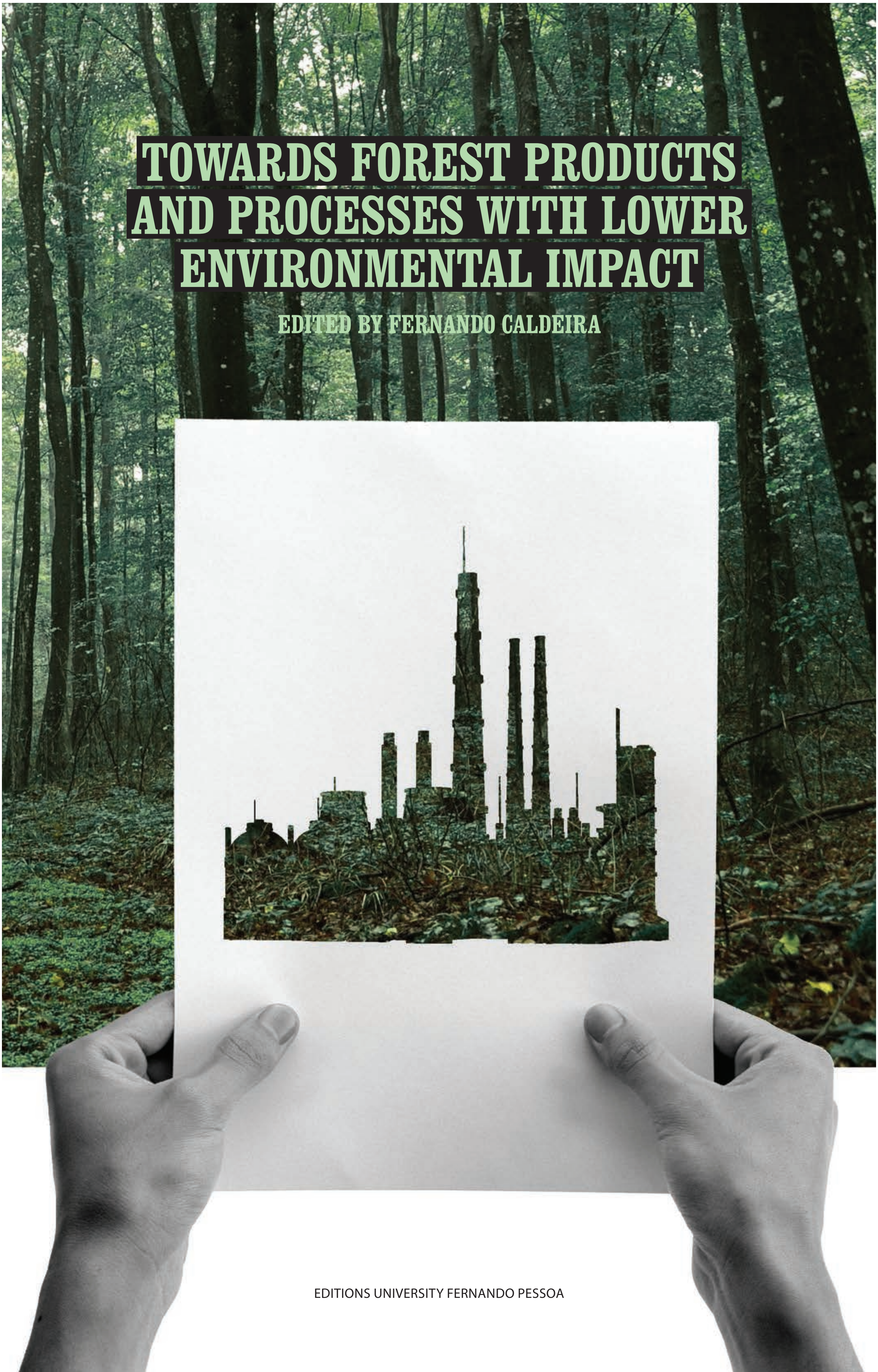
TOWARDS FOREST PRODUCTS AND PROCESSES WITH LOWER ENVIRONMENTAL IMPACT

EDITED BY FERNANDO CALDEIRA



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CHANGES, ENERGY, ENVIRONMENT AND BIOENGINEERING (CIAGEB), FERNANDO
PESSOA UNIVERSITY (UFP), PORTO, PORTUGAL • **JOSÉ VICENTE FERREIRA,**
DEPARTMENT OF WOOD ENGINEERING, SCHOOL OF TECHNOLOGY AND
MANAGEMENT, POLYTECHNIC INSTITUTE OF VISEU, VISEU, PORTUGAL • **MARKO
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EMERITUS PROFESSOR, BIOLOGICAL SYSTEMS ENGINEERING DEPARTMENT,
UNIVERSITY OF WISCONSIN, MADISON, USA
EDITION: **UNIVERSITY FERNANDO PESSOA**
PRAÇA 9 DE ABRIL, 349 / 4249-004 PORTO, PORTUGAL
TLF. +351 225 071 300 / FAX. +351 225 508 269
EDICOES@UFP.PT / WWW.UFP.PT

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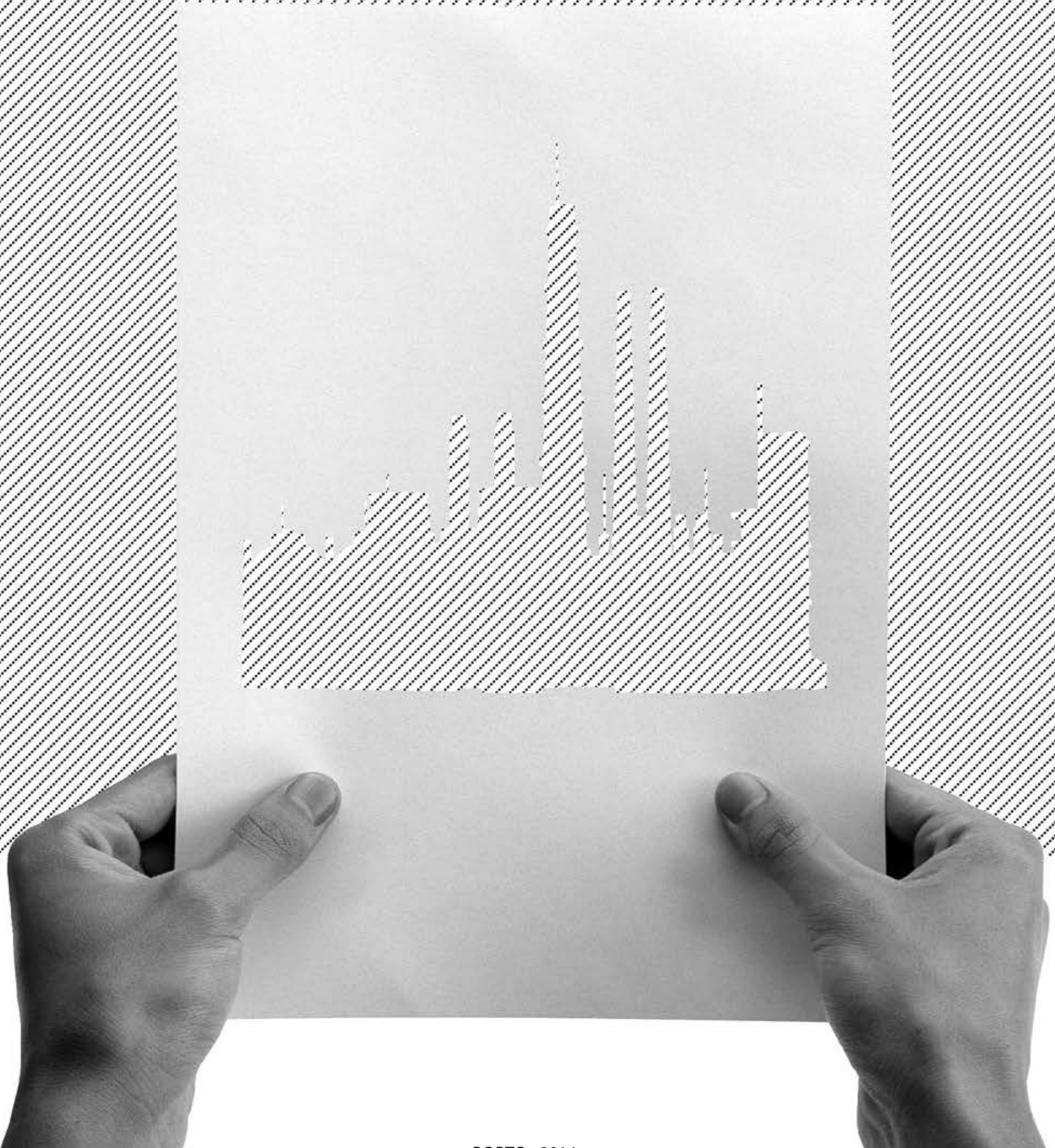

PORTO • 2014

FOREWORD

Society is slowly accepting that our present way of living is not sustainable and is wasteful. Public opinion, the market, legislation and regulations are starting to demand products that have less negative environmental impact, that are more energy efficient and that produce less post-consumer waste.

Aware of that, the forest products industry have been changing their way of working with a higher degree of compatibility with environmental protection. Therefore, forest exploitation needs now to be sustainable; i.e., trees that have been cut are replaced by planting trees; forest production takes place without reducing soil fertility and its capacity to support life, or even helps to reclaim impoverished soils; forests, at the same time they are a source of timber, fibre and chemicals, they do support wild life and traditional human societies. Downstream, the forest products industries must utilise wood more efficiently and recycle wood and fibre wastes more, and control and reduce environmental discharges to the atmosphere, water and soil. Today, when unprecedented high levels of living have been reached for a growing percentage of the world population, the sustainability of such a way of life is questioned. Our past practices have been based on the exploitation of huge reserves of non-renewable fossil fuels and also of non-renewable material sources. Forests and other agricultural lands are part of the solution as a renewable source of materials and chemicals. In a more broad sense, we may speak of lignocellulosics or biomass instead of just wood which includes many types of agricultural products and byproducts.

New solutions for a sustainable, less polluting future come from new ideas and research. Universities and innovative companies have been working to achieve these goals. This book presents a compilation of peer-reviewed papers prepared from ECOWOOD 2012 – 5th International Conference on Environmentally-Compatible Forest Products, that took place at Fernando Pessoa University, in Porto, Portugal, from 5 to 7 September 2012. Topics covered include LCA – Life-Cycle Assessment, EMS - Environmental Management Systems, utilisation of biomass and of less-known plants for lignocellulosics, chemicals from plant sources, wood durability ad new methods for wood and wood products protection, recycling of forest and wood product wastes, utilisation of lignocellulosic wastes for environmental protection, adhesives from renewable chemical sources and formaldehyde issues, and composites and advanced wood-derived materials.

Fernando Caldeira

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01. LCA · LIFE-CYCLE ASSESSMENT

AUSTRIAN RESEARCH PROJECT ECOTIMBER – WOOD, USED IN SUSTAINABLE BUILDING CONSTRUCTIONS (SUBPROJECT OF ECO2)

FRANZ DOLEZAL[1,*], HILDEGUND MÖTZL[2], ALEXANDER DEUTSCH[1]

[1] DEPARTMENT OF BUILDING PHYSICS, HOLZFORSCHUNG AUSTRIA, HFA, 1030 VIENNA, AUSTRIA
[2] AUSTRIAN INSTITUT FOR BUILDING AND ECOLOGY, IBO 1090 VIENNA, AUSTRIA

* CORRESPONDING AUTHOR: TEL: +43-1-7982623; FAX: +43-1-7982623-50; E-MAIL: F.DOLEZAL@HOLZFORSCHUNG.AT

Keywords: LCA, wooden products, sustainability, wooden buildings,
wood frame, solid wood, environmental impact

ABSTRACT

Wood takes up CO2 from the atmosphere while growing and keeps it stored in form of carbon during its entire life-cycle as a building material. Therewith, wood has a great potential to contribute to CO_2-efficient buildings. Nevertheless, important preconditions for a European wide implementation are still missing:

- Standardized calculation methods for CO_2 balances of buildings over the life cycle
- Data for wood and wood based materials
- Consideration of energy or material recycling at the end of life of buildings
- Data for service life and the maintenance intervals
- Investigation of the significance of material based CO_2-balances over the life cycle

Therefore a three years research project was started in Austria in 2010 to gain a better knowledge of environmental impacts of wooden products and houses, considering their whole life cycle. Starting with balancing methods on product level, work continues within the project to building elements like LCAs of walls and floors to the whole building. Existing, commonly used databases for wooden products and elements like dataholz.com have to be updated with latest LCA data and extended by current low energy and low eco-impact constructions.

1. INTRODUCTION

Wood takes up CO_2 from the atmosphere while growing and keeps it stored in form of carbon during its entire life-cycle as a building material. Therewith, wood has a great potential to contribute to CO_2-efficient buildings. Nevertheless, important preconditions for a European wide implementation are still missing:

- Standardized calculation methods for CO_2 balances of buildings over the life cycle
- Data for wood and wood based materials
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- Data for service life and the maintenance intervals
- Investigation of the significance of material based CO_2-balances over the life cycle

Therefore a three years research project was started in Austria in 2010 as part of a European wood wisdom net research project called ECO2 to gain a better knowledge of environmental impacts of and wooden products and wooden houses, considering their whole life cycle. Starting with balancing methods on product level, work continues within the project to building elements like LCAs of walls and floors to the entire building. Considering the extended definition of sustainability with its 3 columns (ecologic, economic and social), results of buildings' LCAs have to be applied on Green Building Labels. Existing, commonly used databases for wooden products and elements like dataholz.com have to be updated with latest LCA data and extended by current low energy and low eco-impact constructions.

The Austrian research project ECOTimber is subdivided into different work packages which are explained in the following:
- WP 1 Methodology of LCA of wooden products
- WP 2 LCAs for wood and wooden products
- WP 3 Application of wood and wood based materials in buildings
- WP 4 Primary energy and greenhouse gas balance of buildings life cycle
- WP 5 Emphasis of building materials within different green building labels
- WP 6-8 Automated updating and extension of dataholz.com with energetically and ecologically optimized constructions

2. **ECOTIMBER**

2.1. METHODOLOGY OF LCAS OF WOOD AND WOODEN PRODUCTS

The applied LCA-methodology is in accordance with the relevant standards (ISO 14040 and ISO 14044; EN 15643-2, EN 15804, EN 15978).

The used LCA-reference-database for building materials from IBO comprises currently more than 500 reference values for building materials. The building materials are assessed step by step from the extraction of raw materials up to the point in time "product at plant" (cradle to gate). So, all previous processes leading to the ready-for-delivery product are taken into consideration. For every process step, material, transport and energy inputs as well as emissions into air, soil, water and waste are determined. The calculations for the building material assessment are carried out with the program SimaPro based on CML2 Baseline 2001.

The generic data from background processes are mostly taken from Ecoinvent data v2.0. Ecoinvent comprises unified and generic LCI data of high quality covering energy, transport, building materials, wood, renewable fibres, metals, chemicals, electronics, mechanical engineering, paper and pulp, plastics, waste treatment and agricultural products. The processes included in the Ecoinvent database represent in most cases the average of currently used technology. The methodology is described in detail in (Frischknecht, 2007). The results will be fed into the LCA reference database.

Special attention is given to the allocation procedures in this project. This comprises the allocation of by-products in wood manufacturing as well as the modelling of the end-of-life process of wood. A literature study concerning different approaches for end-of-life has been carried out. The most convincing methods have been applied to wooden products and are currently under discussion.

In work package AP1 the methodology for the life cycle assessment of timber and timber derived products is defined. Focus is on greenhouse gas emissions and energy consumption. This work package provides the basis for all other work packages.

A more detailed consideration in regard to the selection of the methods which should be applied was necessary for the following topics:
- system borders
- attribution (allocation or system expansion)
- end-of-life
- generic data
- scenarios

Based on the research work the existing LCA-standards (ISO 14040 and ISO 14044) as well as the current standardization drafts of CEN/TC 350 were inspected concerning relevant methodological presettings. These give the frame for our options to specify the methodology.

Result of this work is a comprehensive documentation of the scientific methodological basis. The report addresses LCA-experts and focuses on the interpretation of principles.

2.2. LCAS FOR WOOD AND WOODEN PRODUCTS

Data for the production of wooden products are collected with participating manufacturers. These data will be used for a life cycle inventory analysis of different types of products. From these data, life cycle assessment of the manufacturing processes for wood and wood based materials, including logging and delivering of the products, have been calculated.

For data collection of LCAs of wood and wooden products, interested partners from industry and production were found who provided us with life cycle inventory data of their products. Attention was paid to get data for a wide range of relevant wooden products for the construction sector.

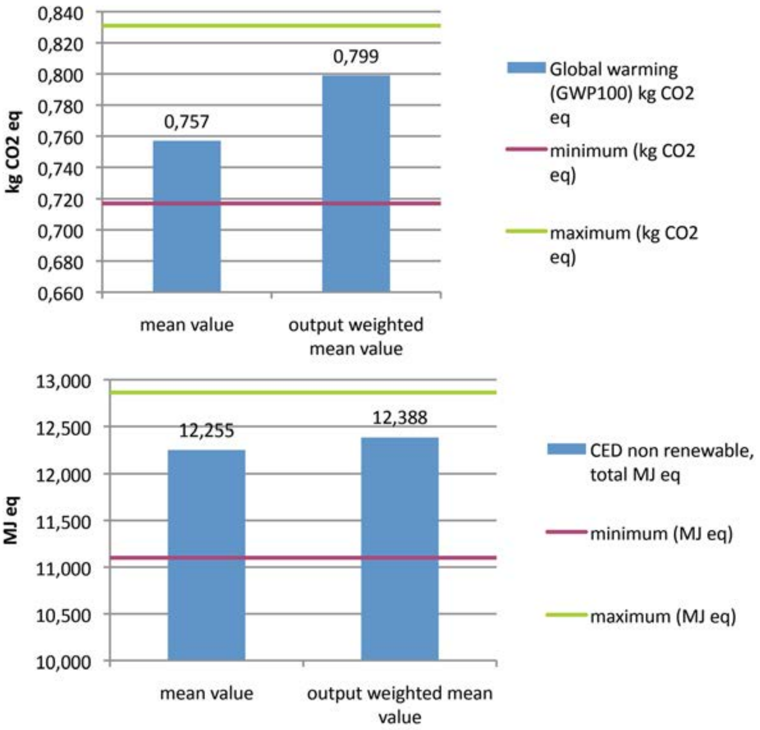
For the following products life cycle inventory data was collected: Cross laminated timber CLT, windows, doors, internal doors, glued laminated timber GLULAM, wooden floors, solid wood boards, cellulose fibre, etc.

Questionnaires had been sent to the companies, covering the following topics: raw material, ancillary input, output, packaging material, production energy, emissions, production waste, wastewater, and additional questions to the entire life cycle: delivery, mounting, use phase, end of life.

To facilitate the start with the questionnaire, a questionnaire-filling-workshop has been organized. This workshop started with a general presentation of LCA, continued with a step by step explanation of the questionnaire and at the end open questions were answered. All Questionnaires of participating partners already returned and at least 1 plant visit for verifying data and last clarifications had been carried out. All LCA calculations were carried out by using Simapro LCA software with Ecoinvent database and in cooperation between Holzforschung Austria HFA and Austrian Institute for Building and Ecology IBO.

After having examined delivered data from industry partners, at least one plant visit had been carried out for each product to check transmitted information on site.

Due to data confidentiality, agreements with participating industry partners, results cannot be published directly. Therefore, mean values of environmental indicators for parquet floors (GWP100 without carbon storage, CED non renewable) are shown in Figures 1 and 2. Figures always show the best and the worst result, the mean value and the output weighted mean value, which gives a better picture of the ecological impact of this wooden product in general. Considering that a wide range of manufacturer participated in this project, results can be seen as quite representative for Austrian wooden products.



Figures 1 and 2: Mean value and output weighted mean value of GWP100 without carbon storage (left) and CED non renewable (right) for 1 kg Austrian parquet floors.

2.3. DATA FOR LOGGING

For this work, on-site measurements in the forest were carried out. Together with calculations, results of the on-site measurements were allocated to timber harvest methods in Austria according to literature. The next step was to compare resulting data to generic data in Ecoinvent database.

In Schwarzbauer (2009) Austrian wood harvest statistics show the use of about 17 million solid meters, without bark, in the Year 2003. Forwarding systems depend mainly on the cutting method, but also on location, stock and size of the forest enterprises (Windsperger, 2010). Usually when cutting is carried out by harvesters, forwarders are used. If trees are cut by chain saws, forwarding is done by cable winch, cable pull and to a small amount by hand. In Pröll (2006) it is mentioned, that cutting in Austria is mainly done by chain saws (80%), the rest with harvesters. Out of this, an average of the last years' harvest in Austria can be calculated. Results, based on harvesting and forwarding methods in Austria compared to Ecoinvent generic data, are shown in Figure 3.

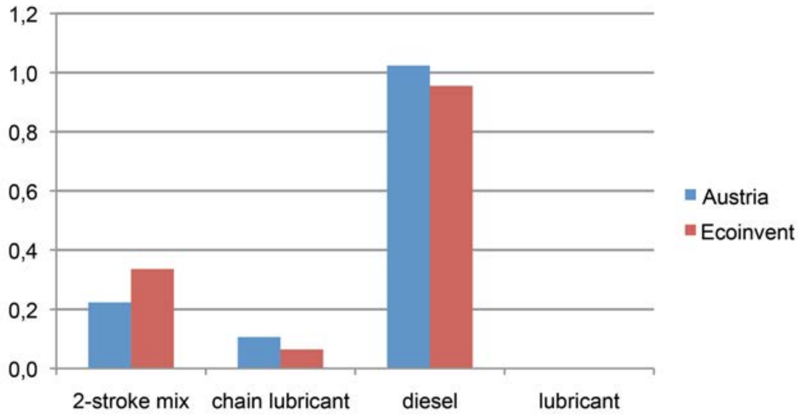


Figure 3: Timber harvesting Austria compared with Ecoinvent - data in liter/solid meter.

A comparison of measured and calculated results with generic data from Ecoinvent shows similar magnitudes. Differences can be detected in forwarding. In general, Ecoinvent calculates only cutting with chain saws. In Austria harvesters are widely (20 %) used, what leads to a higher rate of diesel and reduces rate of 2-stroke mixture within the whole harvesting process. Furthermore it has to be considered, that Ecoinvent only knows application of forwarders. As already mentioned above, only for 19.8 % of the harvest forwarders are used in Austria. The rest is forwarded by cable winch, cable pulls and, a small amount (7.2 %), even by hand (Pröll, 2006).

2.4. LIFE SPAN, SERVICE LIFE, MAINTENANCE

Life span of modern timber buildings nowadays is indicated with at least 100 years in standard ÖNORM B 2320. Assuming continuous maintenance, this period can be extended easily. Life span and service life of a building usually are not always the same and complexity is rising by different service life of building components. Parameters affecting service life of buildings are mainly major changes in function and design, but also profitability, decisions of location and income development. In general economic life span (service life) is significantly shorter than the technical one, what can be shown at some recent examples in Vienna made of massive mineral materials with service lives shorter than 50 years.

Within the research project, HFA developed data which is based on mentioned standards and long-lasting expertise of Holzforschung Austria, considering experiences of producers and users. Furthermore, results of research projects of HFA are taken into account, especially Schober (2010) and Schober (2008). Some single values are taken from literature as for example from Waltjen (2008) and Ritter (2011).

2.5. TRANSPORT

In the questionnaire sent to industrial partners, even questions to transport distances where included. Whilst transports of raw and ancillary materials are included in cradle to gate calculations, transport of the product from factory gate to construction site and construction site to e.g. a recycling site or final disposal, is considered in different modules according to EN 15804. As an example, Figure 4 shows average transport distances of different wood products from factory gate to construction site. Also, the impact of different transport distances of raw materials on the result of LCAs of products was determined and compared to impact of production and use phase. Due to limited space, results are not shown in this paper.

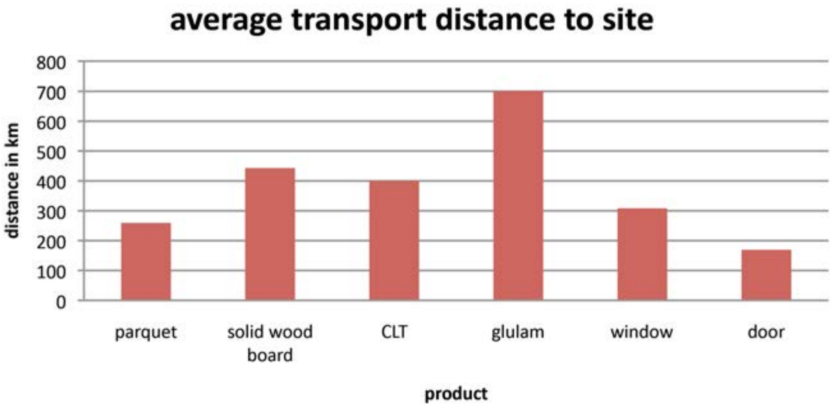


Figure 4: Transport distances of different wood products from gate to site in km.

2.6. CALCULATION OF REFERENCE BUILDINGS

Four different building types were determined according to a European research project called TABULA. For these building types, a couple of existing buildings were looked for. Out of several buildings one for each building type was selected. Energy demands of the buildings are calculated and adapted to different building materials. The aim is to define Zero Energy Houses and then to calculate the whole life cycle of these buildings and compare them in different materials, with different HVAC systems, etc.

Energy performance certificates of 4 different real buildings (one for each building type) were prepared by energy agency and LCA calculations of these buildings are currently carried out. As an example, Figure 5 shows the relation of primary energy demand of the multi storey building of materials and building operation (use phase). It has to be considered that this building is a passive house, located in Vienna.

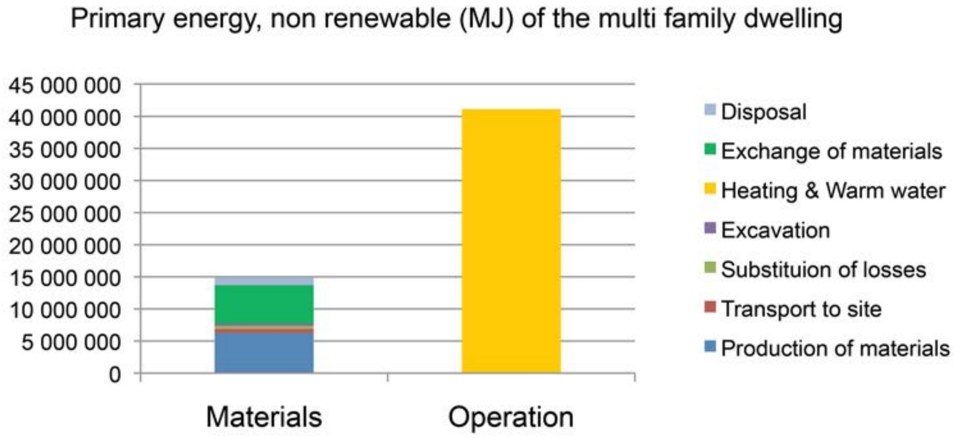


Figure 5: Relation of primary energy demand between building materials and operation of a multi storey building in Vienna.

2.7. UPDATE AND EXTENSION OF DATAHOLZ.COM

Within a previous research project of Holzforschung Austria, a free access internet based catalogue of reviewed timber building components for thermal, acoustic, fire performance requirements and ecological drivers, called dataholz.com (www.dataholz.at), was developed. It's a collection of datasheets for materials, timber components and connections used in timber house constructions. This building physical database for wooden elements is a powerful tool which, meanwhile, is widely used all over Europe, especially in Austria, Italy, Germany, Switzerland, France and Spain with its various language versions. The first task is updating of existing data and establishing of an interface to baubook (www.baubook.info) database (another internet based database with ecological drivers for building materials) for automatic updating.

Moreover, energetically and ecologically optimized components will be added to dataholz.com database and their building physical performances and ecological drivers are calculated and declared.

3. CONCLUSIONS

A common method of LCA calculation could be found at least within Austria's LCA calculation institutions. Within the entire project consortium consisting of 5 different nations and even more different institutions at least essential parameters like e.g. economic allocation method are agreed.

Time and energy consumption of logging in Austria was investigated with the aim to compare it to generic data in Ecoinvent. It could be shown that figures are quite similar, and differences can be explained with slightly different harvesting methods.

Service lives and maintenance intervals for building products, concerning wooden structures, could be determined.

Ecological data and drivers of Austrian wooden products were collected and calculated. A data base with current data was established and average values for production in Austria calculated. Also impact of different transport phases of products was determined and compared to impact of production and use phase.

Reference buildings are calculated and analysis shows ecological impact of different building parts, different phases of the life cycle of a building and the favourable effect of the use of wood as a building material on the environmental impact of buildings.

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5. **STANDARDS**

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LIFE CYCLE ASSESSMENT OF PORTUGUESE WOOD FURNITURE SECTOR

BÁRBARA MATOS* AND JOÃO JOANAZ DE MELO
CENSE – CENTER FOR ENVIRONMENTAL AND SUSTAINABILITY RESEARCH, FACULDADE DE CIÊNCIAS E TECNOLOGIA, UNIVERSIDADE NOVA DE LISBOA, 2829-516 CAPARICA, PORTUGAL TEL: +351–212948397. FAX: +351-212948554

*CORRESPONDING AUTHOR: BA.MATOS@GMAIL.COM

Keywords: Life Cycle Assessment, Portuguese furniture, Ecoblok method; Ecological Footprint

ABSTRACT

Furniture products represent about one percent of global trade, but are also responsible for significant environmental impacts. In Portugal, wood represents more than 40% of total raw materials used in furniture manufacture. Despite difficulties created by the economic crisis, this sector is one of the few with positive trade balance in Portugal. This paper reports on a life cycle assessment (LCA) of Portuguese furniture sector. The LCA used a standard set of environmental pressure indicators, as defined by the Ecoblok method; a synthetic environmental performance index is also used, inspired on the Ecological Footprint concept. The analysis was made at three levels: sector, company and product. The company case study was Movelpartes, a factory belonging to the Sonae Group that makes wood-based furniture in kit. Two products were analysed in detail: the Desk MUS and Shelf AK 027. The analysis of the sector indicated that acquired environmental pressures, embodied in the purchased raw materials, fittings and services, are much higher than the environmental pressures generated on the factory site. Movelpartes Company has an average Ecoblok footprint of 0.3 global ha.year per production unit (a production unit being e.g. a desk or a set of shelves). The Ecoblok footprint of a standard home office is 0.31 global ha.year.

1. INTRODUCTION

Furniture products represent about one percent of global trade (CSIL, 2009). It has a significant environmental impact, due both to the volume of production and its universal use, by business and households alike. It is thus a relevant case study for life cycle assessment (LCA).

In our consumption society, "disposable furniture" became common, like so many other disposable products. This trend has inevitable implications on the environmental impacts of the sector (ISU, 2007). Furniture generates pollution and uses up resources, during its life cycle, mainly in the stages of raw materials production and disposal of discarded furniture (Birkeland, 2004; Curran, 1996; Lewis et al., 2001).

In the EU-27, wood accounts for 30% of raw materials used in furniture manufacture. Major economic pressures for European furniture started with decreasing of world trade barriers, rendering China the biggest exporter of furniture to Europe (Han et al., 2009).

Despite the economic crisis, the Portuguese furniture sector is one of few activities where trade balance is positive and has prospects of further growth. This positive balance, contradicting the European trend, can be a good indicator of competitiveness. However, the industry is threatened by changes in consumer preferences, manufacturing processes, marketing and distribution methods, or relocation of production, who constantly searchs for lower costs; therefore, national companies are now investing in alternate product design and technology, at a competitive price (EGP, 2007). The more traditional Portuguese furniture manufacture, largely based on hardwood work, has been suffering a loss in sales, apparently related to the high costs associated to high quality. Some producers defend that, despite being less used today, hardwood remains one of the most popular materials sought in furniture sector, given its beauty and malleability (Cabaças, 2011).

Consumers are becoming more concerned with environmental issues. Producers understand that it is essential to combine good environmental performance with economic opportunities. LCA and ecodesign may be part of the answer to both. The main objective of this study is to evaluate the environmental performance of Portuguese furniture industry, through LCA at three levels: sector, company and product.

2. THE PORTUGUESE FURNITURE SECTOR

Portuguese forests occupy 3.4 million hectares (40% of the national territory) with pine, eucalypt, cork oak and green oak making the highest percentage of land use (CELPA, 2009).

This industry is dominated by medium, small and micro enterprises: about 60% of the companies employ fewer than 10 workers and are family-based. In 2007 the industry had 34 000 workers (EGP, 2007) and a turnover of 1.4 billion of Euros (UEA, 2009). More than 70% of national production is currently exported. Figures 1 and 2 show the distribution of furniture production in Portugal respectively by category product and by main raw material.

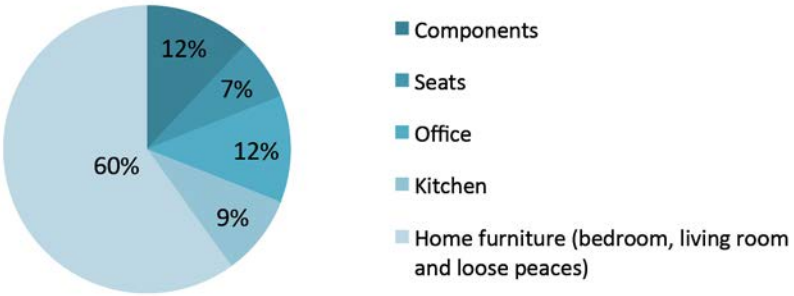

Figure 1: Distribution of products by category. (Source: Cluster do Mobiliário, 2011).

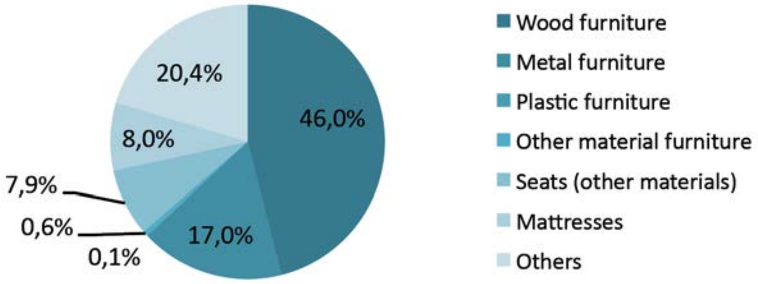

Figure 2: Furniture typology with focus on materials. (Source: Eurostat (a), 2008).

3. METHODS

3.1. ENVIRONMENTAL PERFORMANCE INDICATORS: ECOBLOK METHOD

We used Ecoblok, a method to standardize environmental information with a life cycle oriented approach. It was first proposed by Melo and Pegado (2002) and later developed for a number of applications (e.g. Melo at al., 2007, 2012; Ribeiro, 2009). The method was designed to facilitate transfer of environmental information along the product chain. It allows easy comparison between products and between stages of the life cycle. It follows a mid-point rather then end-point approach, because environmental pressures are much easier and less expensive to measure and standardize. In this we differ from many authors on LCA; our aim is to have an applicable method and robust results, rather than theoretically elegant models that no business will apply because they are too costly and time consuming.

The method uses six key indicators. Each key indicator is computed from measured quantities of environmental variables, weighted by dimensionless equivalence factors (feq), which relay the environmental significance for each variable based on objective criteria. The general equation for the key indicators is: $KI = \Sigma Q_j * feq_j$, where KI is the key indicator expressed in equivalent units, Q_j the physical quantity of variable j, and feq_j is the equivalence factor for variable j. Table 1 describes the key indicators, criteria for equivalence factors and typical measurement units, as applied to products or organizations.

Table 1: Ecoblok key indicators.

Key indicator	Criteria for equivalence factors	Typical units – products	Typical units –organizations
WA – Water abstraction	Water use intensity	m^3/prod. unit	m^3/year
RE – Resource extraction	Stock duration at current rate of extraction	kg/prod. unit	ton/year
LU – Land use	Ecological and social value of land; water cycle; agricultural practice	ha.year/ prod. unit	ha
GH – Greenhouse gas (GHG) emissions	Global warming potential (based on IPCC guidelines)	kg CO_2 eq/ prod. unit	ton CO_2 eq/year
PA – Non-GHG emissions to air	Equivalent hazardousness (based on PRTR: UNECE 2003)	kg NOx eq/ prod. unit	ton NOx eq/year
PW – Emissions to water and soil		kg N total/ prod.unit	ton N total/year

To compare products and life cycle stages the method derives the EcoBlok Index, inspired on the Ecological Footprint concept. Key indicators WA, RE and LU are related by the actual land area that serves the three functions simultaneously; key indicators GH, PA and PW are converted to a virtual global area needed to capture excess emissions.

3.2. FURNITURE SECTOR

The furniture sector analysis was based on two major sources of information: (i) input-output matrix (Eurostat (b), 2008) to analyse the economic relations between the furniture and other sectors, using a 60 by 60+1 matrix according to the NACE (European) and CAE (national) classifications; and (ii) environmental statistics regarding GHG emissions (Eurostat (a), 2008). Figure 3 shows the direct carbon intensity of different economic sectors.

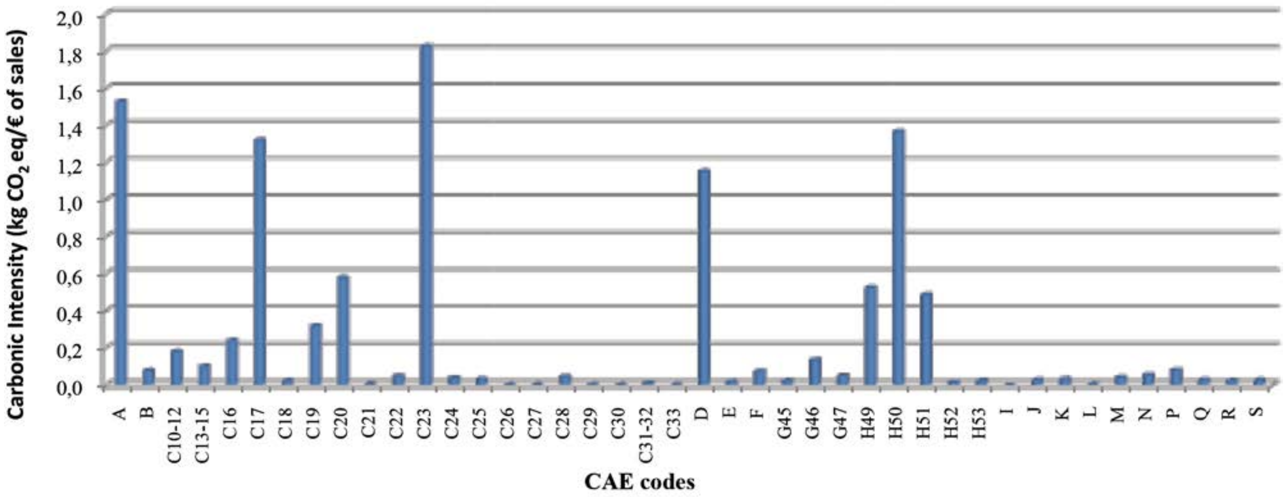

Figure 3: Direct carbon intensity by CAE code. (Adapted from: Eurostat (a), 2008).

We then computed the direct GHG emissions resulting from furniture manufacture and indirect emissions embodied in the life cycle, considering materials and services acquired from other sectors.

3.3. COMPANY: MOVELPARTES

A number of companies were contacted as prospective research partners. The best response came from Movelpartes, a company belonging to Sonae, the largest Portuguese non-financial economic group. The analysis was carried out on the kit furniture factory located at Alcanede, in the Tagus Valley region in Portugal. Employing about 70 workers, Movelpartes transformation of raw materials (main coated wood based panels) produced outside the factory. The company has developed a line of furniture, Make it Better®, which is related to ecodesign practices.

An inventory was performed of direct environmental pressures generated at Movelpartes and significant acquisitions of materials, utilities and other services. A questionnaire was answered by the company for the reference year 2011. Tables 2 and 3 show a synthesis of the data provided by the company. Indirect environmental pressures were derived with the help of the *Ecoinvent Database 2.0.* (Werner et al., 2007). Results were expressed in Ecoblok indicators.

Table 2: Materials acquisitions in 2011. (Source: Movelpartes, 2012).

Materials				
ID	***Ecoinvent* name**	**Real material**	**Amount**	**Unit**
2479	*Medium density fiberboard, at plant*	MDF	153	m^3
2447	*Glued laminated timber, indoor use, at plant*	Melamine coated chipboard	5713	m^3
1840	*Polyvinylchloride, at regional storage*	PVC	2485	ton
1854	*Packaging film, LDPE, at plant*	LDPE	448	kg
1835	*Polystyrene, expandable, at plant*	EPS	730	kg
1695	*Folding boxboard, FBB, at plant*	Cardboard	6593	kg
1802	*Expoxy resin, liquid, at plant*	Glue	11,2	ton

Table 3: Utility acquisitions in 2011. (Source: Movelpartes, 2012).

Others consumptions				
ID	***Ecoinvent* name**	**Description**	**Amount**	**Unit**
705	*Electricity mix*	Electricity	153,0	m^3
1944	*Transport, lorry > 28 t*	Transport	5713,4	m^3
559	*Diesel, burned in building machine*	Diesel consumption	2485	ton
2288	*Tap water, at use*	Water consumption	448	m^3
2262	*Waste water treatment*	Waste water production	730	m^3

3.4. PRODUCTS: OFFICE FURNITURE

Product analysis focused on the Shelf AK 027 and the Desk MUS (Figure 4).

Figure 4: Pieces of furniture analyzed. (Source: Movelpartes, 2012).

A life cycle inventory was performed, covering extraction and production of raw materials (acquired pressures from suppliers), production (in factory), transportation to the store and final disposal. Table 4 shows the main components of the products studied. Table 5 shows estimations of energy consumption used to compute indirect environmental pressures.

Table 4: Components of furniture elements. (Source: Movelpartes, 2012).

Material	**Shelf AK 027**	**Desk MUS**	**Unit**
Chipboard	1.86	3.79	m^2
Edge (PVC)	6.25	7.44	mm
Glue	0.052	0.056	kg
Wood	0.0089	-	kg
Metal	0.11	-	kg
Plastic	0.003	-	kg
Total weight	20	48	kg

Table 5: Energy use in manufacturing processes. (Adapted from: Spitzley, *et al.*, 2006).

Process step	Machinery used	Time (s/operation)
Cut	Multi-saw (20 kWh)	5
Drilling	Drill (2 kWh)	5
Edgebanding	Edge banding (6 kWh)	15
Packaging	Oven	5
Stack up	Lift-truck (30 kWh)	20

The functional unit considered, for both pieces, was: ten years of use of work surface, in a wood office environment (according to the product guarantee). Fugitive emissions or other toxic aspects related to indoors air quality were not accounted for, due to lack of information. Regarding end of life, we considered two cases: landfilling or recycling. Data standardization and expression of environmental performance results were conducted following the Ecoblok method.

To complete the study, the impact of a home office was analyzed, considering the minimum elements of furniture: a desk, a shelf (those previously referred) and a chair.

4. RESULTS AND DISCUSSION

4.1. FURNITURE SECTOR

Indirect GHG emissions (acquired by the furniture sector from different suppliers) are far superior to direct emissions (Figure 5). Together, acquired and added GHG emissions constituted, in 2008, 280 kilotons of CO_2 eq. Total furniture GHG emissions represents, for the same year, 0.4% of total GHG emissions related to all Portuguese economy activities.

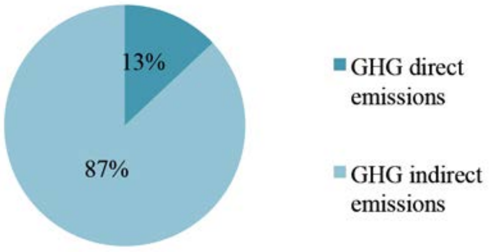

Figure 5: Direct and indirect emissions from the furniture sector.

Figure 6 shows the acquisition of indirect GHG emissions by the furniture industry, taking into account the carbon intensity of products and purchases from each sector, derived from the input-output matrix.

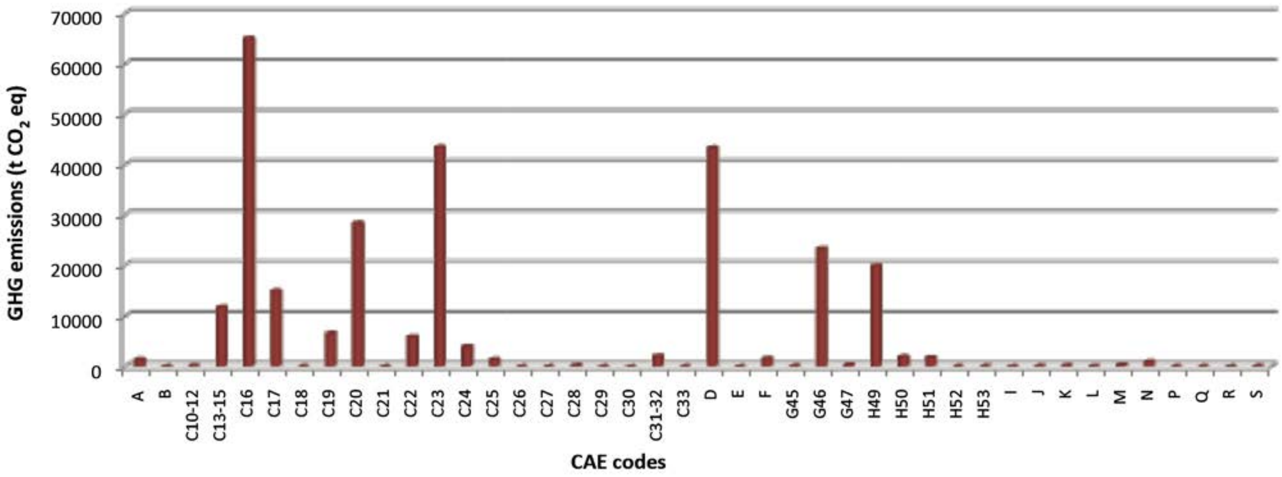

Figure 6: Indirect GHG emissions of furniture industry acquired from other sectors.

High indirect emissions acquired from the wood industry (C 16) seem to be the result of manufacturing processes using chemicals such as paints, resins and varnishes. Other suppliers also associated with high GHG indirect emissions, such as C23 (manufacture of non-metallic mineral products), D (energy production) and H46 (road transportation), owe their magnitude mainly to burning of fossil fuels.

4.2. COMPANY: MOVELPARTES

The computed Ecoblok footprint of Movelpartes is 19267 ha. In 2011 it sold 57 575 product units (PU), each PU being one furniture kit ready to be purchased by the final consumer. This corresponds to a unitary footprint of 0,3 global ha.year/PU. Figure 7 shows the contribution of each environmental compartment, represented by each of the six key indicators, to the overall result. The most significant environmental pressures of Movelpartes are water pollution, land use, resource extraction and greenhouse gas emissions.

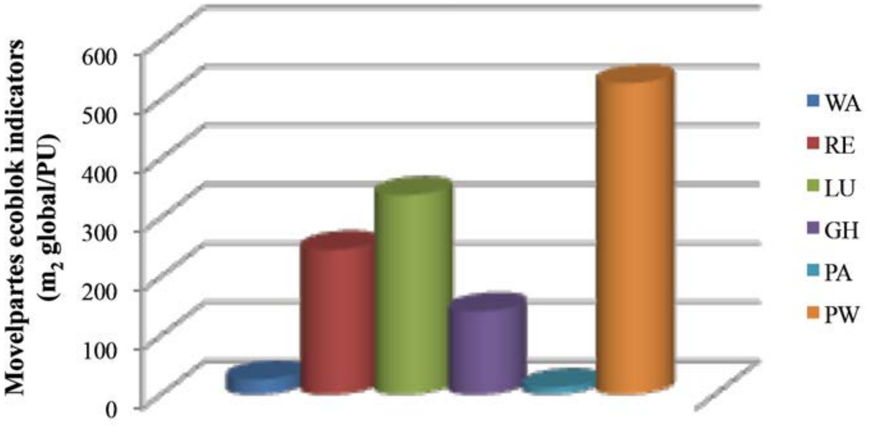

Figure 7: Movelpartes environmental pressures by environmental compartment.

Table 6 shows the environmental pressures resulting from the acquisition of the most significant materials and utilities. The greatest pressures are land use (LU) and pollution of water and soil (PW), which are largely related to environmental pressures that are purchased from chipboard and PVC industries.

Table 6: Ecoblok indicators and Index for Movelpartes

Ecoblok indicators	WA (dam^3/year)	RE (ton/year)	LU (ha eq)	GH (ton CO$_2$ eq/year)	PA (ton NO$_x$ eq/year)	PW (ton N eq/year)	Ecoblok Index (global ha)
Coated chipboard	29,2	8408	1892,8	1163,5	33,5	303	12049
PVC	1202	4924	0,7	4965,6	98,5	282	3833
LDPE	0,05	1,1	0,0	1,2	0,01	0,10	1,0
EPS	0,13	1,7	0,0	2,4	0,03	0,08	1,2
Cardboard	0,46	30,3	3,5	8,6	2,0	2,0	39
Epoxy Resin	4,499	51,5	0,01	74,1	1,0	5,1	53
Electricity	190,6	208	22,0	1466	344,8	14916	1735
Transport	5,4	143	2,9	256,3	71,7	2063	257
Diesel	0,25	4,1	0,06	23,6	8,1	96,2	13
Tap water consumption	11,264	0,68	0,08	1,2	0,3	45,5	6,0
Wastewater production	0,17	2,8	0,07	2,6	1,3	98,4	10,6
Waste production	2,5	6,3	0,2	34	111	12532	1269
Total Indicator	1446	13782	1922	8000	672	30344	19267

To compare Movelpartes performance with the Portuguese furniture sector average we compared carbon intensity. Movelpartes has a carbon intensity of 1.7 kg CO_2 eq/euro of sales, while the sector average is 10.

4.3. PRODUCTS: OFFICE FURNITURE

The product analysis results in an ecological footprint of 1500 global m^2.year for the Desk MUS and 900 global m^2.year for the Shelf AK 027.

Figure 8 shows a comparison between furniture products, taking into account three life cycle phases. The data were normalized for product weight. As was predictable from the company-level analysis, the acquisition of materials and utilities is the phase of the life cycle generating more environmental pressure. Figure 9 shows a comparison with normalized results by environmental compartment. The Desk MUS has a better performance, due to less use of linking elements such as screws and nails.

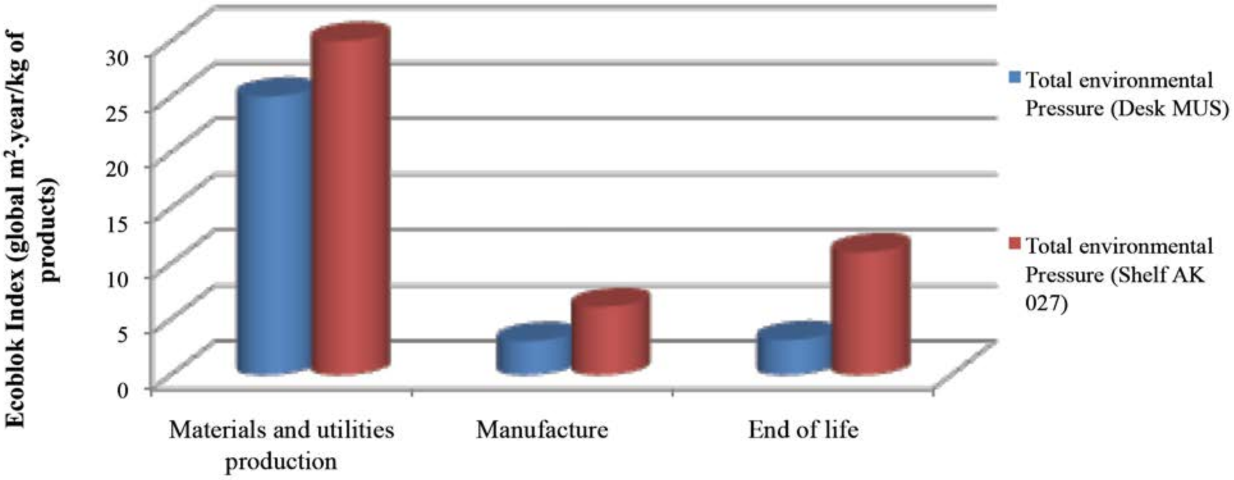

Figure 8: Environmental pressures of desk MUS and Shelf by life cycle phase.

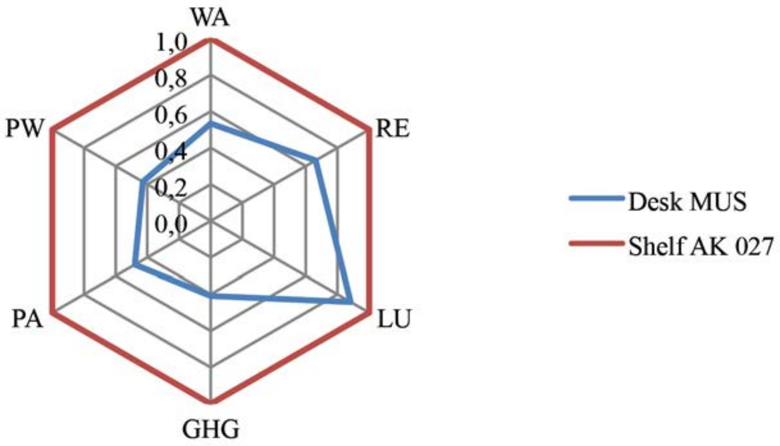

Figure 9: Comparison between desk and shelf
(normalized results: worst case = 1).

The best environment performance of desk MUS were already expected since it belongs to the Make it Better® line, which have more Ecodesign concerns.

Considering a chair with an embodied environmental pressure of 700 global m^2.year, the resulting office represents a total environmental pressure of 3100 global m^2.year.

5. CONCLUSIONS AND RECOMMENDATIONS

The first conclusion of our study was the paucity of environmental information related to furniture production. This absence of data hinders the urgent response to issues of design and innovation.

The study found that GHG emissions are mainly acquired from other sectors, especially because of chemicals used in the wood industry, and fossil fuel burning in power generation and road transport. Energy efficiency, mode of transport and also origin of raw materials are therefore important to the overall environmental impact.

Our company case study, Movelpartes, proved to have a better environmental performance than the sector average, by about 80% in the one indicator we were able to compare, that is carbon intensity.

Design was found to be a critical factor in the ecological footprint of the furniture. Careful design, minimizing environmental-unfriendly practices and materials, can cut environmental pressures by nearly half. Furniture companies are being pressured by a competitive market and should invest in innovative and upscale solutions such as ecodesign.

Using the Ecoblok approach, we were able to compare the weight of different life cycle phases and environmental compartments regarding causes of environmental pressure. Water pollution, land use, resource extraction and greenhouse gas emissions are the most significant pressures. Acquired materials and utilities are the most significant phase of the life cycle. Difficulties to obtain data are ever present, but the Ecoblok method proves satisfactory in simplifying data standardization.

6. ACKNOWLEDGEMENTS

The authors would like to thank: Movelpartes, our major case study; the Sonae group and Millenium bcp who financed research in environmental performance and the development of the Ecoblok method; fellow researchers at CENSE-FCT-UNL, António Galvão and Maria Flôxo Sousa, for discussion and inputs; and the Cluster do Mobiliário Português, for data and moral support.

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COMPARATIVE LIFE-CYCLE ASSESSMENT OF A SINGLE-FAMILY HOUSE: LIGHT STEEL FRAME AND TIMBER FRAME

A.C. COELHO[1], A. LOPES[2], J.M. BRANCO[3,*], H. GERVÁSIO[4]

[1] PHD STUDENT, ISISE, DEPT. OF CIVIL ENGINEERING, UNIVERSITY OF MINHO, CAMPUS DE AZURÉM, 4810058 GUIMARÃES, PORTUGAL
[2] PHD STUDENT, ISISE, DEPT. OF CIVIL ENGINEERING, UNIVERSITY OF COIMBRA, PORTUGAL
[3] ASSISTANT PROFESSOR, ISISE, DEPT. OF CIVIL ENGINEERING, UNIVERSITY OF MINHO, PORTUGAL
[4] ASSISTANT PROFESSOR, ISISE, DEPT. OF CIVIL ENGINEERING, UNIVERSITY OF COIMBRA, PORTUGAL

***CORRESPONDING AUTHOR:** JBRANCO@CIVIL.UMINHO.PT; TEL. +351 253 510 200; FAX: +351 253 510 217

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ABSTRACT

From a sustainability point of view, timber and light steel framing may represent practicable alternatives to concrete structures, due to its lighter weight when comparing with concrete or other common structural systems. This paper presents a "cradle-to-grave" lifecycle assessment for a single-family house built in Kiruna (Sweden), comparing two structural systems: timber frame and light steel framing. Environmental and economical performances were assessed for a 50-year life-span. Environmental assessment showed that steel-frame represents a 41% higher impact on Human Health and 6% higher impact on Acidification, when compared with timber-frame. Economical assessment showed that the life-cycle cost increases 2% for the light-steel option, being the future costs with energy 6% higher than on the timber-frame solution.

1. **INTRODUCTION**

Wooden construction is empirically known for its sustainability. When performing a lifecycle analysis (LCA) of wooden buildings, it must be considered that trees store carbon dioxide in their tissues, in amounts that will only be released by decay or combustion of wood (Buchanan and Levine, 1999). This wood feature is highlighted on long lifespan wood-based products, among which are the main construction industry materials (Karjalainen et al., 1994). Forestry industry has social and economic importance in many regions of the world. Besides that, it also contributes to control soil erosion, helps to regulate the climate and has a decisive role in efficient water cycle and on biodiversity of wildlife and flora. Moreover, wood is a material that requires a relatively low processing power to be prepared for building industry, unlike most building materials. On the other hand, it can be assumed that the transformation process of wood produces virtually no waste, since all the production residues can be used for production of wood-based products or fuel, decreasing the demand for fossil fuels (Sathre and Gustavsson, 2004). Although wooden constructions need maintenance throughout its lifetime, the common wooden building systems allow partial replacement of modules or damaged elements, without compromising the entire structure. The use of wood also contributes to the energy efficiency of buildings, since it is a material with low thermal conductivity. When dismantling a wooden building, the recovered wood can be directly reused in another building, used as raw material for wood-based products, or simply used as biofuel. On landfill, wood is biodegradable and does not constitute any kind of environmental threat, although both combustion and decomposition of wood cause the release of the stored CO_2 back to the atmosphere (Buchanan and Levine, 1999). However, wood is a combustible material. For that reason, some European countries do not allow its deposition on landfill. In these cases, wood residues have necessarily to be burned as biofuel or reprocessed in new products manufacturing. Countries like Sweden, that restrain the landfill of wood, use its residues to generate district heat and electricity, reuse it directly as solid wood, use it as raw material to the production of particleboard, or pulp it to form paper products (Dodoo et al., 2009). This study aims at assessing the environmental and economical performance of both timber-frame and light-steel frame structural systems, to small-scale buildings, like singlefamily houses.

2. LCA APPLIED TO TIMBER BUILDINGS

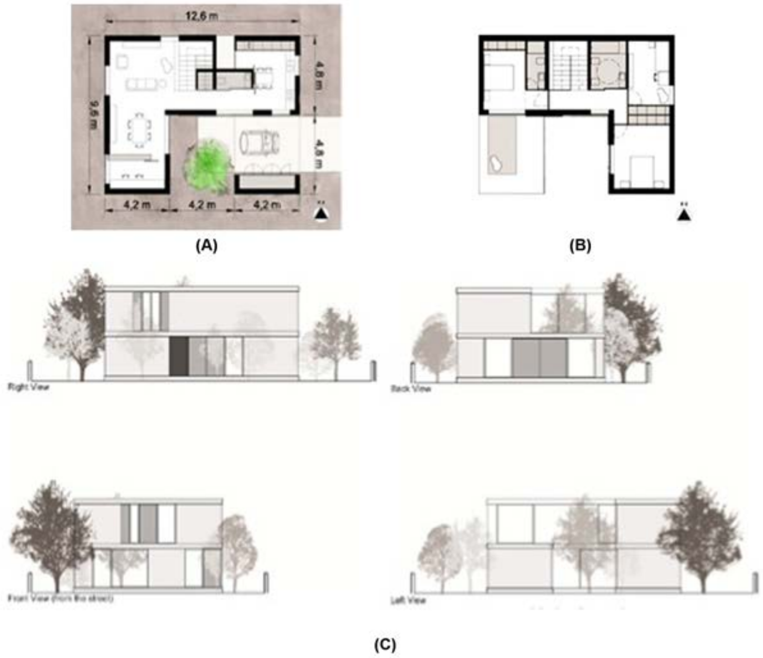
LCA methodology, as prescript by ISO 14040 standard (ISO 14040:2006), is not particularly directed to building assessment. It was designed to assess the sustainability of general products throughout its lifetime, early in an environmental perspective, but more recently also in social and economical perspectives.

One can find some applications of that methodology to timber buildings, like Perez-Garcia et al., (2005) who compared three different structural materials for the same house (timber, concrete and light steel framing), concluding that the timber solution achieved a better score for all the categories under analysis. Buchanan and Levine (1999) and Sathre and Gustavsson (2009) have shown that timber buildings take greater advantage in the low energy processes required to its manufacture, than on the carbon storage itself, considering the whole life-cycle of wood products. Borjesson and Gustavsson (2000) compared greenhouse gas emissions between timber and concrete solutions for a Swedish building, concluding that the timber option decreases Greenhouse Gas (GHG) emissions from 2 to 3 times, assuming that wood waste and logging residues are used to replace fossil fuels. More recently, Nassén (2012) compares the use of concrete versus wood in buildings, from the energy system perspective, concluding that is not clear that the use of wood is a cost-effective option for carbon mitigation, recommending further studies on this subject.

This paper presents a “cradle-to-grave” life-cycle assessment for a single-family house built in Kiruna (Sweden), comparing two structural systems: timber frame and light steel framing. Environmental and economical performances were assessed for a 50-year life-span.

3. CASE STUDY

A single-family 180 square-meter house, built to provide shelter to 4 people during a 50-year period was defined as the functional unit in this study. The building’s area is divided in two floors and all the façades are external, as far as the house is detached from other buildings. It was assumed that the house is located in Kiruna, Sweden, with its main facade turned south. Figure 1 presents the floor plans and the four lateral views.



(A) (B) (C)

Figure 1: Single family-house used as case study. Plan view of the ground floor (a) and first floor and the four lateral views.

The climate in Kiruna is typically polar, with persistent winds, freezing temperatures throughout the year that reach -30ºC, with great duration of night periods during the heating season. The incident solar radiation is very low during the months of October to February, especially throughout the month of December.

The cooling season in Kiruna gives the opportunity to obtain significant solar gains in buildings: the days during the month of June start around 3 a.m. and end around 20 p.m. (about 17 hours of sunlight), although the incident energy is low due to the high latitude. The maximum peak temperature registered in Kiruna has been around 23°C in June, although the maximum hourly average is only 15.4°C during July (1015 ASHRAE weatherfiles).

The temperatures of the ground are extremely low (usually negative) for about 7 months of the year, which emphasizes the importance of heat losses trough construction elements in contact with the ground, on the overall thermal performance of the building.

3.1. METHODOLOGY

The construction materials assessment was based on *BEES (Building for Environmental and Economic Sustainability)* database (Lippiat, 2007), developed by *North-American National Institute of Standards and Technology*. This software complies with the IS0 14040 standard for life-cycle environmental assessment (ISO 14040:2006) and the *ASTM – International Standard life-cycle cost* for economic assessment (ASTM E917–05, 2010). The impact categories considered in the environmental assessment are: Global Warming Potential, Acidification Potential, Eutrophication Potential, Fossil Fuel Depletion, Indoor Air Quality, Habitat Alteration, Human Health, Smog Formation Potential and Ozone Depletion Potential. Results were normalized according to Normalization Values assumed on *BEES* (Lippiat, 2007), which values are presented on Table 1.

Table 1: Environmental balance for each category under study.

Impact	**Normalization Value**
GLOBAL WARMING POTENTIAL	25 582 640.09 g CO2 equivalents/year/capita
ACIDIFICATION POTENTIAL	7 800 200 000.00 millimoles H+ equivalents/year/capita
EUTROPHICATION POTENTIAL	19 214.20 g N equivalents/year/capita
FOSSIL FUEL DEPLETION	35 309.00 MJ surplus energy/year/capita
INDOOR AIR QUALITY	35 108.09 g TVOCs/year/capita
HABITAT ALTERATION	0.00335 T&E count/acre/capita
HUMAN HEALTH	274 557 555.37 g C7H8 equivalents/year/capita
SMOG FORMATION POTENTIAL	151 500.03 g NOX equivalents/year/capita
OZONE DEPLETION POTENTIAL	340.19 g CFC-11 equivalents/year/capita

The energetic balance was performed on *DesignBuilder* software (Design Builder software Ltd., UK), using the *EnergyPlus* dynamic simulation engine (U.S. Department of Energy). Based on a three-dimensional modelling of the spaces that make up the building, systematic analysis of climatic parameters, construction solutions, HVAC systems and its estimated time of operation were defined, aiming towards the fidelity of the results for the imposed conditions. On the other hand, the energy consumption with lighting and domestic appliances was excluded from the analysis.

Climatic data resulting from the research project 1015 ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers), was used in the study compiled into *EnergyPlus* (U.S. Department of Energy) type files obtained from IWEC database (International Weather for Energy Calculations).

Calculations of the heat transfer coefficients were made in accordance with EN ISO 10211 (EN ISO 10211:2007). The studied house is located in the city of Kiruna included in the Norrbottens district (Norrbottens Län) and included in the climate zone I, which is the most rigorous in the heating season, but is also the district where it is legally allowed greater energy consumption with HVAC systems. The legal limit for the building is 150 kWh/m^2/year based on the Swedish BFS 2011:6 BBR18, considering a mixed energetic type use.

In order to simplify the overall thermal simulation performed in *DesignBuilder*, average heat transfer coefficients were determined, which can represent through its multiplication by the element area, the total energy loss observed the element that presents heterogeneities, whether individual or linear. To determine this average values THERM software (Lawrence Berkeley National Laboratory) was used, which complies with the calculation methodology prescribed in EN ISO 10211:2007. The heterogeneities present in the main building blocks, correspond to the structural elements within the walls and slabs which have a linear layout. Cellulose fibre boards were used as insulation. The thermal conductivity coefficient was taken equal to $\lambda R = 0.040$ W/mK.

Given the energetic mix profile in Kiruna, where electricity production has a strong renewable component, electricity was considered for water heating, and the use of District Heating (public heating supply network) was considered for heating.

Economical assessment was performed using the *BEES* database for the materials considered. BEES includes the initial cost of the material and potential maintenance costs that can be predicted for each material. Furthermore, the energy was also expressed as a "future cost", in order to get the final economical balance for each structural option under assessment. A 4% discount rate was applied to future costs, according to the formula:

$$X_{NPV} = \sum (Cn \times q) = \sum_{n=1}^{p} \frac{Cn}{(1+d)^n} \qquad (1)$$

Where X_{NPV} is the net present value, n is the number of years, C_n is the cost in year n, q is the discount factor, d is the real discount rate and p is the period of time considered.

3.2. GOAL AND SCOPE DEFINITION

A single-family house used by 4 people in a 50-year period was defined as the functional unit. The aim of this study is to compare two different light-weight structural systems available to this kind of building: light steel frame and timber frame. For this reason, inventory is detailed for the building shell and main construction options, only excluding some features that are not related to the structural system, like window frames and general fixtures. Although foundations may be dependent on the structural system, as far as they are less demanding for light-weight structure buildings (timber and light steel frame are both light weight structural systems), foundations were not included in this study. The system boundaries, according to BEES database (Lippiat, 2007), includes raw materials acquisition, transport to the factory, manufacture, transport to the building site, construction process, whole life-span maintenance and end-of-life scenario, on a "cradle-to-grave" approach, for all the materials considered in the inventory.

Energetic assessment includes water heating energy consumption, HVAC systems to maintain the requested comfort levels, the passive solar gains, the internal gains from typical domestic activities, the thermal losses through the construction elements and the thermal losses due to natural ventilation. The energy consumption related to lighting and domestic appliances is excluded from the simulation.

3.3. LIFE-CYCLE INVENTORY ANALYSIS

Ground-floor corresponds to a 100.8 square-meter area (Figure 1), with 4 different material layers, from bottom to top: aluminium siding (8 mm), generic cellulose insulation (400 mm), two OSB panels and a layer of natural cork parquet as finishing. The structure is made of framing lumber in the first version under study and light steel on the second version (Figure 2).

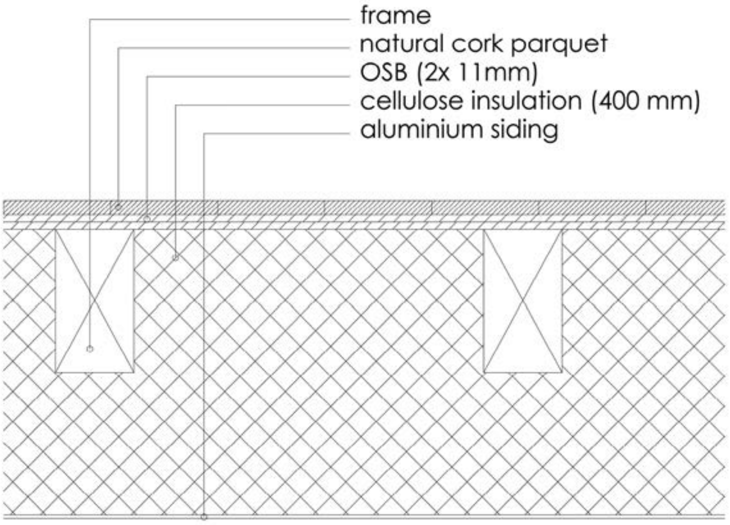


Figure 2: Ground-floor section, first-floor slab (interior/exterior) section.

First floor slab, dividing the two interior floors, corresponds to 59.58 m^2, which section has 4 different layers, from bottom to top: generic gypsum as finishing on the ground floor ceiling, generic cellulose insulation with 150 mm thickness, two layers of OSB panels, and finally, a natural cork parquet as floor finishing to the first floor ground. As in the rest of the building, structure is made of framing lumber on the timber option, and light steel, on the alternative solution under assessment (Figure 3).

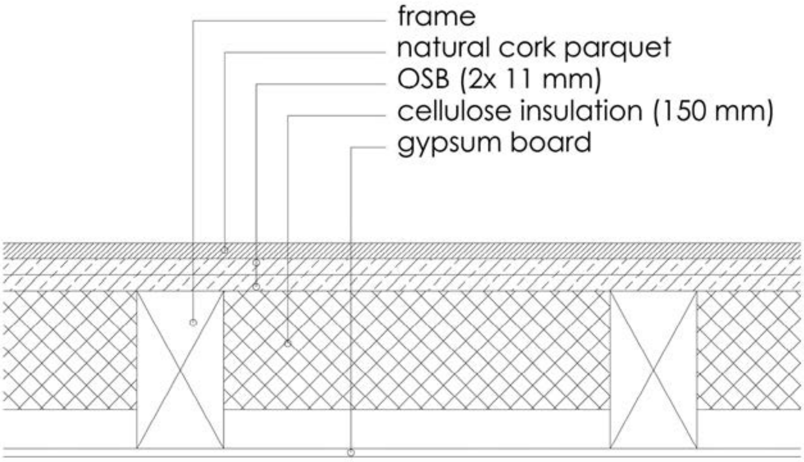


Figure 3: First-floor slab (interior/ interior) section.

First floor slab, dividing the interior space on first floor from the outside on the ground level, corresponds to a 21.06 square-meter area. The designed section repeats the solution formulated to the ground floor slab (Figure 2).

The roof slab (80.64 m^2), due to the building site climate, has large thermal insulation requirements. The assumed solution has 7 material layers, from bottom to top: generic gypsum board to the interior ceiling finish, generic cellulose insulation with 250 mm thickness, two layers of OSB panels, another cellulose insulation layer with 160 mm thickness, an OSB panel on top, to be covered with prime coatings utilithane, with asphalt shingles on top (Figure 4).

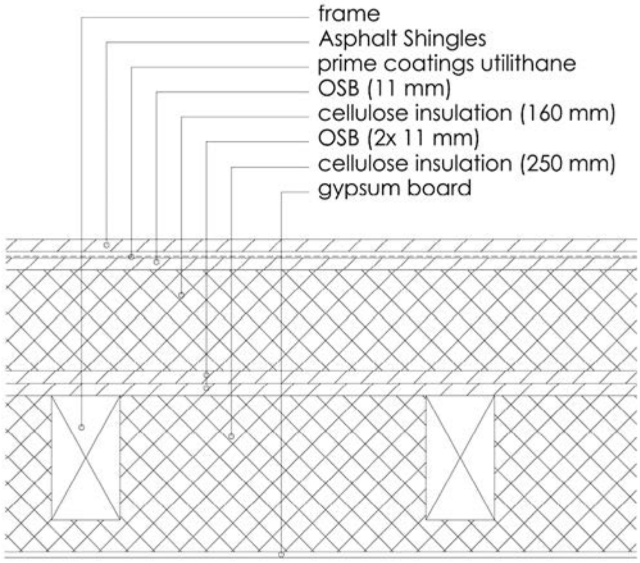


Figure 4: Roof slab (interior/ exterior) section.

The house presents a 20.16 m^2 terrace on the first floor (Figure 1), dividing the exterior above from an interior space below. Its section is similar to the roof section, except on the top, that is covered with a "floating" cedar deck (Figure 5).

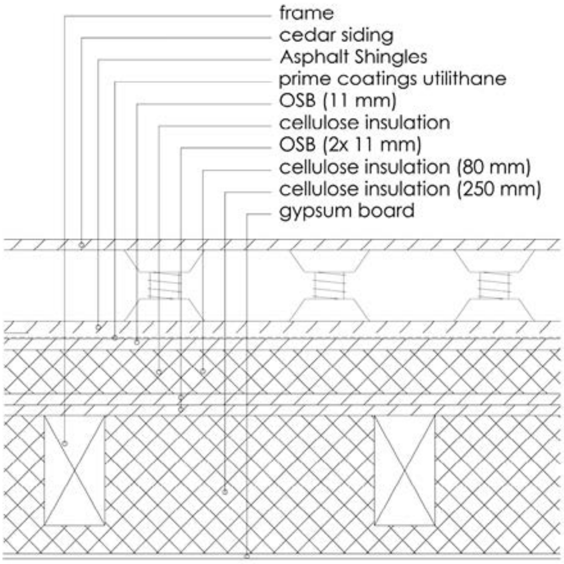


Figure 5: Terrace section (exterior/interior).

External walls correspond to a large share of the whole building materials, an area of 66.40 m^2 of demanding outer shell, to fulfil Kiruna climate needs. Composition is as follows, from the inside to the outside: generic gypsum as interior finishing, generic cellulose insulation (100 mm thickness), one layer of OSB panels, cellulose insulation filling the air gap between the structure (140 mm thickness), one OSB panel layer, sealing with prime coatings utilithane and cedar siding to the external finishing (Figure 6).

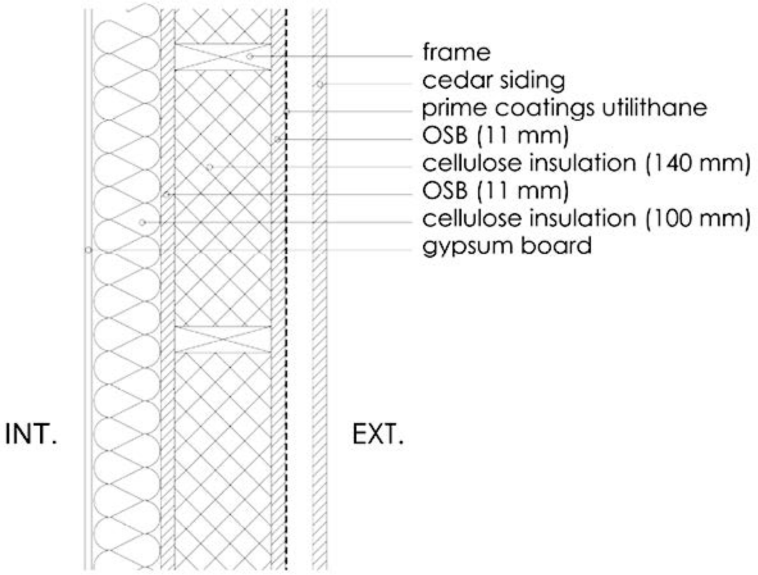


Figure 6: External walls section.

Internal walls correspond to a total area of 110 m^2. According to the building's constructive framework, these are light weight walls, composed by a framing lumber or light steel structure, with the air gap filled with cellulose insulation, limited on both sides with generic gypsum board (Figure 7).

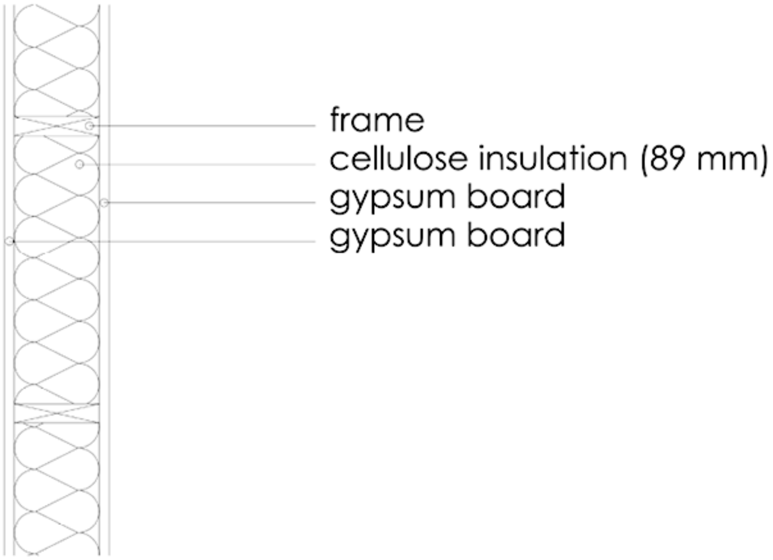


Figure 7: Internal walls section.

3.4. **LIFE-CYCLE IMPACT ASSESSMENT**

3.4.1. **ENVIRONMENTAL IMPACTS**

In this section, the life-cycle assessments of the different impacts are reported for both structural solutions studied: timber and steel frames. Results reporting the environmental impacts are presented in Table 2 and aiming a better analysis of the different impact categories of the house, graphs are used (Figure 8). The environmental impacts presented include all the materials considered in the inventory analysis, in a cradle-to-grave approach, as well as the impacts related to the production of the energy necessary to the 50 years usephase. Energy quantity considered in the environmental impact assessment is according to the energetic balance assessment for both solutions under study, which results are presented in Table 3.

Table 2: Environmental balance for each Impact Category under study.

	timber-frame	light-steel frame
GLOBAL WARMING POTENTIAL	1,31e+01	1,34e+01
ACIDIFICATION POTENTIAL	3,97e-09	4,23e-09
EUTROPHICATION POTENTIAL	2,57e+01	2,57e+01
FOSSIL FUEL DEPLETION	1,80e+01	1,82e+01
INDOOR AIR QUALITY	0,00e+00	0,00e+00
HABITAT ALTERATION	0,00e+00	0,00e+00
HUMAN HEALTH	5,41e+01	9,23e+01
SMOG FORMATION POTENTIAL	4,10e+01	4,10e+01
OZONE DEPLETION POTENTIAL	6,77e-01	6,77e-01

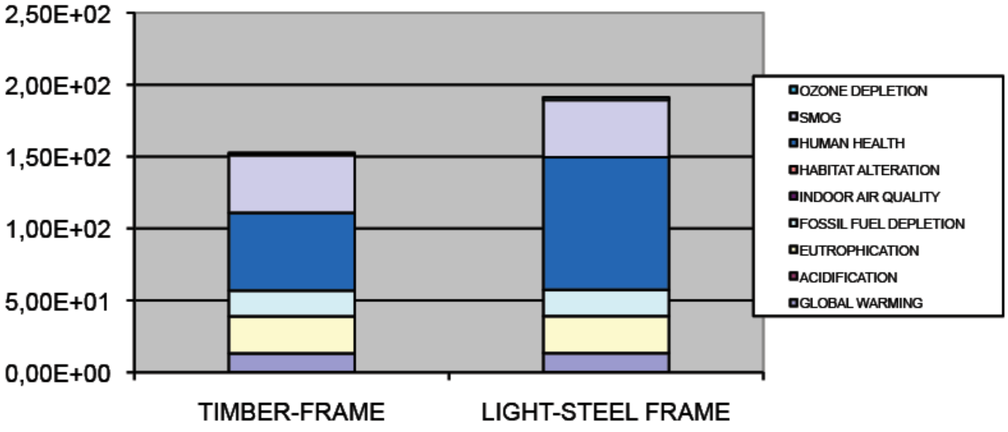


Figure 8: Environmental impacts comparison: timber-frame and light-steel frame buildings under assessment.

Table 3: Energetic balance assessment.

Structural solution	**Total (per year)**	**Electricity (water heating) (kWh)**	**District Heating (kWh)**
Timber frame	Energy Balance	666.7	12376
	Conversion Factor	3.167	1.024
	Primary Energy	2111	12673
		Primary Energy	*Legal Limit*
	Total (per year)	14784 kWh	17875.5 kWh
	Per square-meter	124 kWh/m^2	150 kWh/m^2
Steel frame	Energy Balance	666.7	13316
	Conversion Factor	3.167	1.024
	Primary Energy	2111	13635
		Primary Energy	*Legal Limit*
	Total (per year)	15747 kWh	17875.5 kWh
	Per square-meter	132 kWh/m^2	150 kWh/m^2

3.4.2. **ECONOMICAL IMPACTS**

Economical performance of both solutions under study was assessed according to the procedure described on the "Methodology" section. The total sum includes material acquisition and maintenance, as well as energy costs for the 50-year use phase. Results are presented on Table 4.

Table 4: Economical balance for both alternatives under assessment.

	timber-frame	light-steel frame
FIRST COST	$ 90,040.53	$ 90,480.53
FUTURE COSTS (maintenance)	$ 1,611.66	$ 1,599.43
FUTURE COSTS (energy)	$ 36,803.25	$ 39,044.26
LIFE-CYCLE COST	$ 128,455.44	$ 131,124.22

3.5. DISCUSSION

On the environmental balance, the timber frame building achieved more favourable results, caused by a better performance on three impact categories: *Global Warming Potential* (2% higher impacts on the steel option), *Fossil Fuel Depletion* (1% higher for steel) and *Human Health* (41% higher potential impacts for steel), from the nine categories considered. When it comes to the economic performance, the differences between the two options under study are not significant, even considering the maintenance costs for the use phase. The only remarkable difference is for the energy consumption costs (50 years, considering a discount rate of 4%), that favours the timber option. Therefore, the life-cycle cost balance indicates 2% advantage for the timber house (128,455.44$), comparing with the light steel framing house (131,124.22$). This is due to the better thermal performance of the wood: thermal losses of the light steel house are 6% higher than the timber house ones. Timber house consumes an average 124 kWh/m2 primary energy a year, while light steel frame house consumes 132 kWh/m2 primary energy a year.

4. CONCLUSIONS

Although results for both alternatives remain very close, as a balance we can conclude that the timber house has a more favourable performance both from an environmental and economical point of view. Potential negative effects on *Human Health* are clearly decreased on the timber-frame option, comparing with the light-steel frame. Also the energy requirements are smaller when a timber frame is considered, due to wood better thermal performance when compared with steel.

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ENVIRONMENTAL PRODUCT DECLARATION OF A SOLID OAK PARQUET AND A MULTI-LAYER PARQUET (PRODUCED BY SUBSCRIBERS OF THE FRENCH PARQUET FEDERATION)

CÉCILE HUREL* AND ESTELLE VIAL
TECHNOLOGICAL INSTITUTE FCBA FORESTRY CELLULOSE TIMBER CONSTRUCTION AND
FURNITURE, ALLÉE DE BOUTAUT – BP 227, 33028 BORDEAUX CEDEX, FRANCE

* CORRESPONDING AUTHOR: TEL: +33 (0)5 56 43 63 09 FAX: +33 (0)5 56 43 64 78; CECILE.HUREL@FCBA.FR

Keywords: wood, parquet, Life-Cycle Assessment, EPD, environmental impacts.

ABSTRACT

The issue of sustainable development is broad and of global concern. Consumers and market actors want to have information about the environmental impacts of products. The building sector is a crucial sector for sustainable development. It accounts for a large amount of land use, energy and water consumption, air pollution and impact on climate change. Constructions materials contribute in a significant way to the environmental impact of buildings. The Environmental Product Declaration (EPD) is a tool to communicate on the environmental impact of a product. The quantified data presented in the EPD are calculated according to the Life Cycle Assessment (LCA) methodology which is standardized (ISO standards). The purpose of an EPD is to provide easily accessible, quality-assured and comparable information regarding the environmental performance of products. For now, the development of EPD is voluntary but, in some countries, environmental labelling can be made mandatory in near future. In France, construction materials manufacturers (AIMCC) have committed themselves to produce EPDs for all construction products. In this context, UFFEP (French Parquet Federation) has commissioned FCBA to perform the LCA of two French parquets in order to publish EPDs. This paper presents the methodological choices and the LCA results for solid wood and multi-layer parquets manufactured in France.

1. INTRODUCTION

The European Commission adopted a communication on Integrated Product Policy (IPP) in 2003. One of the main drivers of the IPP is the communication to consumer and market actors of environmental information on products and services. An emphasis is also placed on life cycle thinking in order to have a global approach of environmental assessment, to make comparisons and to avoid pollution transfer.

The industry and the governments have been promoting since then the use of environmental product declarations (EPDs). The EPD corresponds to the environmental profile of a product. It gives quantified environmental data based on Life Cycle Assessment (LCA) information according to the LCA ISO-standards (ISO 14040 and ISO 14044). The development of EPD is voluntary and the purpose of an EPD is to provide easily accessible, quality-assured and comparable information regarding the environmental performance of products.

The building sector is the most advanced in Europe in the definition of a common format for EPD. Standard works are in progress at European level in TC 350 (draft EN 15804 "EPD - Product category rules"). In France, a standard for building product, NF P 01-010 "Environmental quality of construction products - Environmental and health declaration of construction products", is available since 2004. As the green building market is expanding, the need for building products EPDs is growing. These EPDs are in great demand in France with the development of building designed according to High Environmental Quality (HEQ®) requirements. More generally, EPDs are more and more used to assess the contribution of each construction materials on the total impact of the building using softwares such as Elodie (developed by CSTB) and TEAMtm Building (developed by Ecobilan). Today, various construction materials sectors have begun to produce EPDs on a large scale: from the mineral wool insulation to the plasterboard (more than 800 EPDS are available on the inies web site http://www.inies.fr/). Figure 1 presents the life cycle of building products.

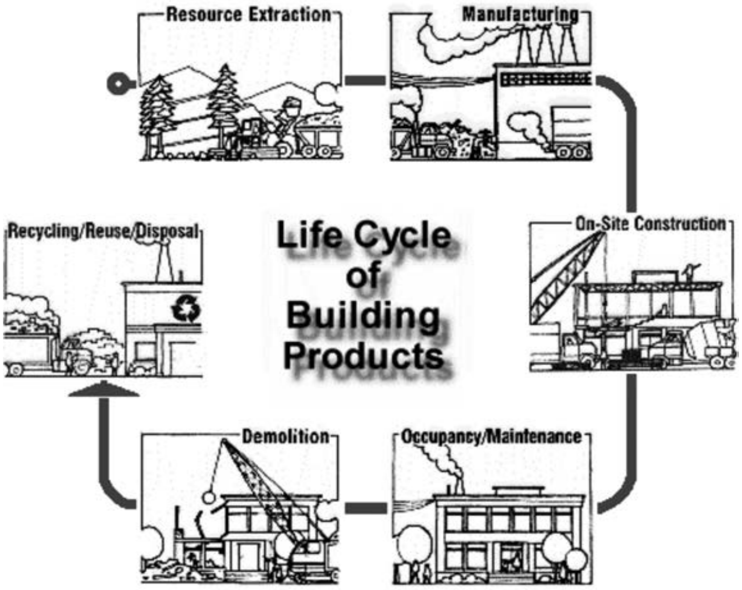


Figure 1: The life cycle of building products.

Recently in France, new laws derived from the "Grenelle de l'Environnement" have broadened the scope of environmental labelling from construction products to all kind of products from food to clothing. A nation wide experimentation has started in July 2011 and is based on LCA data.

At last, wood-based products have many environmental advantages that LCA could reveal:
- Wood is a renewable resource,
- Sequestration of CO_2 by wood in biomass carbon takes an important role in the regulation of greenhouse gases.

In this context, UFFEP (Parquet Manufacturers and Producers French Union) has commissioned FCBA to perform the life cycle assessment of the French parquets in order to publish EPDs according to the French standard NF P01-010 and to improve their environmental performance.

2. MATERIALS AND METHODS

LCA is a methodology to assess the environmental impact of a product. This methodology is based on a quantified inventory of impact sources such as material, water and energy consumption, waste generation and discharges of pollutants in water, air, and soil during the product lifetime. From this inventory, environmental impact indicators are computed. In a practical way, LCA relies on the modelling of physical inflows and outflows at the product system boundaries at each step of the life cycle. It is necessary to do a mass and an energy balance.

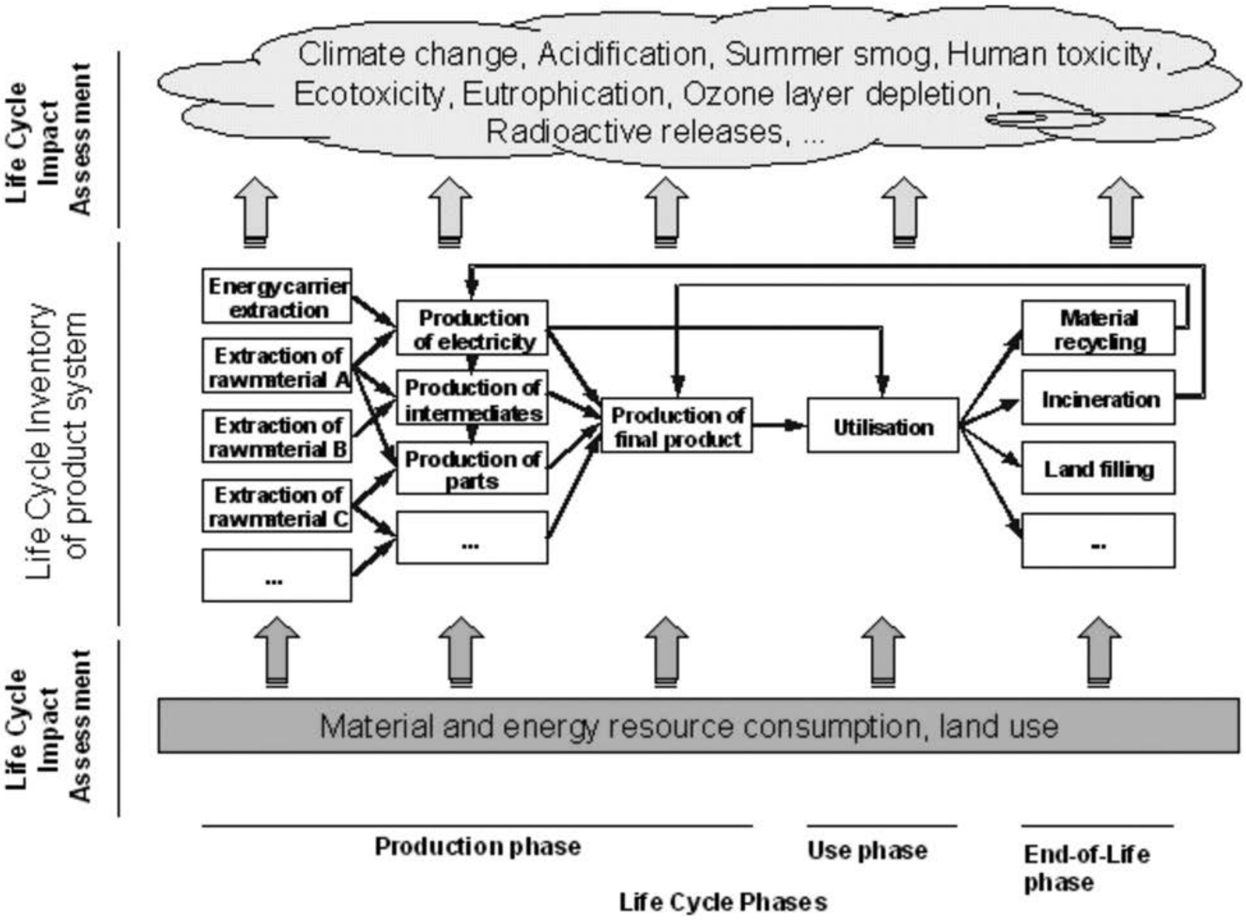


Figure 2: Scheme of a product system's life cycle with data collection of product and waste flows and resources and emissions followed by the impact assessment of the emissions and resource consumption.

French parquets LCAs have been made according to the ISO 14040, ISO 14044 and NF P 01-010 standards. These standards give some rules for the establishment of a LCA. It guarantees that results can be checked and are reliable. ISO 14040 defines four mains steps for a LCA (Figure 3):
- Goal and scope definition,
- Inventory analysis,
- Impact assessment,
- Results interpretation.

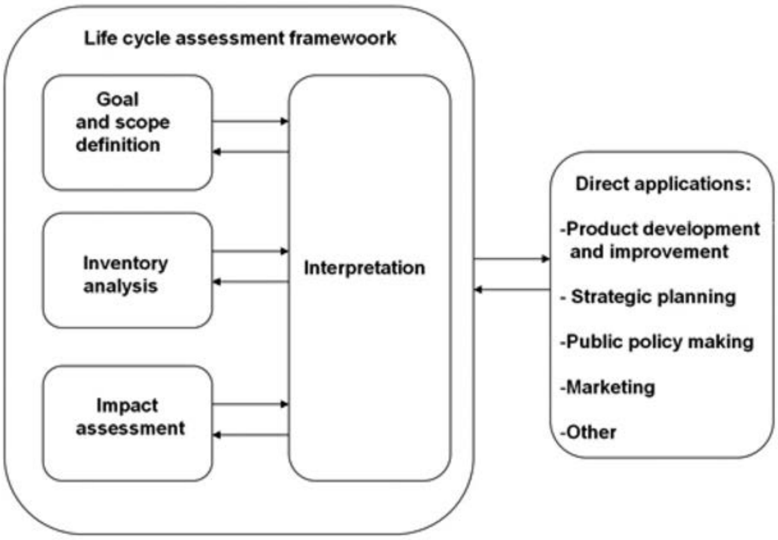


Figure 3: The 4 steps of the LCA.

The first step of the LCA is to define the goal and scope: the functional unit, system boundaries and methodological choices.

Two types of parquets were studied: a solid oak parquet and a multi-layer parquet. Table 1 summarizes the characteristics of the two parquets under study.

Table 1: Characteristics of studied parquets.

Parquet	Type	Thickness	Construction process	Glue	Finish	Service life
Solid wood	Oak	23 mm	Nailed to sleepers	-	Acrylic varnish	100 years (including 6 renovations)
Multi-layer	**Veneer :** oak (3.2 mm) **Core** : 77% HDF panel + 23% plywood (9 mm) **Counter face veneer :** 83% softwood (2 mm) + 17% exotic (1 mm)	13-14 mm	Floating on a PET sub-layer	UF	Acrylic varnish	45 years (including 2 renovations)

The service life of parquets is related to the thickness of the wear layer and the number of renovation. According to NF EN 13226 and NF EN 13489, parquets should be renovated 2 times at least. Functional unit chosen for the French parquets LCAs is 1 m² of parquet as defined in Table 1.

Functional unit is a quantitative performance which characterizes the product function. All the flows and impacts refer to this functional unit.

The parquets life cycle has been divided into five steps: production step, transport to the construction site, construction process, use stage, and end of life. Figures 4 and 5 respectively describe the life cycle and system boundaries of solid parquet and multi-layer parquet.

Data for the solid parquet production were collected from 3 sawmills and 4 parquetries. The amount of solid parquet produced by these companies represents 56% of the UFFEP French parquet production.

Data for the multi-layer parquet production were collected from 2 sawmills and 5 parquetries. The amount of multi-layer parquet produced by these companies represents 100% of the UFFEP French parquet production.The data collected correspond to the production of years 2008 and/or 2009. Data collection was based on a specific questionnaire, site visits, phoning and mailing. Collected data corresponded to materials consumption, energy and water consumption, emissions and waste.

Concerning forestry and harvesting for oak, data come from the FCBA (2011) LCI (Life Cycle Inventory) database according to tree species and specific mechanization rates. Generic data used in this study come from global databases such as Ecoinvent and DEAMtm.

Finally the LCAs have been verified by a third party according to AFNOR verification program.

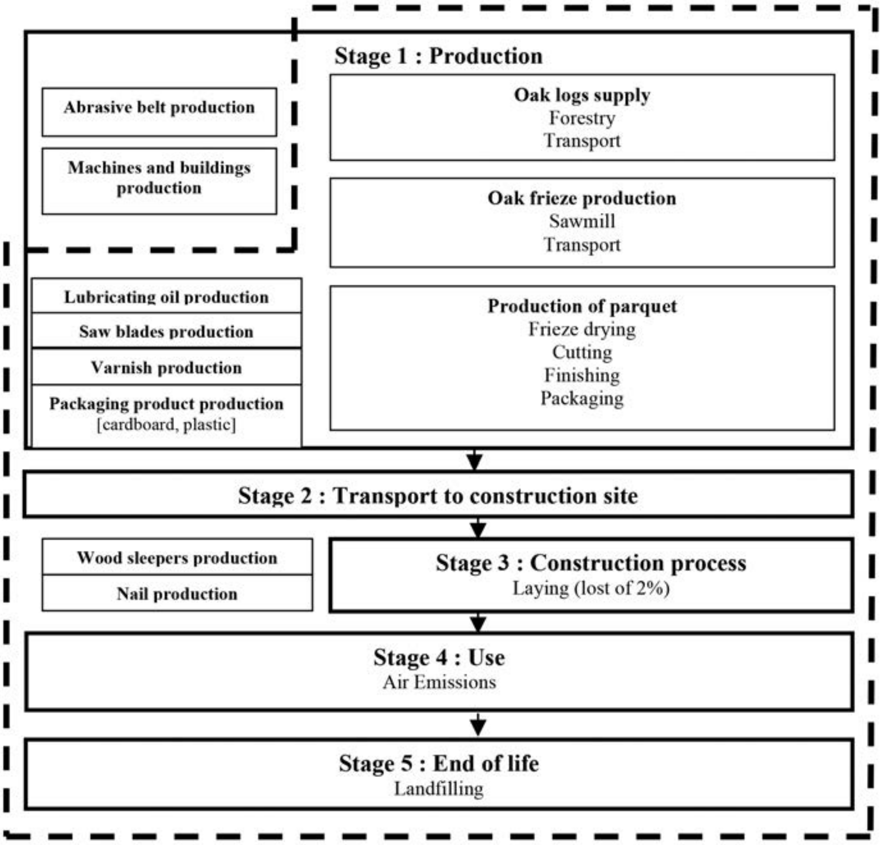


Figure 4: Life cycle and system boundaries of solid parquet (System boundary).

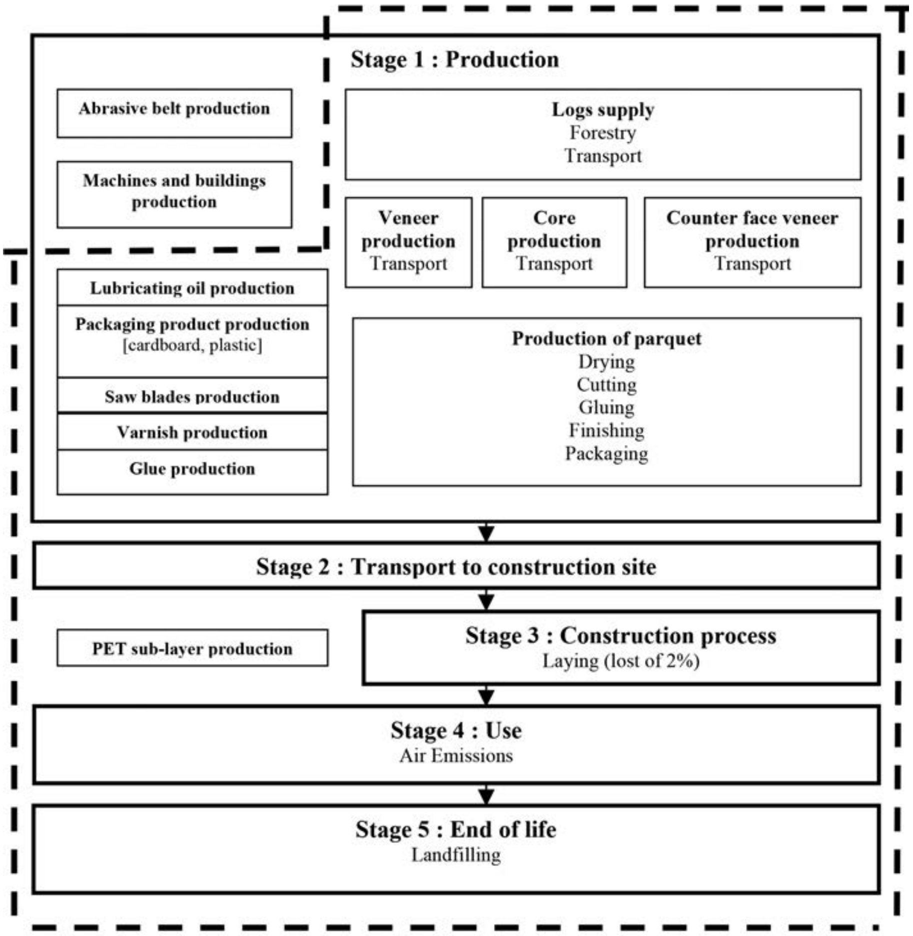


Figure 5: Life cycle and system boundaries of multi-layer parquet (System boundary).

3. RESULTS AND DISCUSSION

Many results have been obtained in this study. In this paper, the most important results are presented about energy, climate change and some other indicators.

3.1. ENERGY INDICATORS

Regarding energy aspects in LCA, there are two types of energy:

- Consumed energy (burned) by the process (processing, transport, heating, ...) called fuel energy,
- Energy contained in the material called feedstock energy, which corresponds to a mobilization of a raw material with a calorific value.

These energies, whether feedstock or fuel, may either come from renewable or from non renewable sources (Figure 6 and Table 2):

- Renewable energy (RE) comes from renewable resources like wind or biomass,
- Non renewable energy (nRE) comes from fossil resources such as oil, uranium, coal or natural gas.

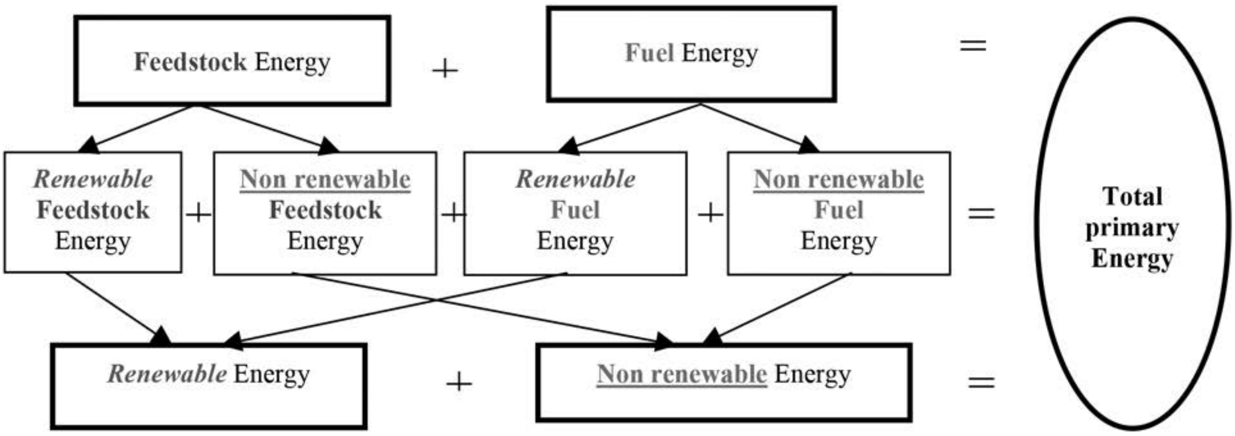


Figure 6: Energy indicators in LCA.

Table 2: Energy results for French parquets.

	Total primary energy (MJ/m²)	Renewable energy (MJ/m²)	Non renewable energy (MJ/m²)	Feedstock energy (MJ/m²)	Fuel energy (MJ/m²)
Solid oak parquet total LCA	868	547	321	429	439
Solid oak parquet per year (100 years)	8.68	5.47	3.21	4.29	4.39
Multi-layer parquet total LCA	659	328	331	210	448
Multi-layer parquet per year (45 years)	14.6	7.28	7.35	4.67	9.97

The consumption of renewable energy represents 50% of the total energy requirement for the multi-layer parquet and 63% for the solid oak parquet.

Table 3 shows the repartition between the different stages of the parquets life cycle.

Table 3: Stages contribution for renewable and non renewable energy indicators.

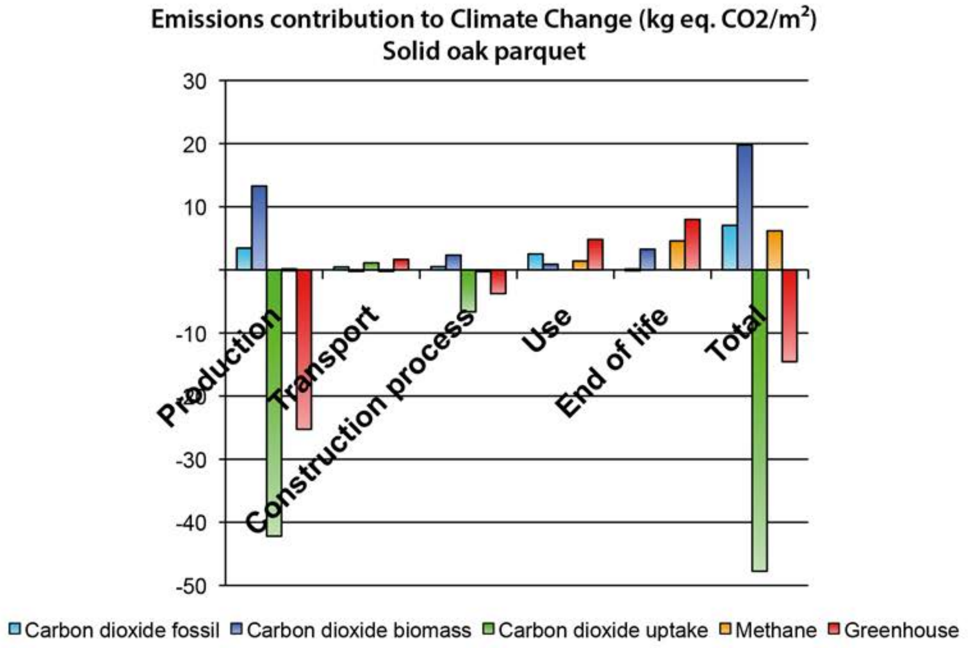
		Production	Transport	Construction process	Use	End of life
Solid oak parquet	Renewable energy	85%	2%	12%	1%	0%
	Non renewable energy	58%	3%	7%	31%	1%
Multi-layer parquet	Renewable energy	95%	2%	3%	0%	0%
	Non renewable energy	86%	3%	1%	10%	0%

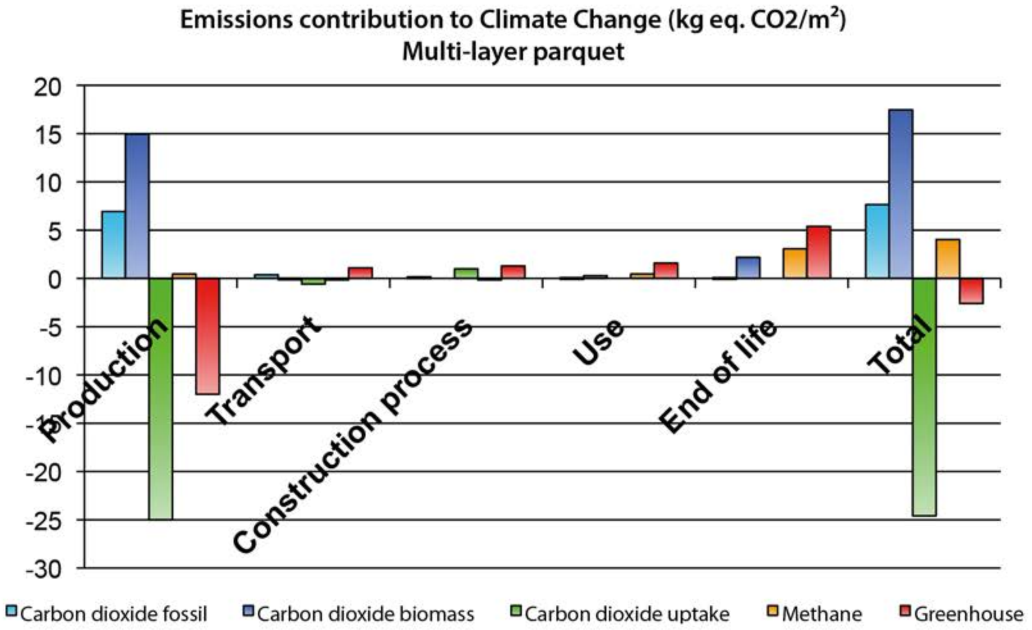
The analysis step by step of the life cycle shows that the production stage is the most impacting for the energy indicators, followed by renovation during use stage concerning non renewable energy. For solid oak parquet, the construction stage with the use of wood sleepers and nails also contributes to energy consumption.

3.2. GLOBAL WARMING INDICATOR

Contrary to minerals or fossil fuel based materials, wood molecules are the result of photosynthesis which is the transformation of carbon dioxide molecules into organic matter using solar energy. As a result, the growth of the tree captures carbon dioxide from the air. In the LCA methodology, this carbon uptake can correspond to an input or a negative emission. The uptake and emissions of carbon biomass were accounted for in this study, because the balance between uptake and emissions was not equal to zero. In the NF P01-010 standard, the reference scenario is landfilling. For wood, degradation in anaerobic conditions is incomplete and carbon contained in the product is stored for an indefinite time. A bibliographical review has been performed based on different publications, including Barlaz (2006), and an average value has been found of 15% degradation rate for wood products.

The global warming indicator includes the greenhouse gases emissions from fossil origin and biomass origin. The biomass part is stable and negative thanks to “definitive” storage of biomass carbon from parquet landfilling at the end of life. The result of the total climate change indicator is negative: -2.64 kg eq. CO_2/m^2 for multi-layer parquet and -14.5 kg eq. CO_2/m^2 for solid oak parquet.





Figures 7 and 8: Main emissions contribution to climate change.

The analysis step by step of life cycle shows that, whatever the type of parquet, the production stage (with energy consumption) and the end of life are the most impacting on climate change.

3.3. OTHER INDICATORS

Table 4 gives results for other LCA indicators.

Table 4: Other impacts results.

	Water consumption (litres / m^2)	Acidification (kg eq. SO2 / m^2)	Photochemical oxidation (kg eq. C2H4 / m^2)	Abiotic depletion potential (kg Sb / m^2)	Eutrophication (kg eq. PO43- / m^2)
Solid oak parquet total LCA	73.3	0.0699	0.0584	0.0652	0.000844
Solid oak parquet per year (100 years)	0.733	0.0007	0.0006	0.0007	8.44 E-6
Multi-layer parquet total LCA	74.6	0.0694	0.0269	0.0819	0.0011
Multi-layer parquet per year (45 years)	1.66	0.0015	0.0006	0.0018	2.46 E-5

For all other indicators, production is also the more impacting stage.

4. CONCLUSIONS

Thanks to this study, eco-profiles of French parquets were established and two EPDs are now available in the INIES database.

One important result is the negative value of the global warming indicator, thanks to the carbon uptake of the wood.

The analysis step by step of life cycle shows that for most indicators, and whatever the type of parquet, the production stage is the most impacting.

To reduce the environmental impacts of parquets, we recommend reducing the production's energy consumption, increasing the part of certified wood and wood yields, and improving the efficiency of the boilers used for wood waste recovery.

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LIFE CYCLE INVENTORY OF HARDWOOD (*EUCALYPTUS*) PRODUCTION IN THE PORTUGUESE FOREST

JOSÉ V. FERREIRA* AND IDALINA DOMINGOS
CENTRO DE ESTUDOS EM EDUCAÇÃO, TECNOLOGIA E SAÚDE, ESTGV, INSTITUTO POLITÉCNICO DE VISEU,
CAMPUS POLITÉCNICO DE REPESES, 3504-510 VISEU, PORTUGAL. TEL: +351232480500; FAX:+351232424651
*CORRESPONDING AUTHOR: JVF@ESTV.IPV.PT

Keywords: Portuguese hardwood, *Eucalyptus*, wooden products, ecoinvent database, life cycle impact assessment (LCIA).

ABSTRACT

The aim of this work is to generate generic life cycle inventory data for Portuguese hardwood *(Eucalyptus)* as material and as fuel. The environmental impact comparison of Portuguese hardwood with the ecoinvent hardwood (beech) is presented as well. The "ecoinvent" database was used where the principal assumptions were changed to include the Portuguese situation. New economic allocation and correction factors to include mass, energy, and carbon dioxide uptake from nature were calculated forming the new inventory tables for round, industrial, and residual wood (Portuguese *Eucalyptus*). The Ecoindicator99 method was chosen to assess the environmental impact and to check the influence of the data adaptation on the life cycle impact assessment (LCIA) final results. The study shows that differences exist between ecoinvent and Portuguese data for the hardwood production in relation to tree species, yield of forest and time from planting trees to final harvesting, length and width of forest roads or total area and land use. The life cycle impact assessment results are similar to round wood but completely different for other kinds of hardwood: Portuguese industrial and residual wood are worse than ecoinvent industrial and residual wood.

1. INTRODUCTION

In Portugal´s mainland, according to data of the 5th National Forest Inventory (DNGF, 2010), the *Eucalyptus* forest covers an area of 740x10^3 ha, representing 23% of all forest stands and 34.7 % of hardwood species in the country. In volume terms, the *Eucalyptus* represents 51% of the total volume of hardwood species. The main species of *Eucalyptus* existing in the country is *Eucalyptus globulus* originated in Australian and Tasmania and used mainly as raw material in the pulp and paper industry (Mendes et al., 2004). Some important data for *Eucalyptus* in Portugal are given in the Tables 1, 2 and 3.

Table 1: Volume, biomass and carbon stored in Portuguese hardwood stands (Source: DNGF, 2010).

Type of Stands	Total Volume Stored ($x10^6 m^3$)	Total Biomass ($x10^6$ ton)	Carbon (C) Stored ($x10^6$ ton)	CO^2 Equivalent ($x10^6$ ton)
Eucalyptus	45.828	36.252	18.126	66.462
Cork oak	24.773	34.925	17.463	64.029
Holm oak	7.566	10.671	5.336	19.564
Other hardwoods	11.882	14.639	7.321	26.839

Table 2: Wood production in Portuguese *Eucaliptus* stands (Source: DGRF, 2006).

	Wood Production ($x10^6$ m^3/yr)		
Function Type	Sawmill	Milling	Biomass for Energy
Quantity	0.1	6.3	0.2
Unit price (€)	40	25	20
Price per function type ($x10^6$€)	4	157.5	4

Table 3: Yield of Portuguese *Eucaliptus* stands (Source: DGRF, 2006; Louro *et. al.*, 2010; Almeida, 2008; Madeira *et. al.*, 2002; Cunha, 2002).

	Yield	
Rotation Length (years)	(m^3/ha.yr)	(m^3/ha)
12	10	120

2. MATERIALS AND METHODS

The "ecoinvent" database (Werner et al., 2007) was used where the main assumptions were changed to include the Portuguese situation.

At the first time, new economic allocation and correction factors to include mass, energy, and carbon dioxide uptake from nature, were calculated.

The new inventory tables for round, industrial, and residual wood (Portuguese *Eucalyptus*) were formed.

The software "SimaPro 7.3.3" (Pré, 2012) was chosen to form the new inventory tables and the "Ecoindicator 99 H/A" method was chosen to check the influence of the data adaptation on the life cycle impact assessment (LCIA) final results.

Most of the data came from the Portuguese studies, but some of them were taken from the "ecoinvent" database, particularly data relating to forest processes.

The land use for hardwood production and forest processes were calculated according to information and assumptions given in Table 4.

Table 4: Land use for Portuguese hardwood (*Eucalyptus*) production and forest processes (adapted from Werner et. al. 2007).

Nr.	Assumption	Unit	Portuguese Hardwood (*Eucalyptus*)	Source	Refers to	Comment
1	Yield	m^3/ha	120	Calculated	Total area including forest roads	Incl. 12% (v/v) bark in total yield
2	Time from planting trees to final harvesting	Years	12	Almeida, A., 2008		
3	Forest road length	m/ha	71.3	Faias et. al. 2007	Total area including forest roads	
4	Forest road width	m	3.5	Florestar, 2007		
5	Forest road area	m^2/m^2	0,0250	Calculated based on (3) and (4)	Total area including forest roads	
6	Yield	m^3/m^2	0,012	Calculated based on (1)	Total area including forest roads	
7	Yield	m^3/m^2	0,0123	Calculated based on (5) and (6)	Forest area excluding forest roads	
8	Land use forest	m^2/m^3	81.3	Calculated based on (7)	Total yield (including bark)	Without forest roads
9	Land use forest roads	m^2/m^3	2.1	Calculated (5)/(6)	Total yield (including bark)	
10	Land occupation forest	m^2yr/m^3	975.6	Calculated (2)x(8)	Total yield (including bark)	
11	Land occupation forest road	m^2yr/m^3	25	Calculated (2)x(9)	Total yield (including bark)	

The following decisions have been made: hardwood is represented by *Eucalyptus*, bark mass equals 12% of hardwood's mass, density for round hardwood is assumed to be 791 kg/m^3 (dry matter) (calculated from Table 1)

The allocation and correction factors to attribute the environmental impacts to the coproducts were calculated according to the method presented in Table 5.

Table 5: Allocation procedure.

	(1) Amount (m^3)	(2) Economic Value (€/m^3)	(3) Revenue (€)	(4) Allocation Factors (-)	(5) Correction (per amount) (m^3)	(6) Correction (per 1 m^3 of wood) (m^3)
Round wood	0.015	40	0.61	= 0.61/25.1=0.024	= 0.015 - 0.024 = - 0.009	– 0.595
Industrial wood	0.955	25	23.86	= 23.86/25.08=0.952	= 0.955- 0.952= 0.003	0.003
Residual wood	0.03	20	0.61	= 0.61/25.1=0.024	= 0.03- 0.024= 0.006	0.202
Total	1.00		25.08			

The allocation procedure was based on the following three parameters: the amount of the given co-products; the economic value of the given co-products; the revenue.

Amount and economic value of round, industrial and residual wood were obtained from Table 2. The following decisions have been made: round wood is represented by sawn wood; industrial wood is represented by milled wood; and residual wood is represented by biomass for energy.

The correction factors can have a positive or negative value and are expressed in the same unit as the amount of wood is expressed in [m^3] because the correction depends on correcting (adding or deducting) the final amount of wood by the value of correction factor.

The flows for "hardwood, standing, under bark, in forest" and flows for "hardwood, stand establishment / tending / site development, under bark" were calculated. Finely, process "softwood, thinning/final cutting, under bark" that delivers the three co-products was calculated and the results are presented in Table 6.

Table 6: Flows for "hardwood, thinning/final cutting, under bark" (adapted from Werner et al., 2007).

Inputs from Technosphere (Module Name)	Remarks	Allocation	Units	Mean value	Source
Hardwood, standing, under bark, in forest	Under bark (1.12 m3 wood including bark		m^3	1.00	Werner et al., 2007
Hardwood, stand establishment / tending / site development, under bark	Under bark		m^3	1.00	Werner et al., 2007
Diesel, burned in building machine			MJ	45.4	Werner et al., 2007
Power sawing, without catalytic converter			H	0.148	Werner et al., 2007
Trailer, production	Assumption: trailer is in use for 15 minutes	To residual wood: 2.5%; to industrial wood: 97.5% (according economic value)	kg	0.417	Adapted from Werner et al., 2007
hardwood, allocation correction, 1	Adds / subtracts the amount of CO2 uptake, resource consumption and embodied energy that is lacking / too much according to economic allocation	100% to residual wood	m^3	0.007	Calculated
hardwood, allocation correction, 2		100% to industrial wood	m^3	0.003	Calculated
hardwood, allocation correction, 3		100% to roundwood	m^3	-0.010	Calculated
Out-puts					
Residual wood, hardwood, under bark, u=80%, at forest road	Under bark		m^3	0.03	Table 5
industrial wood, hardwood, under bark, u=80%, at forest road	Under bark		m^3	0.955	Table 5

The mean values of the hardwood, allocation correction, factors 1, 2 and 3, are calculated based on the corresponding correction (per amount) value from Table 5 multiplied by 1.1 (wood including bark).

3. RESULTS

The results presented in Table 6 are used to obtain the inventory tables for the production of 1 m^3 of different sorts of hardwood: round, industrial, and residual hardwood. The results of the calculations are presented in Table 7.

Table 7: Inventory table for production of 1 m^3 round, industrial and residual hardwood (*Eucalyptus*).

Inputs from Technosphere (per 1 m^3 of wood)	Units	Round Hardwood	Industrial Hardwood	Residual Hardwood
Diesel, burned in building machine	MJ	72.4	45.3	36.2
Power sawing, without catalytic converter	H	0.236	0.148	0.118
Hardwood, stand establishment/tending/site development, under bark	m^3	1.595	0.997	0.798
Hardwood, standing, under bark, in forest	m^3	1.595	0.997	0.798
Hardwood, allocation correction, 3	m^3	-0.666	0.0034	0.226
Trailer, production	Kg		0.426	0.348

The results of the inventory table are entered into the life cycle assessment (LCA) software SimaPro 7.3.3 (Pré Consultant, 2012) in order to perform the impact assessment. The Ecoindicator 99 H/A was the method chosen to assess and compare the environmental impact of Portuguese (PT U) hardwood (*Eucalyptus*) with the ecoinvent (RER U) hardwood (beech). The choice of the LCIA method is rather arbitrary and does not play a key role in the presented analysis. Final results of process comparison are presented in Figure 1.

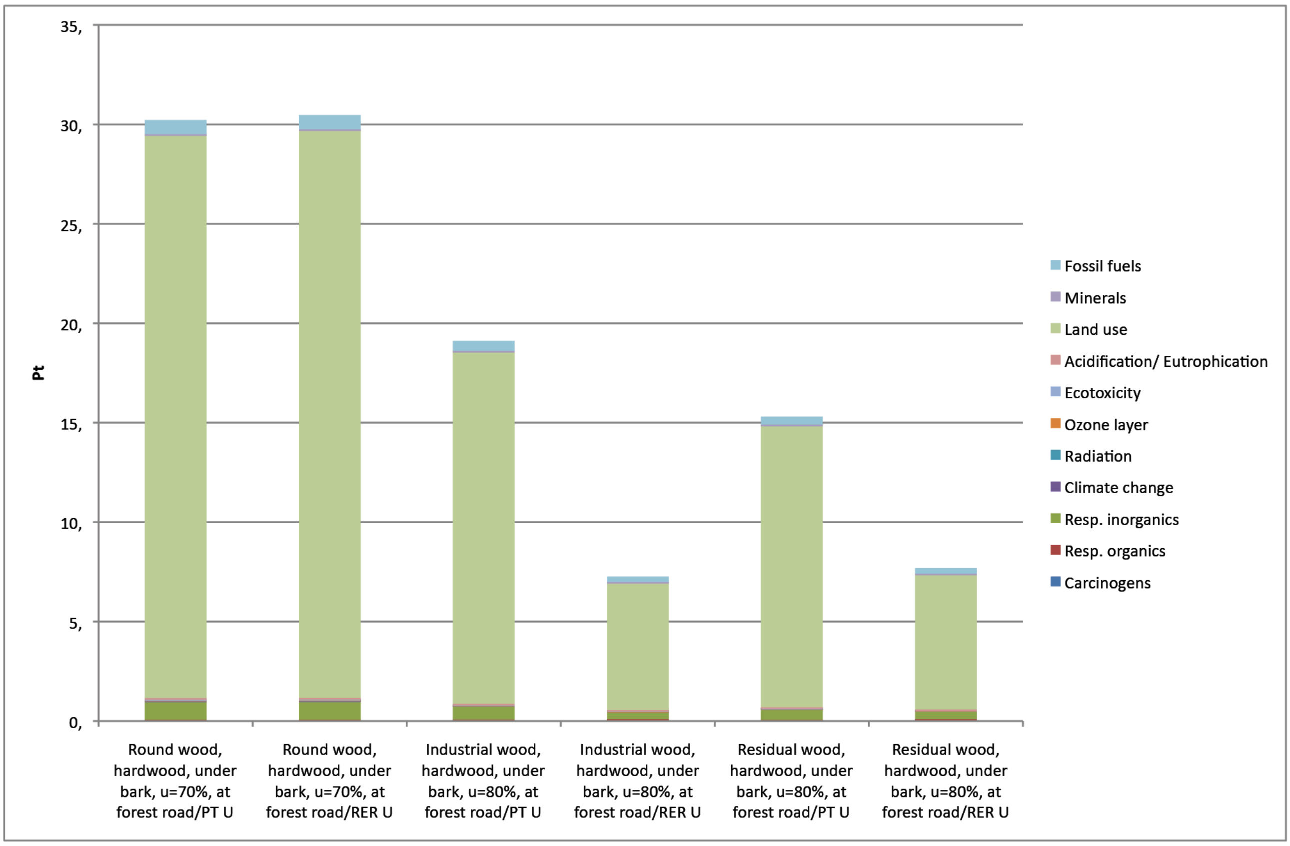

Figure 1: Comparing processes: Portuguese hardwood (*Eucalyptus*) (PT U) vs. ecoinvent hardwood (beech) (RER U); Method: Eco-indicator 99 (H) V2.08 / Europe EI 99 H/A / Single score.

Figure 1 shows that the life cycle impact assessment results are similar to round wood but completely different for others sorts of hardwood: Portuguese industrial and residual wood are worse than ecoinvent industrial and residual wood.

Portuguese industrial wood are worse than ecoinvent industrial wood in all impact categories except for *carcinogens* and *minerals*, where the opposite is true. Portuguese residual wood is worse than ecoinvent in most impact categories except for *carcinogens*, *ecotoxicity* and *minerals*, where the opposite is true. The main discrepancy between Portuguese and ecoinvent results lies in land use.

4. CONCLUSIONS

Three co-products are produced in forest processes: round wood, industrial wood, and residual wood.

At forest road, the environmental impact of Portuguese round, industrial and residual wood, hardwood (*Eucalyptus*), presents 99%, 263% and 199% of the environmental impact of ecoinvent round, industrial and residual wood, hardwood (beech), respectively.

The following reasons probably contributed to obtaining such results: a relevant difference in the yield of beech (784 m^3/ha) and *Eucalyptus* (120 m^3/ha); the time from planting trees to final harvesting (150 years for beech and 12 years for *Eucalyptus*); length and width of forest roads; different amounts and economic values of the particular co-products are attributed in the ecoinvent and Portuguese situation.

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THE ROLE OF ENVIRONMENTAL MANAGEMENT IN THE WOOD INDUSTRY

MARIA ALZIRA DINIS
CIAGEB - GLOBAL CHANGE, ENERGY, ENVIRONMENT AND BIOENGINEERING RDID&D UNIT, FACULTY OF SCIENCE AND TECHNOLOGY,
FERNANDO PESSOA UNIVERSITY, 4249-004 PORTO, PORTUGAL.
CORRESPONDING AUTHOR: TEL: +351-2250 71300; FAX: +351-2255 08269; MADINIS@UFP.EDU.PT

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ABSTRACT

We know that increasing prices of oil, gas and electricity are clearly a great challenge for local industries. On the other hand, in response to climate changes, international legislation has been emphasizing the use of renewable energy resources in Europe. Incentive-based policies, including carbon and fuel taxes will increase the cost of non-renewable fuels, decreasing fossil fuels consumption. Putting a price on greenhouse-effect gases is a reality nowadays, although the European emissions trading system is still relatively recent. At the same time energy efficiency is expected to increase 20% by 2020. Wood resources may then strongly contribute to that goal. In order to achieve it, it is necessary to concentrate the existing expertise and to guarantee the commitment of stakeholders. Energy production requires raw materials to be readily available. Usually, experienced managers are involved in the procurement of fuels. To fulfill the customer's orders, to minimize the production cost and to achieve an efficient delivery sequence are not easy tasks, since it is often necessary to balance the three goals. At the same time, the use of local wood energy resources can help to achieve rural communities development, reducing transport costs and allowing affordable energy to be used and new local tailored markets to be created. In this paper several aspects involving the forest industry are discussed; procurement issues, sustainable development and environmental impacts, are all part of the same aim.

1. **INTRODUCTION**

It is a fact that the central role of business has extended to the political and social actor, and it does not also concern the traditional economic actor role (Li and Toppinen, 2011). As a society, our perception today is that together with economic assessments, the environmental and social impact of business operations must be clearly integrated into decision-making strategy (Christmann, 2004). In US, Europe and Asia, a new consciousness has emerged in terms of social responsibility (Krumsiek, 2003), indicating the need to perform organizational changes in corporate management (Kell, 2003).

According to Li and Toppinen (2011), the forest-based industry, among several other environmentally sensitive factors, has an important role in global sustainable development due to the raw material basis and to industry globalization. Businesses have the obligation to society to operate in ways socially responsible and beneficial. The interaction between stakeholders and other interests is important in the way the forest industry may position itself. A participatory stakeholder approach is also an important step for optimizing the interaction between human and ecological systems (von Geibler et al., 2010).

The main aim of an environmental management system lies, in the assessment of company´s significant environmental aspects, and the interaction the company develops with the environment (Koskela, 2011). That will allow companies to improve their environmental performance. ISO 14000 standard family (ISO, 2004a; ISO, 2004b) defines environmental impacts and environmental aspects, among other terms. While environmental aspects are understood as the ones able to cause environmental changes, environmental changes or impacts may be positive or negative and are caused by activities of a company, affecting water, air or soil (ISO, 2004a) and its identification is crucial (Zobel and Burman, 2004). Significant environmental aspects cause significant environmental impacts (ISO, 2004b). Guidance relating the identification of significant environmental impacts can be found in the ISO 14000 family (ISO, 2004a; ISO, 2004b). Companies clearly need to measure environmental aspects and impacts in order to improve decision-making for the environment, and that demands reliable information (Jasch, 2000). According to Koskela (2011), several different frameworks were developed in order to allow the selection of adequate environmental indicators. In the forest industry, as well as in other kinds of industries, the measurement of top environmental impacts is an essential tool in environmental management. The study conducted by Koskela (2011) through expert interviews covering the Finnish forest industry revealed that the most often mentioned environmental impacts are related to water, energy, air and climate change. Also considered to be the most significant were energy, air and water emissions. The most often mentioned positive environmental impacts were recycling, forest industry products and the use of energy. The author emphasizes that environmental impacts referred were in fact environmental aspects.

Worldwide anthropogenic greenhouse gas (GHG) emissions must be cut in order to limit global warming (Vanneste et al., 2011). In response to that preeminence goal, international legislation, mainly European, relating this concern has come out (European Commission, 2006, 2008, 2009a,b). European Union (EU) aims at achieving a share of 20% renewable energy in 2020 (Eurostat, 2009). According to the International Energy Agency (2008), bioenergy is the largest renewable energy contributor to global primary energy as has the highest potential of all renewable energy sources. Wood plays an important role in this category. It is still the most important energy source for cooking purposes in underdeveloped world (Vanneste et al., 2011). Several studies cited by Vanneste el al. (2011) show the environmental advantages of using wood compared to coal, also in terms of CO_2 emissions reduction. The EU Emissions Trading Scheme (ETS) stimulates the utilization of less carbon intensive fuels - like natural gas – over the use of carbon intensive fuels - as it is the case of coal.

The efficient use of raw materials is very important to the energy production industry. In that sense, forest procurement issues play a crucial role (Palander and Vesa, 2009; Palander, 2011a). The main aim can be achieved through the use of accurate information resulting from optimization methods. Other than mathematical formulations, also heuristics approaches are used. Integrated fuel procurement and energy production is essential to optimize a multiple objective model with conflicting decision principles like cost reduction and increased efficiency. All the procurement process depends on sequence dependencies within the supply chain, together with daily changes affecting the whole decision system (Palander, 2011a; Palander, 2011b). Managers must be able to quickly respond to these changes in real-time, updating their procurement program (Palander and Vesa, 2009). Doing it manually will not allow the decision maker to have time to be aware of all possible implications in the process, with negative consequences in terms of procurement schedules. However, and according to Palander and Vesa (2009) things are still done manually, despite the development of powerful information technology, still today. Since the energy industry as a whole is subject to legislation regarding training and efficiency, forest stakeholders will take benefit from procurement decisions based in holistic energy supply chain models (Palander, 2011a). At the same time, the cooperation of stakeholders is essential in terms of technology selection (Röser et al., 2011). Decisions require a combination of both mathematical formulations together with real-life problems that powerful information technology lacks to achieve. Heuristic approaches are also necessarily used (Palander and Vesa, 2009). Again, in the field of forest fuels procurement, there are daily changes in the supply chain for raw materials that affect the decisions being taken. The processes can be rather complicated and demand for experienced managers to act quickly. When a mixture of some very different material is used, procurement tasks may become rather complicated and the scheduling is too difficult to be handled manually (Palander and Vesa, 2009). Nordic countries, which are so strong in the forest industry field, have thus necessarily developed wood procurement over the last three decades (Mikkonen and Leinonen, 2003).

According to Röser et al. (2011), a key constraining wood fuel market development is confidence. Users lack confidence in and knowledge about existing supply chains and its development will not proliferate in those countries where there is still no further evidence on demand for wood fuels. Supply chains need to be tailored to fit to local circumstances and conditions, as well as the quality of the forest fuel to be produced, and cannot be simply transferred from one country to the other.

2. **SUSTAINABILITY ISSUES**

As mentioned earlier, a very important aspect of the forest industry has to do with corporate responsibility. As seen, the forest-based industry plays a crucial role in global sustainable development, also related with the enduring industry globalization. The Brundtland Commission characterized sustainable development as an intergenerational concept aimed at the continued satisfaction of human needs (United Nations, 1987). As human needs demand the capability of ecosystems to provide services, sustainable development can only be accomplished with the long-term continuity of socio-ecological interaction (von Geibler et al., 2010). Global consciousness relating environmental problems has increased and so, pressure on forest industries increases (Li and Toppinen, 2011). The current global rate of population growth, coupled to the per capita consumption patterns of people in developed countries reveals us that the Earth's carrying capacity (either in terms of resource availability and assimilative capacity for wastes and emissions) is inadequate and cannot sustain the model being pursued. The carrying capacity of Earth *is* finite (Petrie, 2007). Wood is an exceptional raw-material and forest businesses have the obligation to operate in socially responsible and beneficial terms and society defines its boundaries. That is accomplished when a company's intelligently interacts with the surrounding environment, resulting in increased efficiency in environmental performance (Li and Toppinen, 2011). The most perceptible physical environmental effects are caused by the materials and energy being used. The emissions and waste being produced are also directly related to that particular environmental issue. In terms of wood waste, there are studies which clearly show that the addition of wood waste during sewage composting is responsible for controlling the emissions of gaseous pollutants, namely CH_4 and CO_2 (Zigmontiene and Zuokaite, 2010).

We know the energy industry as a whole depends on policy decisions in terms of energy trading and energy efficiency regulation. These decisions are not easy and have to do with analyzing the driving forces behind renewable energy (Palander, 2011b). Sustainability of production systems is a crucial issue for governments, industries and society, particularly in the timber processing and manufacturing sector. With products based on renewable natural resources from forests, this sector is well placed to provide products that enhance long-term environmental, economic and social sustainability (Daian and Ozarska, 2009). Sustainability is a term that it is intuitively easy to understand but not easy to rigorously formalize. Usually it is linked to both ecological and economic perspectives but it may assume a multidimensional concept from the point of view of an industry (Voces et al., 2012). Ecological health, social harmony and economic efficiency are all part of a unified development philosophy (Petrie, 2007). Different kinds of indicators were used by Voces et al. (2012) in order to define the sustainability of an industry: economic, social and environmental types. Fourteen indicators aiming at including the different aspects of the value chain of the European wood manufacturing industry in terms of its sustainability value were used. Portugal figured in the middle term and Estonia was the country with the most sustainable wood manufacturing industry. Clearly, the results obtained directly depend on the indicators selection, as the authors acknowledge. It is important to place the resources sector at the heart of materials value chains, focusing on the role of networks and partnerships in enhancing its contribution to sustainability (Petrie, 2007). Value chains represent important causal links between human activity and environmental change, combining key driving forces for ecological change. The optimization of value chains is an important process to promote sustainable development, since they are conceived to the satisfaction of human needs and combine different driving forces for environmental change (von Geibler et al., 2010). According to the same authors, the development of indicators for an entire value chain must cover environmental, social and economic aspects and can be based on different framework models: dimension-based, policy objective-based, sector-based or cause-and-effect based models. These indicators will allow measuring the quality of decision-making for internal and external stakeholders.

3. ENVIRONMENTAL INNOVATION AND CONSCIOUSNESS

Alfranca et al. (2009) have said that the generation and distribution of knowledge through the innovation process is a basis to economic growth. Like several other industries, wood-based industry also uses some low complexity technologies subject to the markets (OECD, 2005a). In that sense, innovation may surely benefit this industry. OECD (2005b) defines innovation as the implementation of a new or significant improved product, or process, a new marketing or organizational method in business practices. On the other hand, environmental innovations consist in new products or processes aimed at avoiding or at reducing the costs to the environment. Forest certification was first defended by environmental groups as a response to the consequences of forest degradation and deforestation. Then it acted as a way to allow forest management to be sustainable and responsible (Leslie, 2004). A study from Chen et al. (2011) revealed that the motivations behind forest certification in China lied mainly on potential company gains. In this case, the results showed that the level of awareness and acceptance of forest certification was potentially low between wood products manufacturers in China. These results are, according to the same authors, similar to the ones found in Canada, The United States and Malaysia. By obtaining certification, manufacturers are more likely to maintain their current markets or enter more environmentally-conscious ones.

Resource extraction industries are generally characterized by very low conversion efficiencies, high energy intensities, high entropy wastes and emissions, and also by significant adverse environmental impacts – globally contributing to climate change. Petrie (2007) also emphasizes that without adequate awareness and consciousness, the social and environmental costs of continued resource consumption could outweigh the social benefits accomplished.

4. ENERGY REPERCUSSIONS

The transportation costs of each type of energy fuel are a key factor in the procurement industry. On the other hand, putting a price on the emissions of greenhouse gases was not a standard practice before but it will theoretically become increasingly important in the future (Palander and Vesa, 2009). In that sense, the evaluation of all these costs in the energy industry must be accounted for. The increasing prices of oil, gas and electricity strongly influences energy production industry. Wood fuel supply chains are an option to conventional fuels. The lack of confidence is important, since until there is a clear demand for wood fuels, which are creating a new market for wood, the process will not develop. In countries where a local energy source to produce heat and electricity at a competitive price is readily available it is possible to use forest fuels as a competitive source of energy. The quality of forest fuel to be produced is very important. Road transportation or carrying capacity of the soil are factors affecting the selection process, as well as the adequate combustion technology and forest fuel supply chain. We know that a local energy source of power allowing to produce heat and electricity at a sustainable basis will bring positive impacts on local industries and forest owners.

5. THE ENVIRONMENTAL MANAGEMENT CHALLENGE - CONCLUSIONS

The wood forest industry imperatives for sustainable development lie under its own assumed importance. The stakeholder role assumes particular importance since it represents the bridge between human needs and the environment. Environmental management is a tool in forest industry which has the ability to be used by companies in a social responsible way, in order to improve the decision process and allow to measure and control the generated environmental impacts. Social awareness relating sustainable development has evolved in our society and pressure on forest industry has increased lately. International legislation has also addressed this need and is becoming increasingly restricted in all areas relating environmental sustainability. It is now possible to define indicators to assess forest industry sustainability, allowing the measurement of its sustainability value. The optimization of value chains is, at that regard, another way to promote sustainable development.

Procurement issues constitute a fundamental part of the forest industry since the managers must be able to take decisions in real-time and that can only be made possible through the use of optimization software. Regarding this subject, it is also essential for stakeholders to perform a careful technology selection. We have seen before that innovation guided by knowledge leads to environmental control. It may assume many different aspects but it is also a road to sustainable development and social responsibility. In that sense, certification plays an important role, particularly in strong economic emerging nations, like China. At the same time, certification is interconnected with consciousness and one aspect leads to the other and vice-versa, as discussed in this text. It becomes quickly evident that it is not worth to continue acting without environmental consciousness, since it will not pay back.

Thus, the answers to some of the issues discussed in the text are clearly linked to environmental performance and, consequently, environmental assessment. Environmental management is unquestionably and undoubtedly an indispensable tool to achieve the desirable goals, since we have been able to conclude that Earth's carrying capacity *is* finite. We need tools to promote sustainable development, particularly in such an important industry as it is the forest industry case.

Energy is a key issue in our lives today. Its very diverse aspects strongly influence forest production industry, either in terms of transport, procurement issues, or even the resulting climate change consequences. The GHG issues represent one more aspect, between several possible others, to account for in environmental management and sustainable development. Forest industry may generate very different valuable products. In each one of them, the supply chain must me regarded in a sustainable way. Environmental protection and social development need both to be taken into account in terms of value chain, ensuring a fair return involving the forest industry items discussed above.

The theoretical concept of sustainability will only bring long-term success when translated into concrete recommendations, allowing achieving measurable results. That will only be possible when all major society intervenients continue to work together to develop effective strategies.

To conclude, it seems that everything needs to be tailored with a coherent approach to the stakeholder engagement and decision making. In fact, we have seen that reality has become increasingly complex and all discussed aspects are linked and cannot be looked at it in an isolated way. Environmental management comprehends all this.

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02. PLANTS AS SOURCES OF LIGNOCELLULOSICS AND CHEMICALS

ESTIMATED COST AND TIME IN COLLECTING FOREST BIOMASS

TELMA PINTO[1,*], JOSÉ LUÍS LOUSADA[2], GRAÇA LOURO[3], HENRIQUE MACHADO[3], LEÓNIA NUNES[1,2]
[1]AGRARIAN SCHOOL OF VISEU (ESAV) / POLYTECHNIC INSTITUTE OF VISEU (ISPV), PORTUGAL.
[2]CITAB UNIVERSITY OF TRÁS-OS-MONTES AND ALTO DOURO (UTAD), VILA REAL, PORTUGAL.
[3]AUTORIDADE FLORESTAL NACIONAL. LISBOA, PORTUGAL.
* CORRESPONDING AUTHOR: T.PINTO@LIVE.COM.PT

Keywords: productivity, balance, renewable energy, methods, biomass

ABSTRACT

Forest biomass is the sum of the biomass understory aboveground vegetation and biodegradable waste. Collecting these residues reduces the risk of wild fires and the cost of cleaning the forest stands. Also, these residues can be used in the production of energy and consequently open a window of economic profit. Studies about the working time necessary for each forest operation are important to estimate the associated costs and to study the viability of economic and energetic balance. In order to estimate the time spent on the complete cycle of the forest biomass exploration, each operation (baling, bundling, chipping, crushing, and shipping) was evaluated from the beginning to the final industry end users in *Mortágua*, *Águeda* and *Mangualde*, in Portugal The knowledge of these working times is essential to estimate the cost of each operation and to help in the determination of the economic and energetic balance. The data was collected based on continuous real time measurements. The productivity and the economic balance of each operation were calculated taken into account the costs and working time associated. The economic balance was the difference between the total cost of the sum of the operations and the final revenue. The results show a positive economic and energetic balance for all the studied areas.

1. INTRODUCTION

Biomass is the non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms (Ferreira et al., 2009). The forest residues are unused portions of trees like tops and branches left on the ground. These products have several advantages, the possibility to produce energy (bioenergy) being the most important one (Rapier, 2010).

Bioenergy (including forest biomass) is seen as one of the main options to mitigate the greenhouse gas (GHG) emissions and to substitute fossil fuel (Ribas et al., 2008). The Portuguese energy market is based on a large share of imported fuels (oil, coal, and natural gas). The inland energy production is small and it is mainly from renewable sources (Fernandes and Costa, 2010). An important disadvantage of using biomass as an energy resource could be the economic costs associated. To find those costs it is necessary to evaluate the extractive operations and the working time for each operation. So, studies about the viability of economic and energetic balance are necessary (Yoshioka et al., 2006).

The aim of this paper is to analyze methodologies and to obtain the working time and cost of the Forest Biomass (FB) exploration. The knowledge of these parameters is important to study the viability of these operations and to support the decisions by the economic agents. All the times for the necessary operations to extract the FB were measured in 5 sampling plots located in Mortágua, Águeda and Mangualde (Viseu and Aveiro districts) in Portugal. Then it was estimated the economic balance using the individual cost of each operation to calculate the economic balance of the global process and the viability of the process. The collected FB is used to produce energy, so it was elaborated an energetic balance concerning the machinery consumptions (fuel and oils) in all operations and the value of the final energetic production obtained from the energetic transformation of FB.

2. MATERIAL AND METHODS

The field work was developed in September and October of 2010, in 5 different sites located in the districts of Viseu (Mortágua and Mangualde) and Aveiro (Águeda) (Figure 1).

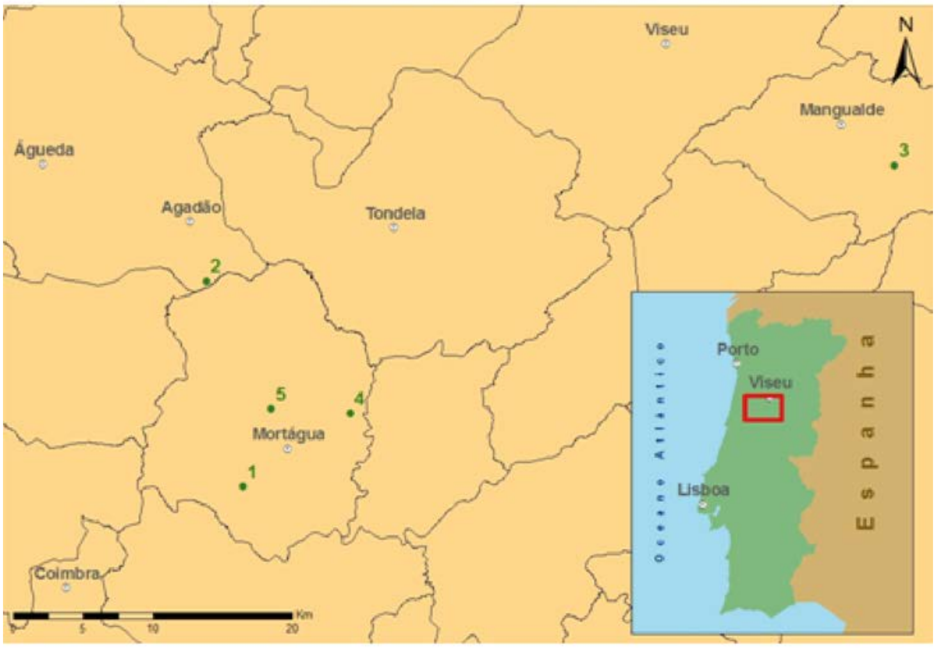

Figure 1: Location of the study area.

The data were collected based on continuous real time measurement. Using this method, it was guaranteed that every partial operation was noticed and registered in a sequential and precise way (CBE, 2008). The slope of each study site was measured in order to characterize each site, and verify its influence in the overall economic and energetic balance. Table 1 presents the parameters of the biomass collected, technical itinerary observed and the parameters measured during the fieldwork in each study site.

Table 1: Selected characteristics of the study area.

Site 1	***Site 2***
Location: district of Mortágua **Area**: 20.9 ha **Slope**: 20.9% **Transporting distance**:55 Km **Characteristics:** Branches and tops of *Eucalyptus globulus* trees. **Field observations**: *technical itinerary 1* Parameters measured and registered operations: *Bundling*, it was taken into account the number of bundles produced during the operation time; *Hauling*. number of bundles collected and operation time in each cycle (loading in a forest, running downward fully loaded on a strip road, unloading alongside a forest road and running upward with no load); *Loading*, it was considered the number of bundles and the time for each loading. The area was divided in terraces	**Location**: district of Águeda **Area**: 42 ha **Slope**: 12.5% **Transporting distance**:42 Km **Characteristics:** *Eucalyptus* trees with ages between 3 and 4 years, in final phase cut due to a *Gonipterus scutellatus* plague. **Field observations**: *technical itinerary 2a* Parameters measured and registered operations: *Hauling*, it was measured the time between each cycle; *Chipping*, it was measured the time of chipping each loading of hauling; *Loading*, it was measured the time needed to load a transportation truck.
Site 3	***Sites 4 e 5***
Location: district of Mangualde **Area:** 5 ha **Slope:** 10% **Transporting distance**:25 Km **Characteristics:** final cut in pine trees and cleaning of the underground vegetation, with leftovers of the understory and pine trees extraction leftovers (branches and tops). **Field observations**: *technical itinerary 2a* Parameters measured and registered operations: *Hauling*, it was measured the time of each cycle; *Chipping* and *loading*, it was measured the time of chipping and loading of a transportation truck.	**Location**: district of Mortágua **Area**: inferior to 1 ha in each site **Slope:** 12% in site 4 e 8% in site 5 **Characteristics:** final cut of Eucalyptus trees, with the leftovers of the wood extraction (branches and tops). **Field observations:** there wasn't identified any complete technical itinerary. Parameters measured and registered operations: *Hauling* and *chipping*, on study site 4 and *Hauling* on study site 5, it was measured the time of each hauling cycle and the associated phases and the time of chipping of each loading, in study site 4; and the time of extraction and associated phases in study site 5.

3. **RESULTS AND DISCUSSION**

Table 2 shows the results in productivity, time (for each operation and for the total in the site) and cost (for each operation and for the total in the site), for each study site and for all the operations. It was verified that the hauling productivity is greatly dependent on the machinery used for the job: in the study sites 1, 3 and 4, there was a forwarder with productivity greater than in study sites 2 and 5, where a tractor-trailer was the main equipment. Considering the chipping, it can be seen that, although the type of equipment is the same in all study sites – a Hussmann mill used in study site 4 leads to a higher productivity than the Willibald hammer mill used in study sites 2 and 3.

Table 2: Productivity (ton.h^{-1}), time spent (min.ton^{-1}) and cost (€.ton^{-1}) for each operation.

Site	Operation	Machine	Productivity (ton.h^{-1})	Time (min.ton^{-1})	System Total (min.ton^{-1})	Cost (€ ton^{-1})	System Total (€ ton^{-1})
1	Bundling	Baler	8.3	7.20	15.1	7.1	18.6
	Hauling	Forwarder	10.6	5.70		3.0	
	Load	Truck transporting with a derrick	27.0	13.00		0.9	
	Transport	Truck	-	-	-	7.58	
2	Hauling	Farm tractor - forest use	4.6	5.70	19.7	11.0	29.0
	Chipping	Mobile chipper (*Willibald*)	15.0	4.00		10.0	
	Load	Farm tractor with a derrick	22.3	2.70		1.0	
	Transport	Truck	-	-	-	7.0	
3	Hauling	Forwarder	15.0	4.00	10.0	4.1	12.9
	Chipping and Load	Mobile chipper (*Willibald)*	10.0	6.00		6.8	
	Transport	Truck	-	-	-	2.0	
4	Hauling	Forwarder	11.5	5.20	-	-	-
	Chipping	Mobile Chipper (*Hussman*)	30.4	2.00		-	
5	Hauling	Tractor-trailer	4.1	14.60	-	-	-

The load productivity seems dependent of the FB type and the load capacity. The load of FB in bundle type appears to be more efficient than the chip type and the productivity of this operation is related with truck load capacity. In site 1, the mean productivity was 27 ton.h^{-1}, using a truck with 22 ton of load capacity. In site 2, there was a productivity of 22 ton.h^{-1} with a truck of 7 ton of load capacity.

Concerning the time of the operations, the hauling is usually the slowest operation and the loading is the quicker. To carry out all operations necessary to extract 1 ton of FB, it was needed approximately 20 min in site 2, 15 min in site 1 and only 10 min in site 3. Concerning the associated costs, the site 2 was the most expensive (29 €/ton), then site 1 (18.6 €/ton) and site 2 was the less expensive (12.9 €/ton). It must be noticed that the transport distance was 77 km, 55 km and 25 km to the sites 1, 2 and 3, respectively.

The economic balance was calculated knowing the difference between the cost of all operations needed to extract FB and the revenue from FB (using the reference value of 30 €/ton). In Table 3 we can see that in the three study cases the economic balance is positive (11.4, 1.0 and 17.1 €/ton for the sites 1, 2 and 3, respectively).

Table 3: Economic balance.

Site	**1**					**2**					**3**			
	Bundling	Hauling	Load	Transport	**Total**	Hauling	Chipping	Load	Transport	**Total**	Hauling	Chipping and Load	Transport	**Total**
Costs (€ ton $^{-1}$)	7.1	3.0	0.9	7.6	**18.6**	11.0	10.0	1.0	7.0	**29.0**	4.1	6.8	2.0	**12.9**
Revenue (€ ton $^{-1}$)	30													
Balance (€ ton $^{-1}$)	11.4					1.0					17.1			

To calculate the energetic balance it was taken into account the fuel and oil specific consumption in each operation to produce 1 ton of FB and its energetic conversions (MJ.ton^{-1}). The heating value of oil is 46 MJ.L^{-1} and the *Eucalyptus* wood heating value is 17500 MJ.ton^{-1}(Luger et al., (s/d)). Table 4 presents the fuel consumption and the energy necessary to produce 1 ton of FB, in sites 1 and 2.

Table 4: Fuel consumption and energetic equivalent in each operation and energetic balance.

	Site 1		**Site 2**	
Operation	Fuel Consumption (l/ton)	Energy equivalent (MJ/ton)	Fuel Consumption (l/ton)	Energy equivalent (MJ/ton)
Bundling/Chipping	2.1	96.6	2.5	115.0
Hauling	1.1	50.6	1.1	50.6
Loading	0.4	18.4	0.4	18.4
Transportation	3.5	161.0	1.6	73.6
Total	7.1	326.6 (a)	5.6	257.6 (a)
Eucalypt calorific power		17500.0 (b)		17500.0 (b)
Global Balance (b)-(a)		+17173.4		+17242.4
Power station production (1/3 (b))		5833.0 (c)		5833.0 (c)
Balance (c)-(a)		+5506.4		+5575.4

To produce 1 ton of FB containing 175000 MJ of energy it was consumed 326.6 MJ (site 1) and 257.6 MJ (site 2). Therefore, and if it was possible to use all BF energy content, the balance was +17173 MJ and +17242 MJ in site 1 and 2 respectively. However, just about 1/3 of the energy contained in the FB can be used to produce electric energy. So, using this FB in a power plant to produce electricity, it is possible to achieve a smaller, but positive energetic balance (+5506 MJ and +5575 MJ to sites 1 and 2 respectively) (Moreira et al., 2010).

4. CONCLUSIONS

The objective of this study was to estimate the productivity of all the operations that take place during the forest biomass harvest. This study also compared the technical itinerary of each study sites with different geological characteristics, distance to end users and type of forest biomass.

The time and cost measured on each study site indicated that site 2 and 3 have different results concerning the total cost of 1 ton of forest biomass. Operations in study site 2 are less efficient because they are slower (about 20 min) and with a higher cost: 29 €.ton^{-1}. Site 3 is the most efficient (it only takes 10 min) with a lower cost: 12.9 €.ton^{-1}. These factors, time and cost, are important to support the decision of which process is better for each location, taking into account the forest biomass type and the operations required.

The energetic and economic balance results indicate the feasibility of the forest biomass extraction, having into account different characteristics of each site (type of biomass, machinery and technical itinerary).

It can be concluded, from the collected data, that there is a positive economic balance in all the situations studied. Study site 3, the closest to the end user, has a higher value (17.1 €.ton^{-1}). A comparison between study site 1 and 2 demonstrate that site 2 has a lower economic balance (1 €.ton^{-1} compared to 11.1 €.ton^{-1}), although it is closer to the end users. The difference between the economic balance of the study site 1 and 2 can be explained by the differences in the geological characteristics and the type of forest biomass.

Regarding the energetic balance, the study sites 1 and 2 have the highest and lowest energy consumption, respectively: site 1 consumes 326.6 MJ.ton^{-1} and site 2 consumes 257.6 MJ.ton^{-1}.

Harvesting the forest biomass is positive within the scope of this study. However, it will be necessary to study the economic and energetic feasibility of the forest biomass harvesting operations in several other locations in order to create a prediction model that could be used as a decision tool to the forest biomass harvesting industry.

5. ACKNOWLEGMENTS

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NEW PRODUCTS FROM HAZELNUT SHELL

L. P. CRUZ LOPES[1,*], J. MARTINS[2], B. ESTEVES[2], L. TEIXEIRA DE LEMOS[1]

[1] DPT. OF ENVIRONMENT, POLYTECHNIC INSTITUTE OF VISEU AND CI&DETS, VISEU, PORTUGAL

[2] DPT. OF WOOD ENGINEERING, POLYTECHNIC INSTITUTE OF VISEU AND CI&DETS, VISEU, PORTUGAL

* CORRESPONDING AUTHOR: PHONE: +351-232 480 636; FAX: +351 232-424 651; LVALENTE@ESTV.IPV.PT

Keywords: Ash, chemical composition, cellulose fibres, hazelnut shells, particleboard, pulp.

ABSTRACT

In this study the complete chemical characterization of hazel nut shells was made and cellulose, hemicelluloses, lignin, ash, tannins and proteins were determined. The cellulose fibers were isolated and characterized by XRD. Pulp was produced and analyzed by FTIR and ^{13}C NMR CP/MAS. Three layer particleboards were made using a urea-formaldehyde resin. The shells were tested in the core and face layers. Density (NP EN 323), water content (NP EN 322), tensile strength perpendicular to the faces (NP EN 319), swelling after water immersion (NP EN 317) and formaldehyde emission (NP EN 717-2) were determined. Chemical analyses revealed that hazelnut shells are composed of lignin (30.2%), cellulose (28.9%), hemicellulose (11.3%), tannins (18.2%) and proteins (6.7%). The chemical composition of the ash (27.7% K and 16.9% Ca) makes them a possible substitute for feldspar in ceramic industry. XRD showed that hazelnut shell has cellulose I fibres with high quality crystalline (69.1%) cellulose. The delignification proved to be very effective producing a pulp almost all composed by cellulose and xylan. Hazelnut shells show a good potential for particleboard production, although only to be used in the face layer.

1. INTRODUCTION

Hazelnut is the fruit of the hazel tree (*Coryllus avellana* L.). It is originally from Anatolia and Greece, but it spread through Europe in the nineteenth century. The biggest producers worldwide are Turkey, representing between 70 and 80% of overall production (USDA, 2010), Azerbaijan and United States. Portugal is in the 16th place of producers ranking, and this crop has 624 planted hectares in the country, and yields about 350 tons of shells annually. In 2003 in Portugal, two regions, namely Beira Litoral and Trás-os-Montes represented almost 90% of all national production with 52% and 37%, respectively (Silva et al., 2005). In Beira Litoral the most representative area is around Viseu, where hazelnut production comes mainly from scattered, often surrounded, associated with other cultures. Hazelnut shells, in this region, are only used for combustion. New uses for this residue are welcome since they might add some value to this by-product and have a positive impact in the producing companies. The aim of this work was to provide new strategies for processing hazelnut shells into value added products such as particle boards, pulp, cellulose fibres or chemicals.

Several authors determined hazelnut shell chemical composition with somewhat different results. In accordance with Demirbas (2001, 2003), hazelnut shell from different Turkish biomass sources has about 30% hemicelluloses, 26% cellulose, 43% lignin and about 3.3% extractives. Saura-Calixto et al. (1983) have presented somewhat different values for Spanish hazelnut shell with 25% hemicelluloses, 37% cellulose and 23% lignin.

Some studies present different uses for hazelnut shell. Several studies refer hazelnut shell as an efficient bio absorbent. (Pehlivan et al., (2009) studied the biosorption of Pb^{2+} ions on hazelnut shells and concluded that these shells are suitable sorbents for the removal of Pb^{2+} ion from aqueous solution. Cimino et al.

(2000) found out that hazelnut shell shows a good efficiency in removing toxic ions such as three- and hexavalent chromium, cadmium and zinc from aqueous solutions similarly to other raw cellulosic materials. Another possible utilization is as a source of natural and effective phenolic antioxidants as reported by Contini et al. (2008). It can be concluded that among the studied wastes that could replace xylan, melon peel has the maximum activity followed by apple pomace and hazelnut shell.

Cöpür et al. (2008) investigated the possibilities of utilizing husk and shell of hazelnut in medium density fiberboard (MDF) production. The results showed that panels could be produced with a mixture of beech (*Fagus orientalis* L.) and pine (*Pinus nigra* V.) fiber (60% and 40%) with hazelnut husk up to 20% addition maintaining the minimum properties required in the standards. However in the case of hazelnut shell a maximum of 10% could be added, because at higher levels the elastic modulus and internal bond strength decreased below the acceptable level.

2. **MATERIAL AND METHODS**

2.1. MATERIALS

Hazelnut shells were provided by Transagri, Lda., a company located in the industrial zone of Mangualde, and wood particles were provided by Sonae Indústria (Oliveira do Hospital). The material was dried at room temperature, milled on a Retsch cross-beater mill SKl, and sieved to *ca* 250-400 µm particles.

2.2. CHEMICAL ANALYSES

The hazelnut shells were characterised regarding the ash content, extractives (in acetone, dichloromethane and in hot water), proteins, tannins, cellulose, lignin and hemicelluloses. The ashes content was determined by calcinations of the material at 525 ºC, according to the standard procedure Tappi T 211 om-12. Metal cations were analysed by ICP after ash wet digestion. The elementary analysis was made on a Leco CHNS-932 Elemental Analyzer.

The extractive content in acetone and dichloromethane were determined by Soxhlet extraction according to the Tappi T 204 om-88. The determination of extractives in hot water was carried out with a solution of ammonium citrate (10 g/L) for 1 hour under reflux (liquid-to-solid ratio 100). The protein content in extractives-free shells, after extraction with acetone, was determined by treatment with 1% pepsin solution in 0.1 M HCl at 37ºC for 16 hours. The tannin content was assessed in extractives- and proteins-free shells by reflux with 0.3% NaOH solution (liquid-to-solid ratio 100) under nitrogen atmosphere for 1 hour. The extracted material was filtered, washed with hot water until neutral reaction of filtrate and dried at 60 ºC to a constant weight. The content of tannins was assessed by the difference in weights of initial and extracted materials. The alkaline extract was precipitated by adding 3M H_2SO_4 until pH 3. After 24 hours, precipitated tannins were centrifuged and washed with water to pH 5. Finally, the tannin fraction was freeze dried. The cellulose was determined by 4 consecutive treatments with HNO_3:EtOH mixture (1:4, v/v) under reflux for 1 h each according to the Kürschner and Höffer method (Browning, 1967). The lignin content in hazelnut shells free of extractives, proteins and tannins was determined by the Klason method with 72% H_2SO_4 (according to Tappi T 204 om-88).

2.3. X-RAY ANALYSIS OF CELLULOSE

The cellulose isolated by the Kürschner and Höffer method was analyzed by X-ray scattering on a Philips X'Pert MPD diffractometer using Cu-Kα source ($\lambda = 0.154$ nm) in the 2θ range 2-40º and scanning step width of 0.02º/scan. Cellulose was analysed as textured sample and the degree of crystallinity was corrected for the presence of non-cellulosic polysaccharides based on sugars analysis (Figueiredo et al., 2010).

2.4. FTIR AND ^{13}C CP/MAS NMR ANALYSES

^{13}C CP/MAS NMR spectra were registered on a Bruker Avance 400 spectrometer (magnetic field of 9.4 T). Samples were spun in a zirconia's rotor at 7 kHz. The acquisition parameters were as follows: proton pulse of 4 µs (90º), contact time of 2 ms, recovery delay of 4 s and 7000 scans were accumulated.

The FTIR spectra were obtained on a Mattson FT-IR spectrometer Model 7300 using KBr pellets at 4 cm^{-1} resolution and acquiring 128 scans per set.

2.5. OXIDATIVE PULPING

The oxidative pulping of hazelnut shells was carried out in closed reactors with a mixture of acetic acid and hydrogen peroxide. The optimization of the reactants ratio, temperature and reaction time was made.

2.6. BOARD PRODUCTION

Hazelnut shells were tested as substitute for wood particles in core and face layers. Standard wood particles are mainly pine, eucalypt, pine sawdust, and recycled wood. The moisture content of the standard mixtures was determined before blending using an infrared balance. The average of the moisture content was 2.5 and 3.5% for face and core layers, respectively. Wood particles and hazelnut shell particles were blended separately with the resin, catalyst and paraffin in a laboratory glue blender with a gluing factor of 6.3% resin solids in the face and 6.9% in the core layers, based on the oven-dry weight of wood particles. The paraffin level was 0.15% solids. Three-layer particleboards (PB) were hand formed in aluminium containers with 220 × 220 × 80 mm^3. The total percentage of board mass was about 20% for the face layers and 60% for the core layer. The pressing was done in a hot-press with 320 mm x 320 mm plates which is controlled by computer and is equipped with four thermocouples, a displacement sensor (LVDT), a load cell, and a pressure transducer. The particles with glue were pressed at 190 °C during 120 s after which, boards were placed in a conditioned room at 20°C and 65% relative humidity (RH).

2.7. DETERMINATION OF BOARD PROPERTIES

After stabilization in the conditioned room the boards were sanded and cut. Some physical properties were determined for both wood and wood+shell particleboards. Density was determined by EN 323 and moisture content (MC) by EN 322. Mechanical properties were also evaluated: internal bond strength (IB) was determined by EN 319 (Determination of tensile strength perpendicular to the plane of the board) and thickness swelling by EN 317 (Determination of swelling in thickness after immersion in water). Formaldehyde content was determined according to EN-717-2 in which the determination of formaldehyde release is done by the gas analysis method.

3. RESULTS AND DISCUSSION

Aiming at a better understanding of hazelnuts shells and the evaluation of its potential as a source of new materials, particularly for obtaining cellulosic pulp, the general chemical composition was evaluated.

Table 1 presents the hazelnut shell chemical composition. The chemical characterization showed that hazelnuts are lignocellulosic materials, in which lignin is the major component (with around 30%), followed by cellulose (with around 29%) and hemicelluloses (11%). Regarding other components, it is important to highlight the high presence of tannins (18%). The extractives are mainly water soluble compounds (3.8%).

Table 1: Chemical composition of hazelnuts shell (% dry material).

Parameters		**Content (%)**
Ashes		4.0
Extractives	Acetone	0.5
	Dichloromethane	0.3
	Water	3.8
Proteins[a]		6.7
Tannins[b]		18.2
Klason Lignin[c]		30.2
Cellulose *Kürscher* and *Höffer*		28.9
Hemicelluloses		11.3

[a] Corrected for extractives in acetone.
[b] Corrected for extractives in acetone and proteins.
[c] Corrected for extractives in acetone, proteins and tannins.

The hazelnut shells ashes content was about 5% with a cationic composition presented in Table 2. It can be seen that potassium (28%) and calcium (17%) are the main cations. This chemical analysis shows that these ashes have the potential to be used as substitutes for feldspar (rich in K, Na, Ca) used in glass and ceramic industries to lower the melting temperature.

Table 2: Cationic composition obtained from ashes.

Elements	%, w/w
Magnesium (Mg)	1.4
Potassium (K)	27.7
Sodium (Na)	0.3
Calcium (Ca)	16.9

Cellulose, the most abundant polymer of hazelnuts shell, was isolated by the Kürscher and Höffer method and characterized by X-ray diffraction to acquire information regarding its crystalline structure. The diffractogram (Figure 1) demonstrates that this cellulose is Cellulose type I with characteristic reflexes at ca. $2\theta = 16$ and 22º. The degree of crystallinity obtained was of about 69% higher than the traditionally obtained from wood, 63-68%. The dimensions of the unitary cell (a, b and c) and the γ angle were: a – 8.0 nm, b – 1.03 nm, c – 7.9 nm and γ - 93º. The value of products of nuts, such as hazelnut shell is an undeveloped theme. This preliminary study allows us to conclude that cellulose recovery is possible, since hazelnut shell has a high percentage of cellulose.

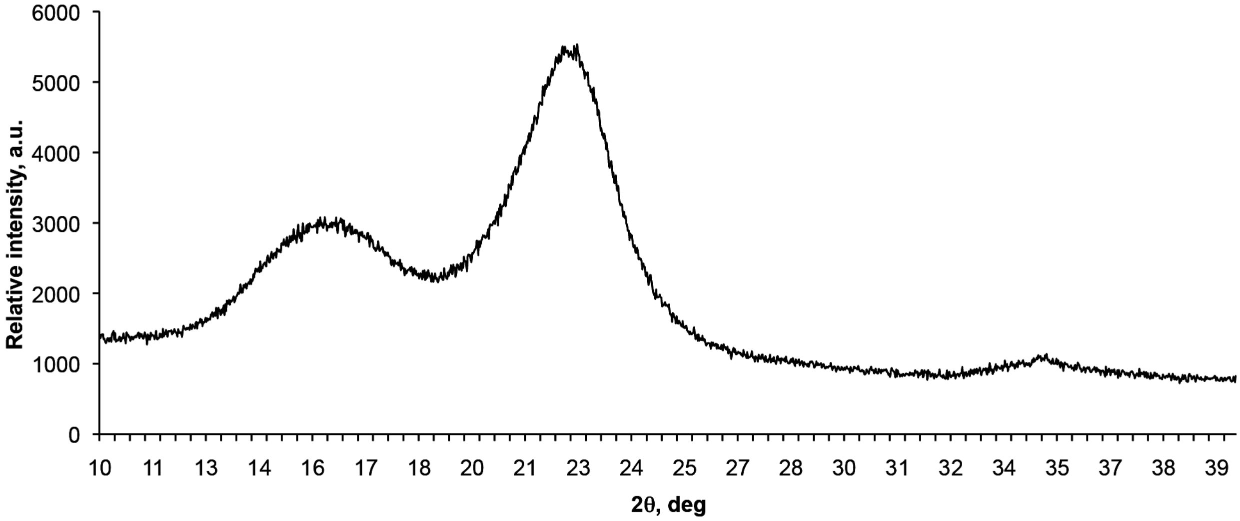

Figure 1: X-ray difractogram of cellullose isolated by the Kürscher and Höffer method.

The parameters were optimized to produce a higher white pulp yield. The best yield (85%) was obtained for the ratio 1: 1: 1.3 (H_2O_2: CH_3COOH : H_2O) at 85 ºC for 12 h.

Pulp was produced and characterized by FTIR (Figure 2) and ^{13}C NMR CP/MAS (Figure 3). In Table 3 we can see the signal assignments for NMR. In Figure 2 we can see that the band at 1510 cm^{-1} assigned to stretching vibrations in the aromatic ring of lignin almost disappears, demonstrating that the conditions applied are efficient in lignin removal. The band around 1630 cm^{-1} also decreases but this band can be overlapped by the band 1700-1550 cm^{-1} of conjugated C = O stretching, and C=C stretching.

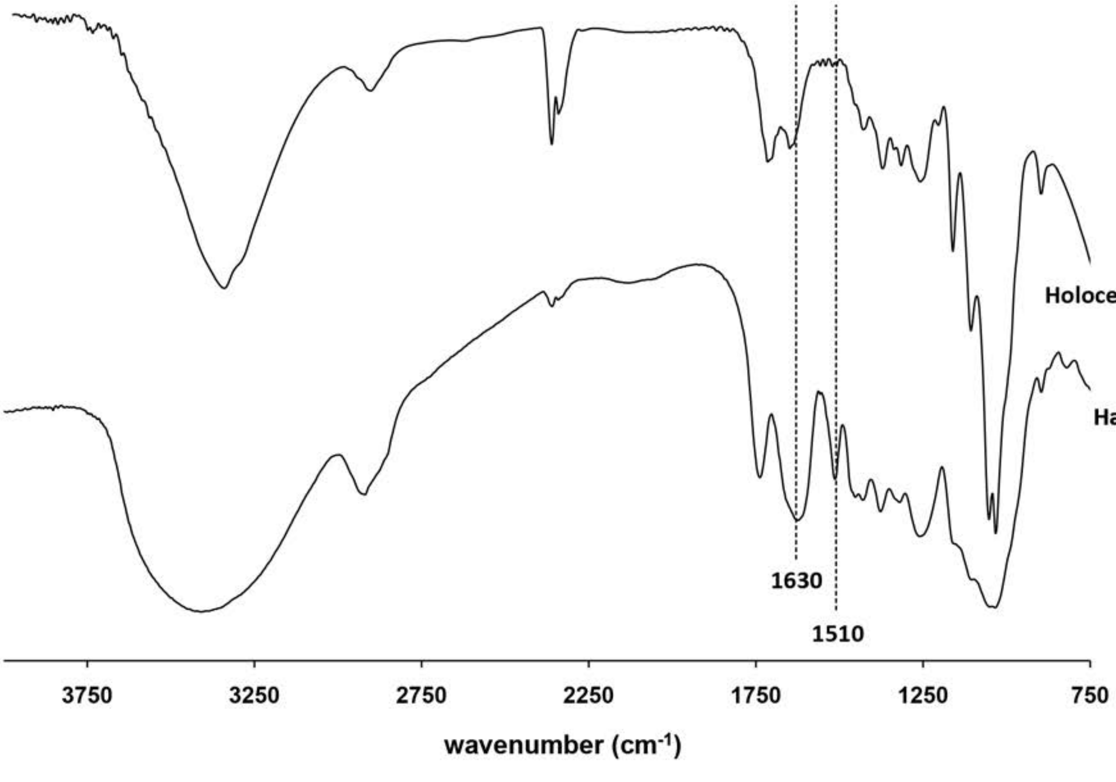

Figure 2: Hollocelulose Fourier transforms Infrared spectroscopy (FTIR).

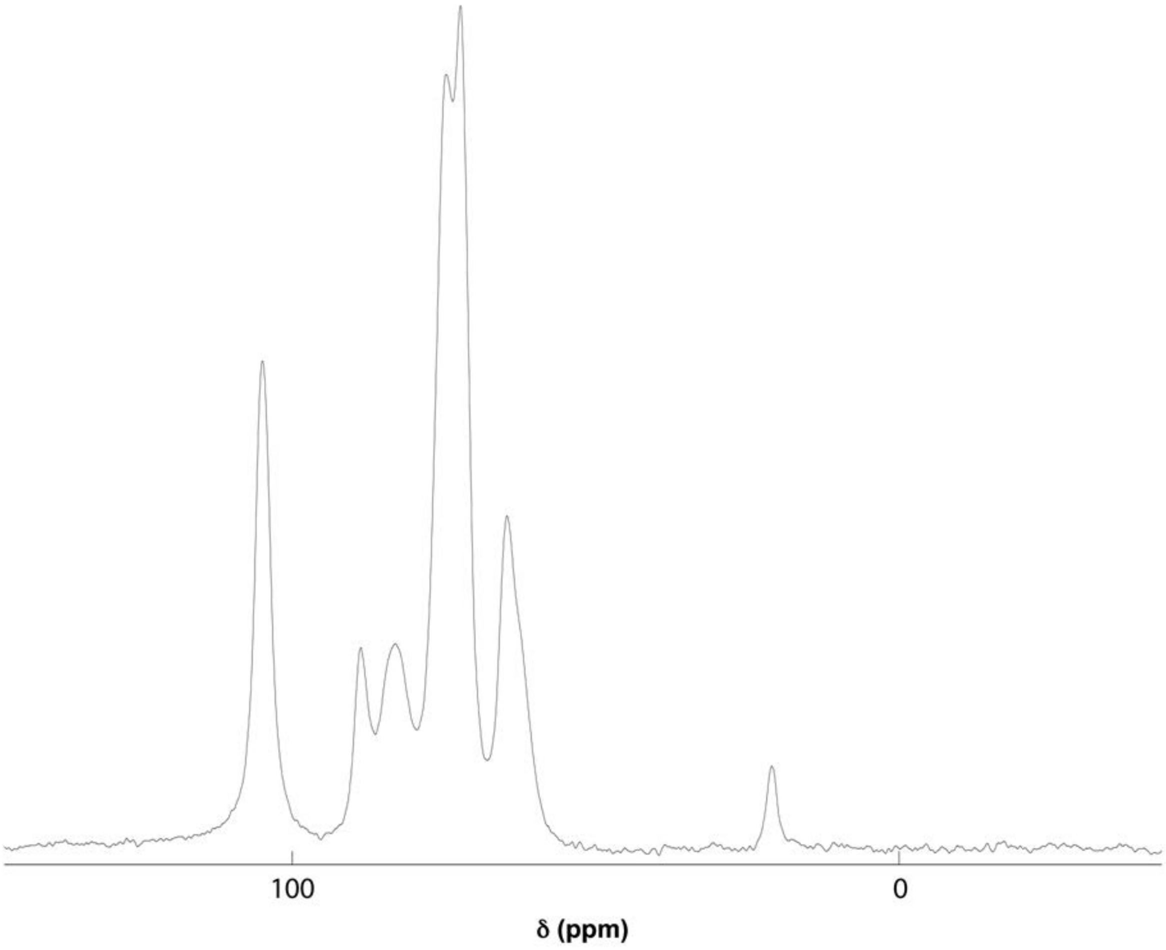

Figure 3: ^{13}C NMR spectrums of holocellulose.

Table 3: Signal assignments for NMR ^{13}C CP/MAS for pulp obtained by oxidative cooking. (Atalla and Vanderhart, 1999).

δ (ppm)	Assignment
21	CH_3 in CH_3COO-
25-35	CH_3 and CH_2 in aliphatic
60-70	C-6 from cellulose; C-5 from xylans
70-81	C-2,3,5 from cellulose; C-2,3,4 from xylans
81-93	C-4 from cellulose
102-108	C-1 from cellulose; C-1 from xylans
174	C=O in CH_3COO-

The ^{13}C NMR CP/MAS shows that the pulp is mainly made of cellulose and xylans. NMR spectrum shows that the treatment is effective in lignin removal since the spectrum does not have the typical lignin peaks.

Hazelnut shells were tested to substitute wood in the core layer of particleboards but due to the round shape of hazelnut shells these boards could not be efficiently pressed. Table 4 presents some mechanical and physical properties as well as formaldehyde content of the boards produced only with wood and with wood particles in the core layer and hazelnut shell particles in the face layer. Both boards were made with the same UF resin and with the same pressing conditions. The internal bonding for wood and wood+shell particleboards were similar (0.25 N/mm^2) which is a normal figure for common wood particleboards. This was to be expected because since hazelnut shell was only used in the face layer, the influence in internal bonding is very limited.

Density was a little higher for wood + shell particleboards but the difference was not significant. The same happened for the thickness swelling behaviour that was higher for wood particleboard but with no significant differences. In relation to formaldehyde, wood+shell particleboard had lower free formaldehyde content, although with no significant difference. Overall, the results show that the particleboard with the incorporation of hazelnut shells in the face layers has better performance than the wood board. Nevertheless the differences are small and more tests are needed to confirm these results. This board would be classified as E2 in accordance to EN 13986 (2004) since formaldehyde is between 3.5-8 mg/m^{3}h.

Table 4: Mechanical and physical properties of wood and hazelnut shells particleboards.

Sample	IB (N/mm^2)	Density (Kg/m^3)	Thicness Swelling (%)	EMC (%)	Formaldehyde content (G = mg/m^{2}h)
Wood particles	0.25	647	42.2	6.8	4.7
Wood particles + Hazelnut shells	0.25	668	40.7	6.7	4.4

4. CONCLUSIONS

In conclusion, hazelnut shell is a lignocellulosic material with 28.9% of cellulose, 11.3% hemicelluloses and 30.2% lignin. Hazelnut shell cellulose was characterized by x-ray diffraction and was found to have a high degree of crystallinity (69.5%). The cooking method used proved to be quite effective in simple material. The optimal conditions were obtained for 12 h at 85 °C and with a ratio 1: 1: 1.3 (CH_3COOH: H_2O_2: H_2O) using 5 grams of hazelnut shells.

Hazelnut shell ash is a by-product with good potential as a substitute of feldspar in ceramic products; for the production a Cellulose type I; for pulp production and for incorporation into wood panels, although only to be used in the face layer.

5. ACKNOWLEDGEMENTS

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PROPERTIES OF PARTICLEBOARDS MADE FROM WILLOW (*SALIX VIMINALIS*)

ARNOLD WILCZYŃSKI[1,*], KRZYSZTOF WARMBIER[1], CEZARY GOZDECKI[1], MAREK KOCISZEWSKI[1], LESZEK DANECKI[2]

[1] INSTITUTE OF TECHNOLOGY, KAZIMIERZ WIELKI UNIVERSITY, CHODKIEWICZA 30 STR., 85-064 BYDGOSZCZ, POLAND

[2] RESEARCH AND DEVELOPMENT CENTRE FOR WOOD-BASED PANELS INDUSTRY, MICKIEWICZA 10 STR., 83-262 CZARNA WODA, POLAND

* CORRESPONDING AUTHOR: WILCZAR@UKW.EDU.PL

Keywords: particleboard, willow, mechanical properties, particle size, urea formaldehyde resin content

ABSTRACT

The objective of this study was to evaluate some mechanical (modulus of elasticity, modulus of rupture, internal bond strength) and physical (thickness swelling) properties of three-layer particleboards with the core layer made from various willow and industrial wood particle mixtures. The effects of willow particle size and resin content in the core layer were also investigated. In general, the willow content and size of willow particles did not affect significantly the particleboard properties. Increasing the urea formaldehyde resin content resulted in improving all properties of experimental particleboards. Mechanical properties meet the requirements of the EN 312 standard for the particleboards of types P1 and P2. The willow *Salix viminalis* can be considered as a substitute for pine wood for manufacturing the core layer of three-layer particleboards.

1. INTRODUCTION

Particleboard is one of the most important wood composites. Continually increasing particleboard production in many countries, including Poland, and limited forest resources make it necessary to use other wooden materials in particleboard manufacturing. One possible raw material can be fast growing shrubs. Such a shrub being cultivated for energy purposes is the willow *Salix viminalis* L. In Poland it is cultivated in about 800 short-rotation plantations on an area of 6,160 ha (Grzybek, 2011). Genetic and breeding studies have been conducted in Poland in order to provide a basis for the development of high-yielding willow cultivars, adapted to the different climatic and soil conditions in Poland (Stolarski et al., 2008; Jeżowski et al., 2011).

Initial Polish studies at the Institute of Wood Technology in Poznań (Frąckowiak et al., 2008) showed that the replacement of 25 % of pine particles with willow ones in the core layer of three-layer particleboards improved their mechanical properties in bending. Sean and Labrecque (2006) investigated the usefulness of Quebec clones of the willow *Salix viminalis*. They studied three-layer particleboards with face and core layers containing from 10 % to 30 % willow, and concluded that the mechanical properties of particleboards with up to 30 % willow particles content were generally greater than those of particleboards made from industrial wood particles. Warmbier et al. (2010) found that the mechanical properties of three-layer particleboards with the core layer made fully from willow particles were worse compared to those with the core layer made from industrial pine particles. The results of the mentioned studies are inconsistent. The first two studies indicate that willow particles as a substitute for industrial particles improve the mechanical properties of three-layer particleboards while the third study indicates that those particles worsen them.

We assume that willow particles as a substitute for industrial wood particles will be used for manufacturing only the core layer of three-layer particleboards. The objective of this study was to evaluate some basic properties of three-layer particleboards with the core layer made fully or partially from the willow *Salix viminalis*.

2. MATERIALS AND METHODS

Raw materials for this study consisted of willow (*Salix viminalis* L.) stems and industrial pine wood particles. Three-year-old stems were collected from the Miescisko plantation in the Wielkopolska Region of Poland. The stem diameter at the base ranged between 28 mm and 35 mm, while the height ranged between 4.9 and 5.3 m. Bark percentage was about 15 % of stem weight. The stems were stored for air-drying to a moisture content of about 12 %, then chipped in a hammer-mill. Industrial pine wood particles used for manufacturing the core layer of three-layer particleboards were supplied by Pfleiderer Prospan Wieruszow (Poland). Both willow and wood particles were then screened by an analytical sieve shaker using 6.3 mm and 1 mm sieves. Particles that passed through the 6.3 mm sieve and remained on the 1 mm sieve (Figure 1) were used as furnishes for the core layer experimental particleboards. The particles were dried to achieve moisture content of less than 3 %. Urea-formaldehyde (UF) resin Silekol®100 (SILEKOL, Poland) was used as a binder. Its density was 1.26 g/cm^3 at 60 % solids. As a hardener, 35 % ammonium chloride solution, which was 1 % of the oven dry weight of particles, was used.

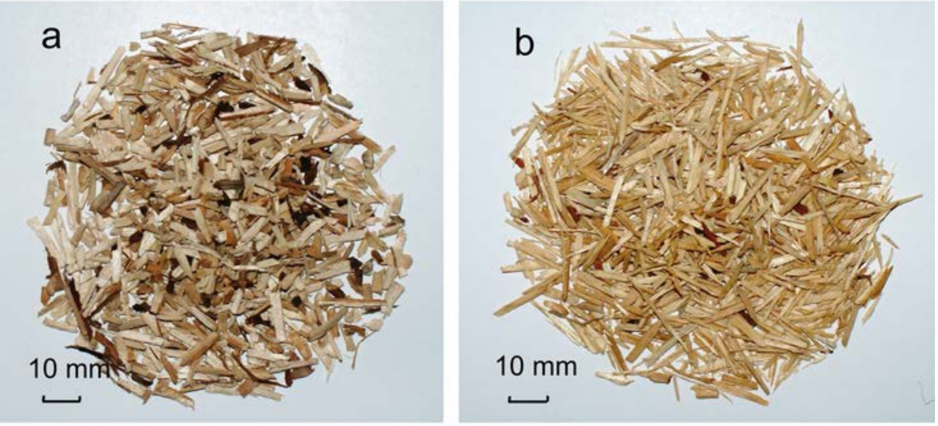

Figure 1: Willow (a) and industrial (pine wood) (b) particles.

The raw material for the face layers of experimental particleboards was industrial fine particles made from pine wood. These particles were dried like those for the core layer, and the UF resin with a content of 10 % was used for preparing the face layers.

Three factors referring to the core layer were taken into account: the willow particle content, resin content and particle size. The experimental design is shown in Table 1. The board manufacturing parameters are listed in Table 2. Four experimental boards were produced for each type of boards.

For comparison purposes, the dimensions of the willow and industrial wood particles used for preparing the core layer were measured. The dimensions were measured for 300 randomly selected particles of each type, and length/thickness and width/thickness ratios were calculated to obtain particle geometric characteristics.

Prior to testing all the boards were stored in controlled conditions (50 % relative humidity and 20 °C) for two weeks. The test specimens were cut from the boards to determine the following mechanical and physical properties according to appropriate EN standards: modulus of elasticity (MOE) and modulus of rupture

(MOR) (EN 310, 1993), internal bond (IB) (EN 319, 1993), and thickness swelling (TS) after 24 h (EN 317, 1993). Test specimens for IB and TS were prepared from the specimens that were formerly tested for MOE and MOR. Eighteen replicates were run for each test.

The obtained data were statistically analyzed. One-way analysis of variance (ANOVA) was conducted to determine the significance of the effect of particleboard type, and Tukey's test was applied to evaluate the statistical significance between mean values of the properties of different particleboards.

3. RESULTS AND DISCUSSION

3.1. PARTICLE GEOMETRY

The dimensions of willow and industrial pine particles used for the particleboard core layer as well as their length to thickness (slenderness) and width to thickness ratios are shown in Table 3. For all size groups of particles, willow particles were shorter but thicker and wider than pine particles. As a result, the slenderness of willow was considerably less than that of pine particles, while the width to thickness ratio of both particles was similar.

3.2. PROPERTIES OF EXPERIMENTAL PARTICLEBOARDS

Mean values of the mechanical and physical properties of tested particleboards are given in Figures 2-5. Error bars represent the standard deviation based on eighteen specimens. The results of the ANOVA test are shown in Table 4. The particleboard type affected significantly all determined mechanical properties (MOE, MOR and IB), and TS.

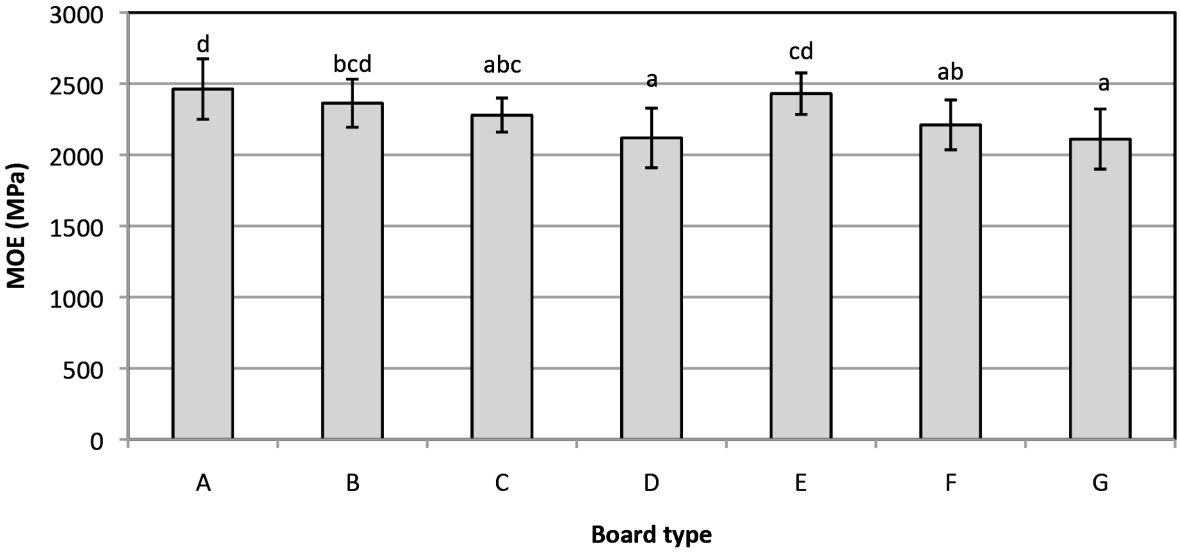

Figure 2: Modulus of elasticity of experimental particleboards (A, B, C, D, E, F, G as shown in Table 1). Mean values with the same letter were not statistically different at the 5 % significance level.

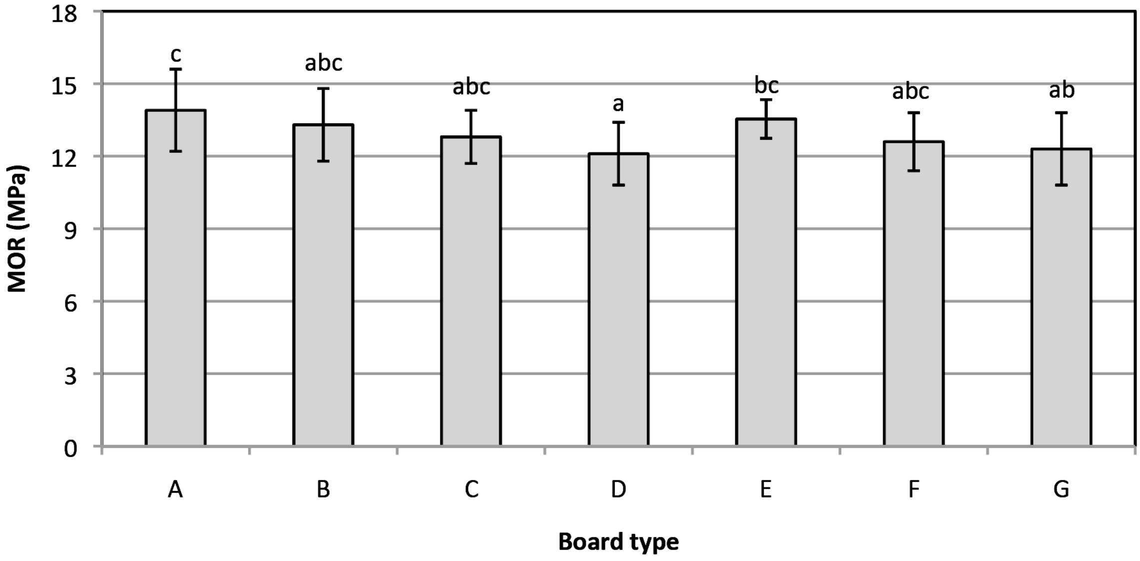

Figure 3: Modulus of rupture of experimental particleboards (A, B, C, D, E, F, G as shown in Table 1). Mean values with the same letter were not statistically different at the 5 % significance level.

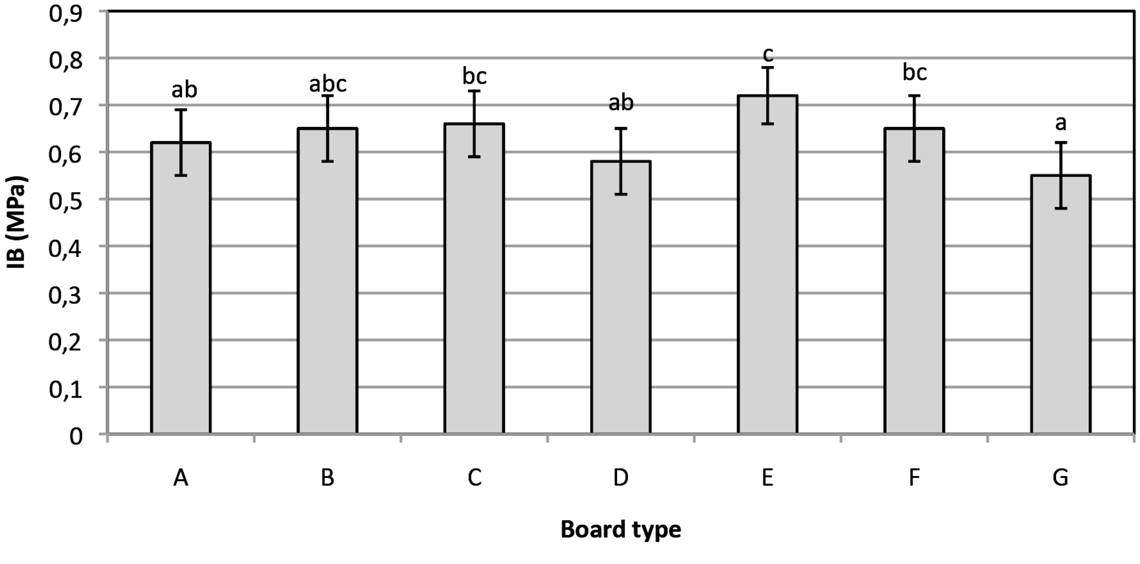

Figure 4: Internal bond strength of experimental particleboards (A, B, C, D, E, F, G as shown in Table 1). Mean values with the same letter were not statistically different at the 5 % significance level.

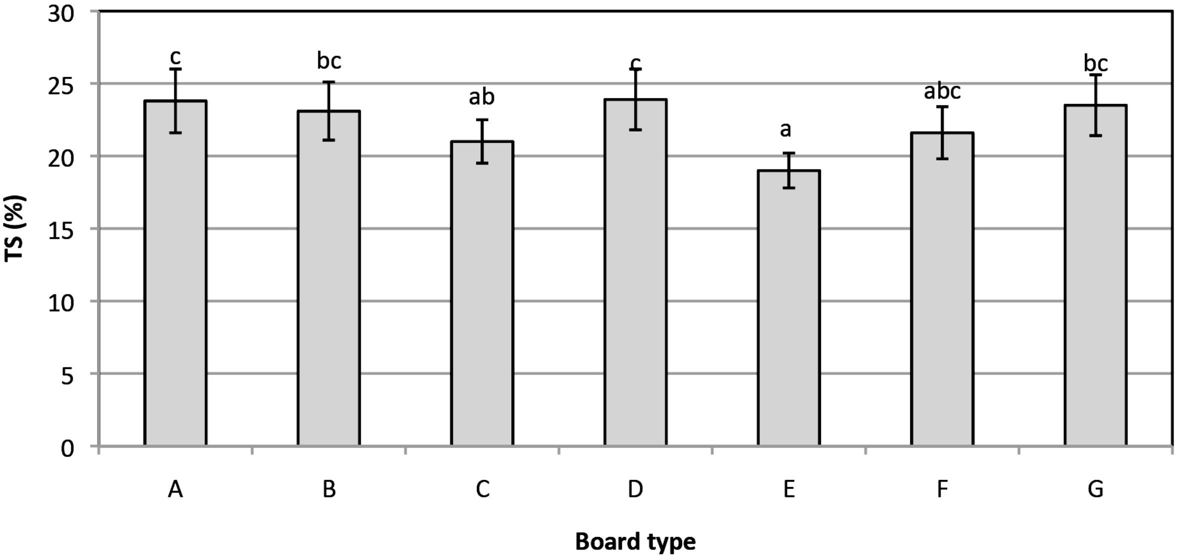

Figure 5: Thickness swelling of experimental particleboards (A, B, C, D, E, F, G as shown in Table 1). Mean values with the same letter were not statistically different at the 5 % significance level.

3.2.1. EFFECT OF WILLOW CONTENT

Particleboards A, B and C with the core layer containing 0 %, 50 % and 100 % willow particles of 2.4 mm - 4 mm, and having a resin content of 8 %, were the basis for assessing the effect of willow content. MOE of particleboards depended significantly on the willow content (Figure 2), and decreased gradually from 2460 MPa to 2280 MPa with increasing this content from 0 % to 100 %. The decrease in MOE was in part caused by willow particle geometry. The slenderness of willow particles (Table 3) was much smaller in comparison to industrial wood particles. According to Rackwitz (1963), increasing the particle slenderness improved MOE and MOR, and worsened IB of particleboards. Another cause of the decrease of MOE was probably the usage of bark which was considerably greater for willow than for industrial wood particles. The negative effect of bark on MOE of particleboards with 22 % and 30 % usage of the willow *Salix viminalis* was also observed by Sean and Labrecque (2006).

The effects of willow content on MOR and IB of particleboards were insignificant (Figures 3 and 4). MOR and IB ranged from 13.9 MPa to 12.8 MPa and from 0.62 MPa to 0.66 MPa, respectively, for the boards with the willow content from 0 % to 100%. The willow content influenced significantly TS (Figure 5) which decreased from 23.8 % to 21.0 % with increasing the willow content from 0 % to 100 %.

3.2.2. EFFECT OF RESIN CONTENT

The basis for evaluating the effect of resin content were particleboards D, C and E with the core layer made only from willow particles of 2.4 mm - 4 mm using the resin content of 6.5 %, 8 % and 9.5 %, respectively. All determined properties depended significantly on the resin content (Figures 2-5). MOE, MOR and IB increased gradually from 2120 MPa to 2430 MPa, from 12.1 MPa to 13.5 MPa and from 0.58 MPa to 0.72 MPa, respectively, and TS decreased from 23.9 % to 19.0 %, with increasing the resin content from 6.5 % to 9.5%.

3.2.3. EFFECT OF PARTICLE SIZE

Particleboards F, C and G with the core layer made from willow particles of 1 mm - 2.4 mm, 2.4 mm - 4 mm and 4 mm - 6.3 mm, respectively, using the resin content of 8 %, were the basis for assessing the effect of particle size. Only IB depended on the particle size (Figure 4), and decreased from 0.66 MPa to 0.55 MPa with increasing the particle size from 2.4 mm – 4 mm to 4 mm - 6.3 mm. MOE, MOR and TS did not depend on this factor (Figures 2, 3 and 5).

3.3. COMPARISON TO EN 312 REQUIREMENTS

Based on EN 312 standard, 1600 MPa is the minimum requirement for MOE of particleboards for interior fitments, including furniture, for use in dry conditions. MOE of experimental particleboards ranged from 2110 MPa to 2460 MPa and was considerably higher than this requirement. The minimum requirements for MOR are 11.5 MPa and 13 MPa for general purpose particleboards for use in dry conditions (particleboards of type P1) and for particleboards for interior fitments, including furniture, for use in dry conditions (particleboards of type P2), respectively. MOR of experimental particleboards ranged from 12.1 MPa to 13.9 MPa, Therefore, all particleboards met the MOR requirement of EN 312 for the particleboard of type P1. Moreover, particleboard B having 50 % willow in the core layer, and particleboard E with the resin content of 9.5 % in the core layer exceeded the MOR requirement for the particleboard of type P2. IB of experimental particleboards ranged from 0.55 MPa to 0.72 MPa, and considerably exceeded the minimum requirements of EN 312 which are 0.24 MPa and 0.35 MPa for the particleboard of types P1 and P2, respectively.

4. **CONCLUSIONS**

Three-layer experimental particleboards were manufactured with the core layer made from the willow *Salix viminalis* as a substitute for industrial particles made from pine wood. In general, the mechanical properties (MOE, MOR and IB) of particleboards with the core layer from willow particles did not differ significantly from those of particleboards with the core layer from pine particles. TS of particleboards with the core layer from willow was significantly smaller. Increasing the resin content resulted in improving all properties of experimental particleboards. In general, the size of willow particles did not affect the particleboard properties. MOE and IB of particleboards with the core layer from willow met the requirements of EN 312 standard for particleboards of type P2, whereas MOR met the requirement for particleboards of type P1. Decreasing the willow content or increasing the resin content in the core layer caused the increase in MOR and a compliance with the requirement of EN 312 for particleboards of type P2. The willow *Salix viminalis* can be considered as a substitute for pine wood for manufacturing the core layer of three-layer particleboards.

5. **ACKNOWLEDGEMENT**

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QUERCUS FRUIT STARCHES: ISOLATION, CHARACTERISATION AND USES

PAULA CORREIA[1,]*, M. LUÍSA BEIRÃO-DA-COSTA[2]
[1] CI&DETS, ESAV, ESCOLA SUPERIOR AGRÁRIA DO INSTITUTO POLITÉCNICO DE VISEU.
QUINTA DA ALAGOA. ESTRADA DE NELAS. 3500-606 VISEU. PORTUGAL.
[2] CEER/SCTA/DAIAT INSTITUTO SUPERIOR DE AGRONOMIA, TECHNICAL UNIVERSITY
OF LISBON. TAPADA DA AJUDA, 1349-017 LISBOA, PORTUGAL.
CORRESPONDING AUTHOR: PAULACORREIA@ESAV.IPV.PT; PHONE: +351232446600; FAX: +351232426536

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ABSTRACT

Quercus rotundifolia and *Q. suber* acorns have high starch contents, about 48%. Acorn starches were isolated from flour by four laboratory- scale methods. The low shear alkaline method using successively three sieves and the enzymatic method were the most promising ones considering the human food usages, since starch showed a high yield, purity and less damaged structure. These methods were optimised and a Central Composite Rotatable Design was used as experimental design. Acorn starches were characterised by morphological, physicochemical, structural and functional properties. Starches showed high contents of amylose and resistant starch, similar to modified starches used in several industries, like gum candies and batters, and like food fibres, respectively. The starches granules were found to be round and oval in shape, with a mean granule size ranging between 9 to 13 μm. They presented a C-type X-ray pattern, with high degree of crystallinity. Thermal analysis revealed that the acorn starches easily suffer transition phenomena as shown by low enthalpy values. The pastes did not present breakdown, which suggests a high paste stability of acorn starches during heating and shearing, like industrial modified cross-linked starches. Thus, acorn starches can improve the texture of food products, providing viscosity, good adhesion and binding properties, with nutritional value.

1. INTRODUCTION

Acorn fruits from *Quercus suber* (QS) and *Q. rotundifolia* (QR) are important forest resources in the Central and Southern regions of Portugal, but they can also be important in Greece, Italy and France (Grove and Rackham, 2001). Most of the fruit production goes to animal feeding, mainly of Iberic pigs.

Starch as a natural component, contributes to the characteristic properties of food products such as texture, viscosity, gel formation, adhesion, binding, moisture retention, film formation and product homogeneity in different products like sauces, puddings, confectionary, and a variety of low-fat products. Approximately 60 million tonnes are extracted annually worldwide from various types of cereal, tuber and root crops (www.zuckerforschung.at), of which roughly 60% is used in foods (i.e., bakery products, sauces, soups, sugar syrups, ice cream, snack foods, meat products, baby food, drinks, fat substitutes) and 40% in pharmaceuticals and for non-edible purposes (Burrell, 2003). The knowledge about the properties of different native and non-conventional starches is of great importance, in order to select the most adequate starch for a specific industrial application and possible substitution of industrial physical, chemical or enzymatic modified starches.

Q. rotundifolia and Q. suber acorns have high starch contents, about 48% (Correia et al., 2009), suggesting that these fruits can be a good alternative to conventional starch resources, such as cereals and tubers.

When these fruits are drying the starch content decreases, to around 32% (Correia et al., 2009), which is nevertheless a high content for a fruit. The properties of starches are not only dependent on the starch source but are also highly dependent on the history of the starch itself as for instance the extraction procedures. It is known that extraction procedures affect both the chemical composition and physical properties of starch, which justify the interest of studying the most suitable one for each individual raw material.

In the literature, acorn starch properties from the fruits of other oak trees, but not *Quercus* species were studied (Stevenson et al., 2006). Since acorns are good sources of starch, these fruits present a large potential for commercial use.

The objectives of the present study were the optimisation of the isolation procedures and also the evaluation the effect of starch isolation method on physic-chemical and structure properties of acorn starches, aiming at finding potential industrial applications for underexploited raw materials, and so resulting on economic profits.

2. **MATERIALS AND METHODS**

2.1. MATERIALS

Quercus suber Lam. and *Quercus rotundifolia* Lam. acorns were collected in "montados", located in Idanha-a-Nova (Centre - East of Portugal). Three sets of 1 kg of each acorn fruit were randomly harvested at maturity stage (December), stored, dried and milled as previously reported by Correia and Beirão-da-Costa (2010).

2.2. CHEMICAL ANALYSIS

The extraction yield (% of starch produced from flours) was determined. The starch purity was evaluated by determining starch content in the extract by the Ewers polarimetric method (ISO/DIS 10520, 1997). Acorn flour and starch isolated by each method was analysed for: moisture, protein, fat, and ash contents (AACC, 2000). The total starch content in the flours was determined by the polarimetric method, as proposed by Garcia and Wolf (1972). The colorimetric method proposed by Juliano (1971), was used to determine amylose content, with amylose content being expressed on a starch basis. Resistant starch (RS) content was determined following the method proposed by Mun and Shin (2006). All reported values are expressed on a dry weight basis (dwb) and all reagents used were of analytical grade.

2.3. STARCH EXTRACTION METHODS

Methods used in starch extraction were selected on the basis of simplicity, efficiency, time consumption and use of low hazard chemicals. The selected methods were based on those proposed by Lim et al. (1992) and Perez et al. (1993) described by Correia and Beirão-da-Costa (2010). Four isolation methods were tested: Low Shear at Alkaline pH method (LSA); High Shear in Water method (HSW); Low shear enzymatic method (ENZ); Low shear alkaline pH and using successively three sieves (A3S). In all cases, centrifugation was performed in a Universal 16 centrifuge (Hettich Zentrifugen Company, Germany) and isolated starches dried in the aforementioned drying chamber, for two days at 40 ºC.

2.4. PHYSICAL ANALYSIS

Scanning electron micrographs (SEM) were taken by with an ISI-D 130 scanning electron microscope (International Scientific Instrument). Starch samples were applied on an aluminium stub using double-sided adhesive tape and the starch coated with gold-palladium (80:20). An accelerating voltage of 10 kV was used during microphotography.

Pasting of acorn starches were monitored in a Brabender (Duisburg, Germany) viscoamylograph at 8% starch concentration suspension, heated from 30 °C to 95 °C, hold at 95 °C for 15 minutes and then cooled till 50 °C.

Thermal characteristics were tested by Differential Scanning Calorimetry (DSC) on a Shimadzu calorimeter (model TA-50WSI, Japan). The instrument was calibrated using indium and deionised distilled water as standards. The samples (7.5 mg) were weighed directly in DSC aluminium pans. Water was added to the starch samples at a ratio of 1:2, and then heated from 25 °C to 100 °C at a 5 °C/minutes rate, and at 30 ml/minute as the flow rate, using nitrogen as carrier gas. Gelatinisation enthalpy ΔH (J/g of dry starch) was determined. The transition kinetics was studied by DSC, using the heat evolution method of Borchardt and Daniels as reported by Danielenko et al. (1985). The method assumes that the reaction follows the relationship (Equation 1):

$$d\alpha/dt = k(T)[1 - \alpha]^n \qquad (1)$$

where $d\alpha/dt$ is the reaction rate; k is the rate constant (s^{-1}); T is the temperature; n is the reaction order, and α is the fractional conversion. The reaction rate $d\alpha/dt$ is obtained by dividing the peak height at a temperature T by the total area. The method also assumes that the dependence of the reaction rate follows the Arrhenius expression (Equation 4):

$$v = -v_0 e^{E_a/RT} \qquad (2)$$

where v is $d\alpha/dt$; v_0 is the constant rate; E_a is the activation energy ($Jmol^{-1}$); R is the gas constant; and T is the absolute temperature.

The analysis of the crystalline structure of the starches was carried out in a Philips diffractometer (X'Pert MPD, Almelo, Netherlands), using CuKα radiation ($\lambda = 0.154$ nm) generated at 40kV and 20 mA, at a moisture content between 8 and 10%. The sample was scanned through the 2θ (diffraction angle) from 3 to 50° at a speed of 8°/minute. The degree of relative crystallinity was determined following the method previously reported by Huang et al. (2007) using the following equation (Eq. 3):

$$\text{Crystallinity degree}(\%) = I_c/(I_a + I_c) \times 100 \qquad (3)$$

where I_a = amorphous area on the X-ray diffractogram, and I_c = crystallized area on the diffractogram.

2.5. STATISTICAL ANALYSIS

A Central Composite Rotatable Design (CCRD) of the experiments was performed with k = 2 for: A3S - centrifuge velocity/ time and ENZ - protease amount/digestion time as independent variables. No previous reports were found between the responses and independent variables and so the established ranges were: centrifuge velocity (CF) 108xg – 2220xg, centrifugation time (Ct) 10-30 min, and protease quantity (EU) 200–1000 units and digestion time (Dt) 2-12 hours. The dependent variables studied included starch yield and purity. Data were fit to second-order polynomial equation (4) for each dependent Y variable, through a stepwise multiple regression analysis using Statistic® vs 6 software:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + b_5x_2^2 \qquad (4)$$

where b_n are regression equation coefficients and x_n the independent variables (Kahyaoglu and Kaya, 2006). Based on the predicted model equations surface plots were generated.

All represent averages of at least three different determinations. Results were analysed using the Statistic® vs 6 software. The data were subjected to one-way analysis of variance (ANOVA) test. The separation of means or significant differences comparisons of all parameters were tested by Tukey's HSD test. The level of significance used for all of the statistical tests was 95%.

3. **RESULTS AND DISCUSSION**

Nutritional composition of acorns fresh flours, without drying, is shown in Table 1. Acorns presented a high quantity of starch, about 47%, followed by protein, 4.1%, for *Q. suber* and *Q. rotundifolia*. Considering the isolation methods, the alkali treatment seems to be quite effective in the reduction of starch fat, protein and ash contents, probably due to an effective protein precipitation and further separation by the use of the sieves. The isolated starches always showed a decrease on amylose content when compared to that found in the original flour, probably caused by the lixiviation/degradation of amylose during the extraction process. Major differences among methods were produced respecting extraction yields. From what has been stated above, it may be concluded that the methods leading to a higher yield were the A3S, followed by the ENZ isolation method. The least efficient was the HSW method, probably due to a greater disruption effect on some compounds that are not further separated. This could be observed by SEM images of the isolated starches are shown in Figure 1.

Table 1: Chemical properties of flour and isolated starches.

Sample	Analysed Parameters (% dwb)	Flour	Isolation Methods					
Quercus. suber			LSA	HSW	ENZ	A3S	$A3S_{OPTIMISE}$	$ENZ_{OPTIMISE}$
	Protein	4.1±0.10	2.2±0.01	2.7±0.05	2.8±0.04	0.9±0.01	0.3±0.02	0.3
	Fat	5.4±0.21	2.1±0.01	2.4±0.01	1.9±0.06	0.8±0.02	0.5±0.01	0.2
	Fibre	2.8±0.06	ND	ND	ND	ND	ND	ND
	Ash	1.7±0.08	0.6±0.04	0.5±0.02	0.3±0.01	0.2±0.01	0	0
	Starch*	30.4±0.81	90.1±2.1	83.6±2.55	91.9±1.05	95.1±0.81	98.1±1.50	97.6±2.00
	Amylose	86.1±1.44	47.6±1.18	48.4±2.33	58.3±2.10	54.4±2.21	57.9±1.33	59.4±0.70
	Resistant starch	43.9±2.01	__	__	__	__	39.2±0.82	30.8±0.69
	Yield	__	18.1±0.6	13.2±0.8	22.1±1.0	25.1±0.6	27.4±0.6	27.3±0.4
Quercus. rotundifolia	Protein	4,8±0.04	1.9±0.05	2.4±0.08	2.4±0.04	1.0±0.01	0.2±0.02	0.3±0.01
	Fat	11.1±0.06	3.1±0.02	3.6±0.07	1.6±0.02	1.1±0.02	0.4±0.03	0.3±0.03
	Fibre	3.0±0.11	ND	ND	ND	ND	ND	ND
	Ash	1.9±0.03	0.6±0.01	0.7±0.02	0.3±0.02	0.2±0.01	0	0
	Starch*	31.6±0.36	91.0±1.31	85.2±1.05	92.8±1.00	95.2±0.50	97.7±0.50	96.8±1.72
	Amylose	83.2±1.0	44.4±0.41	44.3±0.45	51.3±0.77	54.4±0.71	53.4±1.30	54.7±0.42
	Resistant starch	40.0±1.51	__	__	__	__	41.4±1.02	36.8±1.38
	Yield	__	28.7±1.3	25.2±0.8	32.6±1.1	36.6±1.3	28.9±0.8	27.8±1.1

* Starch content in isolated starches is equal to starch purity, expressed in % (dwb). ND – not detected

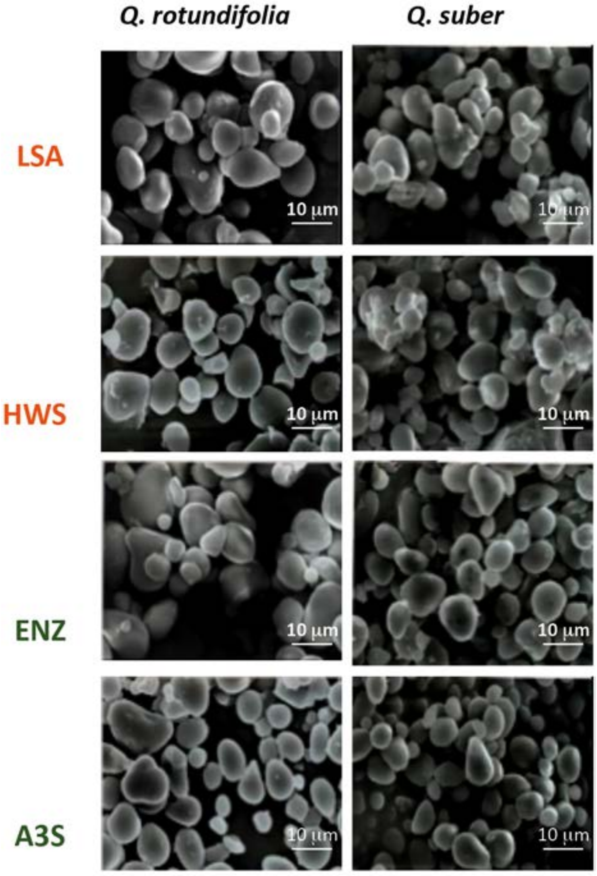


Figure 1: SEM of *Quercus rotundifolia* and *Quercus suber* flour and isolated starches considering the different isolation methods.

Generally, acorn starches presented high gelatinisation temperatures and the methods inducing less damage on acorn starch seem to be the A3S and ENZ methods (Figure 2). No peak consistency was observed for all of the isolated starches, and consequently no breakdown, showing a similar profile to a crosslinked starch suspension (Thomas and Atwell, 1999). This cooked paste stability may show the potential of the starch for use in porridge (Hadimani and Malleshi, 1993). Cold paste consistency increased upon cooling, due to the aggregation of the amylose molecules. This characteristic is estimated by the final consistency. In our study, acorn starches presented high and similar final consistency. Other authors also reported, as the most distinctive acorn starch pastes properties, the high final consistency and setback (Stevenson et al., 2006).

From the above results it was possible to conclude that the A3S and the ENZ isolation methods seemed to preserve in a high degree the starch structure. Thus, they were the chosen ones to be optimised, considering the centrifugation conditions, since this operation unit is used to separate protein and fibre from starch and enzymatic units/ incubation time could influence the yield and purity of isolated starch.

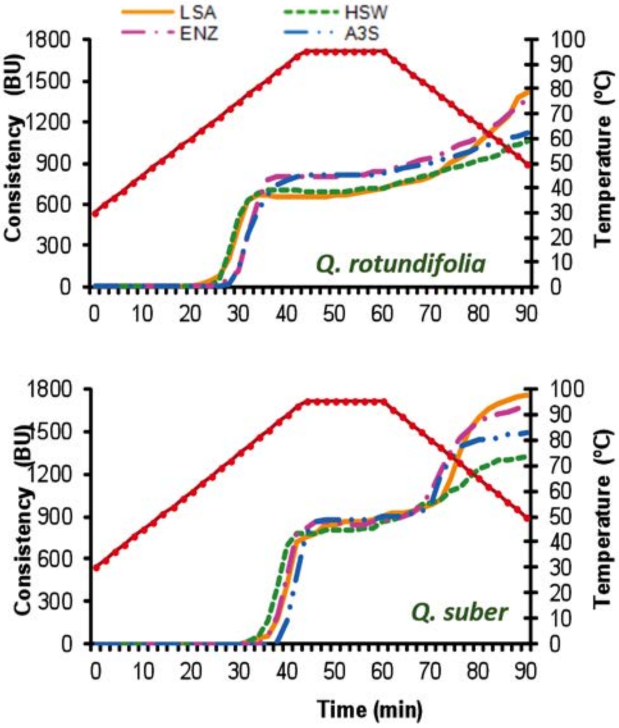


Figure 2: Pasting profiles of acorn starches extracted by different isolation methods (LSA; HSW, ENZ and A3S).

The results of the analysis of variance obtained by the two starch isolation methods for acorn flours from dependent variables fit to Eq. (4) are summarized in Tables 2 and 3. Only parameters adjusted ($p \geq 0.05$) by the model are shown.

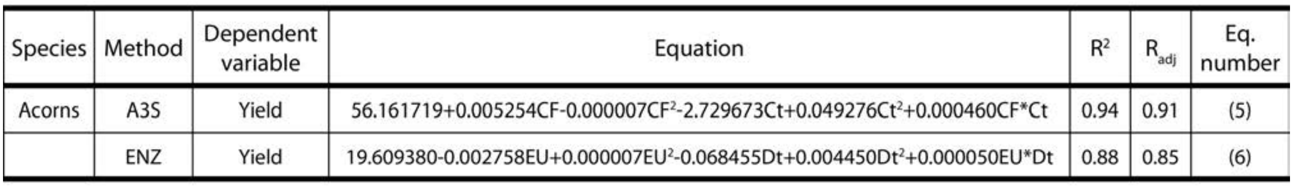
Considering the regression equation coefficients as response parameters of starch isolated from the A3S method, the only equations adjusted from RSM were Eq. (6), with r^2 of 0.94 for acorns (Table 3). Those equations were related with the yield of starch isolation. Purity, in spite of the model, showed a significant fitting ($p \geq 0.05$). RSM regression equations did not adjust, suggesting that higher order interaction and/or other variables not considered in the experimental design may have contributed to a better explanation of the data.

Table 2: ANOVA of yield and purity of acorn starches isolated with A3S and ENZ methods.

			Factor							
			CF[a] (L)	CF (Q)	Ct[b] (L)	Ct (Q)	CF x C t	Lack of Fit	Pure error	Total SS
A3S	Yield	SS	24.1320	92.8437	243.8640	57.6312	95.3555	39.9937	0.7080	396.1433
		df	1	1	1	1	1	3	1	9
		MS	24.1320	92.8437	243.8640	57.6312	95.3555	13.3312	0.7080	
		F	34.0824	131.1259	344.4164	81.3942	134.6735	18.8281		
		p	0.107999	0.055454	0.034270	0.070277	0.054723	0.167445		
	Purity	SS	1.71855	3.8773	5.76231	8.30579	2.33941	11.26010	1.12500	25.4670
		df	1	1	1	1	1	3	1	9
		MS	1.71855	3.8773	5.76231	8.30579	2.33941	3.75337	1.12500	
		F	1.527599	3.446473	5.122054	7.382922	2.079473	3.336325		
		p	0.433065	0.314549	0.264871	0.224503	0.385999	0.377848		

			Factor							
			EU[c] (L)	EU (Q)	Dt[d] (L)	Dt (Q)	EU x Dt	Lack of fit	Pure error	Total SS
ENZ	Yield	SS	7.47996	2.57941	0.00006	0.02331	0.04000	3.35721	0.98000	36.0250
		df	1	1	1	1	1	3	1	9
		MS	7.47996	2.57941	0.00006	0.02331	0.04000	3.35721	0.98000	
		F	7.632608	2.632052	0.000065	0.023784	0.040816	1.141909		
		p	0.221093	0.351657	0.994871	0.902588	0.873092	0.581592		

[a]CF: Centrifugation force; [b]Ct: Centrifugation time; [c]EU: Enzyme units; [d]Dt: Digestion time



Species	Method	Dependent variable	Equation	R^2	R_{adj}	Eq. number
Acorns	A3S	Yield	$56.161719+0.005254CF-0.000007CF^2-2.729673Ct+0.049276Ct^2+0.000460CF*Ct$	0.94	0.91	(5)
	ENZ	Yield	$19.609380-0.002758EU+0.000007EU^2-0.068455Dt+0.004450Dt^2+0.000050EU*Dt$	0.88	0.85	(6)

Table 3: Regression equation coefficients for response parameters of acorn isolated with A3S and ENZ methods.

Regarding acorn starch extraction using the same isolation procedure, not only does the centrifugation force have an effect, but also time was found to significantly affect the yield of starch extract. For acorn flours, the yield of starch isolation decreased when the centrifugation force was higher than 1500xg (Figure 3). Higher velocities of centrifugation gave higher starch extraction yield, but for acorns there is an additional aspect that must be considered. The acorn flour presented a starch content of 31.4%, when dried at 60 ºC (Correia et al., 2009). This means that in ideal extraction conditions the starch extraction yield must be close to this value. From Figure 2 it is possible to see that the optimum centrifugation conditions for acorns will be near 700xg and a duration of 15 minutes, because for different isolation centrifuge conditions not only will starch be present on the extract but also other compounds will. Furthermore, it is very important to guarantee that the centrifuge conditions do not increase the damage of starch granules. Considering these aspects for the tested centrifugation conditions, applied to the A3S method, a centrifugation force of 800xg rpm during 15 minutes should be used in future applications on chestnut and acorn flours.

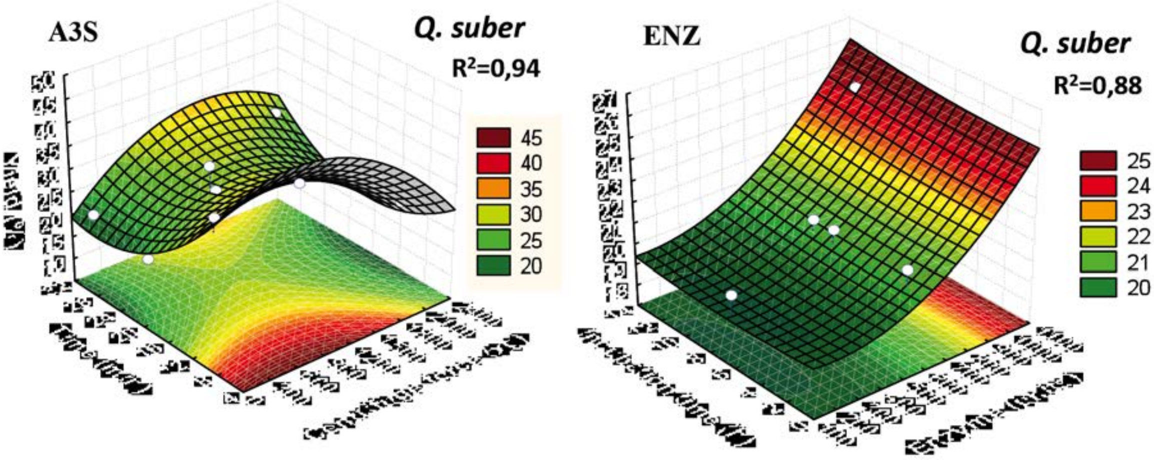


Figure 3: Extraction yield response surfaces for A3S and ENZ isolation methods for acorn starches.

In the ENZ method, as previously mentioned, applied centrifugation conditions were considered as a compromise solution for the A3S method, i.e., 800xg and 15 minutes. Considering the regression equation coefficients for response parameters of starch isolated from the ENZ method, the only equation adjusted from RSM was the one concerning the extract yield with r^2 of 0.88 (Eq. 5, Table 3). This equation was related to the yield of isolated starch. For purity of acorn, the regression equations did not adjust suggesting that higher order interaction and/or other variables not considered in the experimental design may contribute to a better explanation of the data. Only the enzyme quantity had a significant effect on the yield in isolated acorn starch (Figure 3). The starch extract yield increases with increasing amounts of protease (more than 900 units), despite the incubation time. However, considering the cost of the enzyme, we suggest that the conditions that should be used in the isolation of chestnut and acorn starches should be at least 900 units of protease despite the incubation time. In spite of the lack of adjustment in the case of chestnut starch extracts, the general trend was similar to that found for acorns.

Considering the initial starch content in the flours, and the quantity of starch extraction materials, the reached extraction yields and purity were 88.5% and 98.1%, respectively (Table 1). Comparing the modifications applied to the original method, the yield and purity increased 8.4% and 3.1%, respectively. When we compared the optimised results to those obtained by original method, it was possible to reduce the extraction time (by about 30 minutes) and energy costs.

Isolated acorn starches appeared to the naked eye as a light greyish-brown colour powder. Acorn starches granules were found to be round and oval in shape, consisting of medium/ small granules, with a mean granule size ranging between 9 to 13 µm (Figure 4). However, QS starch showed a larger range of sizes, with some granules larger than 60.0 µm in diameter. Soni et al. (1993) also reported for acorn starch granules from *Q. leucotrichophora* a larger diameter. ENZ method seems that had removed/ destroyed larger granules when compared to granule size distribution showed by A3S method. This effect was also reported by other authors in their researches (Daiuto et al, 2005). From the results it is evident that granule diameter of acorn starch varies greatly depending on species and starch isolation methods.

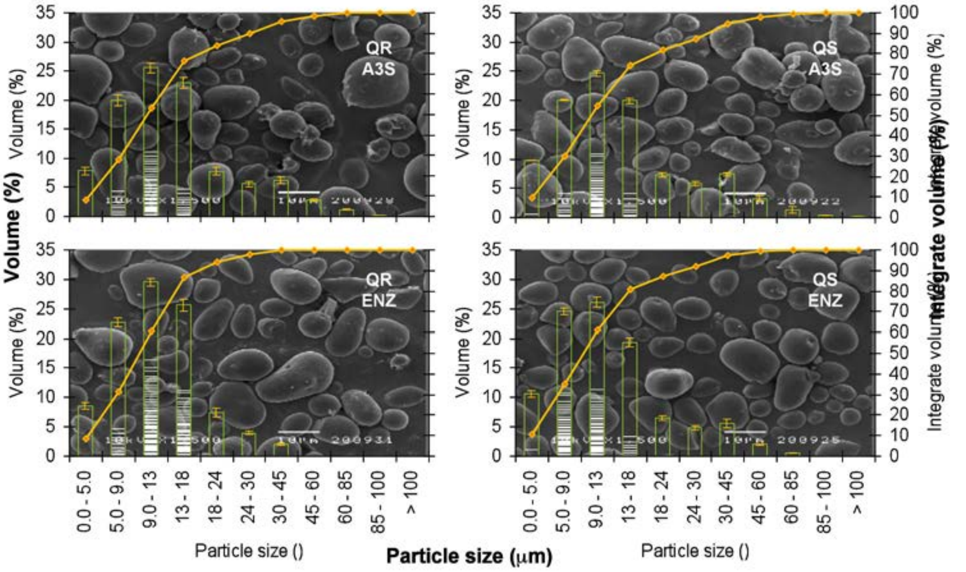


Figure 4: SEM (x1500) and granule size distribution of acorn starch: QR – *Q. rotundifolia*; QS – *Q. suber*; A3S – Alkaline pH and using successively three sieves method; ENZ – Enzymatic method.

The RS values are presented in Table 1. RS content is a measure of indigestible starch and so it is an important parameter from a nutritional perspective. Acorns presented a high content of RS, QS starches presenting the lowest value, 30.8% for ENZ starch isolation method. Acorn starches presented similar RS values to Palmyra starch (32.2%) (Naguleswaran et al., 2010).

The gelatinisation temperature of acorn starch, isolated by A3S optimised method was 72 ºC and pastes did not present breakdown, which suggests high paste stability during heating. Pastes presented a high final consistency and setback. A high setback consistency is associated with cohesiveness of the pastes (Otegbayo et al., 2006) and it is generally used as a measure of the gelling ability or retrogradation tendency of starch (Singh et al., 2009). It must be emphasised that the high consistency that was immediately acquired, when the pastes were cooled, suggests possible new applications of this starch as an alternative to the more conventional products.

The typical DSC (Differential Scanning Calorimetry) traces of gelatinisation for acorn starches are represented in Figure 5. Generally, acorns starches presented low enthalpy values (4.1-4.3 J/g) and E_a (1874-2189 Jmol-1), and the isolation method did not significantly affect these characteristics. Acorn starches generally presented low values of enthalpy and high activation energy, meaning that acorn starches need more energy to achieve gelatinisation, reflecting a strong and better organised structure of molecules in starch granules. The enthalpy (ΔH) values are similar to high-amylose starches, like pea wrinkled starch and other pulsed starches (Hoover et al., 2010), but lower relatively to *Quercus palustris* (Stevenson et al., 2006), meaning a low degree of internal molecular organisation of the granules.

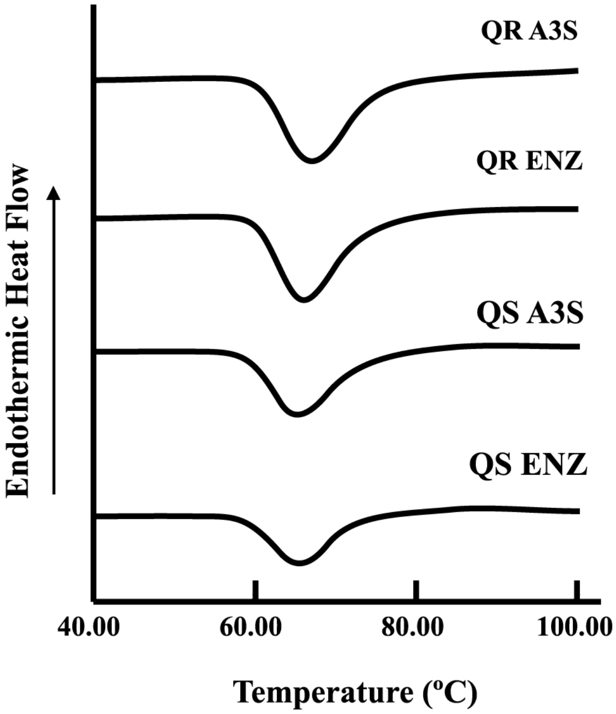


Figure 5: Endothermic transitions of acorn starches. QR: *Q. rotundifolia*; QS: *Q. suber*; A3S: alkaline isolation method; ENZ: enzymatic isolation method.

The X-ray diffraction patterns of starches from acorns are presented in Figure 6. Acorn starch shows a X-ray pattern where the polymorphs were present in varying proportions, whit a strongest diffractions peaks at 2θ of about 17° and 23°, and a few small peaks at around 15°, 20° and 26°. This patterns may be classified as a C-type X-ray pattern (a mixture of "A" and "B" unit cells), but more clearly related to B-type. Concerning crystallinity, no significant differences are presented between acorn starches, showing high percentage of this parameter, when compared for example to pin oak acorn starch (Stevenson et al., 2006). QR starches showed higher crystallinity values, and the A3S method produced also starches with higher degree of crystallinity, which could mean that its original structure is less disturbed.

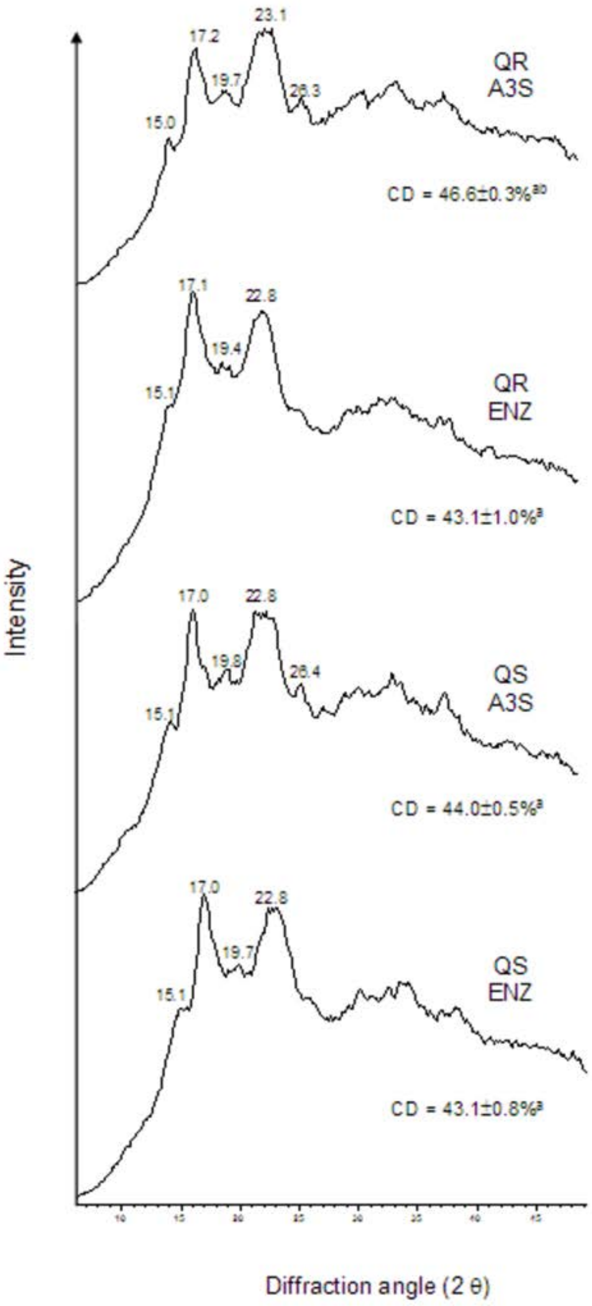


Figure 6: X – ray diffraction patterns of acorn starches. QR – Q. rotundifolia; QS – Q. suber; A3S - Alkaline pH and using successively three sieves method; ENZ – Enzymatic method; DC – Crystallinity degree (%). Data with the same superscript letter are not significantly different ($p<0.05$).

4. CONCLUSIONS

The best isolation method found was the alkaline method at low shear using three sieves (A3S) successively, that was followed by the enzymatic method. These methods were optimised for centrifugation, and enzymatic units/ incubation time, respectively. Starch produced by those conditions showed to be higher in purity and yield, with high contents of amylose and resistant starch. Acorn starches presented high paste consistencies, with higher final and setback consistencies, and did not present a breakdown. Thus, *Q. rotundifolia* and *Q. suber* starch could be classified as tolerant to heating and shearing processes. Furthermore, the physicochemical and functional properties of acorn starches, a non-conventional source, suggest that this product may be used as an ingredients for foods and other industrial applications.

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03. WOOD AND WOOD COMPOSITES DURABILITY AND PROTECTION

OIL HEAT TREATMENT OF TIMBER FOR REDUCED HYGROSCOPICITY

MORWENNA SPEAR[1,*], VALERIE FLEURENTDIDIER[2],
BRONIA STEFANOWSKI[1] AND GRAHAM ORMONDROYD[1]

[1] THE BIOCOMPOSITES CENTRE, BANGOR UNIVERSITY, DEINIOL ROAD, BANGOR, GWYNEDD, LL57 2UW, UNITED KINGDOM.

[2] ENSTIB, 27 RUE PHILIPPE SÉGUIN, B.P. 1041, 88051, EPINAL, CEDEX 9, FRANCE.

* CORRESPONDING AUTHOR: +44 1248 382029, M.J.SPEAR@BANGOR.AC.UK

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ABSTRACT

Thermal treatments of timber using vegetable oil offer a method for effective dimensional stability and durability enhancement, while reducing the brittleness and loss of strength seen in air-based heat treatments. This study considers in detail the moisture relationship of the treated timber, and the parallel contribution to reduction of hygroscopicity due to the presence of the oil, and due to the chemical changes in the timber resulting from the action of heat. Scots pine timber treated at 200 °C for 1, 2 and 3 hours was compared with untreated Scots pine in cyclic conditioning and leaching experiments. Consideration of Equilibrium Moisture Content (EMC) and a modified Equilibrium Moisture Content (EMC_{mod}) revealed interaction of the weight percent gain (WPG) and duration of treatment with the hygroscopicity. To quantify not only the WPG due to oil uptake but also weight loss due to thermal treatment, solvent extraction was performed, revealing surprising results. Helium pycnometry was then performed on extracted treated timber to determine changes in the wood density. This revealed differences in the wood cell wall after 1 h compared to the 2 and 3 h treatments.

1. INTRODUCTION

Heat treatment of wood has been well explored and commercialised in Europe and North America, with increasing interest in this technology being shown in other regions. Many thermal treatments are conducted in air, in steam or in inert gases such as nitrogen (Hill, 2006). The latter of these offer some degree of control over the level of thermally initiated oxidative changes (both physical and chemical) by controlling the level of oxygen present. It has long been acknowledged that high levels of oxidation led to degradation in strength and impact performance of the timber (Rusche, 1973; Kamdem et al., 2002; Gosselink et al., 2004). The intensity of treatment is a function of both treatment temperature and duration, and within this matrix there is a trade off between treatment intensity and excessive oxidation leading to degradation of the material (González-Peña et al., 2004; Hill, 2006; González-Peña et al., 2009).

Oil heat treatments offer a different solution to the issue of oxidation, as the oil excludes oxygen from the timber during treatment, at the same time as providing rapid thermal transfer to the timber by the oil (Sailer et al., 2000; Rapp and Sailer, 2001). Previous studies have reported many aspects of oil heat treatment – temperature, degree of oil permeation into different species of timber, duration of treatment, pressure, vacuum and other process parameters (Sailer et al., 2000; Rapp and Sailer, 2001; Tjeerdsma et al., 2005; Wang and Cooper, 2005; Spear et al., 2006a; Podgorski et al., 2007; Simon et al., 2008; Dubey et al., 2012). Very good performance in fungal decay resistance has been reported for oil heat treated timber (Rapp and

Sailer, 2001; Spear et al., 2006a,b) while the strength properties of oil heat treated timbers are frequently close to the strength of the untreated timber.

This study resulted from investigations into the role of the oil remaining within the treated timber in limiting potential for moisture uptake, and thus the reduced susceptibility to fungal decay due to suppressed moisture content of the treated wood. In permeable species such as pine sapwood the quantity of oil in the cell lumen may be high. For example, WPGs of 89.5-89.9% have been shown for Corsican pine with linseed oil, and 95.5 to 101.7% for rapeseed oil (Spear et al., 2006b), while the WPG is much lower in species with poorer permeability such as Norway spruce (12.3% for linseed oil) (Spear et al., 2006b). Differences between treatment oils are known to occur, and differences with treatment protocol are also significant – treatment with a less severe vacuum reduced the WPG to 50.1% for Corsican pine blocks of the same dimensions as the previous study, again with rapeseed oil (Spear et al., 2006a).

Treatment which leaves less oil within the wood may be desired commercially to minimise materials costs, and to create a lower density product. On the other hand, the quantity of oil which remains in within the wood may have a great influence on the level of decay resistance attained, as moisture availability for fungal metabolism (one controlling parameter) is reduced (Spear et al., 2007). The fungitoxicity of any thermal changes to the timber chemistry is a separate parameter, although studies on extracts from heat treated timber have shown very limited controlling effects on fungal growth (Hakkou et al., 2006; Mohareb et al., 2012). Thirdly there is the reduction in availability of wood polyoses for fungal metabolism due to thermally induced change in the hemicellulose chemistry (Tjeerdsma et al., 1998; Hakkou et al., 2006; Severo et al., 2012).

Two main moisture uptake routes may be considered: the uptake of liquid water by immersion, and adsorption of atmospheric moisture due to humidity gradients. Both of these factors are considered in the two investigations reported and discussed in this paper – the effect of step-wise change in relative humidity to condition treated blocks at three relative humidity levels, and a cyclic soaking and drying procedure to obtain fully saturated wood on percentage uptake of water. In the first study the EMC was determined at each defined relative humidity, along with the dimensional change due to moisture uptake. In the second study a maximum degree of swelling and water uptake was achieved to demonstrate the differences between treatments. Again the dimensional change in radial and tangential direction was recorded as well as the water uptake.

2. **METHODS**

Blocks of Scots pine (*Pinus sylvestris*) sapwood were treated using rapeseed oil for durations of 1, 2 and 3 hours, at 200 °C. The oil was pre-heated to 150 °C prior to introduction of the blocks, meaning that heat treatment started immediately on immersion of the timber in the treatment oil. The temperature of the oil and blocks reached 200 °C within ten to fifteen minutes of immersion, and the time for treatment was timed from the moment that the temperature reached 200 °C.

The blocks for treatment were prepared from Scots pine, and cut to 20 x 20 mm, with these faces having good alignment with the radial and tangential direction of the block. The thickness of blocks in the longitudinal direction was 5 mm. This offers very good accessibility of the treatment oil to the timber structure, giving a maximum uptake of oil and removing any time delay in thermal transfer throughout the sample.

At the end of the cycle the treated blocks were removed from the treatment oil, drained and cooled, then transferred to an oven set to 105 °C over night to ensure no moisture uptake before determination of oven dry weight. Oven dry weight and dimensions were recorded for blocks prior to treatment and after the treatment protocol.

2.1. CONDITIONING EXPERIMENT

Twenty oven dry blocks from each treatment (1, 2 and 3 hours duration) were used with twenty untreated Scots pine control blocks in the conditioning experiment. These were transferred to a desiccator above saturated magnesium chloride solution at 20 °C to provide a relative humidity (RH) of 33% within the chamber. The blocks were weighed daily in the initial stages of the moisture curve, or at intervals of two to three days as necessitated by the working week. Once a stable weight was observed (with a change of less than 0.01% compared to the previous day) this was considered to be the Equilibrium Moisture Content (EMC). The blocks were then measured to determine the swelling at the EMC for 33% RH.

The blocks were then transferred to a desiccator above saturated sodium bromide solution (providing a relative humidity of 58% within the chamber). Weights were again recorded at regular intervals to chart the uptake of moisture and the establishment of equilibrium moisture content. On attainment of EMC at 58% RH, the dimensions were recorded before transfer to a desiccator above zinc sulfate solution (giving a relative humidity of 90%). At this humidity the measurements were taken at two day intervals due to the time lag in establishing the 90% relative humidity in the chamber after opening for each weighing.

2.2. SOAKING EXPERIMENT

Following the full sequence of humidity conditioning stages, ten blocks were selected for a soak test. These blocks were soaked in 100 ml of deionised water by a vacuum process similar to that used in preservative treatment systems. The blocks were placed upright within separate beakers and small glass beads were used to separate them, ensuring good access of moisture to the two large faces of each block. Ballast was added above to avoid disturbing the blocks during handling. The vacuum was established in a desiccator for 15 minutes, before 80 ml of the water was introduced using a separating funnel above the desiccator to fill the beaker. The vacuum was maintained for a further 5 minutes to assist impregnation, then the vacuum was released and the remaining water was added. The blocks were then left for 5 days at room temperature to affect maximum swelling of the wood cell wall by the water.

After the 5 day soak, the water was decanted and the wet blocks were removed, blotted lightly and their weights and dimensions recorded. The blocks were then heated in a 50 °C oven overnight to initiate drying, then dried in a 105 °C oven for the remainder of 2 days. They were then cooled in a desiccator and weighed and measured.

2.3. HELIUM PYCNOMETRY

Specimens were prepared for helium pycnometry by sawing two thin strips (2.75 +/- 0.25 mm) from the side of the 20 x 20 x 5 mm block. The three pieces of wood were oven dried, then placed together in an AccuPyc 1330 Helium Pycnometer and the density of the wood was determined. Twenty purges were used, and ten observed volume measurements, corresponding to ten density values, were used to determine average density.

Samples of untreated wood, and treated extracted wood from each of the three treatment durations, were analysed. In the case of treated extracted wood, a group of five treated blocks (from the same treatment) were placed in a Soxhlet extractor and extracted with 300 ml toluene for 6 hours. The extraction removed the oil, and may have removed other components from the wood. A sample of the extraction liquor was retained for analysis.

3. RESULTS

3.1. WEIGHT PERCENT GAIN CALCULATION

The Weight Percent Gain (WPG) due to treatment for the three durations was calculated according to Equation 1 using the oven dry weight before (W_{unmod}) and after treatment (W_{mod}). Dimensional change in the radial and tangential direction were also calculated as a percentage of the respective oven dry dimension.

$$\mathrm{WPG} = \frac{(W_{mod} - W_{unmod})}{W_{unmod}} \times 100 \qquad (1)$$

Values for WPG and dimensional change are presented in Table 1. It can be seen that the magnitude of radial and tangential dimension change increased as the duration of treatment increased. Longitudinal change is less reliable as the small block dimensions in this orientation mean that small errors in measurement can have a disproportionate effect on observed percentages.

Table 1: Weight percent gain and percentage change in block dimensions due to hot oil treatment. Standard deviation values in parentheses.

Treatment	WPG	Radial change (%)	Tangential change (%)	Longitudinal change (%)
1 hour	69.78 (7.41)	-0.34 (0.71)	-0.92 (0.39)	1.11 (4.54)
2 hour	18.85 (11.41)	-0.78 (0.20)	-1.44 (0.37)	1.02 (5.13)
3 hour	26.96 (5.65)	-0.86 (0.18)	-1.82 (0.32)	0.11 (4.12)

The weight percent gain values follow two competing trends – the uptake of oil leading to an increase in mass, and the anticipated thermal changes in the timber leading to a (smaller magnitude) reduction in mass. This hypothesis is based on the known mass loss for thermally treated wood from air, steam or nitrogen atmosphere treatments. It is proposed that the 1 hour treatment has the smallest thermally induced reduction in mass, and the 3 hour treatment is likely to show the greatest reduction if the weight due to oil could be excluded.

3.2. CONDITIONING STUDY

The uptake of atmospheric moisture during conditioning was plotted for treated and untreated blocks (Figure 1). The conditioning at 33%, 58% and 90% RH continued until equilibrium moisture content was developed at each stage. The values for equilibrium moisture content as calculated according to Equation 2 are presented in Table 2.

$$\mathrm{EMC} = \frac{(W_{cond} - W_{dry})}{W_{dry}} \times 100 \qquad (2)$$

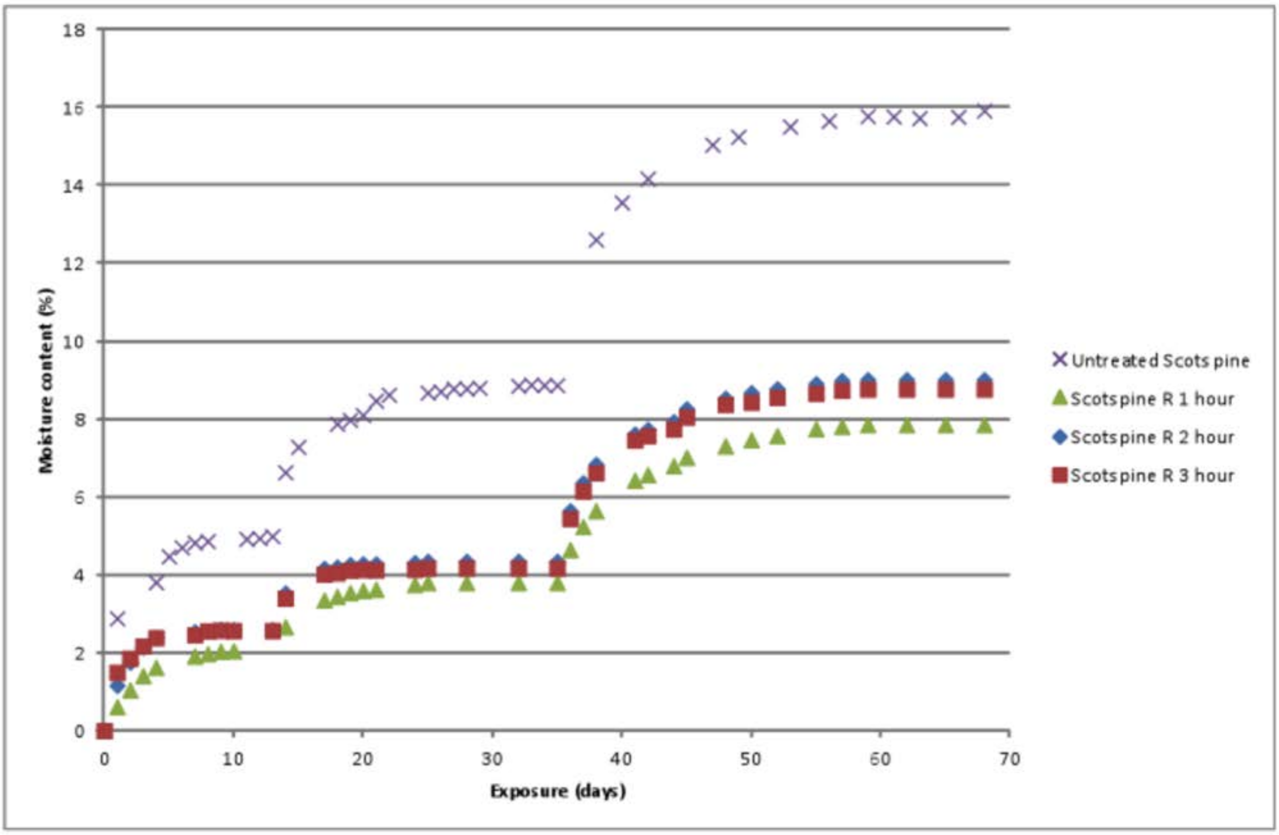

Figure 1: Moisture content developed in treated and untreated Scots pine during the time spent conditioning at 33% RH (days 1-13), 58% RH (days 14-35) and 90% RH (days 36-68).

Table 2: Equilibrium moisture content in Scots pine timber treated with rapeseed oil, and untreated control samples.

	33% RH	58% RH	90% RH
Untreated	4.99	8.87	15.92
1 hour treatment	2.05	3.80	7.86
2 hour treatment	2.59	4.35	9.01
3 hour treatment	2.57	4.17	8.77

It can clearly be seen that each of the three treated timbers developed a lower EMC than the untreated control. The 1 hour treatment appears to have a slightly lower EMC than the 2 and 3 hour treatments. However, this may relate to significant differences in the treated weight, resulting from significantly different WPG values (Table 1). The water uptake must be considered independently of the WPG effects, using EMC_{mod} where the moisture uptake is expressed as a percentage of the weight of the timber prior to treatment (Equation 3).

$$\mathrm{EMC_{mod}} = \frac{(\mathrm{W_{cond\ treated}} - \mathrm{W_{dry\ treated}})}{\mathrm{W_{dry\ untreated}}} \times 100 \qquad (3)$$

Table 3 shows the EMC_{mod}, for each relative humidity studied. This is a good estimate of the quantity of moisture relative to the location where it is most likely to reside, i.e. the wood cell wall.

Using EMC_{mod}, the value for the one hour treatment is shown to be higher than that of the two and three hour treatments (Table 3), as is consistent with the hypothesis that extending treatment period will increase the severity of thermally induced changes within the cell wall, increasing hydrophobicity. It is proposed that in thermal and chemical modification systems, where mass change of the timber is high, the use of EMC_{mod} provides a better benchmark for comparison of the efficacy of the treatment in altering hygroscopicity than the standard EMC calculation.

Table 3: EMC_{mod} of rapeseed oil treated Scots pine timber after conditioning at 33%, 58% and 90% relative humidity.

	33% RH	58% RH	90% RH
Untreated	4.99	8.87	15.92
1 hour treatment	3.51	6.53	12.56
2 hour treatment	3.05	5.12	10.05
3 hour treatment	3.26	5.29	10.63

The anti-swelling efficiency (ASE) of the timber was calculated at EMC for 33, 58 and 90% relative humidity, according to Equations 4 and 5. The radial (R) and tangential (T) dimensions were used for determination of the swelling coefficient (S) rather than volume as the short length of the 20 x 20 x 5 mm samples means small fluctuations in longitudinal dimension have a very strong mathematical effect on the volume. Dimensional stability is principally an issue in the transverse plane of wood rather than the longitudinal dimension, so the use of R and T is justified as these are the primary focus of investigation. S_c is the swelling coefficient for control timber, and S_{mod} the swelling coefficient for the modified timber.

$$S = \frac{(R \times T)_{soaked} - (R \times T)_{dry}}{(R \times T)_{dry}} \times 100 \qquad (4)$$

$$ASE = \frac{(S_c - S_{mod})}{S_c} \times 100 \qquad (5)$$

Table 4: ASE for rapeseed oil treated Scots pine conditioned to EMC at three relative humidities and in the soaked state.

	33% RH	58% RH	90% RH	Soaked
1 hour treatment	47.43	50.57	34.79	28.77
2 hour treatment	49.13	58.21	36.70	34.83
3 hour treatment	40.33	54.80	32.78	33.72

The strongest anti-swelling efficiency was seen at 58% relative humidity for all three treatment systems. This humidity is close to that encountered in buildings, meaning that for many applications the dimensional stability of this heat treated wood could be advantageous. Interestingly the ASE on conditioning up to 90% RH declined, possibly indicating that the chemical changes in the thermal treatment system are not a complete and permanent blocking effect, but a delaying effect, on the moisture uptake. The higher humidity may be sufficient to re-open these pore spaces in the timber, or to provide sufficient enthalpy for hydrogen bonding to occur with atmospheric moisture leading to adsorption and some swelling. Similar effects have been shown for traditional heat treated wood by Almeida et al. (2009).

ASE was also calculated after full immersion of the same set of timber blocks in deionised water for a five day period (Table 4). The values were of similar magnitude to those seen at 90% relative humidity, confirming the trend for swelling at high humidity to be greater than that observed in the humidity range encountered in the built environment.

The weight of water taken up during soaking was calculated, both as a proportion of treated weight, and as a proportion of original block weight. These values are shown in Table 5, and reveal a large difference in the amount of water taken up by the 1 hour treatment compared to the 2 and 3 hour treatments. In previous studies on sticks prepared for DD ENV 807 testing, total saturation of pine was reported after BS EN 84 leaching (Spear et al., 2007), for those samples the water uptake was only 24% of treated weight, again relating to saturation with oil physically restricting moisture ingress.

Table 5: Water uptake (% weight) due to 5 day soak, and uptake as a proportion of available non-wood non-oil volume in the treated and the treated soaked blocks.

	Water Uptake Mass		Water Uptake Volume	
	As % of Treated Weight	As % of Timber Weight	As % of Available Volume Treated	As % of Available Volume Treated Soaked
Untreated	144.24	144.24	123.30	98.18
1 hour treatment	38.32	66.36	166.76	110.49
2 hour treatment	95.87	112.67	111.03	93.76
3 hour treatment	77.86	99.63	115.32	95.06

The volume available for free water to occupy within the 1 hour treated blocks was lower than for 2 and 3 hours, due to the very high weight gain of oil, so volume of available space was also considered (Table 5). The volume of water taken up exceeded the calculated available space, when considering the treated block dimensions. This additional volume requirement was accommodated by the swelling of the wood.

Using treated soaked dimensions, the percentage of available space values were under 100% as might be expected. The exception was the 1 hour treatment, where water displaced oil, giving oil droplets on the leaching liquid surface at the end of the soak test. Thus some of the oil present in 1 hour treated wood is mobile and can be leached or displaced. All treated timbers took up less water than the untreated control blocks.

3.3. EXTRACTION FOR HELIUM PYCNOMETRY

The 20 x 20 x 5 mm blocks were solvent Soxhlet extracted using toluene to remove excess oil, prior to determination of their density by helium pycnometry. The weight lost during extraction was calculated as a proportion of the treated block weight. To allow comparison with the original weight percent gain, the weight loss was also calculated as a percentage of the weight prior to treatment. It can be seen that for the 1 hour treatment a large proportion of the weight gained due to oil uptake was then lost on extraction, although this was not complete, 56.06% was removed, compared to the initial 63.16% weight gain. For the two and three hour treatments there was a larger discrepancy between WPG and weight lost, indicating considerable oil retention even after extraction.

To estimate the oil remaining in the blocks WPG_{extr} was calculated, this was the weight gain after treatment plus extraction determined as a percentage of untreated weight (Equation 6). In all cases WPG_{extr} gave a positive number, indicating net oil gain even after extraction. The values for this are reported in Table 6, alongside the WPG recorded for the subset of five blocks used in the extraction process.

$$WPG_{extr} = \frac{(W_{extracted} - W_{unmod})}{W_{unmod}} \times 100 \qquad (6)$$

Table 6: Weight gain due to oil heat treatment and weight loss on solvent extraction for subset of five blocks from each treatment. WPG_{extr} is the residual weight percent gain after treatment plus extraction.

Conditions	Samples Used	WPG (%)	Weight Loss (% Treated)	Weight Loss (% Untreated)	WPG_{extr} (%)
Rapeseed oil 1 hour	92, 95, 97, 98, 99	63.16	-31.00	-56.06	12.31
Rapeseed oil 2 hour	52, 54, 55, 56, 57	21.03	-10.96	-7.63	7.52
Rapeseed oil 3 hour	121, 122, 123, 124, 125	27.02	-5.27	-9.70	20.31

3.4. HELIUM PYCNOMETRY

The average density values for the solvent extracted wood samples are presented in Table 7. It can be seen that the presence of oil residue in the blocks, even after extraction, reduced the density observed, so in all cases density was lower than that for untreated Scots pine (1.4538 g/cm^3).

Table 7: Density values determined by helium pycnometry.

Sample	Mass (g)	Volume (cm^3)	Density (g/cm^3)
1 hour treatment	1.0859	0.9830	1.1113
2 hour treatment	1.0482	0.8343	1.2584
3 hour treatment	1.0493	0.8277	1.2712
Untreated	0.9331	0.6422	1.4538

It is clear from Tables 6 and 7 that the toluene extraction did not fully remove the rapeseed oil from the treated blocks prior to density measurement. Toluene shows good miscibility with rapeseed oil at room temperature, so had been selected as a suitable solvent, however it proved unable to remove oil from the cellular structure of timber.

The density of the rapeseed oil used for treatments was measured as 0.9238 g/cm^3, while average value observed for the Scots pine wood cell wall was 1.4538g/cm^3. The presence of oil thus reduces the observed density of the cell wall material in the treated extracted blocks. This is especially the case for the one hour treatment, where even after extraction, there was a considerable weight percent gain on the original weight (12.31%) and density was 1.1113g/cm^3.

To investigate the effect of oil on the density further, the WPG$_{extr}$ data for each block was used to calculate the weight of oil and of wood present per block. This data was then combined with the density of rapeseed oil to predict the density of the treated wood cell wall material. The results indicated lower than expected values for all three treatment regimes, with the lowest density being seen in the shortest treatment (Figure 2).

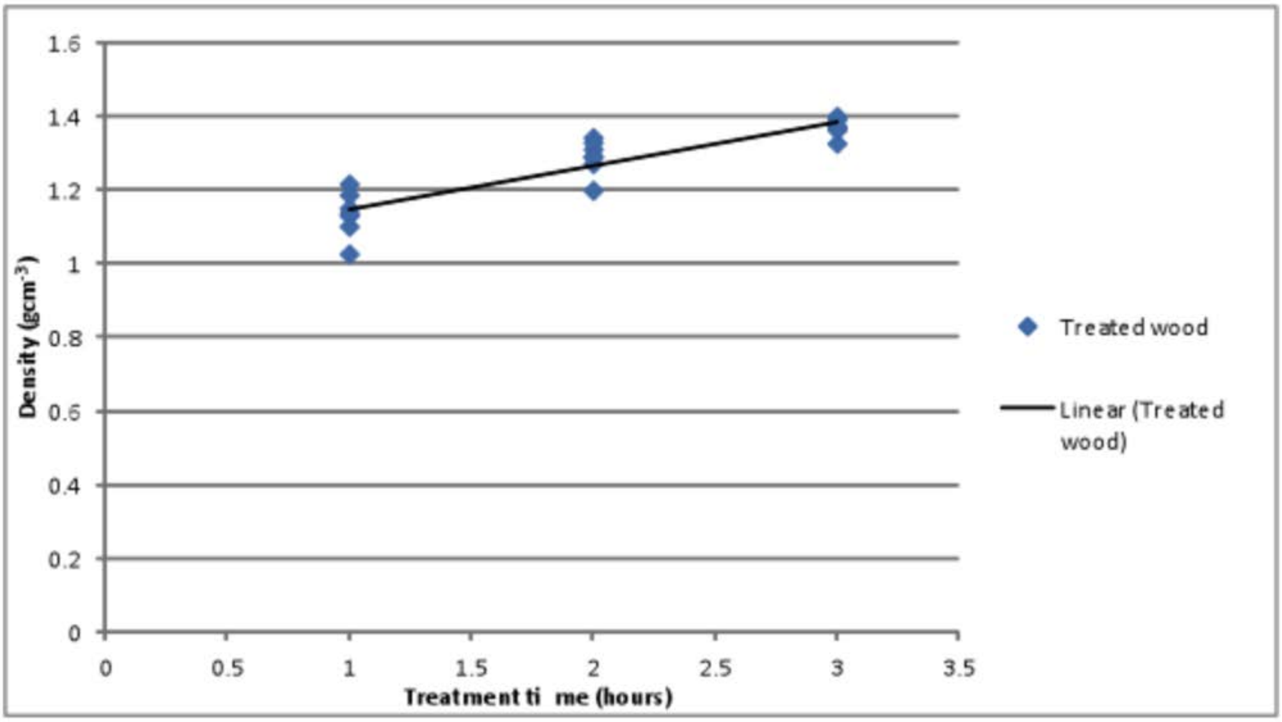

Figure 2: Predicted values for wood density when based on WPG$_{extr}$ and density of unused rapeseed oil.

The positive gradient of the graph for predicted wood density was unexpected, as a loss of density by wood with increased treatment duration was previously believed to occur. The authors acknowledge that WPG$_{extr}$ is not a perfect measure for predicting the quantity of oil present (as any weight loss by the wood on treatment is neglected in WPG$_{extr}$). However, if weight loss by the timber increases the true oil weight above that predicted using WPG$_{extr}$, then although the timber density is increased it is impossible for the weight loss at 1 hour to be greater than that at 2 or 3 hours.

If we assume that weight loss in the wood cell wall increases by a small increment from 1 hour to 3 hours, then the oil can be assumed to be underestimated to a greater extent by WPG$_{extr}$ in the 3 hour data than the 1 hour data. However, this would increase rather than decrease the gradient of the trendline (Figure 3).

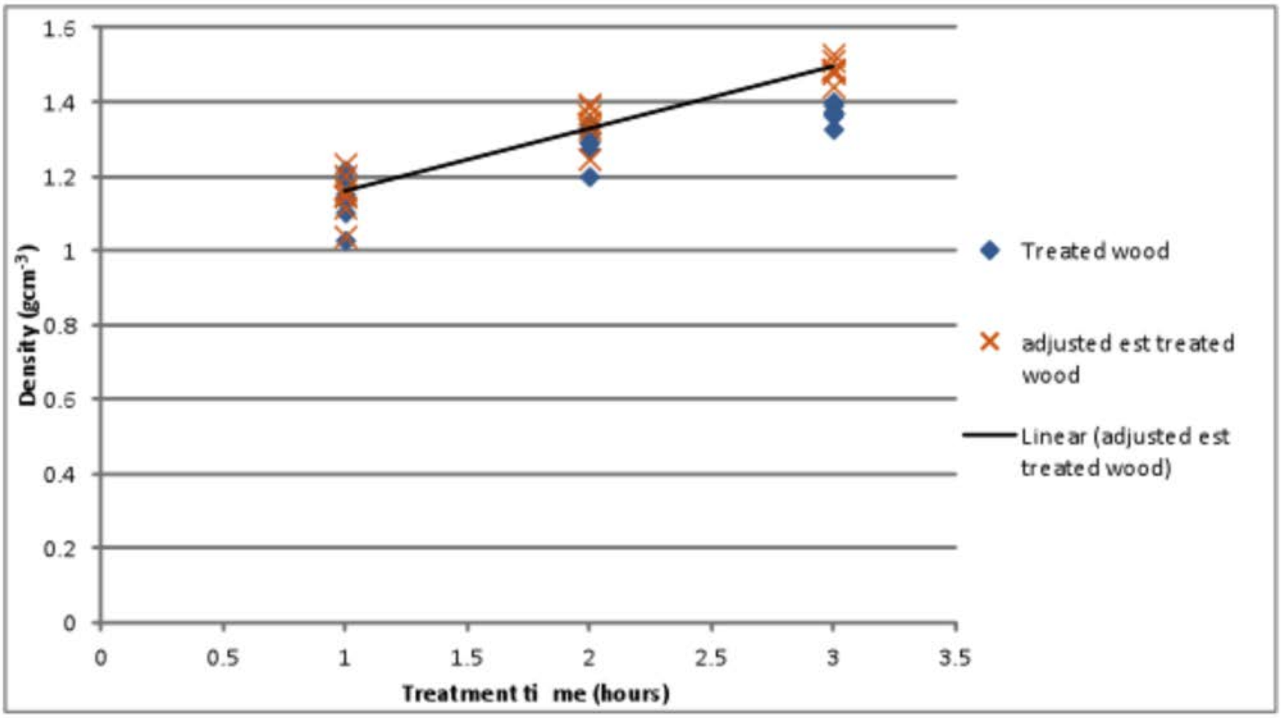

Figure 3: Demonstrating the effect of assuming small, medium and large weight loss for 1, 2 and 3 hour treatment on the wood cell wall density values estimated.

It is more likely that density change at 1 hour is due to the loss of weight being greater than the loss of volume at that point in the treatment. The increase in treatment time then alters the volume and the mass. Previous work with traditional heat treatment by Pfriem et al. (2009) has shown that a lower intensity heat treatment (180 °C spruce) led to a density decrease while higher intensity treatment at 200 °C led to a slight increase. The magnitude of the reported changes were smaller (-6.3%, 180 °C; +4.9%, 200 °C) than shown in this oil treatment study (-21.8%, 1 hour; -11.2%, 2 hours; -5.7%, 3 hours), but this may be due to the absence of oil, and to the treatment duration used in the commercial timber studied by Pfriem.

Further investigation is necessary to separate the volume effect out from the effect of the presence of oil. Work is under way using a different solvent system and density data from additional samples to explore the effect of oil heat treatment on wood cell wall density, and will form the basis for future work.

4. CONCLUSIONS

This study has investigated the relationship of water with oil heat treated wood using techniques which have not been reported previously for this material. It has shown that the EMC for oil treated wood is reduced in a similar manner to conventional heat treated wood, when conditioned at various levels of relative humidity. The level of swelling observed was also suppressed, and anti-swell efficiency (ASE) values of 50 to 58% were shown for the three treatment durations. Both properties indicate a reduced hygroscopicity and thus decreased moisture movement in timber. This property is significant when considering timber for use in environments with fluctuating humidity, such as joinery products for kitchens and bathrooms, but also for exterior windows and doors.

In soaking tests it was demonstrated that the total water taken up was reduced for oil heat treated wood, to a greater extent than conventional thermally modified wood – due to the presence of the oil. Primarily this will be a reduction in the free water, i.e. that is present within the cell lumena and available for flow.

Furthermore, the ASE values recorded for water soak were of similar magnitude to those seen at EMC for 90% relative humidity (with the possible exception of the 1 hour treatment, which was of lower intensity than the 2 and 3 hour treatments, but even here only a reduction of 6% was seen from 90% humidity to full soak). This low swelling relates to a reduction in available hydroxyl-rich pore spaces for hydrogen bonding within the wood cell wall. If swelling can be considered proportional to the capacity for bound water within the wood wall, then the results presented indicate that the oil heat treated wood has a reduced capacity for both free and bound water.

Finally, the study of the density of the cell wall material in untreated and treated Scots pine has shown some interesting results which indicate that the alteration of mass and density in oil heat treated wood is not as simple a two-phase model as often proposed or discussed. It appears that the mass loss by the cell wall may not occur simultaneously with changes in volume during the treatment progression, rather the change in density during treatment time may follow a non-linear trend as mass and volume undergo conflicting changes, thus a positive rather than negative gradient was observed when modelling the wood cell wall density for oil heat treated samples using helium pycnometry data.

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LIQUEFIED LIGNOCELLULOSICS AS A RENEWABLE ALTERNATIVE TO OIL REFINERY-BASED COMPONENTS OF WOOD COATINGS

ARNAUD MAXIME CHEUMANI-YONA[1,2], FRANC BUDIJA[1,2] , BORUT KRIČEJ[1], ANDREJA KUTNAR[2,3], PAVLI PORI[1,4], MATJAŽ PAVLIČ[1], ČRTOMIR TAVZES[2], MARKO PETRIČ[1,*]

[1] UNIVERSITY OF LJUBLJANA, BIOTECHNICAL FACULTY, DEPARTMENT OF WOOD SCIENCE
AND TECHNOLOGY, JAMNIKARJEVA 101, SI 1000 LJUBLJANA, SLOVENIA
[2] ILTRA D.O.O., INSTITUTE OF WOOD SCIENCE AND TECHNOLOGY, AND SUSTAINABLE
DEVELOPMENT, CELOVŠKA CESTA 268, SI 1000 LJUBLJANA, SLOVENIA
[3] UNIVERSITY OF PRIMORSKA, ANDREJ MARUŠIČ INSTITUTE, MUZEJSKI TRG 2, SI 6000 KOPER, SLOVENIA
[4] CHEMCOLOR SEVNICA D.O.O., DOLNJE BREZOVO 35, SI-8290 SEVNICA, SLOVENIA
[*] CORRESPONDING AUTHOR: TEL: +386 1 320 3620; FAX: +386 1 257 2285; MARKO.PETRIC@BF.UNI-LJ.SI

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ABSTRACT

Liquefaction of renewable bioresources for the production of polymers has attracted much attention in recent years. The research is driven by the need for new materials with increased sustainability. While solvolytic liquefaction of wood has already been an issue of extensive research, there is less knowledge on liquefaction of cork, due to its distinctive chemical and physical properties. The industrial processing of cork generates large amounts of cork powder and our investigations exhibited that it can be liquefied using glycerol as the reactive solvent. The liquefaction yield, which is dependent on the catalyst type (acid or base), temperature, reaction time and catalyst content, of up to 73 % was obtained with a cork to glycerol mass ratio of 1:3. Subsequently, some polyurethane type wood coatings were prepared from the liquefied cork and some of their characteristics were determined. However, an important drawback of liquefied lignocellulosics is their dark-brown to black color that could limit their use in preparation of coatings due to aesthetic reasons. So, the possibility of discolouration of liquefied wood with various activator/hydrogen peroxide and laccase model systems was investigated. The most promising results – up to 80 % rate of discolouration - were obtained with the copper(II)/pyridine and potassium carbonate activated hydrogen peroxide. It was shown that the liquefied biomass can be converted into a yellowish product, applicable also for preparation of wood coatings. This paper is a compilation of our selected investigations of liquefaction of wood and cork and of applications of liquefied lignocellulosics in preparation of coatings.

1. INTRODUCTION

Due to negative impacts of usage of fossil based resources on the environment and their potential shortage in the future, utilisation of renewable natural resources is becoming increasingly important. Apart from applications of biomass in a solid form, also gas and liquid based products can be produced and used as a fuel or for organic syntheses (Lin et al., 1997). In recent years, the so-called liquefaction of biomass, including wood, has attracted considerable attention. Liquefaction is one of possible conversion methods of biomass into a liquid state (Demirbas, 2001). It is a thermochemical process – a solvolysis - and can be performed under atmospheric pressure at a moderately elevated temperature. There have been numerous reports in literature on wood liquefaction and possible applications of liquefied biomass and wood (for instance in Kobayashi et al., 2000; Kurimoto et al., 2001; Yamada and Ono, 2001; Doh et al., 2005; Budija et al., 2009; Kunaver et al., 2010). Direct liquefaction processes attempt to produce a product without going through the gas phase (Akdeniz and Gündoğdu, 2007). One of the most frequently applied liquefaction system is based on polyhydric alcohols (Budija et al., 2009). Lin and Hse (2005) used for instance the mixture of polyethylene glycol 400 (PEG 400) and glycerine with the sulphuric acid as a catalyst and with the ferrous salts as additives. In the area of wood science and technology, the major emphasis has been given on applications of liquefied lignocellulosics for wood adhesive resins and adhesives themselves. For instance, polyurethane (PU) as a wood laminating adhesive was prepared from liquefied kenaf core (Juhaida et al., 2010). Lee and Lin (2008) made PU adhesives from polyhydric liquefied Taiwan acacia and China fir. Similarly, wood polyalcohol-based isocyanate adhesives were prepared and synthesised by Tohmura et al. (2005). The liquefied spruce wood was reacted in a condensation reaction in the hot press with different melamine-formaldehyde and melamine-urea-formaldehyde resin precursors and used as adhesives for wood particle boards (Kunaver et al., 2010). Antonović and co-authors (2010) have investigated the influence of urea-formaldehyde resin modification with liquefied wood on particleboard properties. If liquefied wood could be used to produce adhesive resins, one could anticipate the same also for coating binders. However, up to our best knowledge, reports on possible uses of liquefied wood in paint and especially wood coating formulations are rare. An example is the work of Abdel-Mohdy and co-authors (2009) who used a liquefied rice straw as a new resource for paint formulations.

Cork is also an attractive material for liquefaction and subsequent preparation of bio-polymers. At the moment, cork oak stands produce about 280,000 tons of raw cork annually, and the industry processes slightly less than 80 % of this amount into various products, predominantly stoppers (Cordeiro et al., 1998; Silva et al., 2005; Gandini et al., 2006). The industrial processing of cork creates large amounts of cork powder. This by-product could be possibly more efficiently used for the production of bio-polymers, instead of for energy production by burning. However, the same approach as for liquefaction of wood cannot be directly applied to cork, while in addition to cellulose, lignin, hemicelluloses, and extractives, cork contains suberin, which is its main component. Nevertheless, liquefaction of cork was performed by the cyclic carbonate method and the obtained polyols were used for preparation of polyurethanes (Evtiouguina et al., 2001; Evtiouguina et al., 2002).

Several technological barriers have still to be overcome before liquefied lignocellulosic products meet the requirements of the market as a raw material for polymer synthesis. One of them is their colour. Liquefied products have a dark-brown or almost black colour that could limit their use due to aesthetic reasons. This colouration is probably because of the formation of carbonyl groups (C=O) and carbon-carbon double bonds (C=C) during liquefaction. The formation of char is also possible (Jakab et al., 1997). Bleaching of liquefied wood products could be achieved by using hydrogen peroxide or laccase systems. Hydrogen peroxide is a rather weak oxidizing agent in the absence of activators (Jones, 1999; Richardson et al., 2000). Different activators/hydrogen peroxide systems have been developed (Jones, 1999; Araujo et al., 2002; Lane and Burgess, 2003; Yao and Richardson, 2000), and our results with the two of them are presented within this paper: with the copper(II)/pyridine mixture (Cu(II)/pyridine) and with a potassium carbonate (K_2CO_3). In addition, we tested also the discolouration ability of a fungal laccase. Laccases are copper-containing enzymes produced by plant degrading fungi and microorganisms that catalyse the oxidation of various organic substrates. They can oxidize only low-redox-potential compounds such as phenols, polyphenols and anilines. The presence of a redox mediator expands the applicability spectrum of a laccase to non-phenolic substrates (Srebotnik and Hammel, 2000).

This paper is a compilation of our recent selected investigations of liquefaction of wood and cork and of applications of liquefied lignocellulosics for preparation of coatings- (Cheumani-Yona et al., 2012; Yona et al., 2012). The focuses were on the study of liquefaction of cork, on preparation of polyurethane coatings from liquefied cork and their characterisation, and on effectiveness of the hydrogen peroxide or laccase systems for discolouration of liquefied wood with the objective to lighten its colour for the purpose of preparation of aesthetically appealing wood coatings on the basis of liquefied biomass.

2. **MATERIALS AND METHODS**

2.1. LIQUEFACTION OF CORK

A fine cork powder from *Quercus suber* L. (cork oak) that was kindly provided by the Amorim Cork Composites (Amorim, Portugal) was used for liquefaction studies. The cork powder was oven dried at 103 °C for 24 h before each experiment. All chemicals for liquefaction of cork were reagent grade and used without further purifications. The liquefaction experiments were performed using a classical reflux setup, as described for instance by Budija et al. (2009). Glycerol and a catalyst (sulphuric acid or sodium hydroxide) were at first mixed and pre-heated to the predetermined liquefaction temperature (150 °C, 180 °C, or 200 °C, respectively). When sodium hydroxide was used, this mixture was kept at the selected temperature until the complete dissolution of the catalyst. Subsequently, the dried cork powder was added progressively. After the preset reaction time (1 h or 3 h), the liquefied mixture was cooled down to quench the reaction, diluted with methanol and filtered under vacuum through a filter disk (Sartorius filter disks 388 grade/12 µm - 15 µm particles retention). The residual solid was washed with methanol, oven-dried (103 °C, 24 h) and weighed. The liquefaction yield (LY) was calculated on the basis of the part which was insoluble in methanol, using the Equation 1:

$$LY(\%) = \left(1 - \frac{W_R}{W_C}\right) \times 100 \qquad (1)$$

W_R and W_C are masses of the residue and initial biomass, respectively. Three sets of experiments were conducted. Firstly, the effect of a catalyst type (acid or base) was studied by using a cork to glycerol mass ratio (C/G) of 1:10 and 3 % catalyst (mass fraction based on glycerol). The effect of catalyst concentration was afterwards assessed. C/G ratio was kept at 1:10, and the concentration of catalyst increased from 1 % to 5 %. The effect of C/G ratio on LY was finally studied. Based on the results of previous experiments, only sodium hydroxide (5 %) was used in these experiments.

2.2. PREPARATION OF WOOD COATINGS FROM LIQUEFIED CORK AND CHARACTERIZATION OF THEIR PROPERTIES

Liquefaction of cork for preparation of coatings was performed by the acid procedure, similarly as described in the previous paragraphs. However, in this case the solvolysis reagent was polyethylene glycol. Two reaction mixtures were prepared for liquefaction of cork with the ratios of cork to polyethylene glycol of 1:1 and 3:1. The reaction conditions: T = 150°C, duration of 2 hours under stirring, H_2SO_4 as a catalyst (the ratio between the catalyst and the solvent was 1:20). Afterwards, the hexamethylene diisocyanate-trimethylol propane (HDI-TMP) was added to the liquefied product ((LC+PG):TMP 1:1).

The films of polyurethane (PU) coatings prepared from the liquefied cork were applied to both glass and beech substrates with a laboratory film applicator (the wet film thickness of 120 µm). The films were dried at room temperature and at the relative air humidity between 50 % and 60 %. Properties of the films were determined 21 days after application. Resistance of the coatings against alcohol (48 %) and water was determined as described in the standard SIST EN 12720:97 and their adhesion by the standard pull-off test method (SIST EN ISO 4624: 2004).

2.2. PREPARATION OF DISCOLOURED LIQUEFIED WOOD

Sawdust of black poplar (*Populus nigra* L.*)* wood was used for the preparation of liquefied wood. The sawdust was fractionated using a 0.24 mm sieve, and oven-dried at 103 °C for 24 h before liquefaction reaction. Laccase from *Trametes versicolor (EC 1.10.3.2)* was purchased from Sigma Aldrich. All the chemicals were reagent grade and used without further purifications. The liquefied wood was prepared by solvolysis using glycerol as a reactive solvent and sulphuric acid as a catalyst. The liquefaction reaction was performed at 180 °C for 90 min, in a 1 L three-neck reactor, containing wood sawdust (100 g), glycerol (300 g) and sulphuric acid (9 g). After 90 min, the liquefied mixture was cooled down, and diluted with 1,4-dioxane/water mixture (4:1, v/v). The residue of liquefaction was removed by filtration under vacuum through a filter disk (Sartorius filter disks 388 grade/12 µm - 15 µm particles retention). The liquefaction yield was determined by the Equation 1 and it reached the value of 82.5 %. The liquefied wood was obtained after evaporation of dioxane and water, and used for discolouration experiments.

Bleaching with Cu(II)/pyridine: The bleaching experiments were carried out with diluted liquefied wood samples (10 g of liquefied wood in 1 L of a solvent). Two solvents were used: 1,4-dioxane/water mixture (4:1, v:v) where liquefied wood is completely soluble, and pure water (distilled water). The experiments were conducted at room temperature (25 ± 2) °C and in the dark. The pH of liquefied wood solutions was adjusted to almost neutral (6.6 – 6.7) with 40 % aqueous sodium hydroxide solution. 25 ml of liquefied wood solution was introduced in a 50 ml disposable plastic tube, and 100 µl of a 50 mM aqueous solution of copper(II) chloride ($CuCl_2$) and 1 ml of pyridine were added. Addition of $CuCl_2$ and pyridine increased the pH to 6.98 for dioxane/water samples and to 7.96 for water. The tube was sealed and wrapped with an aluminium foil, and hydrogen peroxide was slowly added using a Kd-Scientific continuous flow pump. The injection time was 24 h. The total quantity of hydrogen peroxide added was between 4 % and 80 % with respect to the mass of liquefied wood in the sample. The degree of discolouration and the residual amounts of hydrogen peroxide were determined after 48 h from the start of hydrogen peroxide addition.

Bleaching with K_2CO_3: In the case of bleaching with K_2CO_3, the pH of the samples was also adjusted to almost neutral (6.6 – 6.7) with 40 % aqueous sodium hydroxide solution. 25 ml of liquefied wood solution was introduced in a 50 ml disposable plastic tube, and 100 µl of a 2.5 M aqueous solution of potassium carbonate was added. Addition of K_2CO_3 increased the pH to 8.8 for dioxane/water samples and to 10.40 for water samples. The same procedure as described with the Cu(II)/pyridine reaction was then applied (see above). To study the applicability of the method, oxidation of liquefied wood with K_2CO_3/H_2O_2 was also performed with more concentrated solutions. Liquefied wood (100 g) was mixed with dioxane/water mixture (300 g) in a 2 L reactor, and solid potassium carbonate (15 g) was added. Hydrogen peroxide was added dropwise during 24 h. Rapid addition of hydrogen peroxide caused an intense formation of gases, an increase of temperature and a risk of explosion. After the reaction, residual potassium carbonate was removed by filtration under vacuum through a filter disk (Sartorius filter disks 388 grade/12 µm - 15 µm particles retention). The solvents in the filtrate were evaporated at 80 °C under the reduced pressure. The discoloured liquefied wood samples were re-dissolved in a fresh 1,4-dioxane/water mixture and the pH was adjusted to 6.5 for further precipitation of the salt, filtrated and the solvents evaporated. Discoloured liquefied wood samples were dried at 80 °C for 24 h. The recovered salt was dried in an oven at 105 °C for 24 h, and weighed. About 85 % of the salt (based on potassium carbonate mass initially introduced) was removed.

Bleaching with a laccase: Aqueous suspensions of liquefied wood (1 g/l or 10 g/l) were prepared by mixing 0.2 g or 2 g of liquefied wood and 200 mL of citric acid/sodium hydrogen phosphate buffer (pH = 3). 2.8 U (0.001 g/L; 1U= 1µmol of ABTS oxidized per min, the same buffer and pH value, (25 ± 2) °C) of laccase was added. The experiments were run with a laccase only, or, 1-hydroxybenzotriazole HOBT (1 mM) and 2,2'-azino-bis-(3-ethylbenthiaoline-6-sulfonate) diammonium salt ABTS (1 mM), respectively, were used as a mediator. The reaction samples were incubated in the dark under constant agitation and continuous oxygen supply. After 48 h, the samples were heated at 80 °C for 20 min to deactivate the enzyme.

UV-visible absorption measurements to assess the results of discolouration were performed with a Perkin Elmer Lambda 2 Spectrophotometer (measurement range 300 nm - 900 nm). Liquefied wood absorbs light in the whole visible region (400 nm - 800 nm). Bleaching of the material resulted in a decrease of the absorbance in this region. The absorbance at 400 nm was considered as a reference for the measurement of the degree of discolouration, Disc (%) (Equation 2).

$$Disc\ (\%) = \left[1 - {}^{A_{400}(i)}\big/_{A_{400}(f)}\right] \times 100 \qquad (2)$$

where A_{400}(i) and A_{400}(f) are absorbances of the solution at 400 nm before and after injection of hydrogen peroxide, respectively. The rate of discolouration in the case of the K_2CO_3/H_2O_2 system was also assessed / measured with a spectrophotometer X-rite SP 62 Series-Optronik using a light source type D65. The liquid samples were placed between two glass plates. The thickness between the glasses was 140 µm. The CIELAB parameters (*L**, *a** and *b**) and the colour change (*ΔE**) of liquefied wood after discolouration reaction were determined.

3. **RESULTS AND DISCUSSION**

3.1. LIQUEFACTION YIELDS OBTAINED AFTER LIQUEFACTION OF CORK UNDER VARIOUS CONDITIONS

Two types of catalysts were tested: sulphuric acid (H_2SO_4) for acid catalysis, and sodium hydroxide (NaOH) for base catalysis. LY (Table 1) was generally higher under alkaline (64.5 % to 85.1 %) than under the acidic conditions (43.2 % - 50.2 %). It was significantly sensitive to temperature range under alkaline, but not under the acidic conditions. These observations can be explained by considering cork as a two-component material: suberin (and fatty acids and esters of fatty acid extractives) on one hand and lignocellulosics (and other extractives) on the other hand. It was assumed that almost all lignocellulosics were converted during the first hour of liquefaction at 150 °C. The sum of lignin and carbohydrate contents in cork is around 40 % (Silva et al., 2005). If the amount of some extractives is added, a similar value to the experimentally determined LY is obtained. On the contrary, the range of LY obtained with sodium hydroxide, 61 % - 85 %, was only possible when both suberin and lignocellulosics were liquefied, at least partially. The conversion of suberin under alkaline conditions was expected, more than the conversion of lignocellulosic components, since it is well known that suberin can be depolymerised in alkaline organic alcohols (Cordeiro et al., 1998; Gandini et al., 2006).

Table 1: Yields (%) of liquefaction reactions of cork in acidic (H_2SO_4) and alkaline (NaOH) glycerol (C/G = 1:10; 3 % H_2SO_4 or 3 % NaOH).

Reaction temperature	**Liquefaction yield (%) in dependence of a catalyst and at selected reaction time**			
	H_2SO_4		*NaOH*	
	1 h	3h	1 h	3 h
150 °C	43.2	44.1	64.5	67.3
180 °C	45.5	47.2	72.6	76.2
200 °C	47.4	50.2	81.6	85.1

The influence of the concentration of sulphuric acid or sodium hydroxide on LY is shown in Figure 1. In general, the LY was increased by an increase of the concentration of a catalyst. This effect was more pronounced under alkaline conditions. Up to 92 % LY was obtained at 200 °C and with 5 % sodium hydroxide. It should be mentioned that the liquefied mixtures at higher concentrations of sodium hydroxide tend to become highly viscous (sticky), probably due to recondensation of decomposed natural polymers in the liquefied mixtures. The residues of liquefaction obtained after filtration were in the case of the highest LY maybe just the recondensed products of liquefaction. The increase of LY in dependence of a catalyst concentration under acidic conditions was not so significant (at 150 °C) or even negligible (at 200 °C), confirming the low ability or inability of sulphuric acid to catalyse the liquefaction of cork suberin. The effect of cork to glycerol mass ratio (C/G) on the liquefaction yield is shown in Table 2. As expected, the increase of C/G ratio decreased the yield.

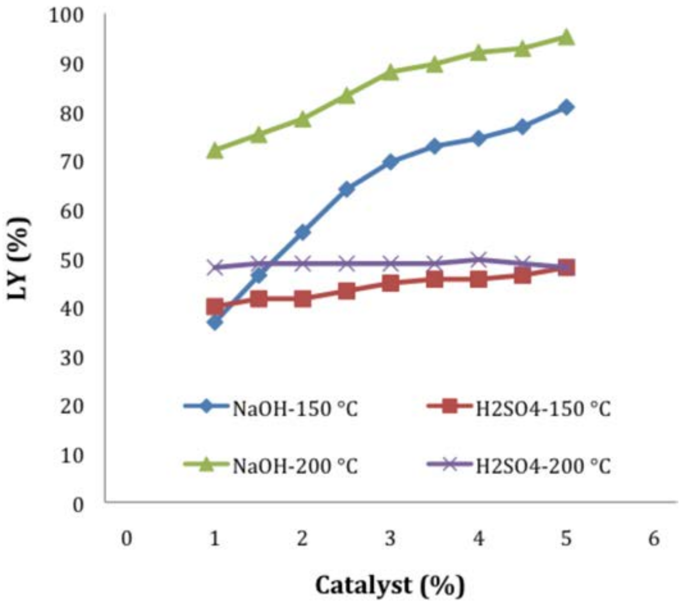

Figure 1: Effect of catalyst concentration on the cork liquefaction yield.

Table 2: Liquefaction yields (%) as a function of cork to glycerol mass ratio C/G (200 °C, 5 % NaOH).

C/G	Yield (%)
1/5	85.2
1/4	78.6
1/3	73.4

3.2. PROPERTIES OF POLYURETHANE COATINGS PREPARED FROM LIQUEFIED CORK

Both types of the polyurethane coatings, prepared from liquefied cork, exhibited quite promising adhesion on the beech wood substrate (Table 3). Namely, according to the longstanding experience of the wood finishing laboratory at the Department of Wood Science & Technology, Biotechnical Faculty, Ljubljana Slovenia, all values higher than 2 MPa can be regarded as the acceptable ones (Kričej, 1976).

Table 3: Results of the pull-off tests.

Substract	Sample	Test	Adhesion (MPa)
Beech	LC / PG (7,5:2,5) TMP 1:1	1	3.90
		2	3.70
		3	3.57
		AVG	3.72
Beech	LC / PG (50:50) TMP 1:1	1	4.15
		2	3.97
		3	3.93
		AVG	4.02

Our previous results on characteristics of polyurethane coatings based on liquefied wood (Budija et al., 2009; Budija et al., 2012) showed that concerning resistance properties, the major drawback of such coatings is their low resistance to water. That is why we tested resistance of polyurethane coatings made from liquefied cork against water and an aqueous solution of alcohol, both on wooden and glass substrates. As can be seen from Table 4, the resistance of the coatings on the glass substrate was poor (1 or 2 – 1 is the worst rating and 5 is the best one). However, in one case, a promising assessment value of 4 was obtained on the beech wood substrate, indicating the sense of further experiments to improve resistance of novel bio-based coatings against liquid water.

Table 4: Resistance to cold liquids.

Substract	Sample	Numerical ratings	
		Alcohol 1 hour	Water 1 hour
Beech	LC / PG (7,5:2,5) TMP 1:1	3	4
	LC / PG (50:50) TMP 1:1	3	3
Glass	LC / PG (7,5:2,5) TMP 1:1	1	3
	LC / PG (50:50) TMP 1:1	1	2

3.3. RESULTS OF THE DISCOLOURATION EXPERIMENTS

The degrees of discolouration are shown in Table 5. Cu(II)/pyridine/H_2O_2 oxidation of liquefied wood was more efficient in water than in the 1,4-dioxane/water mixture. Up to 52.3 % and 71.4 % of discolouration was measured in dioxane/water mixture and in water, respectively. The difference in the degree of discolouration observed between the two solvents can be due to the nature and the stability of Cu(II) complex formed in these solvents. Potassium carbonate-activated hydrogen peroxide has also shown a great ability to discolour liquefied wood (Table 5). A degree of discolouration of 45 % was for example achieved with only 20 % of hydrogen peroxide applied when liquefied wood was treated in dioxane/water mixture. It had been shown that decomposition of hydrogen peroxide in the presence of carbonates generated peroxycarbonate ions (CO_4^{2-}) intermediate oxidant species (Suess, 2010). Such oxidants can induce the oxidation of various organic substrates (Yao and Richardson, 2000; Lane and Burgess, 2003). Contrary to Cu (II)/pyridine/H_2O_2, K_2CO_3/H_2O_2 was more efficient in dioxane/water mixture than in water. Laccase from *Trametes versicolor* was almost not able to discolour the liquefied wood. The rates of discolouration were less than 5 % (Table 6). The addition of redox mediators, ABTS (1 mM) or HOBT (1 mM) also did not significantly improved the results.

Table 5: Bleaching of liquefied wood.

Discoluration System	H_2O_2/Lw (wt%)	Dioxane/water		Water	
		H_2O_{2R} (mg/l)	Disc (%)	H_2O_{2R} (mg/l)	Disc (%)
Cu(II)/pyridine/H_2O_2	4	0	12.0	0	4.7
	20	5	33.0	1	38.0
	40	5	45.3	10	69.3
	80	5	52.3	100	71.4
K_2CO_3/H_2O_2	4	2	8.8	0	15.2
	20	2	43.3	10	27.5
	40	3	52.8	30	32.4
	80	10	80.2	30	38.33

Lw: liquefied wood; H_2O_{2R}: residual H_2O_2; Disc (%): degree of discolouration.

Table 6: Degree of discolouration (%) of liquefied wood treated with the laccase/mediators systems.

Liquefied wood solution	Laccase	Laccase/HOBT	Laccase/ABTS
1 g/l	3.6	3.4	4.5
10 g/l	2.5	2.8	4.1

The colour parameters of liquefied wood before and after the bleaching process with the K_2CO_3/H_2O_2 system are shown in Table 7. The major changes were observed at coordinate parameters *a** and *b**. Liquefied wood tended to become orange (mixture of yellow and red) after oxidation reaction. The brightness (*L**) of liquefied wood was slightly increased.

Table 7: CIELAB parameters and colour change of liquefied wood after bleaching with K_2CO_3/H_2O_2.

Samples	*L**	*a**	*b**	*ΔE**
Lw	23.37	0.19	0.74	0.00
Lwb-40%	35.94	18.20	20.79	29.73
Lwb-80%	38.86	20.42	28.86	37.94

Lwb-40% and Lwb-80%: liquefied wood bleached with 40 % and 80 % of hydrogen peroxide, respectively.

Finally, just to give an impression on colours of liquefied wood and discoloured liquefied wood, in Figure 2, there is an illustration of that.

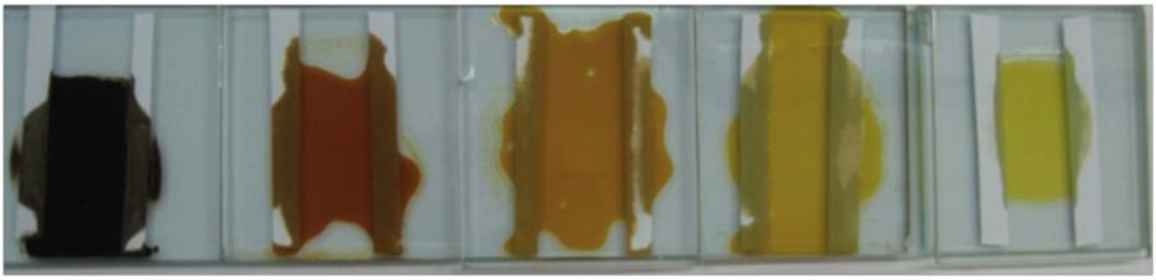

Figure 2: Colour change of liquefied wood during manganese sulphate/sodium bicarbonate activated hydrogen peroxide oxidation as a function of the quantity of hydrogen peroxide applied (from right to left: 0 %, 20 %, 40 %, 60 % and 80 % of H_2O_2).

4. **CONCLUSIONS**

It was shown that cork can be successfully liquefied, either by application of an acid or a basic catalyst. However, it seems that the liquefaction mechanisms are different in both cases, resulting in different liquefaction yields. It was also demonstrated that the liquefied cork is a potential bio-resource for preparation of polyurethane wood coatings. Some of their properties were quite promising, so that we believe that continuation of these investigations has sense. Also, our studies showed that one of important drawbacks of liquefied wood when to be used for preparation of coatings, its dark brown colour, can be successfully overcome. By application of a proper bleaching system, a considerable discolouration rate could be achieved.

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TESTING OF NON-DESTRUCTIVE METHODS AND WOOD NATURAL AND CONFERRED DURABILITY FOR DRYWOOD TERMITES (*CRYPTOTERMES BREVIS* (WALKER)) DETECTION AND CONTROL

SÓNIA DUARTE[1], CATARINA AMARAL[2], MIQUEL GAJU[3], LINA NUNES[1,4,*]
[1]LABORATÓRIO NACIONAL DE ENGENHARIA CIVIL, AV. BRASIL 101, 1700-066 LISBOA, PORTUGAL
[2]LABORATÓRIO REGIONAL DE ENGENHARIA CIVIL, RUA DE S. GONÇALO S/N, 9500-343 PONTA DELGADA
[3]ZOOLOGY DEPARTMENT, UNIVERSIDAD DE CÓRDOBA, CÓRDOBA, SPAIN
[4]AZOREAN BIODIVERSITY GROUP, CITA-A, UNIVERSIDADE DOS AÇORES, TERCEIRA, AÇORES, PORTUGAL
[*]CORRESPONDING AUTHOR: LINANUNES@LNEC.PT

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ABSTRACT

The invasive drywood termite *Cryptotermes brevis* (Walker) was accidentally introduced in the Azorean Islands (Portugal), causing severe damage to furniture and structural timber in buildings. Investigation on efficient methods for drywood termites control is crucial to the definition of future directions in integrated pest management strategy and for preservation of wooden structures in the Azorean Islands. Blocks of eight wood species (white tola, kambala, sucupira, European silver fir, redwood, Australian blackwood, Southern blue gum, Japanese cedar) and two wood derived products (oriented strand board – OSB; medium-density fibreboard – MDF) were exposed to drywood termites inside a house with an active infestation. One organic solvent (propiconazole: 1.22% + permethrin: 0.24%) was applied to all wood species and OSB; MDF was not submitted to any treatment. Two different methods for organic solvent application were used: by brushing or by immersion. Drywood termites attack was evaluated through the observation of: sealed or no sealed holes in wood or wooden products, pellets or termites presence. A redundancy analysis was performed and six variables were considered significant: no treatment, OSB, MDF, Australian blackwood, February and Southern blue gum. OSB was severely attacked, since it had the highest number of holes in wood, although some of those holes were not sealed, as for MDF, indicating possible difficulties in drywood termite foundation of new colonies. Some wood species showed 100% effectiveness against drywood termite attack after: a) organic solvent application (sucupira and white tola); b) organic solvent applied by immersion (Australian blackwood, European silver fir, Japanese cedar and kambala); c) organic solvent applied by brushing (redwood and Southern blue gum). Kambala and Southern blue gum heartwood had the lowest number of holes in the blocks. However, wood derived products (OSB and MDF), although revealing a high number of holes, the number of non sealed ones was high, as well as for Japanese cedar. The choice of termite natural more resistant wood species, treatment products and application methods (specific to each wood species) is important for *C. brevis* control in Azorean Islands, and should be locally evaluated before their implementation. Non destructive techniques for termite detection are very important for early prevention and control measures. A microwave detection device and an acoustic detection device were tested for termite detection. The acoustic emissions potential in detecting early infestation of *C. brevis* should be further investigated.

1. INTRODUCTION

Drywood termites are social and cryptic insects which live entirely in the wood, both nesting and feeding there. Drywood termites infest wooden structures and elements during dispersal flights. When termites land they search for a pair and select a nesting site in wood, building a copulation chamber which is then sealed to enable the formation of a new colony. Since they have the ability to thrive in wood with low moisture content, they may attack all kinds of dead and dry wood, as structural timbers, furniture, flooring and other wooden articles (Myles et al. 2007). *Cryptotermes brevis* (Walker) (Isoptera: Kalotermitidae) distribution is vast, due to secondary introductions, since they are present in all continents, except Antarctica, while their endemic habitat was identified in the Pacific coastal desert of South America (Scheffrahn et al., 2009).

C. brevis presence in Europe was reviewed by Nunes et al. (2010) which added data on their presence in continental Spain (Barcelona) and Portugal (Lisbon), together with previously identifications in other European countries as well as in Portuguese islands of Madeira (Mateus and Goes, 1953) and Azores (Borges et al., 2004).

The archipelago of Azores is made of nine main islands in the North Atlantic Ocean, located about 1,500 km west from Lisbon, in Portugal mainland. The strategic position of the archipelago of Azores (halfway between Europe and North America) has led to the use of these islands as stopping point for airplanes and ships, which facilitates possible biological invasions. *C. brevis* is actually a well-established and concerning pest in Azores, already identified in five islands, and whose economical and patrimonial damages concerns both citizens, authorities and scientific community (Borges and Myles, 2007; Guerreiro et al., 2009).

C. brevis control strategies should be pursued by different techniques enabling, for example, the prevention through the use of natural or increased wood durability. Studies on natural durability of wood species against drywood termites have been published by different scientific teams, since the results are highly dependent on termite species and for different locations (for example, Minnick et al., 1973; Kartal and Green, 2003; Martins et al., 2008). Increased durability conferred by wood preservatives application is also a common practice although the effectiveness vary according to wood species, active ingredient (and/or other product) or methodology used (Scheffrahn, 2001; Usta et al., 2009; Köse et al., 2011; Hadi et al., 2012; Holt et al., 2012).

Together with prevention and control strategies, early detection of termite infestations before recommendation of treatment procedures for drywood termites would enable the determination of infestation extent and the delineation of areas for future treatment procedures (Su and Scheffrahn, 2000). Visual inspection is the normal procedure for drywood termite detection, although it is not 100% effective, so it should be accomplished with other sophisticated methods, as moisture meters, electronic odour devices, acoustic emission detectors or infrared heat detectors, for enhancing the reliability of termite detection (Evans, 2002; Oliver-Villanueva and Abián-Pérez, 2012). Currently, non-destructive detection methods, together with traditional visual inspections are advisable, since the integrity of wooden elements is maintained. Different non-destructive detection methods are being used, as acoustic emission, microwave or heat detectors (Evans, 2002; Indrayani et al., 2007; Oliver-Villanueva and Abián-Pérez, 2012). Acoustic emission, for example, detects the production of elastic waves due to the release of strain energy which is stored in the wood and is released by termites feeding (Matsuoka et al., 1996; Indrayani et al., 2007).

The aim of this work was to analyze new techniques for *C. brevis* prevention (through wood natural durability analysis), control (through the efficacy analysis of one organic solvent) and detection (through the evaluation of two different detection methods).

2. MATERIALS AND METHODS

Four heartwood blocks of each eight wood species: white tola (*Gossweilerodendron balsamiferum* Harms), kambala (*Milicia excelsa* Benth. & Hook. f.), sucupira (*Bowdichia nitida* Spruce ex Benth), European silver fir (*Abies alba* Mill.), redwood (*Sequoia sempervirens* (D. Don) Endl), Australian blackwood (*Acacia melanoxylon* R. Br.), Southern blue gum (*Eucalyptus globulus* Labill.), Japanese cedar (*Cryptomeria japonica* (L. filius) D. Don) and two wood derived products: oriented strand board – OSB and medium-density fibreboard – MDF, were exposed to drywood termite *Cryptotermes brevis* (Walker) attack inside the attick of a house with an active infestation of *C. brevis* in the city of Ponta Delgada, São Miguel, Portugal. A number of holes were previously drilled in the blocks, since it may facilitate *C. brevis* installation.

Besides no treated blocks, one organic solvent (propiconazole: 1.22% + permethrin: 0.24%) was applied to the wood species and OSB; MDF was not submitted to any treatment. Two different methods for organic solvent application were used: by brushing or by immersion.

Visits were done monthly from January to December 2010, except for November (two visits) and September (three visits). Wood and wood derived products moisture content was assessed with a moisture meter; presence of living termites and pellets was annotated. After the swarming season (May – August), the wood blocks were investigated for the presence of sealed previously done holes and new holes.

A multivariate redundancy analysis (RDA) followed by a stepwise regression was performed to investigate the effect of different wood species and wood derived product, treatment and moisture content of wood or wood derived product on drywood termite attack. Statistical significance of the canonical axes was evaluated by Monte Carlo permutation test ($p < 0.05$). The analysis was performed in CANOCO 4.0 software (Ter Braak and Smilauer, 2002).

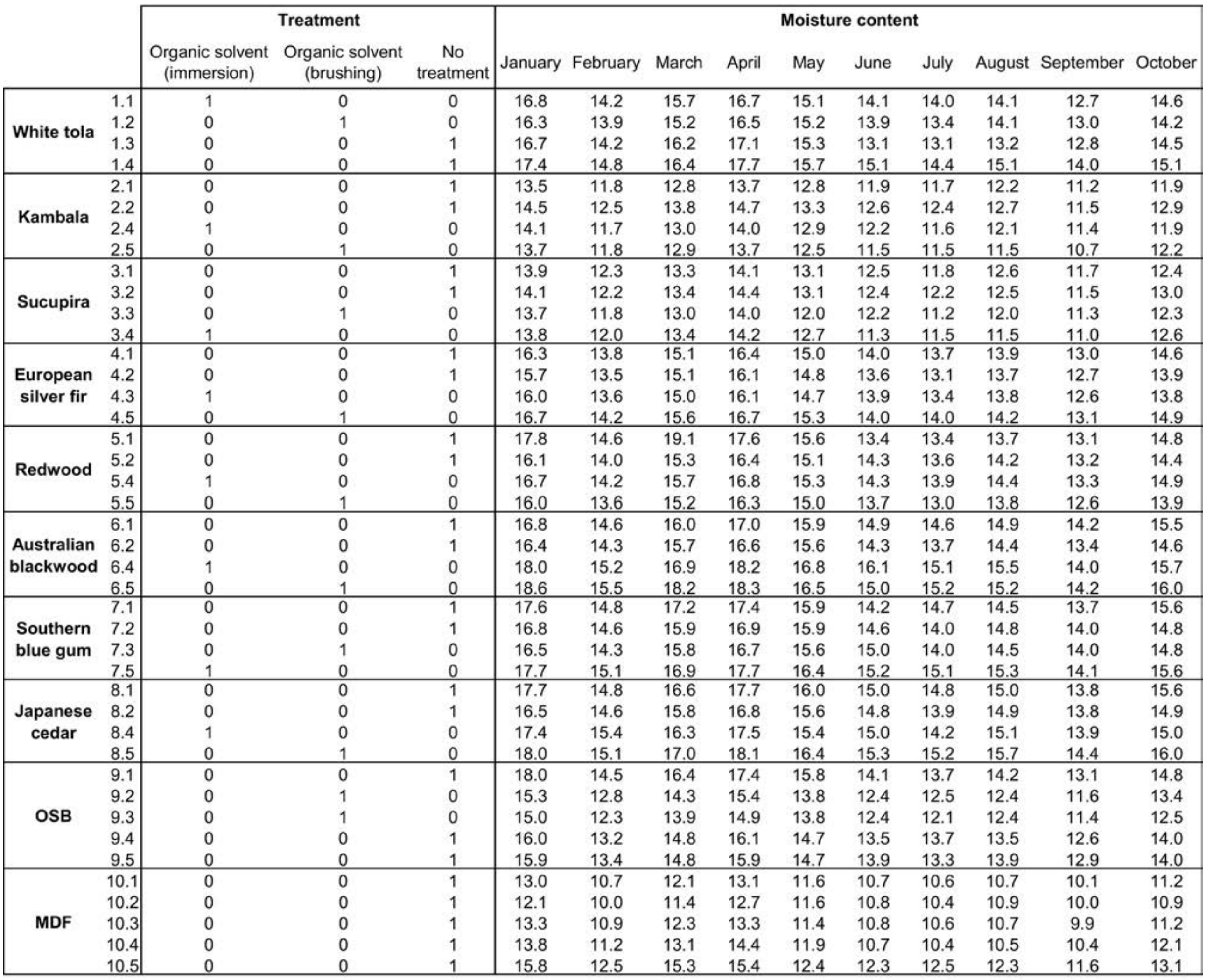
Termite activity signs were investigated after swarming season, only for non-treated samples of each wood species or wood derived product.

Microwave and acoustic emission commercial detectors were used and results were confirmed with further inspection of termite signs of infestation.

3. RESULTS

Wood or wood derived products moisture content values were clearly divided into a humid season (January to May) and a dry season (June to October), except for February since its moisture content levels were low in comparison to January or March (Table 1).

Table 1: Treatments applied to the monitored wood species or wood derived products, and average moisture content measured monthly between January and October 2010.



		Treatment			Moisture content									
		Organic solvent (immersion)	Organic solvent (brushing)	No treatment	January	February	March	April	May	June	July	August	September	October
White tola	1.1	1	0	0	16.8	14.2	15.7	16.7	15.1	14.1	14.0	14.1	12.7	14.6
	1.2	0	1	0	16.3	13.9	15.2	16.5	15.2	13.9	13.4	14.1	13.0	14.2
	1.3	0	0	1	16.7	14.2	16.2	17.1	15.3	13.1	13.1	13.2	12.8	14.5
	1.4	0	0	1	17.4	14.8	16.4	17.7	15.7	15.1	14.4	15.1	14.0	15.1
Kambala	2.1	0	0	1	13.5	11.8	12.8	13.7	12.8	11.9	11.7	12.2	11.2	11.9
	2.2	0	0	1	14.5	12.5	13.8	14.7	13.3	12.6	12.4	12.7	11.5	12.9
	2.4	1	0	0	14.1	11.7	13.0	14.0	12.9	12.2	11.6	12.1	11.4	11.9
	2.5	0	1	0	13.7	11.8	12.9	13.7	12.5	11.5	11.5	11.5	10.7	12.2
Sucupira	3.1	0	0	1	13.9	12.3	13.3	14.1	13.1	12.5	11.8	12.6	11.7	12.4
	3.2	0	0	1	14.1	12.2	13.4	14.4	13.1	12.4	12.2	12.5	11.5	13.0
	3.3	0	1	0	13.7	11.8	13.0	14.0	12.0	12.2	11.2	12.0	11.3	12.3
	3.4	1	0	0	13.8	12.0	13.4	14.2	12.7	11.3	11.5	11.5	11.0	12.6
European silver fir	4.1	0	0	1	16.3	13.8	15.1	16.4	15.0	14.0	13.7	13.9	13.0	14.6
	4.2	0	0	1	15.7	13.5	15.1	16.1	14.8	13.6	13.1	13.7	12.7	13.9
	4.3	1	0	0	16.0	13.6	15.0	16.1	14.7	13.9	13.4	13.8	12.6	13.8
	4.5	0	1	0	16.7	14.2	15.6	16.7	15.3	14.0	14.0	14.2	13.1	14.9
Redwood	5.1	0	0	1	17.8	14.6	19.1	17.6	15.6	13.4	13.4	13.7	13.1	14.8
	5.2	0	0	1	16.1	14.0	15.3	16.4	15.1	14.3	13.6	14.2	13.2	14.4
	5.4	1	0	0	16.7	14.2	15.7	16.8	15.3	14.3	13.9	14.4	13.3	14.9
	5.5	0	1	0	16.0	13.6	15.2	16.3	15.0	13.7	13.0	13.8	12.6	13.9
Australian blackwood	6.1	0	0	1	16.8	14.6	16.0	17.0	15.9	14.9	14.6	14.9	14.2	15.5
	6.2	0	0	1	16.4	14.3	15.7	16.6	15.6	14.3	13.7	14.4	13.4	14.6
	6.4	1	0	0	18.0	15.2	16.9	18.2	16.8	16.1	15.1	15.5	14.0	15.7
	6.5	0	1	0	18.6	15.5	18.2	18.3	16.5	15.0	15.2	15.2	14.2	16.0
Southern blue gum	7.1	0	0	1	17.6	14.8	17.2	17.4	15.9	14.2	14.7	14.5	13.7	15.6
	7.2	0	0	1	16.8	14.6	15.9	16.9	15.9	14.6	14.0	14.8	14.0	14.8
	7.3	0	1	0	16.5	14.3	15.8	16.7	15.6	15.0	14.0	14.5	14.0	14.8
	7.5	1	0	0	17.7	15.1	16.9	17.7	16.4	15.2	15.1	15.3	14.1	15.6
Japanese cedar	8.1	0	0	1	17.7	14.8	16.6	17.7	16.0	15.0	14.8	15.0	13.8	15.6
	8.2	0	0	1	16.5	14.6	15.8	16.8	15.6	14.8	13.9	14.9	13.8	14.9
	8.4	1	0	0	17.4	15.4	16.3	17.5	15.4	15.0	14.2	15.1	13.9	15.0
	8.5	0	1	0	18.0	15.1	17.0	18.1	16.4	15.3	15.2	15.7	14.4	16.0
OSB	9.1	0	0	1	18.0	14.5	16.4	17.4	15.8	14.1	13.7	14.2	13.1	14.8
	9.2	0	1	0	15.3	12.8	14.3	15.4	13.8	12.4	12.5	12.4	11.6	13.4
	9.3	0	1	0	15.0	12.3	13.9	14.9	13.8	12.4	12.1	12.4	11.4	12.5
	9.4	0	0	1	16.0	13.2	14.8	16.1	14.7	13.5	13.7	13.5	12.6	14.0
	9.5	0	0	1	15.9	13.4	14.8	15.9	14.7	13.9	13.3	13.9	12.9	14.0
MDF	10.1	0	0	1	13.0	10.7	12.1	13.1	11.6	10.7	10.6	10.7	10.1	11.2
	10.2	0	0	1	12.1	10.0	11.4	12.7	11.6	10.8	10.4	10.9	10.0	10.9
	10.3	0	0	1	13.3	10.9	12.3	13.3	11.4	10.8	10.6	10.7	9.9	11.2
	10.4	0	0	1	13.8	11.2	13.1	14.4	11.9	10.7	10.4	10.5	10.4	12.1
	10.5	0	0	1	15.8	12.5	15.3	15.4	12.4	12.3	12.5	12.3	11.6	13.1

All wood species/ wood derived products were attacked by *C. brevis*, although different levels of attack were detected within different wood species/wood derived products and/or treatment applied, as well as for modes of application. The organic solvent treatment was generally effective in preventing high levels of drywood termite colony foundation in this study (Table 2). Some blocks showed 100% effectiveness against drywood termite attack after: a) organic solvent applied by brushing and by immersion (sucupira and white tola); b) organic solvent applied by immersion (Australian blackwood, European silver fir, Japanese cedar and kambala); c) organic solvent applied by brushing (redwood and Southern blue gum). Kambala and Southern blue gum had the lowest number of new holes. However, for MDF and OSB blocks, a higher number of holes made by termites was recorded, especially no sealed holes, as well for Japanese cedar. Southern blue gum was the only wood species in which no sealed holes were detected, followed by sucupira, in which only one sealed hole was detected, although no tunnelling observed indicate that the colony was not successfully installed. Comparing both application methods, immersion had a slightly better performance in wood protection from drywood termite attack, since the average number of holes done and/or sealed by termites was higher in blocks with application of organic solvent by brushing (Table 2). Sucupira and southern blue gum wood species have higher average density than the other studied species while Australian blackwood showed the highest average moisture content.

Table 2: Number of previously made holes sealed in superior or lateral part of the samples and number of holes made by drywood termites, sealed and no sealed for the different wood species/wood derived products and treatments applied. The heat detector and the acoustic emissions (AE) detector results as being true (v) or false (x) detections.

		Organic solvent (immersion)	Organic solvent (brushing)	No treatment	Superior zone	Lateral zone	Sealed	No sealed	Heat detector		AE detector	
White tola	1.1	1	0	0	0.0	0.0	0	0			0	v
	1.2	0	1	0	0.0	0.0	0	0	1	x		
	1.3	0	0	1	100.0	75.0	2	9			0	x
	1.4	0	0	1	95.0	100.0	0	4	1	v		
Kambala	2.1	0	0	1	85.0	100.0	0	0	1	v		
	2.2	0	0	1	70.0	25.0	1	8			1	v
	2.4	1	0	0	0.0	0.0	0	0	0	v		
	2.5	0	1	0	5.0	0.0	0	3			0	x
Sucupira	3.1	0	0	1	80.0	50.0	0	1				
	3.2	0	0	1	100.0	100.0	1	0			1	v
	3.3	0	1	0	0.0	0.0	0	0	1	x		
	3.4	1	0	0	0.0	0.0	0	0			0	v
European silver fir	4.1	0	0	1	85.0	50.0	4	14			0	x
	4.2	0	0	1	90.0	100.0	1	2	1	v		
	4.3	1	0	0	0.0	0.0	0	0	0	v		
	4.5	0	1	0	5.0	0.0	1	4			0	x
Redwood	5.1	0	0	1	60.0	50.0	1	18			1	v
	5.2	0	0	1	90.0	100.0	9	39				
	5.4	1	0	0	5.0	0.0	1	1				
	5.5	0	1	0	0.0	0.0	0	0	1	x		
Australian blackwood	6.1	0	0	1	100.0	100.0	0	14			0	x
	6.2	0	0	1	95.0	75.0	0	0	1	v		
	6.4	1	0	0	0.0	0.0	0	0	0	v		
	6.5	0	1	0	5.0	25.0	1	0			1	v
Southern blue gum	7.1	0	0	1	75.0	25.0	0	11			1	v
	7.2	0	0	1	95.0	100.0	0	0	1	v		
	7.3	0	1	0	0.0	0.0	0	0	1	x		
	7.5	1	0	0	5.0	0.0	0	0			0	x
Japanese cedar	8.1	0	0	1	65.0	50.0	7	38			0	x
	8.2	0	0	1	80.0	75.0	2	10	1	v		
	8.4	1	0	0	0.0	0.0	0	0	1	x		
	8.5	0	1	0	10.0	0.0	0	6			0	x
OSB	9.1	0	0	1	90.0	66.7	10	52			0	x
	9.2	0	1	0	0.0	0.0	0	12			0	v
	9.3	0	1	0	0.0	0.0	1	6	0	v		
	9.4	0	0	1	90.0	66.7	15	109	0	x	0	x
	9.5	0	0	1	73.3	0.0	2	16	0	x	0	x
MDF	10.1	0	0	1	76.7	33.3	2	56	0	x		
	10.2	0	0	1	86.7	66.7	6	38	0	x		
	10.3	0	0	1	80.0	100.0	0	4	1	v		
	10.4	0	0	1	66.7	66.7	0	63			0	x
	10.5	0	0	1	73.3	0.0	3	43			0	x

The RDA performed resulted in six significant variables: no treatment (F = 81.78; P = 0.002), OSB (F = 6.10; P = 0.004), MDF (F = 3.98; P=0.008), Southern blue gum (F = 3.16; P = 0.022), February (F = 3.03; P = 0.032) and Australian blackwood (F = 2.75; P = 0.038). The model created explained 88.6% of total data variability.

Three blocks did not show any termite tunneling – sucupira, Southern blue gum and OSB, although living termites were present in this last block. White tola and Kambala only had galleries in the previously perforated zone, where termites had facilitated access to wood interior.

For the detection methods used, the microwave detector indicated 50% of truly observed termite absence, while termite presences were correctly detected in 42% of cases. For acoustic emissions, only 19% of indications on termite absence were true, although it detected correctly 100% of drywood termite presence (Table 2).

4. DISCUSSION

MDF and OSB high attack levels may be explained by the non treatment of MDF and the application of organic solvent only by brushing in OSB. Despite the high number of holes newly drilled by drywood termites in these wood derived products, the majority of them were not sealed. This fact may be due to initial colony installation stage when wood was opened, or these wooden substrates were not favourable to termite colony foundation and installation. Data on termite activity showed that termites were installed and tunnelling in MDF but not on OSB. Investigation on this issue should be pursued. MDF was already tested, but for subterranean termites, showing low resistance to their attack despite the wood species involved in its processing (Kartal and Green, 2003). Unsal et al. (2009) observed that in *Pinus sylvestris* wood panels the attack of *Reticulitermes flavipes* (Kollar) was influenced by processing conditions such as pressure, temperature and time of exposure to treatment. Investigation on the possibility of adding new effective termiticide materials or products, or the refinement of the processing conditions, which shall also be both environmentally sound and health safe, to the wood derived products in order to increase their resistance to *C. brevis* attack and other biological degradation agents is advisable (Kartal and Green, 2003; Usta et al., 2009; Köse et al., 2011; Holt et al., 2012; Ustaomer et al., 2012).

The heartwood of the two Australian origin wood species – Australian blackwood and Southern blue gum – showed to be resistant to drywood termite attack in this study. These wood species may not have been preferred by the termites, since a great variety of woody substrates were available, enabling them to choose the favourites and to form new colonies. The holes made by termites were in lower number in these two wood species, in comparison with other substrates, except for Sucupira, which also showed a good resistance to *C. brevis*. Sucupira is the only species of this study with South American origin, and it also showed resistance to *C. brevis* infestation. Azorean *C. brevis* population endemic origin was probably located also in South America, attacking mainly dead wood in living trees (Scheffrahn et al., 2009; Ferreira, 2011). These two facts may be important for explaining the sucupira resistance to drywood termite attack observed in this study, as if termite and sucupira original territories overlap, sucupira trees may have evolved defences against termite attack, for example in the form of extractives, which have proven to repel termites action on wood (Nunes et al., 1994). Santos (1982) tested the susceptibility of Amazon wood species to *C. brevis* and showed that sucupira was in the group of most resistant species.

The data about tunnelling behaviour of termites and other signs of their activity showed that for sucupira and Southern blue gum, termites avoided the attempt to form new colonies and install. On the contrary, termites were observed tunnelling in Australian blackwood. This may be related with the high density of the species, while the Australian blackwood high moisture content and lower density may have influenced the *C. brevis* attack behaviour. On the other hand, redwood, European silver fir and Japanese cedar were clearly preferred for drilling new holes and for occupying previously made ones, as well as the percentage of sealed holes is higher, which supposedly indicate the formation of new colonies. Sapwood of the late species was already pointed out as one of *Cryptotermes* favourite wood species (Borges and Myles 2007, Hadi et al. 2012).

On the other hand, pine species had been pointed out as resistant to *C. brevis* (Minnick et al. 1973), while Scheffranh and Rust (1983) found antitermitic and feeding deterrent properties of *Pinus lambertiana* Dougl. towards drywood termite *Incisitermes minor* (Hagen). The utilization of mixed sapwood and heartwood blocks may be one explanation for the termite preference for redwood in this study, since the major part of extractives accumulates in the trees heartwood (Ragon et al., 2008).

In February, wood and wood derived products moisture content values decreased, comparing to the other "humid" season months. Wood moisture content, as well as temperature, is important for all termite species, including drywood termites (Indrayani et al., 2007). This may explain why Australian blackwood had severe tunnelling, since it was the species with highest levels of moisture content. However, MDF had low moisture content values and was severely attacked. Drywood termite behaviour should be analysed through different variables, not only wood moisture content, but also wood species, wood density, and temperature.

Organic solvent application was effective in preventing high levels of *C. brevis* colony foundation in comparison with no treatment, at least when different wood and wood derived products, treated or no treated, were available to termites. On the other hand, non treated wood/wood derived products were significantly more vulnerable to termite attack and formation of new colonies (higher number of sealed holes). Application of organic solvent by brushing showed a weaker effect on prevention of termite attack than application by immersion, as already advised by Myles et al. (2007) for *C. brevis* in Azores. The application of this product, especially by immersion or double vacuum treatment, if possible, may be an important measure to decrease the levels of *C. brevis* attack and colony foundation in Azores.

In this study, the detection method which stood out was the acoustic emission, since it detected correctly all termite presences later observed. But the false positive detections may induce errors and application of control measures to a non existing infestation by drywood termites. Treated wood was indicated by Lewis et al. (2004) as inducing in more false detections than non treated wood, due to possible termite behaviour changes. The direct contact and the type of sensor attachment to wood substrate are critical for obtaining correct termite detections (Lewis et al., 2004). Wood anisotropy may also introduce variation in detection results, together with natural surrounding noisy environment (Rosa et al., 2010).

These results indicate the urgent need to further investigate appropriate calibration of these electronic devices for different locations, conditions and wood properties, in order to allow their correct application. Acoustic emissions signals are difficult to work with, due to the usual noisy environment and to wood anisotropy. Also, the direct contact between wood and sensors must be ensured in order to use correctly this simple method of non-destructive detection of drywood termites (Rosa et al., 2010).

5. CONCLUSIONS

According to the results obtained and the discussion done, the heartwood of two wood species stand out as more resistant to *C. brevis* attack: sucupira and Southern blue gum. This last result should nevertheless be taken with extreme care has normal construction practice in Azores involves the use of blue gum round timber and therefore prone to high levels of degradation by the termites. This is particularly severe when small diameter round wood is used.

The wood derived products resistance to termite attack shall be increased, since they are easily attacked by *C. brevis*, although the majority of colonies did not succeeded in establishing themselves in the test specimens; processing conditions and/or the addiction of termiticide products or materials should be further investigated. The general use of heartwood instead of sapwood should be preferred in heavily attacked areas for new construction or wooden furniture. The use of an organic preservative instead of no treatment is advisable as it might decrease the levels of *C. brevis* attack and colony foundation in Azorean wooden articles.

Detection techniques application should be refined in terms of local application in order to achieve better results in terms of real termite detections.

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INFLUENCE OF COPPER-ETHANOLAMINE BASED WOOD PRESERVATIVES COMPOSITION ON THE PERFORMANCE AGAINST WOOD DECAY FUNGI IN LABORATORY AND IN FIELD CONDITIONS

MIHA HUMAR*,1, BOŠTJAN LESAR1,2,3, NEJC THALER1
1. UNIVERSITY OF LJUBLJANA, BIOTECHNICAL FACULTY, JAMNIKARJEVA 101, SI-100 LJUBLJANA, SLOVENIA
2. SILVAPRODUKT D.O.O., DOLENJSKA CESTA 42, 1000 LJUBLJANA, SLOVENIA
3. MONTAŽNA GRADNJA TADEJ ZIMIC S.P., U., BRATOV KOMEL 29, 1210 LJUBLJNA - ŠENTVID, SLOVENIJA
* CORRESPONDING AUTHOR: MIHA.HUMAR@BF.UNI-LJ.SI; TELEPH.: +386 1 320 3638; FAX: +386 1 423 5035

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ABSTRACT

Wood is one of the most important building materials. Particularly, when used outdoors, it is exposed to weathering and biotic degradation. The majority of European wood species is nondurable wood so it has to be additionally protected in order to ensure sufficient service life. In spite of many drawbacks, copper based wood preservatives are still one of the most important solutions for preservation of wood. There are not many other alternatives for preservation of infrastructural wood in ground contact in Europe as well as in the US. In our research, service life of wood exposed outdoor in the third use class, determined with double layer test, was investigated. These results of the real case scenario were compared to results of laboratory tests. In the first part of the investigation, Norway spruce wood specimens were impregnated with seven different copper-ethanolamine based solutions. In parallel laboratory tests were performed. Specimens were impregnated with one of the copper-ethanolamine solutions, artificially aged according to EN 84 procedure, and then exposed to two brown rot fungi (*Gloeophyllum trabeum* and *Antrodia vaillantii*) and one white rot fungus (*Trametes versicolor*) according to the EN 113 procedure. Efficacy against wood pests is the most important parameter of wood preservatives, followed by fixation. Results of the laboratory tests show that fixation of copper-ethanolamine based preservatives is significantly affected by its composition. Field test data and laboratory experiments clearly show that addition of the co-biocides to copper-ethanolamine performance is essential to ensure the efficacy against copper tolerant fungi. Furthermore, addition of other chemicals considerably improves fixation as well. The results of the six year lasting field testing of copper based solutions show that these treatments significantly prolong service life of wood.

1. INTRODUCTION

Copper-based preservatives have been successfully applied for wood preservation for more than two centuries. In the past they had been combined with chromium compounds to enable fixation in wood and arsenic to improve performance against copper tolerant fungi and insects (Richardson, 1997). Due to arsenic toxicity, its use is no longer desired in the majority of European countries, thus it was generally replaced with boron. The situation changed further with the introduction of the Biocidal Products Directive (BPD). BPD directive limits the use of chromium in wood preservatives and so the need for development of new solutions for fixation of copper arose (Humar et al., 2006). Amines are one of the most appropriate replacements for chromium. Particularly ethanolamine is reported as the most promising amine source in several researches, and it is used already for some emerging preservative systems including alkaline copper quat (ACQ), copper dimethyl-dithio-carbamate (CDDC), copper hydroxyquinolinolate (Cu-HDO) and copper azole (CA) (Cao and Kamdem, 2004). However, fixation of copper-ethanolamine based preservatives is still not comparable to fixation of copper-chromium ones. Emissions of copper from wood impregnated with copper-amine preservatives can be reduced with proper copper-amine molar ratio and addition of different hydrophobic agents. Octanoic acid (OA) is one of the chemicals that significantly decreases copper leaching from impregnated wood. This carboxylic acid has multiplicative effect. Beside hydrophobic, OA forms new complexes with copper-amines which are less soluble in water and do not leach from wood as much. Additionally, octanoic acid has fungicidal effect itself, which results in improved quality of impregnated wood (Humar et al., 2005).

Although copper-amine preservatives have been utilized for more than two decades, complete performance of this system is still not completely elucidated. One of the questions is: are the results of the laboratory testing comparable to the results of the field testing? In order to answer this question, our specimens were exposed to outdoor conditions and parallel samples were assessed in the laboratory. The aim of this research was to obtain correlation between laboratory and field test for various copper treated materials, and to compare them with performance of naturally durable materials. Service life data will be the basis for carbon footprint calculation which will be one of the most important criteria for decision in green public procurements.

2. MATERIALS AND METHODS

2.1. TREATMENT SOLUTIONS USED

For impregnation, six different inorganic wood preservative solutions were used as resolved from Tables 1, 3 and 4. They consist of the following ingredients: copper(II) sulfate, ethanolamine, alkyl dimethyl benzyl ammonium chloride, boric acid, and octanoic acid. For leaching test and fungicidal tests, samples were impregnated with copper concentration of 1%, while for double layer tests solutions of two different strengths were prepared to achieve two different retentions as resolved from Tables 4 and 5 and Figure 3. Impregnation was performed according to the full cell process (vacuum 0,2 bar, 20 min; pressure 9 bar, 120 min; vacuum 0,2 bar, 10 min). Uptake of treatment solutions was determined gravimetrically.

Table 1: Composition of various preservative solutions used in this respective experiment. Prior impregnation, aqueous solutions were diluted to achieve targeted retention.

Preservative Solution	Mass of the Respective Active Ingredient in 1000 g of Preservative Solution				
	$CuSO_4 \cdot 5H_2O$ (CuS)	Ethanolamine (EA)	Octanoic acid (O)	ADBAC*	Boric acid (B)
	(g)	(g)	(g)	(g)	(g)
CuS	39.3	-	-	-	-
CuEa	39.3	57.7	-	-	-
CuEaO	39.3	57.7	8.1	-	-
CuEaQO	39.3	57.7	8.1	10	22.7
EABQ	-	57.7	8.1	10	22.7

* alkyl dimethyl benzyl ammonium chloride

2.2. WOOD DECAY TEST

After impregnation, specimens were conditioned for four weeks in the laboratory conditions, first week in the closed chambers, second and the third week in the half open chambers and the fourth week in the open chambers as prescribed by the relevant standard EN 113 (2004). Fungicidal properties of steam sterilized wood impregnated with different biocidal solutions, and untreated wood samples, were determined according to the EN 113 (2004) procedure with two brown rot fungi (*Antrodia vaillantii* and *Gloeophyllum trabeum*) and one white rot fungus (*Trametes versicolor*) on Norway spruce (*Picea abies*) wood samples of dimensions 15 mm x 25 mm × 50 mm. After 16 weeks of fungal exposure specimens were isolated and mass losses were gravimetrically determined and expressed in percentages of the initial mass.

2.3. LEACHING TESTS

Leaching was performed according to the modified ENV 1250-2 (1994) procedure. In order to speed up the experiment, two modifications were applied: three specimens instead of five were placed in one (single) vessel and water mixing was achieved with shaking on a non-rotatory shaker instead of a magnetic stirrer. Nine specimens per concentration/treatment were put in three vessels (three specimens per vessel) to have three parallel leaching procedures. Afterwards, specimens in the vessel were positioned with a ballasting device that prevents them from floating. 300 g of distilled water were added and the vessel with its content was shaken with the frequency of 60 min^{-1}. Water was replaced six times in four subsequent days as proposed by standard ENV 1250-2. Leachates from the same vessel were collected and aggregated. Afterwards, X-ray fluorescence spectroscopy (Twin-x; Oxford instruments) analysis of the leachates was performed. Percentages of leached copper were calculated from the amount of retained copper determined gravimetrically and amount of copper in collected leachates.

2.4. PERFORMANCE OF WOOD IN OUTDOOR CONDITIONS

In parallel spruce wood specimens were exposed in use class 3 conditions according to the double layer test method (Rapp and Augusta, 2004; Augusta, 2007). 10 specimens were grouped together in double layer test setup 500 mm above ground. Decay was visually evaluated and rated as prescribed by EN 252 standard (2004) (Table 2).

Table 2: Grading system for decay (Rapp and Augusta, 2004; SIST EN 252, 2004).

Rating	Description	Definition
0	Sound	No evidence of decay. Any change of colour without softening has to be rated as 0.
1	Slight attack	Visible signs of decay, but of very limited intensity or distribution: - changes which only reveal themselves externally by very superficial degradation, softening of the wood being the most common symptom, to an apparent depth in the order of one millimetre
2	Moderate attack	Clear changes to a moderate extent according to the apparent symptoms: - changes which reveal themselves by softening of the wood to a depth of approximately 1 to 3 millimetres over more than 1 cm^2 per stake.
3	Severe attack	Severe attack - marked decay in the wood to a depth of more than 3 millimetres over a wide surface (more than 20 cm^2) or by softening deeper than 10 mm over more than 1 cm^2 per stake
4	Failure	Impact failure of the stake

Figure 1: Test set up of the specimens exposed in use class 3 conditions according to the double layer test method after one year of exposure.

Figure 2: Development of the fungal mycelia on the control specimens. Please note darkening as the sign of severe degradation of the wood.

2.5. COPPER LEACHING FROM WOOD EXPOSED IN USE CLASS 3 CONDITIONS

One of the purposes of this research was to estimate copper leaching from impregnated wood. Therefore, Norway spruce wood specimens (1,5 cm × 2,5 cm × 30 cm) were vacuum and pressure impregnated with preservative solutions CuEaQO of two different concentrations, namely of 0,25% and 0,125%. There was only one testing solution chosen for this test setup, due to the limited area of the field test site and limited number of specimens. After four weeks of conditioning in laboratory conditions (T = 23 °C; RH = 75%), samples were exposed 0,5 m above ground. After predetermined periods resolved from Table 5, samples were isolated. Oven dried samples were ground into particles that could pass 1 mm sieve with Retch cutting mill SM 2000 and pressed into tablets (r = 16 mm; d = 5 mm) with Chemplex press for further analysis. Copper in wood sawdust was determined with an XRF spectrometer (XRF TwinX, Oxford instruments). Measurements were performed with PIN detector (U = 26 kV, I = 112 µA, t = 360 s) on five parallel specimens. Percentage of leached copper was determined as the ratio between retained copper (calculated from the uptake of preservative solution) and remained copper determined with XRF.

Climate in Ljubljana is Oceanic, bordering on a Humid subtropical climate zone with continental characteristics such as warm summers and moderately cold winters. July and August are the warmest months with daily highs generally between 25 °C and 30 °C, and January is the coldest month with the temperatures mostly oscillating around 0 °C. The city experiences 90 days of frost per year, and 11 days with temperatures above 30 °C. The precipitation is relatively evenly distributed throughout the seasons, although winter and spring tend to be somewhat drier than summer and autumn. Yearly precipitation is about 1,400 mm, making Ljubljana one of the wettest European capitals. Thunderstorms are very common from May to September. Snow is common from December to February; on average, there are 48 days with snow cover recorded each winter season. The city is known for its fog, which is recorded on average on 64 days per year, mostly in autumn and winter.

3. RESULTS AND DISCUSSION

One of the main criteria of wood preservatives is their efficacy against target organisms. In Central Europe, fungi are predominant reasons for failure of wooden constructions (Brischke et al., 2013). Therefore, this paper focuses predominantly in the fungicidal resistance of the copper-amine preservatives, although insecticidal properties are expressed as well (Pohleven in Humar, 2006). The second criterion that indicates the quality of wood preservatives is leaching. Low leaching is important to ensure efficacy, as well as for environmental reasons.

The data presented in the Table 3 shows that copper treatment, without fixatives, does not enable sufficient protection against wood decay fungi, as the majority of the copper is removed from wood in the process of leaching. The remaining copper is not sufficient to control brown rot fungi (*G. trabeum* and *A, trabeum*), but it can ensure protection against copper sensitive fungus *T. versicolor*. Addition of the ethanolamine considerably reduces copper leaching, what clearly reflects in the increased performance against *G. trabeum*. However, copper itself is not sufficient to stop the growth of the copper tolerant *A. vaillantii*. In order to stop this fungus, addition of secondary biocides is required. There were two secondary fungicides applied in this research. One was boron, which primarily role was to control the insects. Presumably, most of the boron leached from wood during artificial ageing, and the remaining concentration was not sufficient to stop growth of *A. vaillantii*. Therefore, quaternary ammonium compound (ADBAC) was introduced in the second step. From the data in Table 3, it can be resolved that only combination of all these compounds ensured sufficient fixation of copper biocides and on the other hand guarantees sufficient performance against wood decay fungi. Besides already mentioned ingredients, octanoic acid was introduced into the preservative solution as well. The main reason for this is the fact, that octanoic acid improves fixation of copper ethanolamine preservative solutions in wood. Octanoic acid forms complexes with copper-amine that are much more leaching resistant compared to the normal copper-ethanolamine complexes (Humar et al., 2005). Furthermore, octanoic acid makes surface more hydrophobic, what reduces leaching as well. It is rather interesting that the aqueous solution without copper (EaOQ) protects wood against wood decay fungi to a rather good extent. This indicates, that quaternary compound is fixed in wood and does not leach from wood even during severe leaching procedure like EN 84.

Table 3: Leaching of copper ingredients (cCu = 1%) from impregnated specimens determined according to the standard procedure (SIST EN 1250-2) and mass losses of impregnated and leached (SIST EN 84) Norway spruce wood specimens exposed to wood decay fungi according to mini-block procedure. Standard deviations are given in the parenthesis.

Preservative Solution	Composition of Preservative Solution					Percentage of Leached Cu (%)	Mass loss (%) Fungi		
	Cu sulfate	Ethanolamine	Octanoic acid	Boric acid	*ADBAC		*Gloeophyllum trabeum*	*Antrodia vaillantii*	*Trametes versicolor*
CuS	X					48.2 (1.5)	14.4 (4.3)	27.2 (3.1)	2.2 (0.2)
CuEa	X	X				3.5 (0.2)	9.3 (3.3)	29.8 (4.3)	1.0 (0.5)
CuEaO	X	X	X			2.4 (0.3)	1.4 (0.4)	20.9 (4.2)	1.3 (0.2)
CuEaOB	X	X	X	X		3.2 (0.1)	1.5 (0.3)	20.5 (2.3)	1.1 (0.4)
CuEaOQ	X	X	X	X	X	4.1 (0.4)	0.4 (0.4)	0.2 (0.1)	0.4 (0.1)
EaBQ		X	X	X	X	-	0.0 (0.1)	0.3 (0.2)	1.4 (0.9)
Spruce						-	32.1 (5.6)	20.1 (3.7)	18.4 (4.1)
Beech						-	48.2 (2.7)	17.6 (1.5)	42.2 (2.1)
Larch						-	16.1 (0.9)	3.7 (0.9)	-
Oak						-	0.7 (0.2)	0.9 (0.6)	1.6 (0.4)

* * alkyl dimethyl benzyl ammonium chloride

In the second step, we were interested if performance of copper-ethanolamine based preservatives in laboratory is comparable to the performance in the outdoor conditions. Performance of the copper-ethanolamine preservatives was compared to the performance of classical copper-chromium based solution and with naturally durable wood species like European larch and English oak. When comparing laboratory and outdoor data, it should be considered that in the laboratory impregnated specimens were exposed to the pure fungal cultures in sterile conditions, while in the outdoor tests synergistic effect of abiotic and biotic factors influences the performance of the impregnated wood. Wood is not exposed to fungi and leaching alone, but also to temperature variations, bacteria, UV-degradation… Therefore, only field testing reflects pure performance of impregnated and non-impregnated-wood.

Table 4: Retention of copper-ethanolamine preservative solutions and performance in double layer application. Samples were exposed outdoor between 7. 4. 2006 and 10. 7. 2012.

Preservative solution / wood species	Target retention (kg/m^3)	Retention (kg/m^3)	***Rating***					
			2007	**2008**	**2009**	**2010**	**2011**	**2012**
CuEaQO	4.9	4.0	0	0	0	0	0	0
	19.6	18.1	0	0	0	0	0	0
CuEaO	1.2	1.3	0	0	0	0.1	1.3	3.4
	5.6	5.6	0	0	0	0	0	0
	14.9	12.7	0	0	0	0	0	0.1
CuS	1.4	1.1	0	0	0	0.1	0.4	1
	5.6	6.5	0	0	0	0	0.1	0.8
CuEa	3.4	2.1	0	0	0	0.3	0.6	0.5
	13.8	10.9	0	0	0	0	0	0
EaBQ	3.5	3.4	0	0	0.1	0.4	1.4	3.4
	14.0	8.9	0	0	0.5	0.5	0.7	0.8
CCB	4	4.1	0	0	0	0	0.1	0.1
Spruce 06*	0	0	0.2	0.8	1.8	2.8	3.2	3.6
Spruce 07**	0	0	-	1.4	2.5	3.7	4	-
Spruce 08***	0	0	-	-	0	0.2	0.4	1.9
Larch	0	0	-	-	0	0	0	0
Beach	0	0	-	1.2	2.5	3.0	3.3	3.8
Oak	0	0	-	0.3	0.1	0.1	0	0.4

Spruce 06*- Control. un-impregnated specimens exposed 7. 4. 2006
Spruce 07** - Control. un-impregnated specimens exposed 28. 5. 2007
Spruce 08*** - Control. un-impregnated specimens exposed 19. 6. 2008

Results presented in Table 4 show that impregnation of wood with tested wood preservative solutions considerably improve performance of impregnated spruce in outdoor conditions. Un-impregnated spruce was exposed in outdoor tests in different time frames in spring of 2006, 2007 and 2008. It is rather surprising, that some specimens from the 2006 are still exposed in the field test site, while all the specimens that were exposed in the field test site in the 2007 were completely decayed after 4 years of exposure. Similar performance was determined with beech wood specimens as well. Beech wood was almost completely degraded after 5 years of exposure (Table 4). Decay of beech wood is a bit slower than decay of spruce, as beech wood is denser and so fungi need more time to consume the material. In contrast; there were almost no signs of decay on larch and oak wood samples, which clearly confirms good decay resistance of those two materials for above ground applications. This data are in line with reports in the EN 350-1 (1994) standard.

All treatments significantly increased performance of impregnated wood in use class 3 applications. However, there are considerable differences between tested preservatives. For example, spruce wood treated with preservative solution based on boric acid and quaternary ammonium compounds had its lifecycle prolonged only for a few years, but after leaching of the boric based ingredients from wood and potential bacterial degradation of quaternary ammonium compounds, decay started. Similar influence of copper leaching was determined with copper sulfate (CuS) treated wood. As long as at least low copper contents were present in wood, wood was protected against wood decay fungi (Thaler et al., 2011). When copper is leached, decay proceeds, similarly as determined in the laboratory specimens after artificial ageing. Furthermore, with specimens impregnated with higher Cu concentrations (retention = 6,5 kg/m^3), decay was delayed in comparison to the samples with lower Cu retention (retention = 1,1 kg/m^3). This was expected and is in line with the laboratory results, where lower concentration of copper did not prevent but even promote fungal growth (Pohleven and Humar, 2006). Even if copper is combined with ethanolamine, it does not ensure complete protection, if retention is too low (retention = 2,1 kg/m^3 of CuEa or 1,3 kg/m^3 of CuEaO). Field test data clearly show that in order to ensure protection of copper ethanolamine preservatives, copper must be combined with additional co-biocides like quaternary ammonium compounds. Good combination of biocides resulted in sufficient protection of wood even in case the stakes were impregnated with solutions of the lowest concentration. However, it has to be considered that double layer exposure offers extremely good conditions for fungal development, as there is water trapped between the samples. Without water traps considerably better performance is expected. At vertically exposed stakes, there are no signs of decay after three years of exposure even with susceptible beech or spruce wood specimens. Double layer test, however, represents the worst case scenario and should be interpreted as such.

Results of the copper leaching from the specimens exposed in outdoor aboveground application are resolved in Table 5. From the values determined with unexposed specimens it can be seen that there is a slight difference between concentration of copper determined from uptakes of preservative solution and values determined with XRF. This data somehow indicate, that "copper losses" of 4 % with specimens impregnated with aqueous solutions of lower concentrations, or 8% with specimens impregnated with aqueous solutions of higher concentrations were measured. These differences appeared to be due to different methodological approaches, variability of the material, selective penetration of water, crystal deposits on the surface that were brushed off… However, considering this experimental mistake, it can be concluded that statistically insignificant copper losses were determined with specimens impregnated with lower concentration of copper-ethanolamine preservative solution, between 2 % and 11 % of copper was emitted from wood in 18 weeks of exposure. So at the very moment it can not be confirmed if leaching is significant or not due to the huge variation of the results.

Table 5: Copper leaching from Norway specimens exposed in above ground applications. For impregnation aqueous preservative CuEaQO was used.

Copper concentration	Weeks of exposure	Copper loss (%)
0.125 %	0	4
	4	-2
	7	5
	12	5
	18	-2
0.25 %	0	8
	4	14
	7	10
	12	19
	18	12

These results are in line with laboratory leaching studies as well (Figure 3). These results clearly indicate that copper leaching increases with concentration of active ingredients in treatment solutions. The reasons for this originates in the fact, that the number of easily accessible fixation sites is limited, so there is not enough easily accessible functional groups available to achieve sufficient fixation with specimens impregnated with the highest copper concentrations. Furthermore, aqueous solutions of higher concentrations contain more ethanolamine, that could cause undesired depolymerisation of lignin, resulting in more prominent leaching from wood (Humar and Žlindra, 2007).

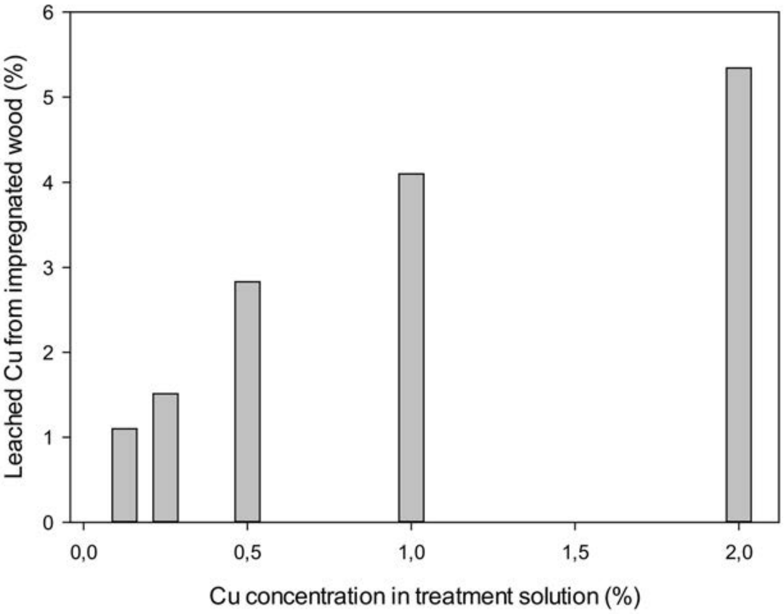

Figure 3: Influence of copper concentration on leaching of copper from Norway spruce wood impregnated with copper-ethanolamine based aqueous solution CuEaQO according to the standard EN 1250-2. Molar ratios between different active ingredients were the same in all treatment solutions.

4. CONCLUSIONS

Service life of the wood is influenced by several parameters. In use class 3 conditions, service life of Norway spruce wood is between 4 and 6 years. Similar service life is determined for beech as well. On the other hand larch wood and oak heart wood expressed insignificant signs of microbiological degradation after four years of exposure. Impregnation of wood with copper based biocides increased performance of the impregnated wood significantly. After 4 years first spruce samples, were completely degraded, while there was no sign of decay present on properly treated copper wooden samples. However, if leachable biocides are used, or if biocides in too low retentions are applied, decay is not prevented but only delayed for 1 to 3 years. One of the most important findings of this research was that laboratory experiments offer good estimation of the outdoor performance if applied correctly.

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AN ACCELERATED LABORATORY AGAR METHOD TO DETERMINE THE RESISTANCE OF PARTICLEBOARDS MADE FROM SAWMILL WASTE OF AMAZON WOOD SPECIES AGAINST DECAY FUNGI

MARIA APARECIDA DE JESUS [1,*], JESSICA SOUZA DA COSTA [2], SETSUO IWAKIRI [3], BASÍLIO FRASCO VIANEZ [1], ANDRÉ LUIS WILLERDING[4]

[1] NATIONAL INSTITUTE FOR AMAZON RESEARCH –INPA/ TECHNOLOGY AND INNOVATION COORD
.– COTI. AV. ANDRÉ ARAÚJO, 2936. ALEIXO. CEP: 69.060-001. MANAUS, AM – BRAZIL.

[2] BIOTECHNOLOGY /AMAZONAS FEDERAL UNIVERSITY. AV. GEN. RODRIGO OTÁVIO JORDÃO, 3000. CEP: 69.077-000. MANAUS - AM, BRAZIL.

[3] PARANÁ FEDERAL UNIVERSITY. R. AV. LOTHÁRIO MEISSNER, 900. JARDIM BOTÂNICO. CEP: 80.210-170. CURITIBA, PR – BRAZIL.

[4] AMAZON BIOTECHNOLOGY CENTER (CBA), AV. DANILO AREOSA, 690 DISTRITO INDUSTRIAL, 69075351 MANAUS, AM, BRAZIL.

* CORRESPONDING AUTHOR: TEL: +55 92 36433077, RANNA@INPA.GOV.BR

Keywords: Particleboard, tropical woods, decay fungi, biodeterioration resistance.

ABSTRACT

This bioassay was developed to evaluate the natural resistance of particleboards made from sawmill waste of tropical wood species: *Scleronema micranthum* Ducke (Cardeiro), *Ecclinusa guianensis* Eyma (Caucho), *Scleronema* sp. (Castanha-de-paca), *Copaifera multijuga* Hayne (Copaíba), *Ocotea* sp. (Louro), *Ocotea guianensis* Aubl (Louro-espinho), *Caryocar villosum* Pers. (Piquiarana), *Couratari oblongifolia* Ducke & R. Knuth (Tauari) and *Virola surinamensis* Rol. Warb (Virola). The resistance of particleboards were evaluated by the agar block method, using fungi: *Pycnoporus sanguineus*, *Trametes villosa* and *Lenzites trabea*. Five replicate blocks (2.5 x 2.5 x 0.9 cm) were labeled, stored at 25 °C, weighed and sterilized for 15 min. at 120 °C. *Pinus taeda* and *Simarouba amara* Aubl. (Marupá) were used as controls. The samples were all simultaneously exposed to each test fungus, on Petri dishes holding malt agar extract with particles of *Mauritia flexuosa* (Buriti) at 28ºC, 70% relative humidity (RH), for 16 weeks. After the test, the weight loss of the particleboard samples was calculated. The findings show *Ocotea* sp and *C. villosum* to be the most and least resistant to decay fungi. This knowledge is important to evaluate these wood species viability for being used as alternatives to replace the traditional species for manufacturing particleboards. Furthermore, this product could benefit the environmental landscape, since it diminishes, or even ends, the rate of wood wastage disposal.

1. INTRODUCTION

The best use for forest wastes generated by timber industrial processing is being increasingly sought for throughout the world. Even though Brazilian industries try to control and prevent the loss of raw material, most of them wind up just discarding it (Feitosa, 2007). According to Da Costa et al. (2005) a substantial portion of these wastes is used for direct generation of energy for industrial and domestic use. A feasible alternative for reducing wastage could be its sustainable utilization as raw material for manufacturing wood products, which will aggregate more value to it than just by using it for generating energy (Mendoza et al., 2010). Therefore, there is already a great concern on searching for a better application of this timber byproduct so as to meet its increasing demand (Melo et al., 2009).

The particleboard manufactured from planted *Eucalyptus* spp and *Pinus* spp shows to be the most industrialized and consumed in the southern and southeastern regions of Brazil (Iwakiri et al., 2012). However, pine plantations are not able to meet the increasing demand of wood processing industry, which increases the need to use alternative timber species (Mattos, 2008).

In Northern Brazil, holding higher forest species diversity, forest residues are mainly employed for generating energy for industrial and domestic use, especially in the Amazon. However, this adds very little value to the final product, as compared to what can be achieved by the traditional panel industry (Mendoza et al., 2010). There is a large amount of wood waste, such as sawing cants sawings, bark, sawdust, shavings, chips, among others (Iwakiri et al., 2012). Out of the 8.4 million m^3 recovered from logs nearly 1.6 million m^3 were used for coal production; another 2.7 million m^3 for power generation and 2.0 million m^3 for various uses. The remaining 2.1 million m^3 were burned or thrown out as refuse (Hummel et al., 2010).

Timber exploiting in regions, such as the Amazon have generate a large amount of waste, and faced serious problems. The wood waste utilization could be an alternative for manufacturing panels bearing regional perspectives of sustainability for furniture and forest product industries, and contribute to minimize the environmental impact of these lignocellulosic materials as well as bring forth a new economic alternative in the Northern region of Brazil, by creating new jobs and increasing the local population's income.

Iwakiri et al. (2012) evaluated the tropical wood waste-manufactured particleboard quality. They found that their physical and mechanical properties indicate them to be adequate for wood byproduct manufacturing. These findings meet the European Standards (EN) requirements and show to rise above those found on *P. taeda* used as the referential timber. On account of these good results, the authors recommended these Amazonian wood species as assorted particleboard manufacturing alternatives.

However, it must be emphasized that like other lignocellulosic materials, particleboards are also susceptible to decay by fungi belonging to Agaricomycetes and Basidiomycetes, most of which present an enzymatic lignocellulolitic complex able to exert decay on the three main natural polymers: cellulose, hemicelluloses and lignin, causing brown and or white rot on wood. The latter can efficiently degrade and even mineralize the most resistant natural polymer, lignin, whereas the former degrades the wood hemicellulose rapidly, leaving only lignin behind (Hammel and Cullen, 2008).

Decay fungi can severely affect the economic value of wood, along with its usefulness, as well. Therefore, further studies are needed to increase the knowledge on biodegradation as a whole, so as to produce a higher quality product. Data on the natural resistance to decay fungi presented by tropical wood are more restricted to solid than wood waste byproducts (Cardias, 1985; INPA, 1991; and Jesus et. al., 2008) and panels made of *Pinus* sp and *Eucalyptus* sp. (Okino et al., 2007 and Melo et. al., 2010), *Eucalyptus grandis* and *Bambusa vulgaris* (Stangerlin et al., 2011), *Hevea brasiliensis* (Willd.: A. Juss.). Müll. (Rubberwood) (Okino et al., 2009), among others. Thus, the main aim of the present study is to evaluate the sawmill waste tropical wood species-manufactured particleboards natural resistance against decay fungi, under laboratory conditions, in order to enhance the reusing ability of wood waste, preventing its degradation and correcting the use of the final product, without compromising the forest diversity.

2. MATERIALS AND METHODS

The experiment was carried out at the Wood Pathology Laboratory/INPA and the particleboards were manufactured at the Wood Panels Laboratory / Paraná Federal University/UFPR. Waste from Amazonian tree species, *Caryocar villosum* Pers. (Piquiarana), *Copaifera multijuga* Hayne (Copaíba), *Couratari oblongifolia* Ducke & R. Knuth (Tauari), *Ecclinusa guianensis* Eyma (Caucho), *Erisma uncinatum* (Cedrinho), *Ocotea guianensis* Aubl. (Louro-espinho), *Ocotea* sp. (Louro), *Scleronema micranthum* Ducke (Cardeiro), and *Virola surinamensis* Rol. Warb. (Virola) were obtained from local sawmills in the outskirts of Itacoatiara, Amazonas, Brazil, and were used to manufacture the particleboards with urea-formaldehyde resin (UF) mixture with solid content of 65%, pH 7.8 and Brookfield viscosity of 450 cP, with the ammonium sulfate at a ratio of

3%. Data on the above mentioned tropical wood species physical and mechanical properties are similar to those found in literature pertaining to planted and natural grown forest. Mean perpendicular tension, elasticity and rupture modulus values of the above mentioned tropical wood species corroborate with those established by European Standard EN (Iwakiri et al. 2012).

Sound particleboard samples with no finish were obtained through cutting them into (25.0 x 25.0 x 10.0 mm) blocks. All samples were sanded to prevent future striping. Figure 1 shows particleboard and Marupá samples. Five replicates per wood species / treatment for each fungus were used and these were placed in an air conditioned room at 20 ± 3 °C and 65 ± 5% RH in order to reach equilibrium moisture content prior to testing. This material was weighed once a week until it reached constant weight (W_1). All samples were sterilized for tree times for 15 min. at 120°C.

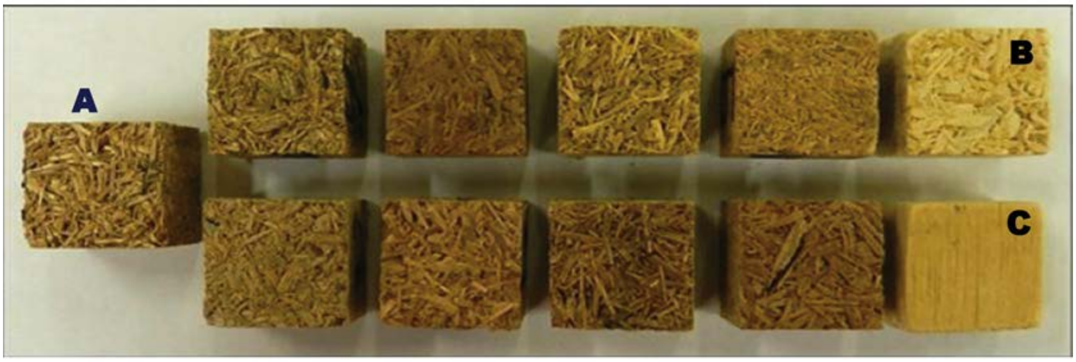

Figure 1: Particleboard samples made from Amazonian waste wood species (A), *P. taeda* (B), and solid wood of *S. amara* (C).

Decay fungi tested in this study *Pycnoporus sanguineus* (L.: Fr.) Murr. (LPM 408), *Trametes villosa* (Fr.) Ryv. (LPM 406) (white rot) and *Lenzites trabea* Pers.: Fr. (LPM 368) (brown rot). These fungi were acquired from the Microorganisms Culture Collection of the National Institute for Amazon Research – INPA.

The present experiment used an alternative accelerated fungal test with malt-extract agar under laboratory condition proposed by Jesus et al. (2002). The particles of *Mauritia flexuosa* (Buriti) were sterilized at 121°C for 20 min. on three successive days. Then, 20 g of Buriti particles were added to the sterilized malt-extract agar medium, still liquid, poured onto the Petri dish (150 x 20 mm), until reaching a minimum depth of 4 mm to 5 mm. When the medium got solidified, five inoculums of fungi were placed on the dish. The cultures were conditioned at 28ºC and 70% RH until the Buriti was heavily colonized by vigorous mycelial fungi. Five particleboard samples made from each wood species were then placed on the surface of fungus-colonized medium culture. For comparison, low durability solid wood samples of *S. amara* (Marupá) (25.0 x 25.0 x 10.0 mm) that were cut from the sapwood, and particleboards made from *P. taeda* with the same dimensions, were used as controls. The wood-fungi cultures were kept at 28ºC and 70% RH for 16 weeks.

Following this period, all micelium traces remaining on particleboard surfaces were carefully brushed off. The particleboards were placed under the same pre-test conditions so as to reach the constant weight (W_2). The weight loss was calculated by the difference between the initial weight (W_1) and the final weight of the samples exposed to fungi (W_2), and expressed as percentage of the initial sample weight (i.e., weight loss in %), based on the values of weight loss of each treatment by the arithmetic mean of 5 particleboard samples for each decay fungus species $[(W_1 – W_2)/W_1] \times 100$). The class of natural resistance against decay fungi showed on Table 1 was rated according to American Society for Testing and Materials (ASTM D 2017-05, 2005) based on particleboard weight loss mean values. Experimental design was at random with 11 wood species x 3 decay fungi species. Anova and average were compared by Turkey at the 5% significance level test, performed to evaluate the natural resistant of particleboards against decay fungi.

Table 1: Natural durability classes, according to the ASTM D 2017-05, 2005.

Natural Durability Class	Weight Loss, mean (%)
Highly Resistant	0 to 10
Resistant	11 to 24
Slightly Resistant	25 to 44
Non-Resistant	45 or above

3. RESULTS AND DISCUSSION

Weight loss mean values of particleboards and controls, as exposed to white and brown rot fungi, as well as natural durability class to decay fungi of Amazon wood, complying to ASTM D 2017 (2005), are listed on Table 2. All particleboards made from Amazonian waste wood species showed to be resistant to *L. trabea*, whereas the mean weight loss varied from 9.45% to 21.79%. But *Ocotea* sp., with the weight loss of 9.45%, has been classified as highly resistant to *L. trabea* as well as to *S. amara* (6.88%), lower than that obtained by Jesus and Abreu (2002) and Da Costa et al. (2005). Conversely, *L. trabea* caused the highest weight loss on particleboards made from *P. taeda* (38.86%) (Table 2). Similar weight loss was also reported to *P. taeda* panels attacked by *L. trabea* by Okino et al., (2007).

Table 2: Weight loss mean values and the class resistance of particleboards made from Amazon wood species and controls as exposed to decay fungi under accelerated test in laboratory, following 16 weeks.

Wood species	Natural durability classes according to weight loss % wood decay fungi					
	White rot fungi				Brown rot fungi	
	PS	Class	TV	Class	LT	Class
Caryocar villosum Pers.	37.51^{a}	S.R	39.14^{a}	S. R	21,79^{b}	R
Copaifera multijuga Hayne	8.68^{c}	H. R	41.68^{a}	S. R	14,54^{b}	R
Couratari oblongifolia Ducke & R. Knuth	29.73^{a}	S. R	28.02^{a}	S. R	12,27^{b}	R
Ecclinusa guianensis Eyma	23.19^{a}	R	28.16^{a}	S. R	11.88^{b}	R
Erisma uncinatum Warm.	29.19^{a}	S.R	26.89^{a}	S. R	10,69^{b}	R
Ocotea guianensis Aubl.	27.07^{b}	R	39.38^{a}	S. R	11,65^{c}	R
Ocotea sp.	18.94^{b}	R	30.90^{a}	S. R	9,45^{c}	H. R
Scleronema micranthum Ducke	20.24^{b}	R	32.69^{a}	S. R	15^{b}	R
Virola surinamensis Rol. Warb.	30.68^{a}	S. R	34.51^{a}	S.R	10,81^{b}	R
Pinus taeda L.	11.74^{b}	R	39.88^{a}	S.R	38,86^{a}	S. R
Simarouba amara Aubl.	23.75^{b}	R	33^{a}	S.R	6,88^{c}	H. R

Note: fungi species (PS= *P. sanguineus*, LT= *L. trabea*, TV= *T. villosa*); the natural durability classes according to ASTM D 2017, 2005, R = Resistant; SR = Slightly Resistant; H.R.= Highly Resistant; Numbers followed by same letter do not differ significantly by Turkey test ($p < 0.05$).

Particleboards produced from nine wood species and *P. taeda* exposed to *T. villosa* showed to be slightly resistant, since their weight loss ranged from 26.89% to 41.68%. While the particleboards were rated from slightly resistant to resistant to *P. sanguineus*, as their weight loss varied from 8.68% to 37.51%, samples of particleboards made from *C. multijuga* (8.68%), were highly resistant to *P. sanguineus*. When comparing the weight loss by all particleboards one can see that *T. villosa* caused more decay than the other two decay fungi tested and particleboards made from most Amazon waste wood species could be rated as slightly resistant to *P. sanguineus* and *T. villosa* (white rot fungi) and resistant to *L. trabea* (brown rot) (Table 2).

Data on the particleboards resistance against decay fungi is paramount in order to indicate the best wood species for panel manufacturing. It is known that decay fungi might reduce the timber mechanical resistance (Olfat et al., 2007). However, there is a lack of data pertaining to Amazonian wood species and their byproducts' natural resistance to decay fungi, under laboratory conditions (Alves et al., 2006). By comparing the studied solid wood resistance to decay fungi, we found that *V. surinamensis, C. oblongifolia* and *E. uncinatum* to be non durable to decay fungi according to Neves et al. (2002), IPT, (1989, 2003), respectively. While *C. villosum* presents high natural durability (Araújo, 2012).

Likewise, the natural resistance of wood byproducts, solid wood, plywood and mixed cement-bonded particleboards manufactured from six clones of *H. brasiliensis* against *L. trabea* and *Trametes versicolor* were evaluated by Okino et al. (2002). As a result, all wood byproducts showed to be slightly resistant to decay fungi. Okino et al. (2003) also tested the resistance of flakeboards made from four clones of *H. brasiliensis* to the same fungi species and they all showed to be slightly resistant, as well. The findings obtained in the present study point out particleboards produced from these Amazonian wood species to be ranging from highly to slightly resistant to decay fungi.

According to statistical analysis, the weight loss brought about by all three decay fungi species tested on particleboards made from nine wood species differs significantly. Yet, there were no significant differences on weight loss of particleboards made from *S. micranthum*, *E. uncinatum*, *C. multijuga*, *O. guianensis* and *C. oblongiflora* deteriorated by (*P. sanguineus*, *T. villosa* and *L. trabea*), under accelerated laboratory test (Figure 2). The particleboards made from *V. surinamensis* and *C. villosum* presented slight differences on their weight losses (25.338% and 32.82%) respectively, as compared to the above mentioned wood species. However, particleboards from *Ocotea* sp showed the best natural resistance performance, whereas those from *C. villosum* showed the greatest susceptibility to decay fungi (Figure 2).

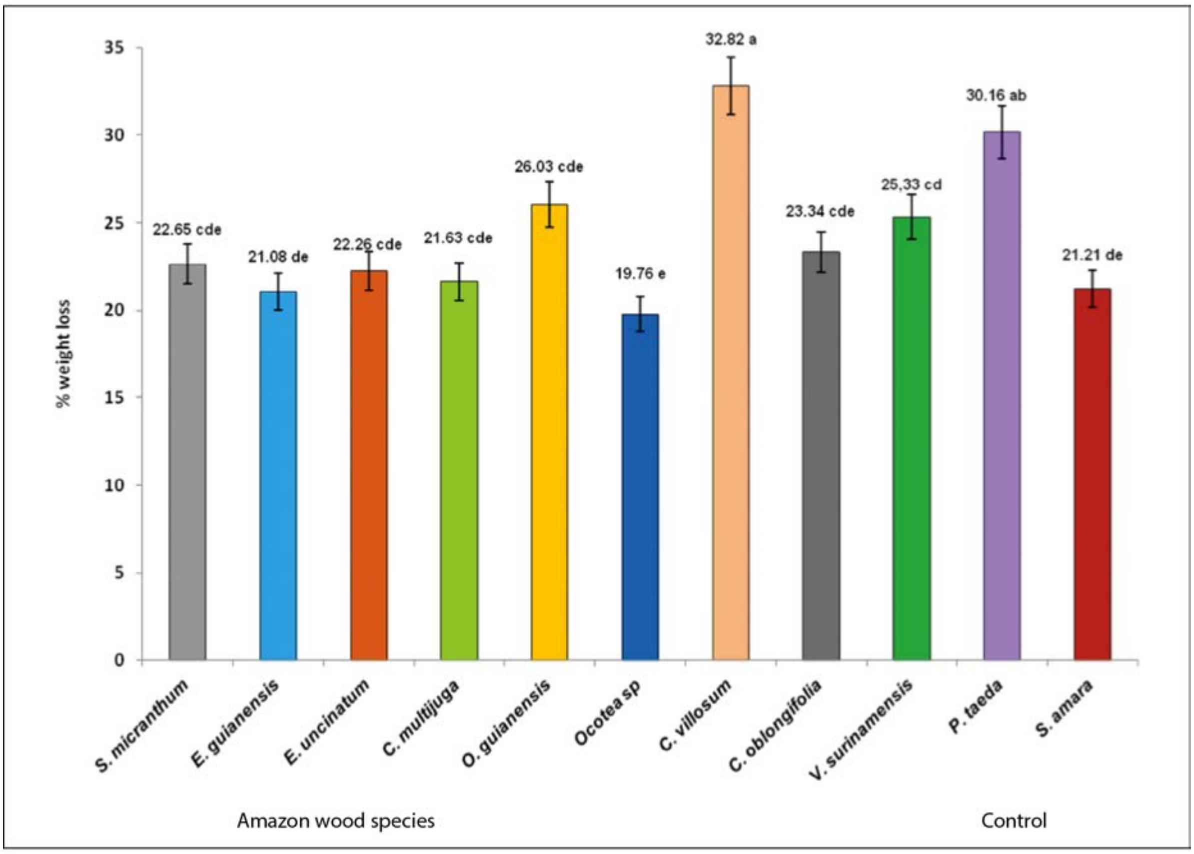

Figure 2: Weight loss mean values of particleboards made from Amazonian waste wood species and controls, brought about by all three decay fungi(*P. sanguineus, L. trabea* and *T. villosa*), under accelerated test in laboratory, following 16 weeks. Bars represent means and lines are mean standard deviations (n =5); treatments with the same letter do not differ by the Turkey test at the 5%.

Comparing the weight loss caused by each fungus on particleboard made from every wood species, through the Turkey test at the 5% level, one can find them to present no significantly different weight loss values, when exposed to *L. trabea*. Except for *P. taeda* which was severely attacked by *L. trabea* and presented the highest weight loss value (38.86%). Conversely, the lowest weight loss value (6.88%) was observed on *S. amara* decayed by *L. trabea* (Table 2). Studies investigating the wood's natural resistance to decay fungi have demonstrated *L. trabea* to cause the highest weight loss on solid wood and byproducts and *Pinus* as well as brown rot fungi species to prefer decaying conifers rather than hardwoods (Okino et al., 2010).

There were no significant weight loss differences shown by all particleboards made from wood species attacked by *T. villosa*. However, *T. villosa* demonstrated to cause higher weight loss on particleboards made from *C. multijuga*, *O. guianensis* and *C. villosum* (41.68%, 39.38%, 39.14%), respectively. Similar weight loss brought about by *T. villosa* was observed on *P. taeda* (39.88%) and *S. amara* (33.0%), as well (Table 2).

Likewise, the Turkey test at the 5% level pointed out all particleboards exposed to *P. sanguineus* to present differences on their weight loss values. However, particleboards from *S. macranthum*, *O. guianensis, C. multijuga,* and *Ocotea* sp showed no significant differences in weight loss, while presenting lower weight loss than *C. villosum*, *C. oblongiflora*, *E. guianensis* and *Virola surinamensis*. *P. sanguineus* showed to cause the highest and lowest weight loss on particleboards made from *C. villosum* and *E. uncinatum*, respectively. Regarding the weight loss caused by *P. sanguineus*, *T. villosa* and *L. trabea* on particleboards produced from all wood species and control, one can observe *T. villosa* (34.02%), *P. sanguineus* (23.70%) and *L. trabea* (14.89%) to cause decreasing weight losses (Figure 3). These findings point out particleboards made from Amazonian waste wood species to be more resistant than *P. taeda* to (brown rot fungi) *L. trabea* (Figure 3).

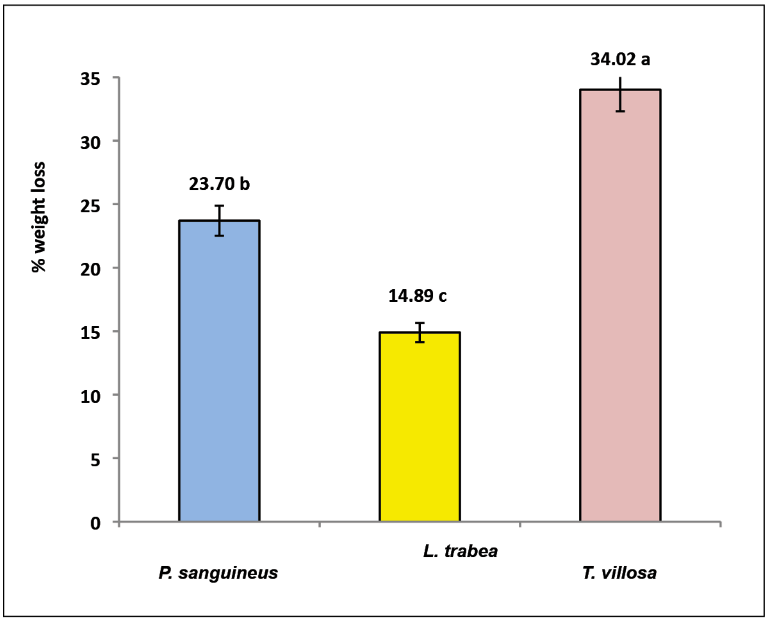

Figure 3: Weight loss mean values brought about by each fungus (*P. sanguineus*, *L. trabea* and *T. villosa*) on all particleboards made from Amazonian waste wood species and controls, under accelerated test in laboratory conditions, following 16 weeks. Bars represent means and lines their standard deviation (n =5). Means followed by the same letter do not differ by the Turkey test at the 5%.

The weight loss brought about by brown and white rot fungi differs significantly on particleboards made from nine Amazonian wood species, whereas brown rot fungi caused lesser weight loss than white rot fungi on all particleboards (Figure 4 and 5). This data agrees with what is reported in literature, since white rot fungi cause greater mass loss and are particularly effective at deteriorating wood (Curling and Murphy, 2002). When comparing the weight loss data from all particleboards made from different wood species and controls exposed to *P. sanguineus*, *T. villosa* and *L. trabea*, most of them showed to be slightly resistant and resistant to *T. villosa* and *L. trabea*, respectively, ranging from highly to slightly resistant to *P. sanguineus*. Particleboards attacked by all three tested decay fungi, presented under 50% weight loss values (Figure 2), which are below those recommended by ASTM D 2017 (2005). The use of sawmill waste from these Amazonian wood species for manufacturing particleboard shows to be feasible due to their satisfactory natural resistance against decay fungi.

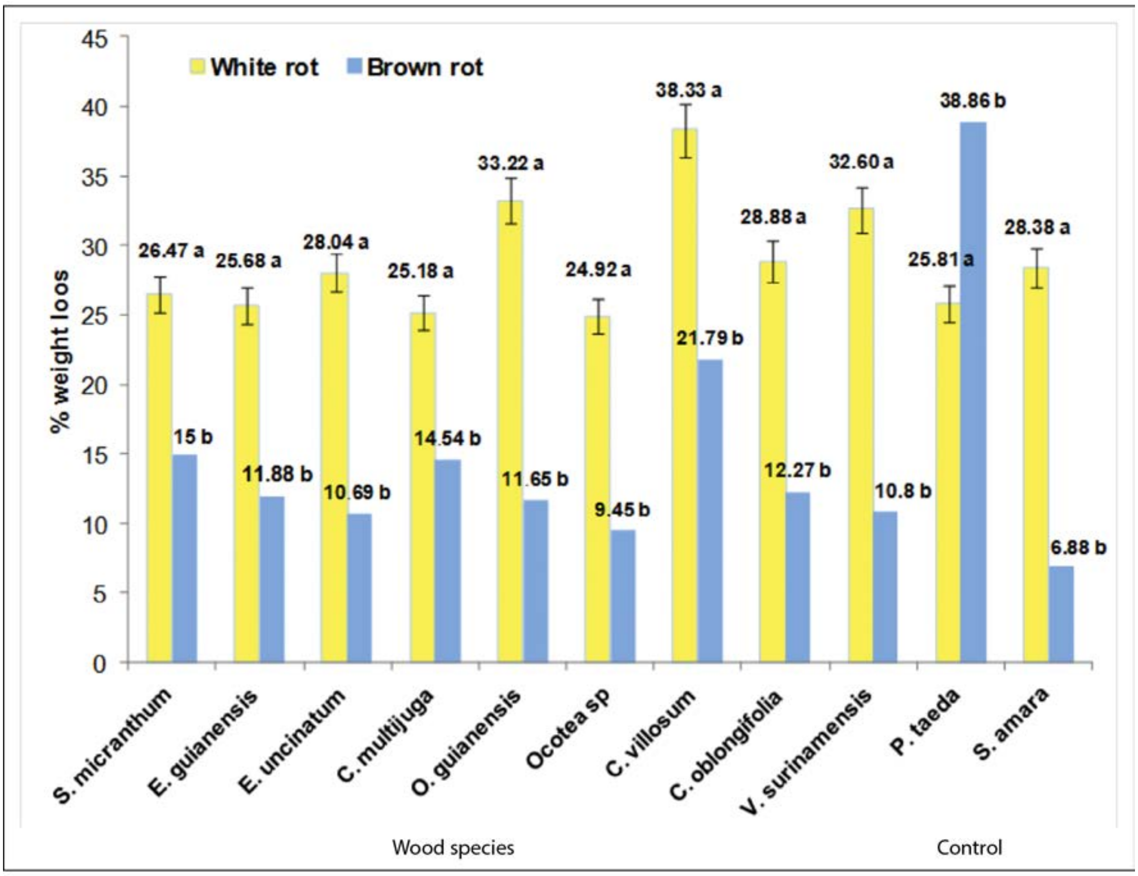

Figure 4. Weight loss mean values of particleboards made from Amazonian waste wood species and controls as exposed to brown and white rot fungi, under accelerated test in laboratory conditions, following 16 weeks. Bars represent means and lines their standard deviation (n =5). Means followed by the same letter do not differ by the Turkey test at the 5%.

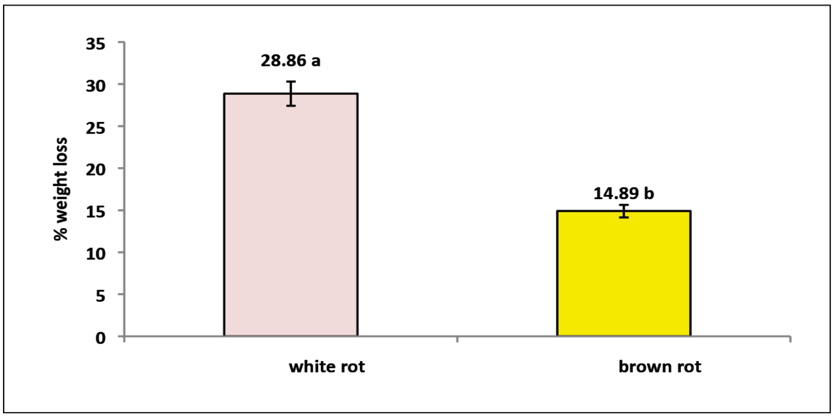

Figure 5: Weight loss mean values brought about by brown and white rot fungi on all particleboards made from Amazonian waste wood species and controls tested in laboratory conditions, following 16 weeks. Bars represent means and lines their standard deviation (n =5). Means followed by the same letter do not differ by the Turkey test at the 5%.

Microscopy analysis showed *L. trabea* to attacck particleboard samples with hyphae by branching through wood elements presenting a distinctive darker color. While *T. villosa* as well as *P. sanguineus* hyphae grew as much. Particleboards made from *O. gianensis*, *C. villosum*, *E. uncinatum*, *C. villosum* and *Ocotea* sp attacked by *T. villosa* and *S. micranthum* as well as by *P. sanguineus* differ little in color, showing to be lighter-colored and to disintegrate easily. On the other hand, the biossay showed particleboards samples made from *Ocotea* sp and *O. guianensis* to be prone to humidity-induced swelling. Conversely, particleboards from both species presented, lower water absorption mean values (18.43% and 22.44) within 24 hours, respectively (Iwakiri et al.; 2012).

4. CONCLUSION

The findings obtained from particleboards made from Amazonian wood species exposed to decay fungi, differ for each fungus but indicate most of them to be slightly resistant to *T. villosa* and resistant to *L. trabea*, ranging from highly to slightly resistant to *P. sanguineus*. Particleboards made from *Ocotea* sp showed the best natural resistance, whereas those from *C. villosum* showed the greatest susceptibility to decay fungi. No particleboards should be considered to be nonresistant to decay fungi. In light of the particleboards natural resistance against decay fungi, the use of waste wood from *S. micranthum*, *E. guianensis*, *S.cleronema* sp., *C.multijuga*, *Ocotea* sp., *O. guianensis*, *C. villosum*, *C. oblongifolia* and *V. surinamensis* stands out as an assorted particleboards manufacturing alternative.

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EFFECTS OF DETERIORATION ON DENSITY AND COMPRESSIVE STRENGTH PARALLEL TO FIBRES IN CARDEIRO WOOD (*SCLERONEMA MICRANTHUM*)

RAIMUNDA LIÉGE SOUZA DE ABREU, BASÍLIO FRASCO VIANEZ, JORGE LUIS MONTEIRO DE MATOS, SUELY DE SOUZA COSTA, CLAUDETE CATANHEDE DO NASCIMENTO, BEATRIZ RONCHI-TELLES AND CECI SALES-CAMPOS
NATIONAL INSTITUTE FOR AMAZON RESEARCH DEPARTMENT OF TECHNOLOGY AND INNOVATION,
AV. ANDRÉ ARAÚJO, 2936 - ALEIXO. CEP 69060-001 . MANAUS, AMAZONAS, BRAZIL.
FEDERAL UNIVERSITY OF PARANÁ. WOOD TECHONOLOGY – PHYSICAL AND MECHANICAL PROPERTIES. AV.
PROF LOTHARIO MEISSNER, 3400 – JARDIM BOTÂNICO. CEP 80210-170 CURITIBA, PARANÁ, BRASIL.
*CORRESPONDING AUTHOR: TEL: 55 92 3643 3075; RAIABREU.INPA.GOV.BR.

Keywords: Amazon wood, tree trunk sections, exposure in contact with forest ground, heartwood.

ABSTRACT

The forest species *Scleronema micranthum* (Ducke) Ducke is frequently found in upland forests, mainly on the outskirts of Manaus, Amazonas, Brazil. Although there are studies on its physical and mechanical properties, research about the influence of biotic and abiotic factors on deterioration of the wood of this species is non-existent. Therefore, the objective of this study was to evaluate the influence of wood degradation of *S. micranthum* on basic density and compressive strength parallel to fibers, when exposed in contact with forest ground. Five trees were used from which, 45 cross section (wood cylinders) 30 cm long were cut from three different positions of the trunk (base, middle and upper position). For the determination of basic density and compressive strength parallel to fibers, six samples were cut from each wood cylinder in a tangential orientation, measuring 2 cm x 2 cm x 3 cm and 5 cm x 5 cm x 20 cm, respectively. These tests were carried out with sound wood cylinders exposed on the ground of the forest for 12 and 24 months. Statistical analyses were made using descriptive statistics, analysis of variance and simple linear regression. The results indicate that the exposure time of the samples in contact with forest ground changed these properties. At the end of 24 months it was observed that the percentage of density reduction was lower than the reduction of compressive strength parallel to fibers. The decrease in density within the three stem positions ranged from 21.9% to 29.9% and compressive strength from 40.37% to 62.04%. Comparison between samples taken from different positions for both, sound and deteriorated samples, showed little variation in the values of these properties.

1. **INTRODUCTION**

The forest species *Scleronema micranthum* (Ducke) Ducke commonly known as cardeiro, belongs to the family Bombacaceae. Its wood has good workability and is used in the wood industry in the manufacture of furniture, general carpentry, joinery works, partitions, light construction, finishes, plywood, decorative veneers, etc. (CPPF INPA, 1991). It is a medium to large tree, its height varies from 23 to 40 m and the diameter from 25 to 80 cm. The heartwood is light brown and glossy; the sapwood has a light yellow color, 5 to 8 cm thick; regular grain, coarse texture; indistinct smell and taste; the parenchyma presents banded or concentric lines; few medium to large size pores, some of them blocked by tyloses or oily resin; two types of rays: wide and narrow (Loureiro et al., 1979). In laboratory tests this species proved to be resistant to fungi *Pycnoporus sanguineus* and *P. fumosus*, moderately resistant to *Lenzites trabea* and not resistant to termites of the genus *Nasutitermes* (CPPF INPA, 1991). Its density ranges between 0.55 and 0.60 g/cm^3, module of elasticity between 11600 a 19140 MPa and compressive strength parallel to fibers between 23 to 25 MPa (INPA/CPPF, 1991; Nascimento, 2000; Oliveira, 2006).

Wood is the only material in which the chemical composition, anatomical characteristics, physical and mechanical properties and natural durability are interrelated (Winandy, 1994; Simpson and TenWolde, 1999; Chowdhury et al., 2007).

The physical and mechanical properties of wood are important parameters to define its quality and final use (Scanavaca Jr and Garcia, 2004). The density is one of the most important physical properties, because it characterizes the quality of wood and also affects all other properties (Kollmann and Côté, 1968). Compression parallel to fibers, which is one of the mechanical properties most correlated with density, is also widely used to determine wood applications (Araújo, 2002; Lin and Fu, 2008).

The natural durability of wood is directly related to the wood species, the amount of heartwood and sapwood, extractives, density, moisture content, conditions of use, among others (Panshin and Zeew, 1980).

Woods exposed to weathering are subjected to decay and this affects the durability and the physical and mechanical properties of wood. In this condition, in addition to weathering, they are also decayed by fungi and insects that after long periods of exposure will cause loss of resistance and durability (Shupe et al., 2006).

Tests with chemically-treated and untreated wood, whether in contact or above ground, in forests or urban environment, aiming to analyze the relationship between decay and various wood properties, have been conducted in several countries (Torres, 1994; Machek et al., 1997; 2004; Grinda and Göller, 2005; Lin et. al., 2007; Pfeffer et al., 2008; Meyer et al., 2012). In Brazil, the existing research works were carried out by Venson (2000) and by Trevisan et al. (2007).

In the Amazon region, the existing research works refer only to physical and mechanical properties of sound wood, including basic density and compressive strength parallel to fibers (Paula et al., 1986; INPA/CPPF, 1991; 1993; IBAMA, 1993; Nascimento, 1993; Nascimento and Garcia, 1995; Nascimento et al., 1997; Oliveira, 2006). Reserch studies about the forest species *Scleronema micranthum* were carried out by INPA/CPPF (1991), by Nascimento (2000) and Oliveira (2006).

Based on what was stated above, this work aimed at evaluating the effect of degradation of cardeiro wood (*Scleronema micranthum*) on density and compressive strength parallel to wood fibers when it is exposed for 24 months in ground contact in primary forest.

2. MATERIAL AND METHODS

2.1. EXPERIMENTAL AREA

This work was carried out at the ZF-2 Experimental Station, Nacional Institute for Amazon Research-INPA, located at km 50, BR-174 (Manaus-Boa Vista, Brazil) (2° 35 ‘ 45 “; S 60° 12 ‘ 40 “W). According to RADAM (1978) and Bastos et al. (1986), the area has a slightly wavy terrain; the climate is categorized as Am type, according to the Köppen classification; the annual average temperature of the coldest month is always above 18ºC; the relative humidity is very high and the annual average ranges from 84% to 90%; the rainfall is greater from December to May and the annual average is 2,097 mm. According to Ferraz et al. (1980) and Higuchi et al. (1998) the soil of the region is clayey, and it can be classified as Oxisol and Ultisol The vegetation of the area is influenced by the Rio Negro basin, characterized by possessing heterogeneous forests. The height of trees varies from 30 to 40 meters (Hueck, 1972).

2.2. PREPARATION OF THE SAMPLES AND LAYOUT OF THE EXPERIMENT

Five trees of *S. micranthum* were used with an average diameter of 58 cm, free from insect and fungal attack. The tree trunk was divided into three positions: base, middle and upper and from each position a cross section (wood cylinder) measuring 30 cm in length was cut and labeled (Abreu et al., 2009), totaling 45 samples. Immediately after each tree was felled, 15 wood cylinders of sound wood were randomly taken for measurements of basic density and compression parallel to fibers. Afterwards the other wood cylinders were randomly plotted in contact with the forest ground on the same place where the trees were cut, to be submitted to biodeterioration for twenty-four months. During that period, 15 wood cylinders were removed from the forest after each period of 12 months of exposure, for determination of basic density and compressive strength parallel to fibers. For removal of the wood cylinders from the forest, these samples were randomly chosen so that they systematically included samples from all positions of all trees.

In most studies of wood deterioration, wood mechanical resistance evaluation is done by the determination of the module of elasticity (Machek et al., 1997). According to Yang and Evans (2003) and Scanavaca Jr and Garcia (2004) this is one of the most important mechanical properties to make this assessment. On the other hand, Lin et al. 2007 stated that compressive strength parallel to fibers is also an important parameter to evaluate the stiffness and strength of wood. Furthermore, the existence of few works using this method was an important factor for choosing this technique in the present work. Trevisan et al. (2007) Li et al. (2007), and Lin and Fu (2008) are some of the authors that carried out studies using this approach.

2.3. DETERMINATION OF DENSITY AND OF COMPRESSION PARALLEL TO FIBERS

For the determination of basic density and compressive strength parallel to fibers, samples were taken from heartwood of healthy cross section (wood cylinders), from heartwood of cylinders exposed in the field after twelve months and from heartwood of cylinders after 24 months of exposure. Six samples measuring 2 cm x 2 cm x 3 cm (Figure 1A) and six measuring 5 cm x 5 cm x 20 cm (Figure 1C) were cut from each wood cylinder for basic density and for compressive strength tests, respectively. All samples with the longest dimension in the longitudinal direction. Sampling was carried out in five trees, in all positions of the tree, totaling 270 samples for each test.

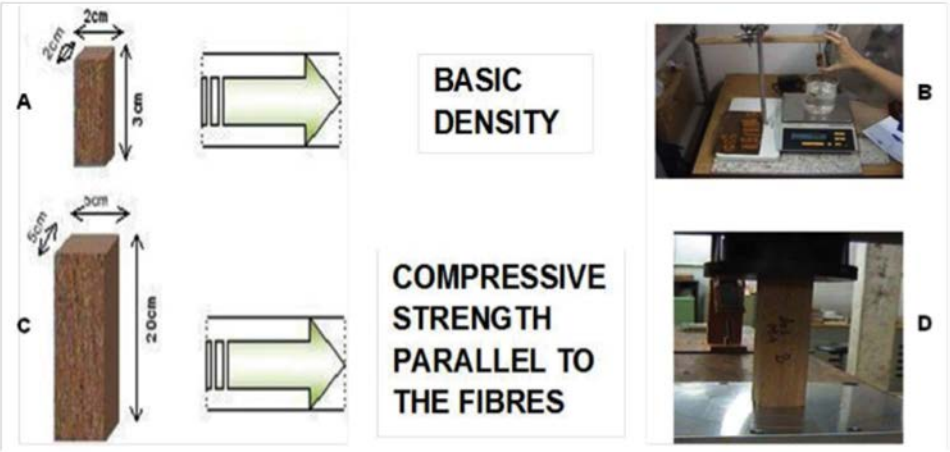

Figure 1: Representation of samples for analysis of basic density (A and B) and compressive strength parallel to fibers (C and D) of *Scleronema micranthum*.

For basic density calculation, the volume of green wood and the weight of dry wood were used, in accordance with the recommendations of the Pan American Standards Commission (COPANT 1971a). To obtain the volume of green wood, the specimens were submerged in a container with water for a period of 10 days, for saturation. After that, each saturated sample was fixed to a support, submerged into a beaker with water level at the top of the scale (Figure 1B) and the volume of green wood was obtained from water displacement (Vital, 1984). For the calculation of the weight of dry wood, the same samples were dry in an oven at 103 ± 5 °C, until the weight remained constant. The accuracy of the scale used for these measurements was 0.001 g. The density was calculated using the following formula (1).

$$Db = \frac{Ps}{Vv} \quad g/cm^3 \quad (1), \quad \text{where}$$

Db = Basic density

Ps = Weight of dry wood

Vv = Volume of green wood

For the test of the compressive strength parallel to fibers, each sample was subjected to a load at one end, applied at constant speed, up to its maximum resistance, using a Instron Universal Testing Machine, with a capacity of 50,000 kg (Figure 1 D). The loading speed used to determine the limit of compressive strength was calculated in accordance with the recommendations of the ASTM (1995) standard, based on the dimensions of the samples and a constant speed of 0.09 mm/min, according to equation (2), in accordance with COPANT (1971b).

$$Vc = 0{,}003 \text{ cm/cm of length/min } (2)$$

Compressive strength parallel to fibers was calculated by the formula (3):

$$Fc = \frac{Fc_{\max}}{A_0} \quad kgf/cm^2 \quad (3), \quad \text{where:}$$

Fc = Compressive strength parallel to fibers

$Fc_{\max}$ = maximum compressive force applied to the wood sample

A_0 = initial area of compressed cross section

2.4. STATISTICAL ANALYSIS

For the statistical analysis of the results of the measurement of density and compressive strength parallel to fibers, the mean value, the standard deviation and the percentage of weight loss of the samples of *S. micranthum* wood were initially calculated in the three positions of the tree trunk (base, middle and top) for each of the time periods evaluated (zero, 12 and 24 months). The next step was the analysis of variance (ANOVA) for the comparison of the averages of the samples in the different positions of the trunk, for the same time periods of the test and also for the interactions (position and time period). Finally, for each parameter, a linear model was fit for time periods with [log(x+1)] transformation and positions, as well as for each of the positions, by means of simple Linear Regression, applying a t-test with 95% confidence level.

All these analyses were carried out using the MiniTab Statistical Software.

3. RESULTS AND DISCUSSION

Table 1 presents the average values of density of *S. micranthum* wood samples in three positions of the tree trunk for each time period of evaluation, as well as the percentage of density reduction. It can be observed that the averages of these parameters obtained with samples from different positions in the trunk were very similar, in spite of the fact that sampling was carried out from different position of the trunk and from five different trees. According to the standard deviation of density in each position *versus* time period, the largest variations in relation to the average were observed in the last evaluation period. The percentage of weight reduction was more noticeable as the exposure time of the samples increased. The biggest reduction in density occurred at the upper position (29.96%) between 12 and 24 months of exposure of the wood samples in contact with forest ground.

Table 1: Average values of basic density (± standard deviation) and percentage of density reduction of wood samples of *Scleronema micranthum*, in three positions and in three time periods.

Periods / Position in the tree trunk	0 month	12 months	Density Reduction(1) (%)	24 months	Density Reduction (2) (%)	N
Lower	0.59 ± 0.0064	0.484 ± 0.028	17.966	0.378 ± 0.048	21.901	90
Middle	0.59 ± 0.0036	0.494 ± 0.028	16.129	0.381 ± 0.052	22.874	90
Upper	0.59 ± 0.0069	0.494 ± 0.025	16.129	0.346 ± 0.064	**29.960**	90
Whole trunk	0.59 ± 0.0057	0.491 ± 0.027	16.638	0.368 ± 0.057	25.051	270

(1) Percentage of wood density reduction between 0 and 12 months.
(2) Percentage of wood density reduction between the periods of 12 months and 24 months.
N = Number of samples

The values of compressive strength parallel to fibers are shown in Table 2, where a similar trend is observed for the averages and percentages of compressive strength reduction. From the standard deviation it can be seen that, for this parameter, there was greater data dispersion within each position and in each period of exposure. With respect to the percentage of reduction the smallest value was obtained in the upper position (40.37%), in the same period of exposure (24 months).

In general when there was a reduction in density the same occurred to compression parallel to fibers. In this work the reduction in density followed a pattern, namely the reduction increased from base to upper position. The value of compressive strength parallel to fibers in the period of 24 months did not followed this pattern in the upper position of the tree, in which the reduction was smaller than in the other positions. Trevisan et al (2007), also analyzed these two properties in logs of *Eucalyptus urophyla*, *Pinus elliotti*, *Melia azedarach* and *Inga marginata*, exposed to deterioration for 12 months. He also noted that there was no proportional reduction between density and compression parallel to fibers.

Table 2: Average values of compressive strength parallel to fibers (± standard deviation) and percentage of compressive strength reduction of wood samples of *Scleronema micranthum*, in three positions in three time periods.

Periods Position in the tree trunk	0 month	12 months	Strength reduction (1) (%)	24 months	Strength reduction (2) (%)	N
Lower	598±49	399±42	33.23	252±103	58.58	90
Middle	588±52	395±63	32.94	243±76	62.04	90
Upper	603±49	350±87	41.95	249±89	**40.37**	90
Whole trunk	596±159	381±156	36.07	248±168	53.61	270

(1) Percentage of compressive strength reduction between 0 and 12 months.
(2) Percentage of compressive strength reduction between the periods of 12 months and 24 months.
N = Number of samples

ANOVA results confirmed that there is significant difference in density values between the time periods of exposure of samples on the field ($p < 0{,}001$) and between the time *versus* position($p = 0{,}001$), but there is no difference between positions. On the other hand, the data on compressive strength parallel to fibers indicates that there was a significant difference between the time periods of exposure of samples on forest ground ($p < 0{,}001$).

Analysis of variance of the regression of the values of density and compressive strength parallel to fibers show that data can be estimated by the simple linear model by adjusting the relationship between density and compressive strength parameters, with the exposure time of the samples on forest ground.

Figure 2 shows data density for all positions in relation to periods of time. It can be stated that the regression equation, $Y = 0{,}5990 - 0{,}1389X$ explains that in the absence of deterioration, the average density of healthy wood samples is estimated to be $0{,}5990\ g/cm^3$ and for each period of twelve months of exposure there is a loss of $0{,}1389\ g/cm^3$. This same reasoning can be extended to the positions, separately. In relation to the variation of this parameter in the positions there is similarity of the values obtained from different positions of the tree trunk (Figures 3, 4 and 5). The biggest variations were observed during the last period of exposure on forest ground. It can be seen that in all positions there are values that do not follow a straight line pattern, especially when analyzing all data together, since the values obtained from the upper position are smaller. The smallest gradual loss of density was obtained at the upper position ($0{,}0101\ g/cm^3$) and also after 24 months several density values ranging between ($0{,}22\ g/cm^3$ and $0{,}30\ g/cm^3$ were observed, but the lowest density after 24 months was obtained in the middle position ($0{,}21\ g/cm^3$), emphasizing that these factors are not related.

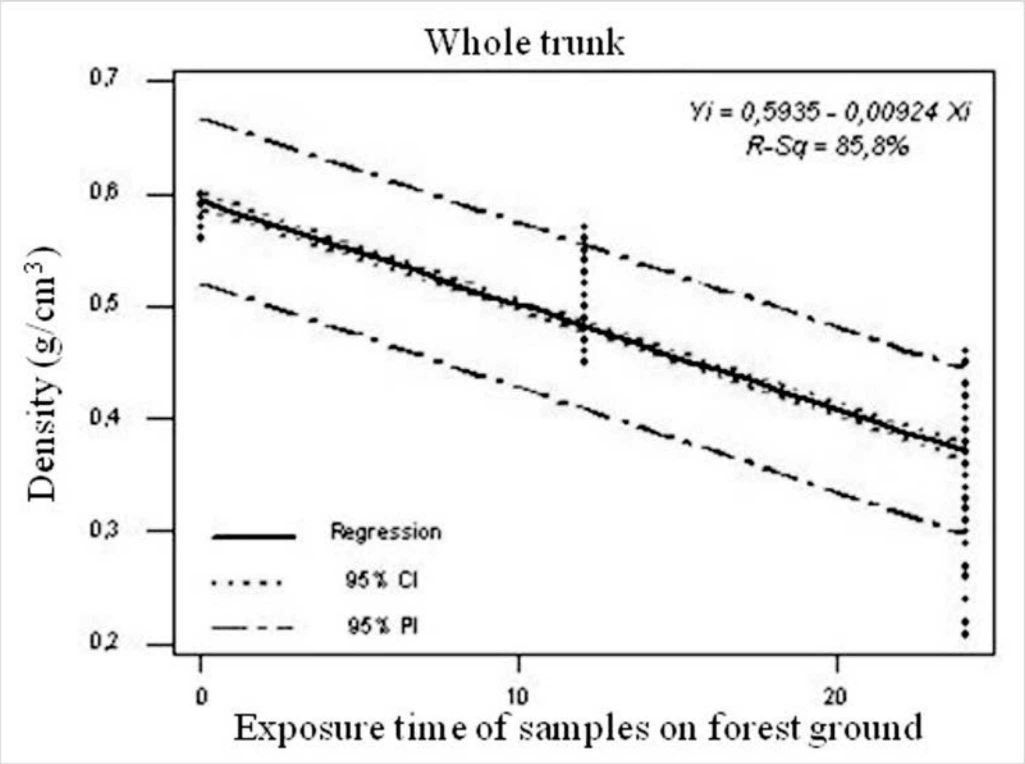

Figure 2: Density variation of all wood samples of *Scleronema micranthum* during twenty-four months of exposure on forest ground.

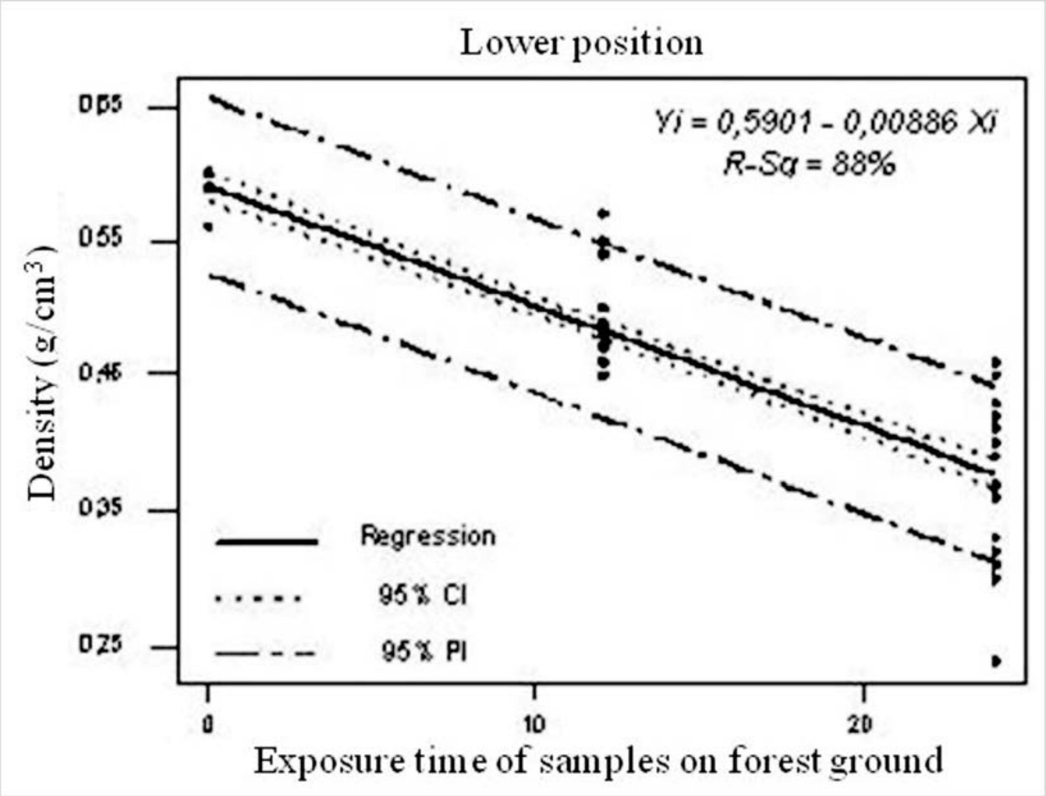

Figure 3: Density variation of wood samples of *Scleronema micranthum* in the lower position of the tree trunk during twenty-four months of exposure on forest ground.

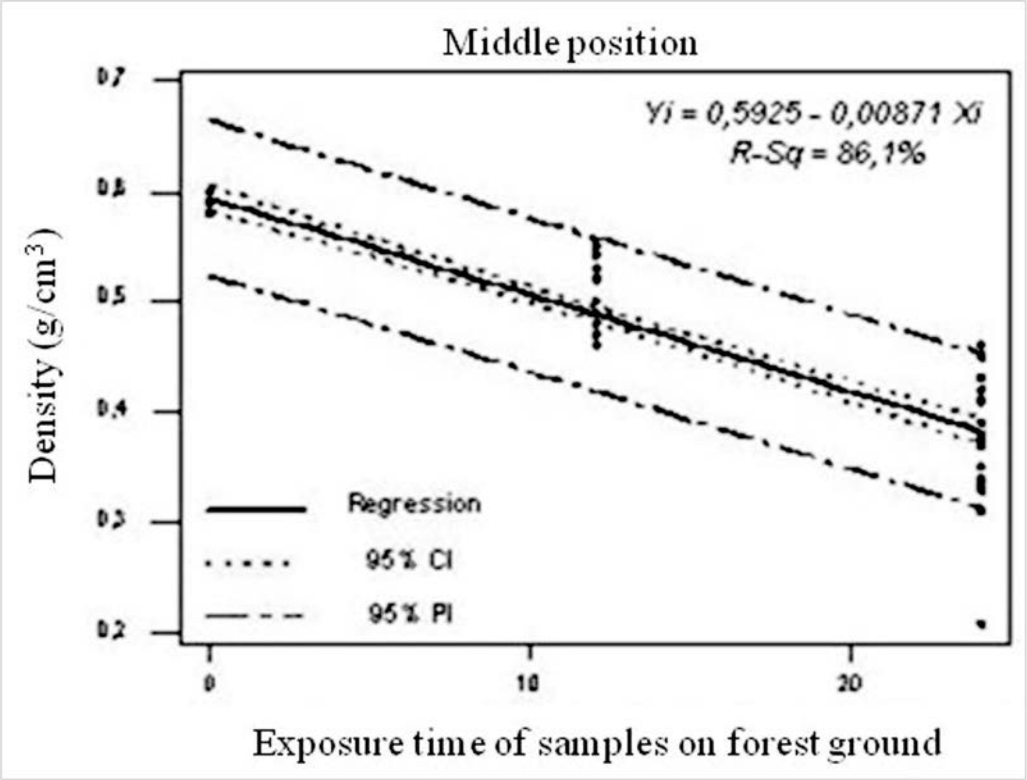

Figure 4: Density variation of wood samples of *Scleronema micranthum* in the middle position of the tree trunk during twenty-four months of exposure on forest ground.

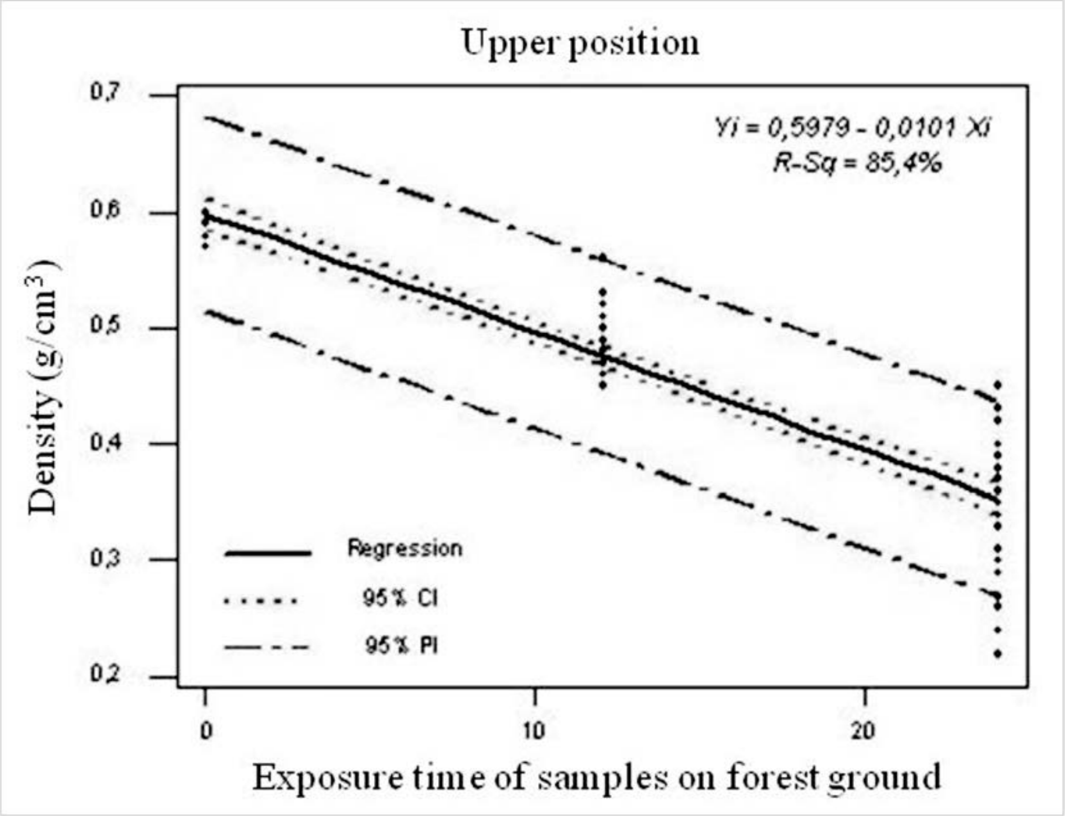

Figure 5: Density variation of wood samples of *Scleronema micranthum* in the upper position of the tree trunk during twenty-four months of exposure on forest ground.

For the parallel regression of compression resistance parallel to fibers (Figure 6), the equation $Y = 604,0 - 233,3X$ means that without any deterioration, the average compression resistance of healthy wood samples is estimated to be $604,0$ *Kgf/cm*^{2} and for each period of twelve months of exposure there is a loss of $233,3$ *Kgf/cm*^{2}. It can be seen that the variation of this parameter between positions on the tree trunk (Figures 7, 8 and 9) presented the same trend of density. In this case, there was no difference in the gradual loss of resistance between positions. As the ANOVA has not detected any significant difference between the positions along the trunk, the model can be used with all samples.

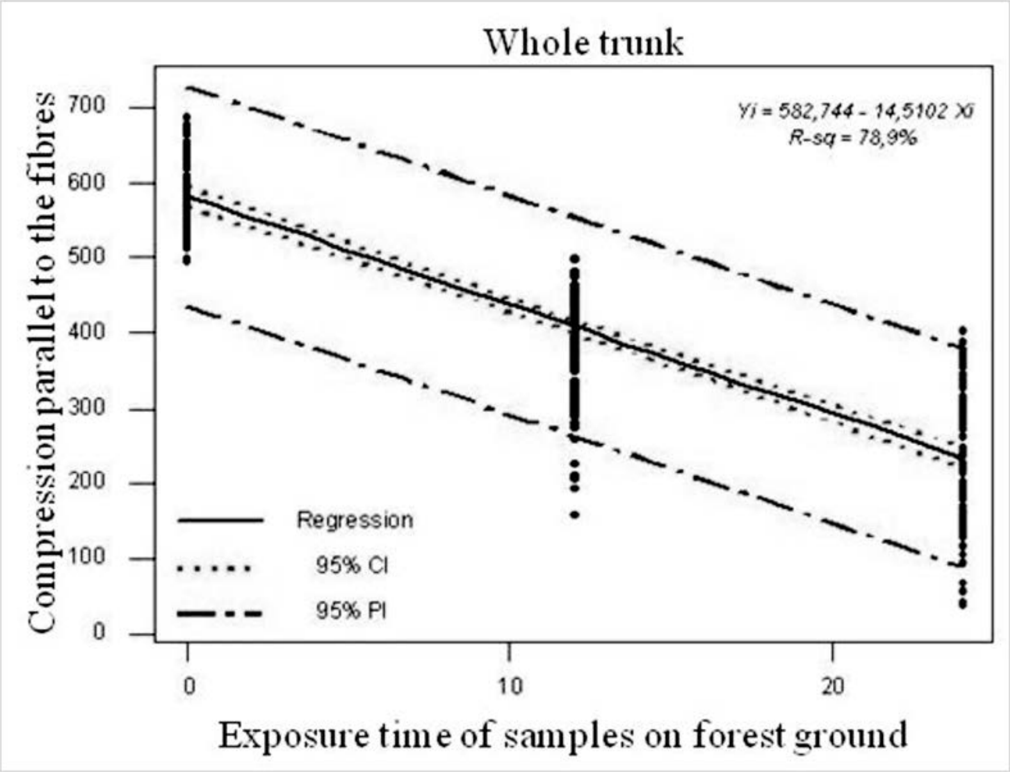

Figure 6: Variation of compressive strength parallel to fibers of all wood samples of *Scleronema micranthum* during twenty-four months of exposure on forest ground.

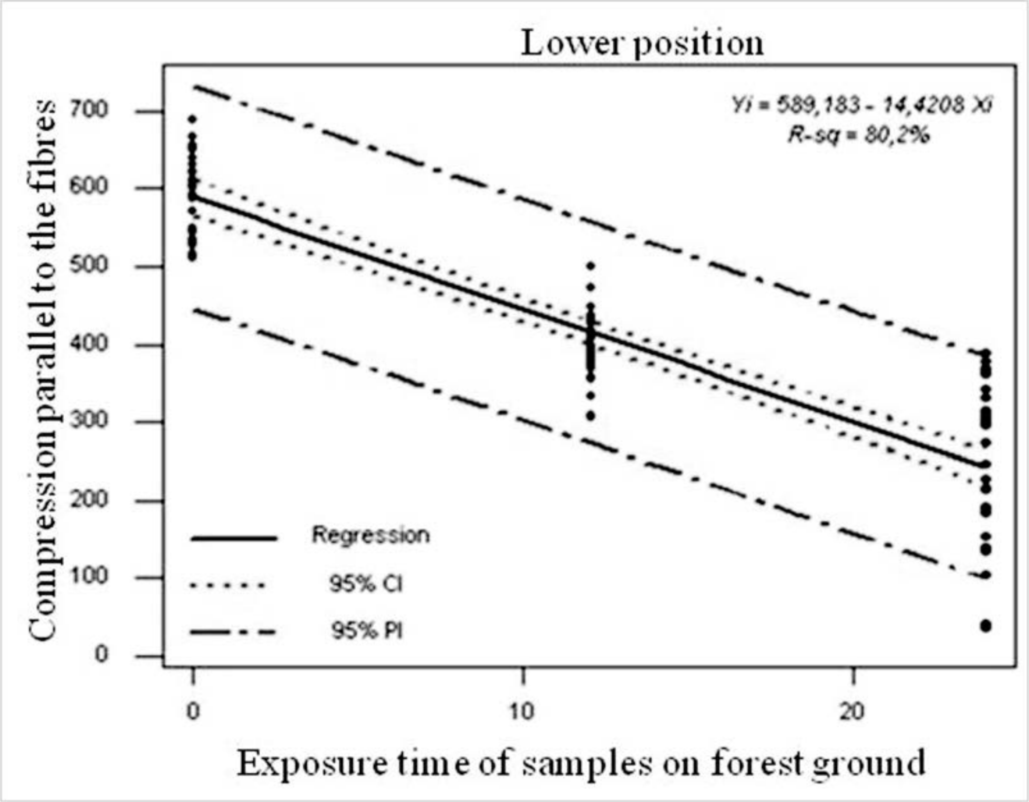

Figure 7: Variation of compressive strength parallel to fibers of wood samples of *Scleronema micranthum* in the lower position of the tree trunk during twenty-four months of exposure on forest ground.

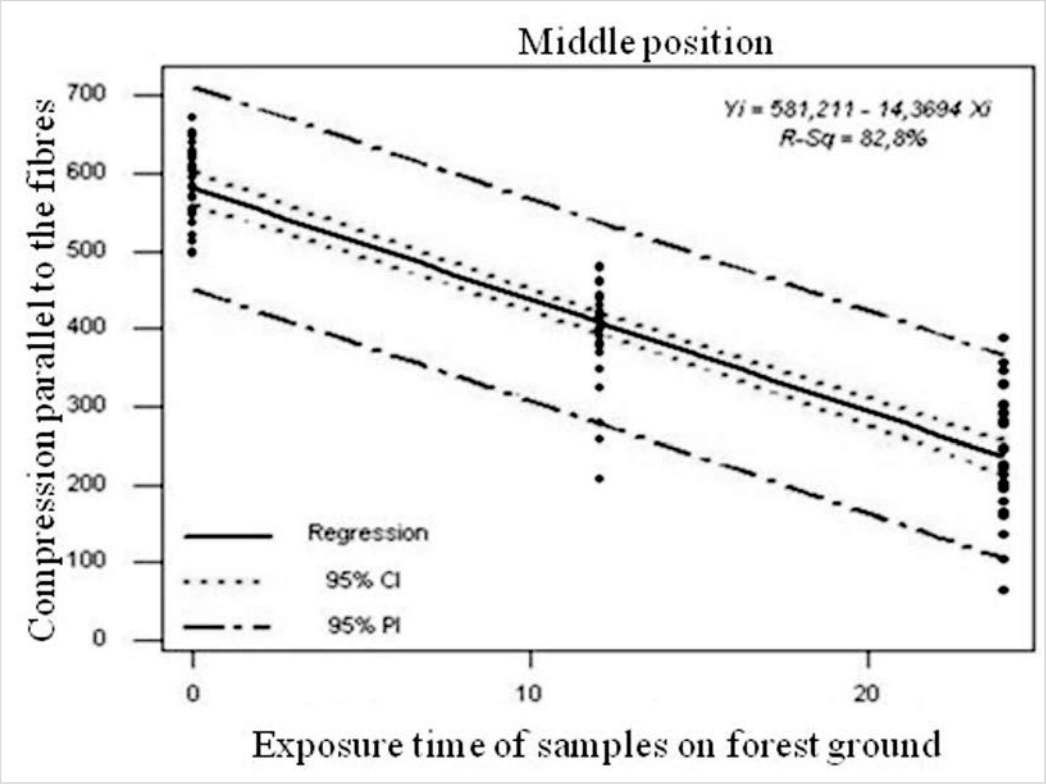

Figure 8: Variation of compressive strength parallel to fibers of wood samples of *Scleronema micranthum* in the middle position of the tree trunk during twenty-four months of exposure on forest ground.

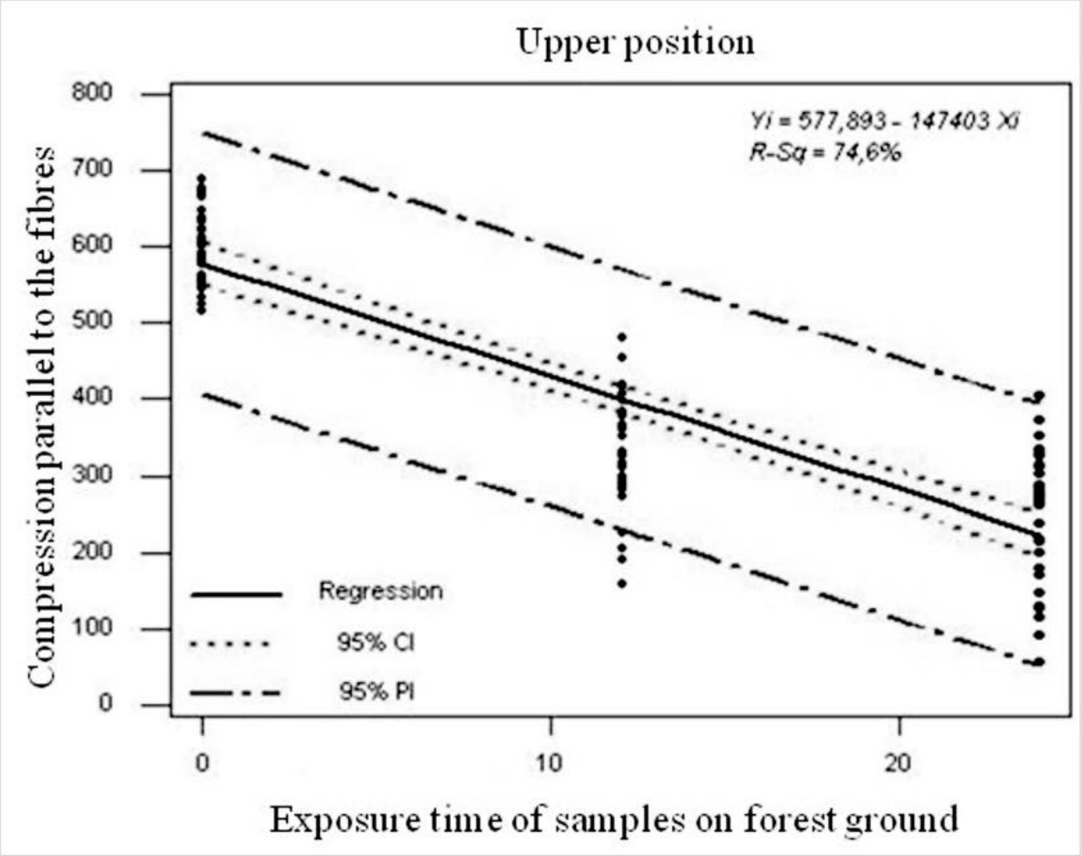

Figure 9: Variation of compressive strength parallel to fibers of wood samples of *Scleronema micranthum* in the upper position of the tree trunk during twenty-four months of exposure on forest ground.

According to the Figures 2 to 9, many values of density and compressive strength parallel to fibres were out of the fitted line and also out of the confidence interval of the model. The coefficient of determination found in all analyses indicates that the reduction in values of density and compressive strength parallel to fibers is not fully explained by time variation. One can infer that there are other factors that may be influencing these variables, such as the attack of organisms like bacteria, fungi and insects, and also abiotic factors and those inherent to the tree, mainly the ones related to its anatomical characteristics.

The analyzed variables showed some uniformity along the tree trunk in relation to the exposure time (Figures 2 to 9). A slightly higher variation was observed within each position and each time separately (Tables 1 and 2). Uniform density along the trunk was also detected by Nascimento (2000) and by Oliveira (2006) when they evaluated healthy samples of this wood species, analyzing the entire length of the tree trunk.

These authors observed that density varied from 0.52 to 0.63 *g/m* ^{3}, showing less variability along the tree trunk (CV between 6.28 and 12.39%) and that this variability is in accordance with the model "density decreases as the height of the tree increases", proposed by Panshin and Zeeuw (1981). The same trend was observed by Nascimento (2000) when the density of another species of the Amazon region, *Qualea paraensis* Ducke, was also evaluated.

For compressive strength parallel to fibres, Nascimento (2000) has also noted that *S. micranthum* presented uniformity along the upper half of the tree trunk, and variations presented in the lower half positions may be related to the presence of resin canals, although these channels have not influenced basic density. According to Panshin and Zeeuw (1981), the resin canals are intercellular canals, oriented in the longitudinal and transverse directions and when subjected to any mechanical stress, show a small decrease in resistance due to its structure.

The exposure time of the samples of *S. micranthum* in contact with forest ground caused reduction in density and compressive strength parallel to fibers. It was observed that the percentage reduction of density was smaller than that of compressive strength parallel to fibers. This result is consistent with those observed by Venson (2000) and by Trevisan et al. (2007), when they observed a worsening of these two properties. The first author used *Pinus taeda* logs stored for six months on the forest ground, where he observed a reduction of 4.3% in density and 14.7% in compressive strength parallel to wood fibers. The second author submitted samples of *E. urophyla*, *P elliotti*, *M. azedarach* e *I. marginata* to weathering for 12 months and also observed reductions from 5 to 14% in density and from 20 to 42% in parallel compression to fibers.

Torres (1994) evaluating the density of wood of *Cyrilla racemiflora* L. divided into four classes of deterioration, noticed significant reduction in density only in the samples of class four, which is the last stage of deterioration. This class presented logs without bark and twigs, in contact with the ground, with soft wood easily penetrated by a sharp object.

Lin et al 2007 exposed 20 *Pinus palustris* piles in soil moistened to 80% for 230 days, aiming to compare wood deterioration as a function of compressive strength versus dynamic MOE. These authors noted that not all stakes suffered the same level of deterioration and that the reduction in compressive strength reached over 60%. It was also found a correlation of 0.884 between the averages of compressive strength losses and losses of MOE.

Regression analyses indicated that time was not totally responsible for reducing the density and compressive resistance parallel to the wood fibers and that these variables showed no significant variation along the trunk. The factors inherent in the tree are those that influence to a lesser extent density, since, in general, length and diameter of wood anatomical structures such as fibrous elements also decrease towards the top of the tree trunk with small variations (Nascimento, 2000). Therefore, the deterioration by xylophagous organisms along with the abiotic factors may have contributed to the reduction of density and compressive strength parallel to fibers of cardeiro.

According to the results presented in Tables 1 and 2 there was an average reduction of more than 20% in density and approximately 63% in compressive strength parallel to fibers in the wood of *S. micranthum*. Based on this aspect and on the results of the analysis of infestation intensity, it can be inferred that the wood samples of cardeiro have been attacked by termites and beetles, and also colonized by staining, mold, and decaying fungi.

The insects found throughout the first year of wood exposure in the forest were beetles of the family Curculionidae, mainly of the genus *Xyleborus* and *Euplatypus* and Cerambycidae family (*Psapharochrus longispinis, Jamesia globifera* and *Steirastoma melapogenys*). The termites were represented by the Rhinotemitidae family (*Heterotermes tenuis*, *Coptotermes testaceus* and *Rhinotermes marginalis*) and Termitidae with the main species: *Nasutitermes similis*, *Cylindrotermes parvignathus*, *Cornitermes weberi* and *Planicapritermes planiceps*. In the second year some species of beetles of the genus *Xyleborus* and termites *H. tenuis*, *R. marginalis*, *Cylindrotermes parvignathus* and *N. similis* remained on the wood cylinders. It was also observed the presence of the species *Neocapritermes angusticeps* and *Nasutitermes surinamensis*.

The main fungi that were found, both in the first and in the second year, were: *Trichoderma* spp., *Lasiodiplodia theobromae*, *Paecilomyces* spp., *Penicillium* spp., *Aspergillus* spp., *Scopulariopsis* spp., *Monocillium* sp., *Gliocladium* sp., *Fusarium* sp., *Phialomyces* sp., *Diplococcium* sp. and *Cladosprium* sp.

Although the samples have been attacked by insects that have caused damage by the construction of galleries, these organisms are not mentioned in the literature as agents of the process of reduction in physical and mechanical properties of wood, since their attack normally occurs in the bark, sapwood and subcortical regions considered to have low resistance to biodeterioration and are therefore less-used commercially (Oliveira et al., 1986). This statement might be based on the fact that there is very little research about wood deterioration caused by insects and its relationship with these properties (Torres, 1994).

Despite that, the damage caused by insects in wood facilitates the decomposition by microorganisms, contributes to material loss by leaching and improves aeration of wood, allowing aerobic respiration. Insects create a spatial heterogeneity in wood, allowing the entry of microorganisms and affecting the distribution of nutrients by translocation and defecation (Torres, 1994).

In the decay process of the wood, fungi are considered the main decomposers of physical and mechanical properties of this material. Generally speaking, the fungal attack occurs when wood moisture content is above 20%, but the ideal condition for colonization is when the wood moisture content is above the fiber saturation point. For this reason, the fungal attack is common in freshly cut logs, pieces of newly sawn wood or wood exposed to the environment with high humidity. At this point, the cell walls are completely saturated and the cell lumens have no free water (Galvão and Jankowsky, 1985).

It is well known that biotic and abiotic factors have influence on the occurrence of xylophagous organisms, as well as, on their performance in the process of decomposition of wood. In this context, Cavalcante (1985) says that the wood exposed to different environments responds differently, since each of these environments has its peculiarities related to food availability, competition, natural predators, humidity, solar radiation, aeration, temperature, soil, among others. All these factors acting together in this organic matter are crucial to its durability.

The analysis of all the above factors is of fundamental importance for the understanding of the mechanisms that govern the process of deterioration involving the relationship between intrinsic and extrinsic factors to wood. Thus, the elucidation of the relationships between the various types of organisms that inhabit this raw material and its implications is a prerequisite to develop meaningful indicators to monitor and manage the forests and their products (Schwarze et al., 2000). Allied to this, the studies of decomposition of wood in the field can guide the use of this material in damp and shady places, providing appropriate subsidies to its best use.

4. CONCLUSION

The wood of the forest species *Scleronema micranthum* when exposed in contact with forest ground for 24 months, presented considerable reductions in density and in compressive strength parallel to fibers, mainly in this last property. For this reason, this wood species should not be used in severe conditions like the one used in this study, where the risk of attack of insects and microorganisms are high. In order to achieve a long life span, the use of this wood in outdoor environments should be avoided.

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ANTIFUNGAL POTENTIAL OF EXTRACTS FROM BARK OF AMAZON WOOD TO DECAY FUNGI

MARIA APARECIDA DE JESUS*, CRISTIANO SOUZA DO NASCIMENTO,
BASILIO FRASCO VIANEZ, CECI SALES – CAMPOS
NATIONAL INSTITUTE FOR AMAZON RESEARCH –INPA/ TECHNOLOGY AND INNOVATION COORD.–
COTI. AV. ANDRÉ ARAÚJO, 2936. ALEIXO. CEP: 69.060-001. MANAUS, AM – BRAZIL.
*CORRESPONDING AUTHOR: TEL: +55-92-3643-3077; RANNA@INPA.GOV.BR

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ABSTRACT

The development of new natural products as alternative to conventional wood preservatives would help to reduce the impact of introducing synthetic chemicals in the environment. The objective of this study was to evaluate the antifungal activity of Amazon wood bark extracts against decay fungi, such as *Lenzites trabea* Pers.: Fr., *Pycnoporus sanguineus* (L.: Fr.) Murr. and *Trametes villosa* (Fr.) Ryv. Hydro-alcohol extract solutions were prepared from bark of nine plant species at 0.5 % to 1 % concentrations. Culture medium with and without plant extracts, and (1:1) water/ethanol solution were evaluated for all fungi. Four replicates of each treatment were tested simultaneously during 12 days at 27ºC. The Antifungicidal Index (AFI) was determined considering the average for each treatment tested and using the values of the fungi colony area (cm^2) obtained after twelfth days of incubation. *Cassia leiandra* Benth outer bark extracts, *Hidrochorea corymbosa* Barneby and *Swartzia panacoco* Cowam inner bark and *Triplaris surinamenis* Cham. outer bark extracts at 0.5% concentration presented 100% AFI for *L. trabea*, *P. sanguineus* and *T. villosa*. AFI ranging nearly to 100 % was obtained from *Virola surinamensis* (Rol.) Warb inner bark extracts on both (0.5 % and 1 %) concentrations, as well as *O. macrophylla* and *P. santalinoides* inner bark extracts at 0.5% and 1%, concentrations, respectively, presented AFI of nearly 100% to decay fungi. Despite the high AFI value presented by all plant extracts tested, no decay fungi died, suggesting the bioactive compound present on the extracts should be under low concentrations. Further phytochemical screening need to be carried out in order to determine the bioactive compounds present on all plant species above mentioned, as well as their wood preserving potential.

1. INTRODUCTION

Decay fungi susceptibility is an intrinsic characteristic displayed by each wood species. Anti-fungicidal bio-actives derived from plant extracts are known to be a promising approach for protecting the wood from being attacked by decay fungi. Antifungal activity of heartwood extracts from *Juniperus, virginia, J. occidentalis* and. *J. aschei* has been evaluated by Tumen et al. (2013) against the decay fungi: *Postia placenta* (Fries) Lars. & Lomb., *Trametes. versicolor* (L.: Fr.) Quel. and *Irpex lacteus* Fr.. They found that only the extract from *J. aschei* presented high bio-activity on all the three tested decay fungi. Likewise, purified primary metabolites from *Anethum graveolen* (Dill Weed), *Pelargonium* graveolens (Egyptian geranium) *Rosmarinus* officinalis (Spanish rosemary) and *Thymus* zygis (White thyme) were tested for their antifungal activity by Clausen, et al. (2010). Results showed that thymol and borneol obtained from *T.* zygis and *R.* officinalis, respectively, inhibited the growth of *P. placenta*, *L. trabea* (Pers.: Fr.) Murr. (brown-rot) and, *T. versicolor* (white-rot fungus). Also, heartwood extracts from *Afzelia africana* J.E. Smith, *Erythrophleum suaveolens* (Guill & Perr.) Brena and *Milicia excelsa* (Welw.) CC. Berg. presented high potential for suppressing attack from *L. trabea, Coridopsis polyzona Pers. Ryv.* and *Trametes cinqulata* Fr. (Onuorah, 2002).

Amazon plant species provide a rich source for bioactive compounds. Considerable number of tropical timber extracts and their derivatives have been reported to present high antifungal properties against decay fungi (Jesus et al., 2006, 2008; Nascimento et al., 2008; Brand et al., 2006; Bossardi and Barreiros, 2011), among others. Due to the pharmacological potential along with the high feasibility for being utilized in the Amazon timber processing industry, research studies have been carried out targeting mainly on wood technology, addressing the development of sustainable wood byproducts that will bring forth a fresh alternative for the forest products industry in the Northern region of Brazil.

Heartwood and bark extracts acquired from different plant species have displayed significant antifungal potential against decay fungi. However, many of them have not been readily accepted on account of the chemical toxicity, low efficacy or cost effective potential. To attain this goal, each natural wood preservative's environmental feature and economic viability must be evaluated and compared with the traditional chemical wood preservatives being commonly used (Brand et. al., 2006). These problems call for the need of new fungicidal compounds to be used by the forest-products industry (Bossardi and Barreiros, 2011). Hence, this research makes part of an ongoing project on searching for bioactive compounds from Amazon plants aiming to evaluate the bark extract antifungal activity against wood decay fungi.

2. **MATERIAL AND METHODS**

2.1. LOCATION AND PLANT MATERIAL

Botanical materials, such as flowers, leaves, and bark from all tree species were collected at different locations in the Archipelago of Anavilhanas. The Archipelago of Anavilhanas has the largest Forest Reserve in South America. It covers a 350,000 hectares area in the lower Rio Negro region between the counties of Manaus and Novo Airão in the State of Amazonas, Brazil (Lat. 1º00' 3º00' S; Long. 61º31' 64º00' W). The archipelago is formed by hundreds of islands and countless lakes in an over 90 km long and 15 km wide area (SEMA, 1977).

Each botanical material was identified, and a herbarium specimen voucher for each species, was deposited at the Herbarium at the National Institute for Amazon Research – INPA, and the wood samples were added to the Amazon Wood Collection/INPA. Bark from tree species: *Cassia leiandra* Benth (Mari - mari), *Dalbergia inundata* Benth (Cipó de Tucunaré), *Hidrochorea corymbosa* Barneby (Faveira do Igapó), *Ormosia macrophylla* Benth (Olho de Cabra), *Pterocarpus santalinoide*s DC (Mututi), *Swartzia panacoco* Cowam (Coração de Negro), *Swartzia polyphylla* DC (Arabá), *Triplaris surinamenis* Cham. (Tachi vermelho) and *Virola surinamensis* (Rol.) Warb (Virola) have being used in the experiments.

2.2. PLANT EXTRACT PREPARATION

From each tree species, the outer and inner bark was removed, dried, ground into sawdust, and put into a polyethylene bag. Plant material processing and extract production followed the procedures described by Jesus et al. (2008), as follows: 300 g of sawdust was macerated with 95% ethanol at room temperature for 20 days. This step of the procedure was done twice. The mixture was filtered and the crude extract was concentrated in a rotary evaporator, under reduced pressure at 40-45ºC, until the solvent evaporated. The extract was lyophilized to remove all water and the ethanol. The stock solution from the crude extract was freshly prepared in distilled and sterilized (1:1) water/ethanol to determine its solubility. Next, the hydro-alcohol extract solutions at 0.5 and 1% were prepared to be evaluated on bioassays.

2.3. ANTIFUNGAL ACTIVITY OF PLANTS EXTRACT ON SOLID MEDIUM CULTURE

The antifungal activities of plant extracts were evaluated using the same procedures as described in Jesus et al. (2008). Tested decay fungi were *Pycnoporus sanguineus* (L.: Fr.) Murr. (LPM 408), *Trametes villosa* (Fr.)

Ryv. (LPM 406) (white rot) and *Lenzites trabea* Pers.: Fr. (LPM 368) (brown rot). These fungi were acquired from the Microorganisms Culture Collection of the National Institute for Amazon Research – INPA.

Wood samples (3.0 x 28.0 x 32.0) mm of *Simarouba amara* Aubl (Marupá) were then placed on the surface of malt-extract agar medium and the fungus was then inoculated close to the wood. The plates were kept at 28ºC and 70% relative humidity (RH) until the Marupá wood samples were heavily colonized by vigorous mycelia. The purpose of this step was to get inoculum with high lignocelluloses' potential. An inoculum from this culture was placed on malt-extract agar medium. After the fungus has grown, mycelia inoculums with vigorous aspect were selected, in order to guarantee the sensitivity of the extract efficacy test.

The bioassay procedure was similar to that described by Jesus et al. (2008). In short, 2 mL from each plant hydro-alcohol extract solutions at 0.5 and 1% was added to 18 mL of malt-extract agar medium and placed on a Petri dish and it was then homogenized. When the medium got solidified, four inoculums of the fungus were distributed equidistantly on the Petri dish. Culture malt-extract agar medium with and without (1:1) water/ethanol solution that dissolved the extracts tested had been used as controls, in order to verify its antifungal effect as a negative control to decay fungi. Four replicates per treatment were run simultaneously. The Petri dishes were maintained at 27ºC, and at 70% RH.

Measurements were taken of fungi radial mycelium growth (mm), in the linear and vertical direction, with a calliper MyCAL6CS, Mitutoyo, digital model every 3 days up to the 12th day, which is the period of time needed for fungi full development in all Petri dish controls. The diameter was determined by averaging the two measurements mentioned above. The area of the fungi colony (cm^2) was calculated based on the mean radial mycelium growth value (mm) of four replicates for each extract and solvent. Antifungicidal Index (AFI) was calculated using the formula [1 – {Treatment / Control }]*100. Treatment stands for culture malt-extract agar medium with extracts and control indicates (culture malt-extract agar medium without extracts and culture malt-extract agar medium with (1:1) water/ethanol solution. The extract presenting an AFI value of 100% can be considered to have fungicidal potential against decay fungi.

The inoculums that seemed to die on the bioassay had been placed in malt extract agar-medium again, and maintained for two weeks under the same conditions as already described, for mycelium reactivation. Following this, the inoculums were observed microscopically to verify whether the fungi had grown or not. The latter were considered to be dead. Therefore indicating the extract's fungicidal potential. Conversely, when they grew, it indicated the extract's fungistatic potential.

3. RESULTS AND DISCUSSION

The antifungal activity against decay fungi reached 100% of AFI for *L. trabea*, *P. sanguineus* and *T. villosa* was obtained from *C. leiandra* outer bark extracts, *H. corymbosa* and *S. panacoco* inner bark, all at 0.5% concentration; and *T. surinamensis* outer bark extracts at 0.5% concentration (Table 1). AFI nearly 100% was found on *V. surinamensis* inner bark extracts on both (0.5 and 1%) concentrations, as well as *O. macrophylla* and *P. santalinoides* inner bark extracts at 0.5% and 1% concentrations, respectively, presented AFI of nearly 100% to decay fungi (Table 1).

Table 1: Antifungicidal Index % (AFI) of extracts from Amazon plant species against decay fungi, after 12 days in an accelerated test in laboratory conditions.

	Bark	Conc.	Antifungicidal Index (AFI) (%)		
			Fungus		
			L. trabea	***P. sanguineus***	***T villosa***
Cassia leiandra	Inner	0.5%	99.35	99.89	99.99
		1%	93.86	99.86	100
	Outer	0.5%	100	100	100
		1%	99.00	99.81	100
Dalbergia inundata	Inner	0.5%	95.32	98.96	99.60
		1%	99.76	100	100
	Outer	0.5%	79.48	81.48	100
		1%	98.48	100	100
Hidrochorea corymbosa	Inner	0.5%	100	100	100
		1%	99.97	99.97	100
	Outer	0.5%	97.19	98.05	99.71
		1%	98.49	99.22	100
Ormosia macrophylla	Inner	0.5%	97.29	99.97	100
		1%	61.48	98.66	99.59
	Outer	0.5%	82.86	91.67	95.45
		1%	97.76	99.59	99.99
Pterocarpus santalinoides	Inner	0.5%	93.30	99.61	100
		1%	100	100	99.76
	Outer	0.5%	94.64	97.24	98.76
		1%	94.44	98.99	99.39
Swartzia panacoco	Inner	0.5%	100	100	100
		1%	97.93	98.93	99.0
	Outer	0.5%	97.28	99.89	99.99
		1%	40.73	98.59	99.75
Swartizia polyphylla	Inner	0.5%	40.24	100	100
		1%	97.96	98.40	99.59
	Outer	05%	71.62	100	100
		1%	98.25	100	100
Triplaris surinamensis	Inner	05%	97.65	98.75	99.74
		1%	96.13	97.65	98.46
	Outer	0.5%	100	100	100
		1%	71.48	83.76	99.48
Virola surinamensis	Inner	0.5%	99.99	99.99	100
		1%	99.99	100	100
	Outer	0.5%	95.88	100	100
		1%	87.38	100	100
Control	--		0.0	0.0	0.0
Negative Control (water/ethanol)	-	1:1	0.0	0.0	0.0

Data from all extracts tested against decay fungi showed that most plant species have presented higher AFI values for inner than for outer bark extract at 0.5% concentration (Table 1). When comparing the AFIs values obtained from bark extract from all wood species against all three decay fungi, it was observed that AFIs did not differ amongst the bark extracts to both fungi, *P. sanguineus* and *T. villosa* (Figures 1 and 2).

However, the AFIs from *L. trabea* (brown rot) were lower than those presented by the former to the bark extracts (Figure 3). These results indicate that bark extracts from all wood species tested present higher antifungal activity to white rot fungi (*T. villosa* and *P. sanguineus*) than to brown-rot fungi, *L. trabea.* Probably due to *L. trabea.* degraded more compounds than white rot fungi. Conversely, heartwood oils from both *Juniperus virginiana* and *C. japonica* contain mostly sesquiterpenes and are both active against *L. trabea* suggesting the role of sesquiterpenes in this resistance (Eller et al., 2010).

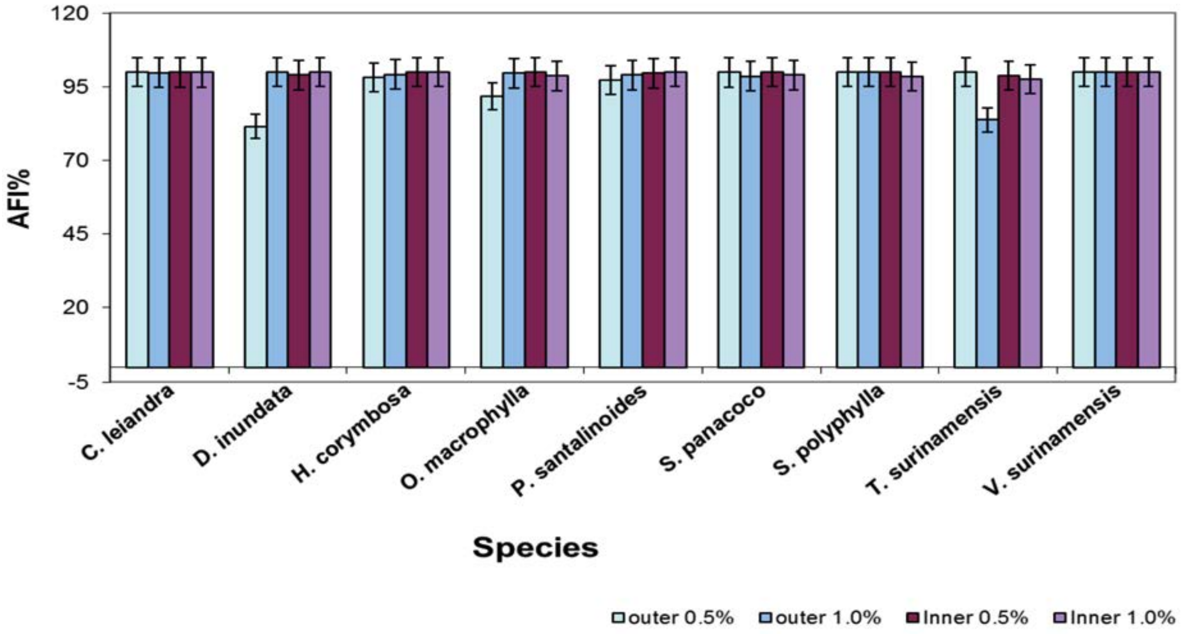

Figure 1: Antifungicidal Index (AFI) values of inner and outer bark extracts against *P. sanguineus.*

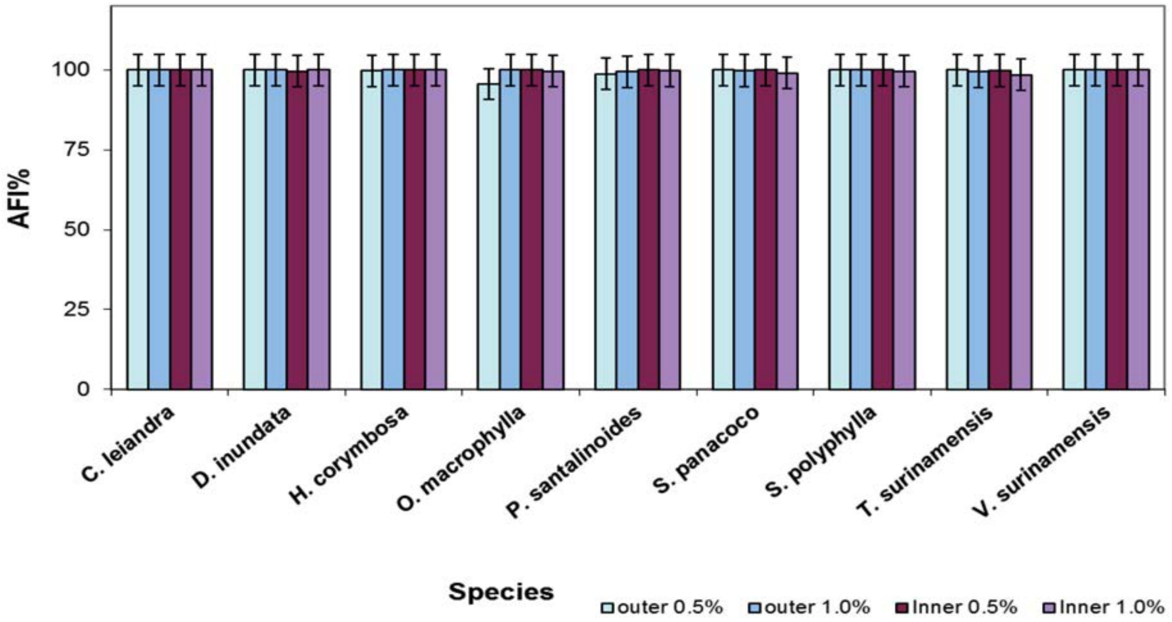

Figure 2: Antifungicidal Index (AFI) values of inner and outer bark extracts against *T. villosa.*

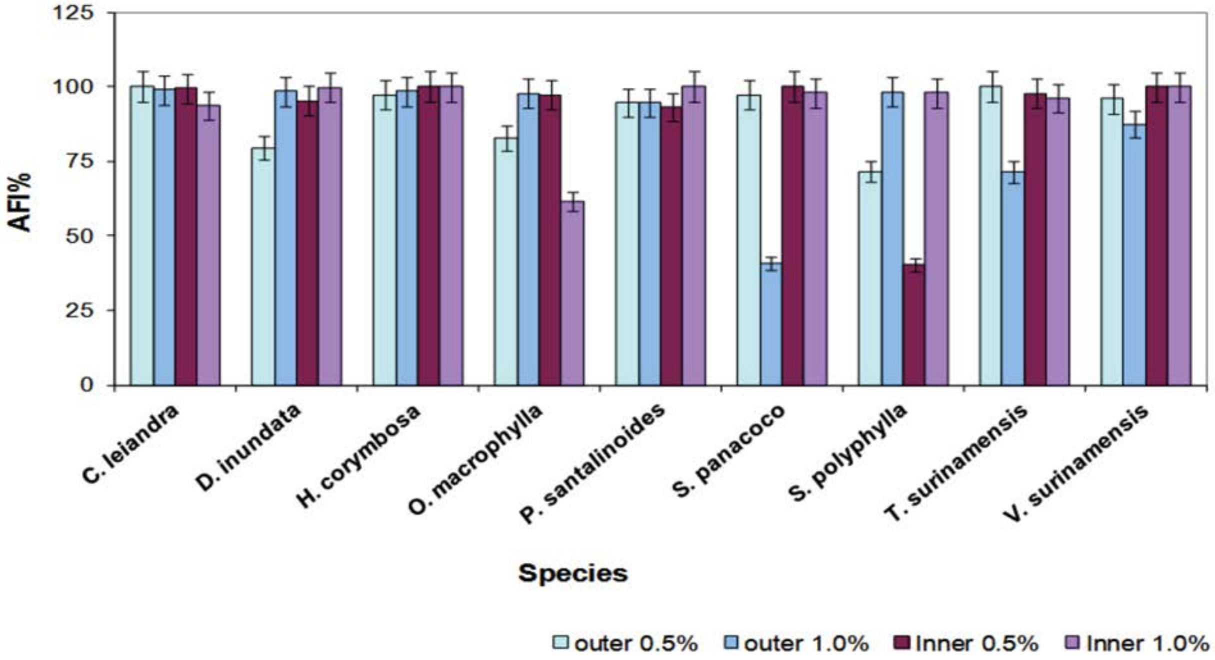

Figure 3: Antifungicidal Index (AFI) values of inner and outer bark extracts against *L. trabea*.

The plant extracts are not water soluble, thus they were dissolved into (1:1) water/ethanol solution. This solution was used as control to confirm that ethanol was not lethal to fungi. All tested fungi were grown on (1:1) water/ethanol solution (Figure 4), suggesting the solution to have no effect at all on the development of decay fungi. The extract's solubility has been reported to be one of the factors contributing to reduce or increase its antifungal potential, as well as interfering on the crude plant extracts antimicrobial potential. The extract's low solubility may mask its fungistatic activities. Archer et al. (1995) considered compound solubility to be responsible for interfering on the test's final results.

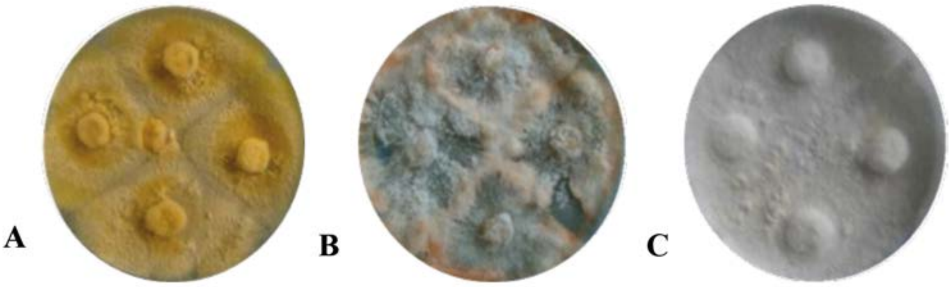

Figure 4. Micelial fungi aspects when grown on culture medium added with (1:1) water/ethanol solution: *L. trabea* (A); *P. sanguineus* (B); and *T. villosa* (C).

In general, the fungi growth was atypical when in contact with the plant extract at any tested concentrations. For instance, *P. sanguineus* has developed a little when in contact with *S. polyphylla* extracts and had formed a halo. This suggests that lignocellulolític enzyme could be produced by the fungus. Also, *L. trabea* and *P. sanguineus* developed little and disorderly in contact with *H. corymbosa* and *P. santalinoides* extracts (Figure 5). This behavior contrasted with that of *T. villosa*, which had grown on all the Petri dishes, apparently to escape from the extract.

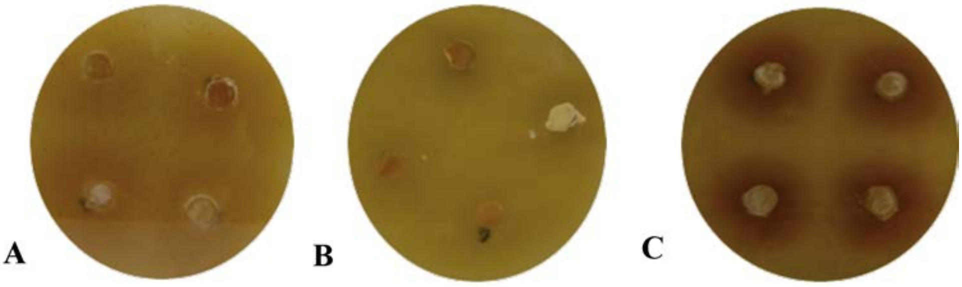

Figure 5. Micelial *L. trabea* fungi growth on *H. corymbosa* inner bark extracts at 0.5% concentration (A); *T. villosa* has grown very little on culture medium with *P. sentorinoides* inner bark extracts at 5% concentration (B); and *P. sanguineus* on *S. polyphylla* outer bark extracts at 1% concentration (C).

Phytochemical compounds of most bark extracts from all tested plants species were characterized to be condensed tannins, saponins, triterpenes, steroids and cyanogenic heterosides, flavones, chalcones, and catechins (Jesus, 2003; Barbosa et al., 2006; Arruda et al., 2010; Morais et al., 2012). Out of all these compounds, the tannins and the saponins were reported to have biocidal effects, which may be associated to high fungistatic potential, present on extracts obtained from *S. panacoco*, *S. santalinoides*, *T. suriminamenis* and *V. surinamensis***.**

Despite the high AFIs values found on *H. corymbosa*, *C. leiandra*, *P. santalinoides, S. panacoco*, *T. surinamensis* and *V. surinamensis* extracts on all three tested decay fungi species, none of them were able to kill the fungi. But the fact that the growth of fungi was inhibited indicates that these extracts may present fungistatic activity, probably on account of the low bioactive compound concentrations. One possible use of this information is to better adjust the extract concentration on future biossays.

The high antifungal potential presented by the above mentioned plant species against decay fungi indicates the need for further phytochemical screening so as to identify the bioactive compounds that may be impregnated into wooden blocks in order to confirm their resistance against decay fungi as well as characterize their wood preservative potential.

5. **CONCLUSIONS**

Most plant extracts presented significant fungistatic effect against *T. villosa*, *P. sanguineus* and *L. trabea* fungi. The highest AFI value was obtained with outer bark extracts of *C. leiandra*, and inner bark extracts of *H. corymbosa* and *S. panacoco*, at 0.5% concentration. Also, high AFI potential occurred with outer bark extracts of *T. surinamensis*, at 0.5% concentration on all three decay fungi tests. One hundred (100%) of AFI was obtained with *V. surinamensis* inner bark extracts on both (0.5 and 1%) concentrations, as well as *O. macrophylla* and *P. santalinoides* inner bark extracts at 0.5% and 1% concentrations, respectively, presented AFI values of nearly 100% to decay .fungi.

The high AFI values indicate that the above mentioned Amazon plant extracts present high antifungistatic potential against decay fungi. Bioactive compounds as well as derivatives from *V. surinamensis* and *C. leiandra* can be isolated and identified. Furthermore, they should be previously evaluated against decay fungi through a specific methodology in order to determine their fungicidal properties. In case they show to be positive, further studies should be undertaken on wood block tests so as to determine their wood preservation efficacy and acceptability as natural wood preservatives.

5. ACKNOWLEDGEMENTS

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04. LIGNOCELLULOSIC WASTES: RECYCLING AND APPLICATION IN ENVIRONMENTAL PROTECTION

REJECT FIBRES FROM PAPER MANUFACTURE AS AN ALTERNATIVE MATERIAL FOR FIBREBOARDS

ELENA TIKHONOVA[1], MICHAEL LECOURT[1] AND MARK IRLE[2]

[1]FCBA, 38000 GRENOBLE, FRANCE

[2]LUNAM UNIVERSITÉ, ECOLE SUPÉRIEURE DU BOIS, B.P. 10605, 44306 NANTES CEDEX 3, FRANCE

Keywords: Wood-based panels, fibreboard, hardboard paper rejects, paper sludge, recycling

ABSTRACT

This paper presents a short analysis on the feasibility and benefits of using reject fibres from paper recycling as an alternative material for fibreboards. The reject fibres were characterised in terms of fibre size and the proportion of non-fibrous material present. Wet process hardboards were produced containing different proportions of reject fibres. The boards were tested according to EN 310, EN 317, EN 319 and their density profiles were measured. From the results obtained it is suggested that the inclusion of reject material should be limited to 5-10% of the panel weight.

1. **INTRODUCTION**

Within the wood sector the paper industry is the largest recycler in Europe (Anon., 2012). The essential raw material for paper making is cellulose fibres from wood. Using recovered paper for new products extends the life cycle of the wood fibres. The recycling process includes sorting and cleaning of the recovering materials. The operations often cause wastes that generally equal about 30 % of manufacturing volume (Ishimoto et al., 2000). The rejects, despite the high content of wood fibres are normally incinerated or disposed in sanitary landfills.

Several researchers have studied the possibility of paper reject recycling (WRAP, 2004; Geng et al., 2007; Taramian et al., 2007; Ochoa de Alda, 2008; Migneault et al., 2010; 2011). Some have reported that paper sludge is a potential alternative material for fibreboards. The chemical and physical characteristics of the paper rejects vary depending on the type of recycled paper and at which cleaning step in recovery process they are generated (Usherson, 1992).

The objective of this study was to investigate the possibility of recycling paper manufacture rejects into fibreboards, specifically hardboards (wet process products) and medium density fibreboards (MDF, dry process products).

2. **MATERIALS AND METHODS**

Two types of industrial paper rejects were analysed here: the rejects obtained after cardboard recycling (OCC rejects) and rejects from newspaper and magazine paper recovering. Samples from the latter were obtained at each of the three main steps of the recovering process, i.e. after fine screening, coarse screening and flotation.

The first analysis consisted of fibre fractionation by fibre size using a Bauer McNett apparatus as described in the method TAPPI 233 cm-06 using the screens with following openings: 2.38 mm; 1.18 mm; 0.595 mm and 0.105 mm. The results were compared to those for virgin fibres made using FCBA's pilot-scale defibrator using a schedule designed for hardboard manufacturing.

The second analysis was the measure of ash content according to TAPPI 211 om-07 and TAPPI T413. The ash content was measured at a lower combustion temperature from that defined by TAPPI 211 om-07: 425 °C was applied instead of the required 525 °C in order to prevent early $CaCO_3$ destruction in the analyzed material (proposed and developed at the Centre Technique du Papier, France).

In order to facilitate the inclusion of paper rejects in the panels a three layer board structure was used, where the rejects were used in the central layer. The mattresses, or webs, were wet formed using an automatic sheet former designed for paper manufacture. For the 3 layer boards, three webs were produced separately and then stacked one on top of the other. Only the core layer contained paper rejects and the proportion was varied as follows: 0, 20, 50, 80 %.

After formation the mattresses were compressed and hot pressed into the boards. The target thickness of the boards was (4 ± 0.2) mm. The panels were hot pressed at 190 °C and 5 MPa for 7 minutes. After pressing and cooling, the panels were cut into specimens as described in EN 310, EN 317 and EN 319. Before testing, the samples were conditioned to constant weight in a control environment of 65 % relative humidity at 20 °C.

3. RESULTS AND DISCUSSION

The results obtained after fibre sorting (Figure 1) show that the fibre size depends on the source of the fibres. The same conclusion could be made regarding the ash content (Figure 2): the amount of non-fibrous compounds varies as a function of the fibre source.

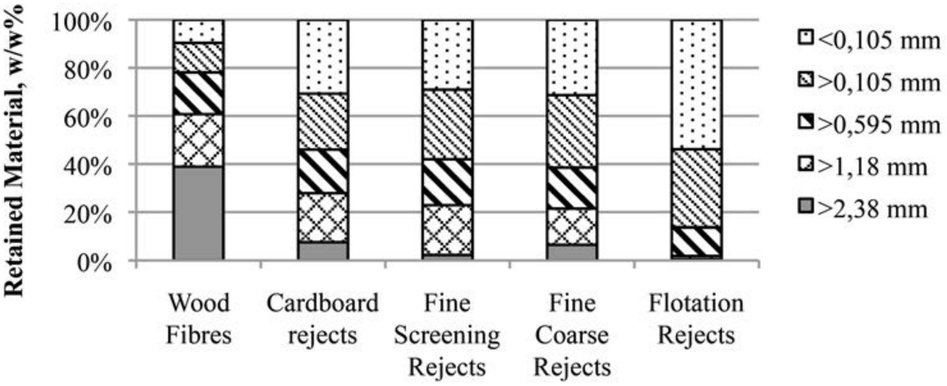

Figure 1: Fibre size distribution after fibre fractionation.

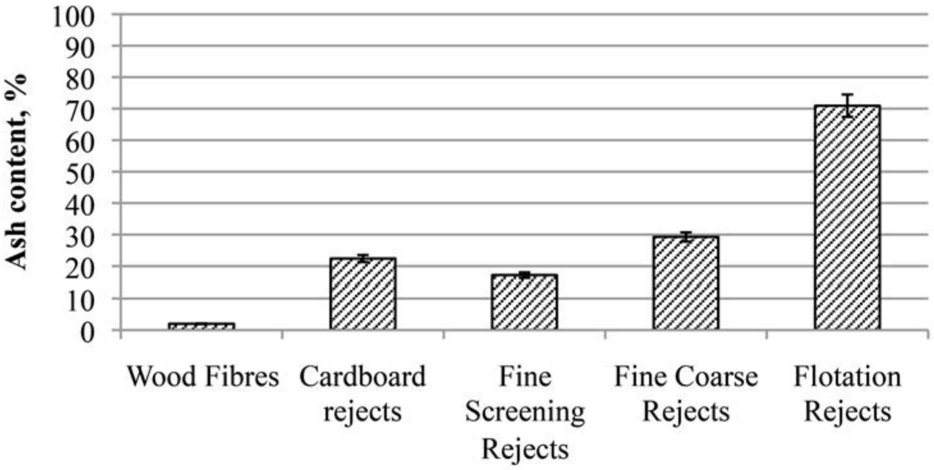

Figure 2: Ash content assessment.

The reject inclusion affected mechanical properties. Generally, the properties were only negatively affected at the 80 % substitution level. As an example, the MOR results obtained from hardboard panels containing newspaper and magazine paper rejects are shown in Figure 3.

The internal bond (IB) strength was also reduced with increasing of reject content. The effect is attributed to the change of board density. The latter tended to increase with reject content because the rejects generally contain more small elements compared to virgin wood fibre. The density profiles of the boards clearly show that the densities of the core layers containing rejects were 2 – 2.5 times higher than those layers made using only virgin wood fibres. Because the rejects were concentrated in the middle layer, the rupture was often occurred in the surface layers and the values were lower than those required by EN 317.

On the other hand, since some of the rejects contain more non-fibrous compounds, they showed positive effect on the thickness swelling.

Following these results it is considered that the optimal amount of the rejects to include in boards should be in the range of 5 % - 10 %. Additional experimental work is needed to verify this conclusion.

Regarding the growing amount of the rejects and the demand of raw materials for wood composites, it could be concluded, that the results could be useful in the future to reduce the landfilling and incineration volumes, which have serious environmental consequences.

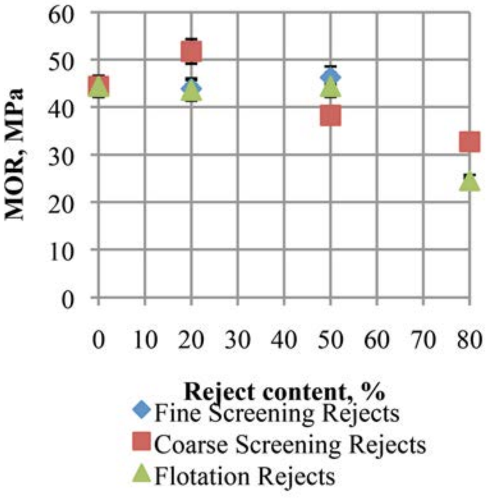

Figure 3: Modulus of rupture of 3 layer boards with paper rejects in the core.

4. CONCLUSIONS

The conclusions of this study are as follows:

- The raw material characterization confirmed the variation of fibre size and chemical composition between rejects obtained from different sources.
- The rejects from paper recycling contain a much higher proportion of small fibres and inorganic materials
- There are clear correlations between paper reject characteristics and board performance.
- Rejects from paper recycling are a viable raw material for hardboard manufacture.
- The optimal amount of the rejects is considered to be 5 % - 10%.

5. ACKNOWLEGMENT

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IMPACT AND WATER RESISTANCE OF RATTAN COMPOSITES PRODUCED WITH RICE HUSK ASH AND WELDERS' CARBIDE WASTE AS PARTIAL REPLACEMENT FOR PORTLAND CEMENT

ABEL O. OLORUNNISOLA* AND ADEBIYI I. OGUNDIPE
WOOD PRODUCTS ENGINEERING UNIT,
DEPARTMENT OF AGRICULTURAL & ENVIRONMENTAL ENGINEERING
UNIVERSITY OF IBADAN, NIGERIA
*CORRESPONDING AUTHOR: TELEPHONE +234- 803 472 4945; ABELOLORUNNISOLA@YAHOO.COM

Keywords: cement-bonded composite, roofing sheet, rattan, rice husk ash, lime.

ABSTRACT

The health hazards associated with the use of asbestos has resulted in renewed interest in the development of roofing and ceiling materials from cement reinforced with vegetable fibres. Rattan - cement composite roofing sheets were manufactured using rice husk ash (RHA) and welder's carbide waste (lime) as a partial replacement for cement at 0 %, 5 %, 10 % and 15 %, replacement levels. Hammer-milled and air-dried rattan cane (*Laccosperma secundiflorum* (P.Beauv.) Kuntze) particles retained on 2 mm sieve were dry-mixed with ordinary Portland Cement and sand at a cement : rattan : sand mixing ratio (by mass) of 1:2:0.05. Water was then added at a water : cement ratio of 0.5. Composite samples of 100 mm x 100 mm x 6.5 mm produced were cured in water for 28 days and then subjected to impact strength and water absorption tests. The results obtained indicated that the composites produced without partial replacement of cement were quite heavy, having a density of 3,262 kg/m^3 at 7.4 % moisture content. The corresponding impact strength, water absorption and thickness swelling (both at 24 hours) were 4.9 N/mm^2, 7.4 % and 3.5 %, respectively. RHA and lime had virtually the same effects of a slight increase in moisture content, water absorption and thickness swelling; an acceptable reduction in density, and a minimal reduction in impact strength of the composites. The properties of the composites produced with the addition of RHA (up to 5%) and welder's carbide waste (up to 10 %) compared favourably with those reported in literature for asbestos sheets. The studies are on-going to determine the long term behaviour of the roofing sheets under exposed field conditions. The preliminary laboratory test results indicate that partial replacement of ordinary Portland cement with RHA or welder's carbide waste is feasible in the manufacture of low cost rattan-cement composite roofing sheets in developing countries such as Nigeria where disposal of rice husk and welder's carbide waste constitutes an environmental menace.

1. INTRODUCTION

Asbestos - cement roofing sheets and ceiling boards have been in common use in Nigeria and elsewhere for several decades due to their relatively low cost and the thermal comfort they provide. However, the health hazard that asbestos poses to factory workers, residential occupants and stored food items, has resulted in renewed interest in the development of more environmental friendly, low-cost, efficient and effective alternatives for cement - composites reinforced with vegetable fibres and wood particles (Swamy, 1990; Ramirez-Coretti et al., 1998; Nabi, 1999; Savastano Jr. et al., 2003). A notable advantage of such composites is that they can be produced in nearly all desired practical sizes and can be sawn, bored, nailed, and painted. However, the choice of fibre or particle is often based on local availability, processing cost, and compatibility with Portland cement (due to the inhibitory effect of the starch and other compounds content of organic materials on cement setting).

A locally available fibre and particle source for cement composite manufacture in Nigeria is rattan cane, a climbing spiny palm, presently used largely for the furniture manufacture. As noted by Olorunnisola *et al.* (2005a), over 30 % of rattan stems harvested at a particular time for furniture manufacture is wasted. Besides, only about 20 % of the over 600 known rattan species produce the most sought-after fine quality canes and are, therefore, of a commercial value. The remaining species with low quality canes are not utilised due to inflexibility, tendency to breakage, and poor mechanical properties. Several studies on rattan applications in concrete and cement bonded composites have been reported (Olorunnisola and Adefisan 2002; Lucas and Dahunsi, 2004; Olorunnisola et al., 2005a, b; Olorunnisola, 2007; Olorunnisola, 2008; Adefisan and Olorunnisola 2012). The properties of cement-bonded composites from *Laccosperma secundiflorum*, one of the most common species in Nigeria have also been compared with composites manufactured from agricultural residues (Table 1).

Table 1: Properties of cement-bonded composites manufactured from selected agro-forestry materials.

Board Properties	**Sawdust of Various Wood Species**	**Maize (*Zea mays*) Stalk Particles**	**Coconut (*Cocos nucifera*) Husk Particles**	**Rattan (*Laccosperma secundiflorum)* Particles**
Density (kg/m^3)	1200	1200	990 - 1200	1360
MOR (N/mm^2)	2.0 – 4.0[a] 8.7 – 11.2[b]	3.1- 5.4	4.3 - 7.4	7.0
MOE (N/mm^2)	1250 – 3000[a] 3000 – 4000[b]	6409	4253	3350
Water absorption after 24 hrs (%)	18.0[a] 28.0[b]	25.7	22.1	2.5
Thickness swelling after 24 hrs (%)	0.16[a] 0.43[b]	0.88	0.6	0.5

Note: a = 100% sawdust-cement panel, b = 3-layered boards incorporating flakes.
Source: Owonubi and Badejo (2000), Olorunnisola (2010).

A major challenge in cement and concrete composite manufacture in Nigeria is the rising cost of Ordinary Portland Cement (OPC) which has fluctuated between US$ 225 and US$ 250 per tonne (i.e., 23 - 25 cents per kilogramme) in the last two years (Olorunnisola, 2012). The local consumption of cement in the country in 2009 alone was estimated at about 19 million tonnes. However, only 9.6 million tonnes was produced locally while nearly 10 million tonnes had to be imported. To achieve the low cost objective in composite manufacture there is therefore the need to identify materials suitable for partial replacement of OPC without compromising strength and durability. Potential materials include welder's carbide waste (lime) derived from ethylene (C_2H_2) gas, by the action of cold water on calcium carbide during metal welding and cutting operations, and Rice Husk Ash (RHA) obtainable from rice processing residues. The use of rice husk ash and carbide waste as pozzolanas, (i.e., materials containing reactive silica and/or alumina which on their own have little or no binding property but, when mixed with lime in the presence of water, will set and harden like cement), has been widely reported in literature (Omoniyi, 2009; Ogundipe, 2009). The utilization of both residue materials in cement-bonded composite manufacture could promote waste management and reduce environmental pollution.

The objective of this preliminary study was to evaluate the effects of lime and rice husk ash on the impact strength and sorption properties of rattan-cement composites for possible use as roofing sheet in residential and agricultural buildings.

2. MATERIALS AND METHODS

2.1. MATERIAL COLLECTION AND PREPARATION

Mature, freshly harvested samples of *Laccosperma secundiflorum* canes obtained from rattan cane sellers were duly identified in the herbarium of Department of Botany, University of Ibadan. The canes were cross - cut into about 5 cm long billets, air dried for four weeks and pulverized in a hammer-mill. The particles obtained (Figure 1) were subsequently screened. Only particles retained on the 2 mm sieve were used for production.

Figure 1: Sieved rattan particles.

Welders' carbide waste (Figure 2) collected from a metal work shop was air dried for seven days, pulverized and screened with 75 micrometers British Standard (BS) sieve. The particles were further air dried for 21 days to average moisture content of about 1.5 % (dry basis). Rice *(Oryza sativa* L.) husk (Figure 3) was collected from a rice mill and burnt to ashes completely at a temperature of 600 °C in an incinerator (Figure 4). The ashes were sieved through British Standard Sieve (BS) of 75 micrometers . The portion passing through the sieve was used.

Figure 2: Welders' carbide waste.

Figure 3: Un-processed rice husk.

Figure 4 : Rice-husk ash.

Fresh ordinary Portland cement was purchased from the open market in Ibadan in 50 kg bag. It was stored in air tight container prior to use. The distilled water used was stored at room temperature (20±2) °C. The fine aggregates used consisted of river sand, collected from the bank of Awba Dam at the University of Ibadan. The sand was washed with potable water and air - dried for three days in an open enclosure, and screened with a set of sieves. Only sand that passed through the sieve size of 2 mm were used.

2.2. RATTAN - CEMENT – COMPOSITE PRODUCTION

The rattan - cement composites were produced using flat sheet moulds 100 mm (length) x 100 mm (breadth) x 6.5 mm (thickness). Mixing proportions for cement : sand; cement : rattan particles; and cement : water content (by weight of cement) were fixed at 1:2; 1:0.05 and 0.5, respectively.

Air dried rattan particles were manually mixed in a container with sand and cement. Distilled water was then added. Composites were produced using corrugated concrete mould, 500 mm (length) x 300 mm (breadth) x 6.5 mm (thickness). The cement-sand-rattan-water composite mixture was spread on a vibrating table, 660 mm (length) x 480 mm (breath) x 50 mm (thickness) using a bricklaying knife. The vibration time was 60 seconds. The cast was thereafter moved to the mould and covered with water - proof polyvinylchloride (PVC) sheet. Each composite was demoulded after 48 hours and cured under fresh water in a plastic reservoir at room temperature (20±2) °C for 6 days. The samples (Figure 5) were then stacked horizontally in a ventilated chamber at the same room temperature and relative humidity of (70±5) % for 3 weeks.

Figure 5: Rattan-cement composites.

2.3. MOISTURE CONTENT AND DENSITY DETERMINATION

The moisture content of the composites was determined by oven-drying at (100±5) ^{0}C. The density was computed based on the standard mass and volume ratio.

2.4. IMPACT STRENGTH TEST

The impact strength test was conducted on three replicate flat sheet samples of dimension 1000 mm x 100 mm x 6.5 mm at room temperature using an impact pendulum tester at an average velocity of 3 m/s and 90^0 swing angle. The energy involved in breaking the sample was determined by the height differences of the pendulum before and after the impact, which implies that all the energy lost by the pendulum is consumed in breaking the sample. The impact tester measured the sample strength by the fall of a steel ball (4.5 kg) from maximum height of the ball. Each sample was placed on steel the reinforced base of the impact machine and was subjected to weight drop at different heights. At each impact the face of the sample was checked, the height of ball was increasingly varied for further impacts, until the sample completely ruptured.

2.5. WATER ABSORPTION AND THICKNESS SWELLING

Water Absorption (WA) and Thickness Swelling (TS) were determined in accordance to RILEM (1984) recommendations. The air dried samples (100 mm x 100 mm x 6.5 mm) were immersed in clean, potable water. Their weights were measured with an electronic balance before and after 24 hours of soaking. WA as expressed in percent was determined using the Equation 1:

$$WA = \frac{Ws - Wo}{Wo} \times 100 \qquad (1)$$

Where:

Ws = Mass (kg) of sample after 24 hours

Wo = Mass (kg) of air dried sample.

Thickness in five points and weight of each of the three replicate samples were measured. The samples were immersed in fresh, potable water at (20±2) ^{0}C for 24 hours. After 24 hours of soaking, the samples were removed and thickness in same five points and weight were measured using digital vernier calliper and electronic balance, respectively. The values measured for TS were the average of the five points. TS was calculated using Equation 2:

$$T = \frac{TS_S - TS_O}{TS_O} \times 100 \qquad (2)$$

Where:

TS_O = thickness (mm) before soaking.

TS_S = thickness (mm) after 24 hours of soaking

3. RESULTS AND DISCUSSION

3.1. MOISTURE CONTENT AND DENSITY OF THE RATTAN COMPOSITES

The moisture contents of the rattan particles, carbide waste, RHA and the composites were 1.4 %, 1.5 % and 0.9 % respectively. As shown in Table 2, the moisture content of the different composite samples ranged between 7.4 % and 12.8 %. Addition of RHA and carbide waste generally increased the moisture content of the composites, but much more so by RHA than carbide waste. This may perhaps be attributable to hydrophilic nature of RHA, which caused them to absorb moisture (Aznizam et al., 2005).

Table 2: Properties of the rattan – cement composites.

Ordinary Portland Cement Replacement Level	Moisture Content[1] (%)	Density[1] (kg/m³)	Normalized Density[2]
Control (0%)	7.4	3262	1.00
5 % RHA	8.3	3119	0.96
10 % RHA	12.8	3028	0.93
15 % RHA	13.1	2916	0.89
5 % Carbide Waste	8.0	3457	1.06
10 % Carbide Waste	10.4	3218	0.99
15 % Carbide Waste	12.0	3169	0.97

[1] Mean of three replicate samples

[2] The normalized specimen density equals the average specimen density divided by the average density of control specimen.

The densities of the composites varied from 2,916 kg/m^3 for composites containing 15 % RHA to 3,459 kg/m^3 for the control. These values compare favourably with those reported by Sarja (1988) for structural wood fibre concrete and Omoniyi (2009) for bagasse-reinforced cement composite roofing sheets. The densities of the composites generally decreased as RHA and carbide waste contents increased from 0 % to 15 %. However, the densities of the composites containing 5 % to 10 % carbide waste were higher than that of the control. Presumably, the higher density of specimens containing carbide waste is a reflection of lesser void spaces and more continuous bonding with cement.

3.2. IMPACT STRENGTH

The mean impact strength values of the composites ranged between 1.0 N/mm^2 and 4.0 N/mm^2 (Table 3). Composites manufactured using 100% OPC had the highest impact strength (4.0 N/mm^2), followed by those produced with 5 % carbide waste and 5 % RHA inclusions, respectively. RHA had a more pronounced negative effect on the impact strength of the composites than carbide waste, another indication that carbide waste may be a better replacement than RHA for ordinary Portland cement in composite manufacture.

Table 3: Impact strength of the rattan – cement composites.

Ordinary Portland Cement Replacement Level	Impact Strength[1] (N/mm²)
Control (0 %)	4.0
5 % RHA	3.4
10 % RHA	2.4
15 % RHA	1.2
5 % Carbide Waste	4.0
10 % Carbide Waste	3.9
15 % Carbide Waste	3.0

[1] Mean of three replicate samples.

A weak but positive linear correlation ($R^2 = 0.39$) was observed between impact strength and density of composites containing carbide waste. In contrast, a strong positive correlation ($R^2 = 0.95$) observed between impact strength and density of composite roofing sheets produced with partial replacement of cement with RHA indicating density may be a good determinant of the impact strength of rattan - cement composite roofing sheets containing RHA.

3.3. WATER ABSORPTION (WA)

The 24 h WA values are presented in Table 4. The values obtained varied from 7.4 % to 13.3 %. These values compare favourably with published data on WA in cement-bonded composites manufactured using agricultural and forestry residues such as maize stalk, coconut husk, coffee husk, arhar stalks, and rattan furniture waste (Oyagade, 2000; Ajayi, 2002, 2003; Olorunnisola and Adefisan, 2002; Okino et al., 2004; Olorunnisola, 2006; Aggarwal et al., 2008).

Table 4: Water absorption and thickness swelling of the rattan – cement composites.

Ordinary Portland Cement Replacement Level	Water Absorption[1] (%)	Thickness Swelling[1] (%)
Control (0 %)	7.4	3.5
5 % RHA	8.3	3.7
10 % RHA	11.4	3.7
15 % RHA	13.1	4.0
5 % Carbide Waste	7.9	3.5
10 % Carbide Waste	10.4	3.6
15 % Carbide Waste	12.0	3.6

[1] Mean values of three replicate samples

The control samples (with no replacement of cement) had the least WA of 7.4 %, while composites manufactured with 15 % RHA exhibited the highest water absorption. Replacing OPC with RHA and carbide waste generally increased the WA. However, composites manufactured with carbide waste inclusion generally absorbed less water than those manufactured with RHA inclusion. This finding could be attributed to their higher density and hence lower porosity. It also seems to suggest that carbide waste has less affinity for water than RHA. A further statistical analysis (Figure 6) indicated a linear correlation ($R^2 = 0.553$) between the density and WA of the samples.

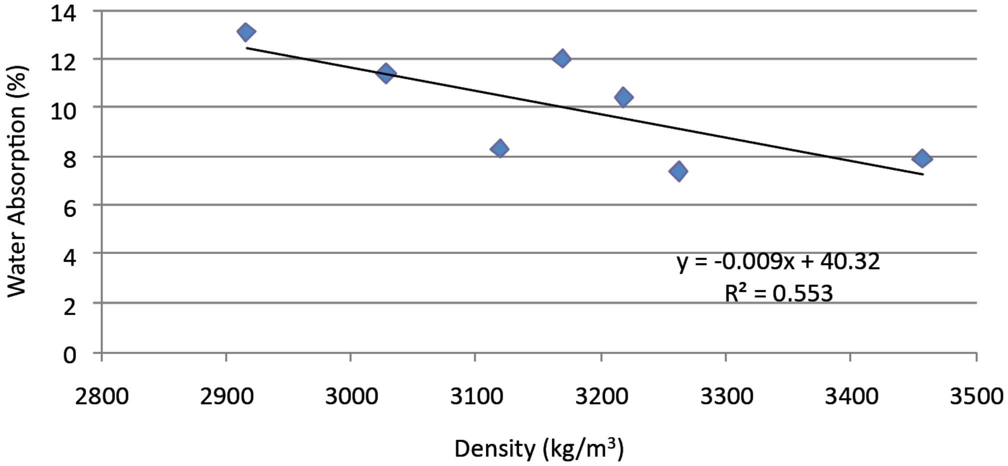

Figure 6: Correlation between density and water absorption of the composites.

3.4. THICKNESS SWELLING (TS)

The 24 h TS values, that are presented in Table 4, were relatively low, varying from 3.5 % to 4.0 %. A plausible reason for this is that the boards were not under appreciable stress/strain recovery since they were not subjected to any serious pressure during manufacture. Also, these values compare favourably with TS values reported for cement-bonded composites (Olorunnisola et al., 2005a, b; Olorunnisola, 2007; Olorunnisola, 2008; Adefisan and Olorunnisola, 2012). Composites containing RHA exhibited relatively higher TS than the control and samples containing carbide waste.

Since thickness swelling is a good measure of the dimensional stability of wood-cement composites. The relatively low TS of the composites suggests that they would be stable if exposed to water at room temperature and they could therefore be explored as a roofing sheet material. Statistical analysis (Figure 7) indicated a linear and positive correlation ($R^2 = 0.777$) between the density and TS, and a weaker positive correlation ($R^2 = 0.517$) between the WA and TS of the samples (Figure 8).

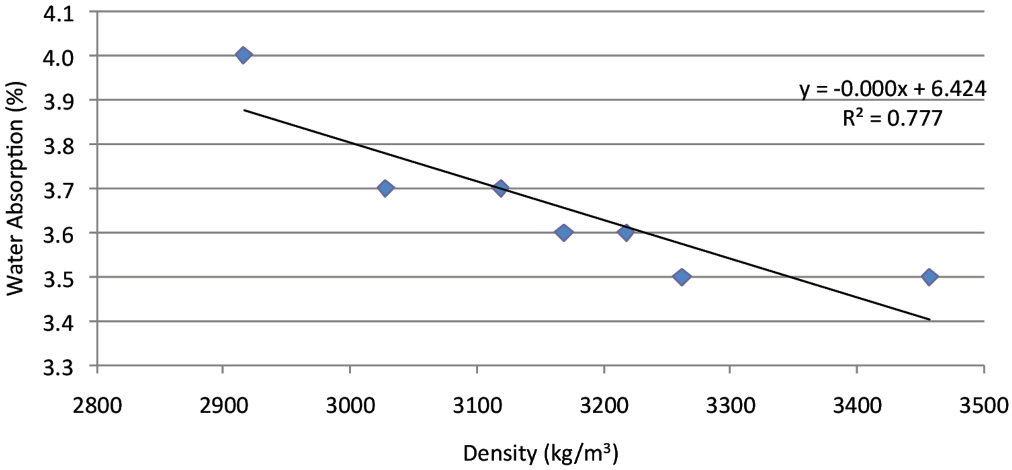

Figure 7: Correlation between density and thickness swelling of the composites.

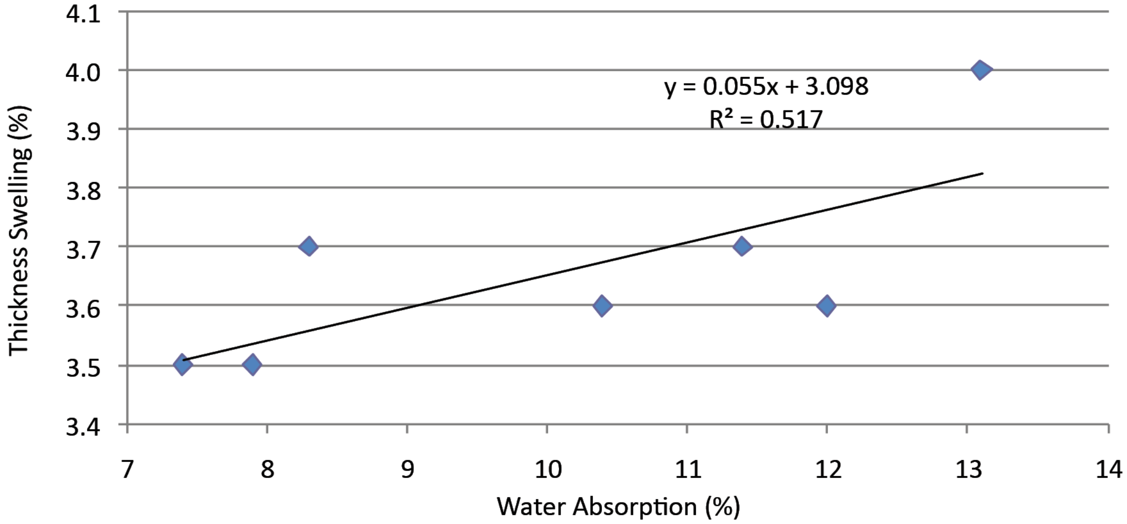

Figure 8: Correlation between water absorption and thickness swelling of the composites.

4. CONCLUSIONS

The following conclusions can be drawn from this preliminary study:

There exists a high possibility for partial replacement of ordinary Portland cement with both rice husk and ash carbide waste in the manufacture of rattan-cement composites.

Partial replacement of ordinary Portland cement with up to 5 % of rice husk ash and 10 % of carbide waste should not impact negatively on the impact strength and water resistance properties of the rattan-cement composites.

The relatively low water absorption and thickness swelling of the composites suggest that they could be explored as potential roofing sheet materials.

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WOOD-PLASTIC COMPOSITE AS A NEW WAY OF RECYCLING POST-CONSUMER PARTICLEBOARDS

CEZARY GOZDECKI[1,*], ARNOLD WILCZYNSKI[1], MAREK KOCISZEWSKI[1], STANISŁAW ZAJCHOWSKI[2]
[1] INSTITUTE OF TECHNOLOGY, KAZIMIERZ WIELKI UNIVERSITY, CHODKIEWICZA 30 STR., 85-064 BYDGOSZCZ, POLAND
[2] FACULTY OF CHEMICAL TECHNOLOGY AND ENGINEERING, UNIVERSITY OF TECHNOLOGY AND LIFE SCIENCES,
SEMINARYJNA 3 STR., 85-225 BYDGOSZCZ, POLAND
* CORRESPONDING AUTHOR: GOZDECKI@UKW.EDU.PL

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ABSTRACT

The objective of this study was to evaluate the usefulness of recycled wood particles, made from post-consumer particleboards, as a substitute for wood flour for manufacturing wood plastic composites (WPCs). Two kinds of experimental WPCs were prepared using polypropylene and polyethylene as a matrix and recycled wood particles as a filler. For comparison, WPCs with typical wood flour were prepared. The mechanical properties in tension and in bending, and the impact strength of WPCs were assessed. The results showed that WPCs with milled post-consumer particleboards had mechanical properties similar to composites with wood flour. Post-consumer particleboards can be useful for manufacturing WPCs.

1. INTRODUCTION

Particleboards are one of the most commonly used wood-based panels, particularly in the furniture industry. Nowadays, furniture production continually increases and life-cycle of furniture becomes shorter. As a result there are more and more post-consumer particleboards which make a serious problem for the environment. One of the possible ways of recycling these boards is using them for manufacturing wood-plastic composites (WPCs) (Kikuchi, 2000; Ashori and Nourbakhsh, 2009; Ferreira et al., 2010).

Mechanical properties of WPCs depend on many factors. Among the most important ones is the wood particle size. Typical WPCs are filled with small particles or short fibres. The effect of the size of small wood particles, smaller than 1 mm, on WPC mechanical properties was investigated several times (Zaini et al., 1996; Stark and Berger, 1997; Stark and Rowlands, 2003; Khalil et al., 2006; Salemane and Luyt, 2006; Cui et al., 2008; Migneault et al., 2008; Bouafif et al., 2009). Studies on the effect of the size of large wood particles, greater than 1 mm, on WPC mechanical properties have been carried out by Chen et al. (2006) and Gozdecki et al. (2011, 2012) among others. Generally, they have observed that tensile and flexural properties of WPCs increased with increasing the size of wood particles.

Investigations into possibilities of using waste wood materials for producing WPC were made by, among others, Boeglin et al. (1997), Stark (1999), Kajaks et al. (2001), Winandy et al. (2004), Gozdecki el al. (2007), Ashori and Nourbakhsh (2009). The composites produced by them were characterized by the properties similar or better to those of typical WPCs filled with wood flour.

On the other hand there are few investigations into a possibility of using waste particleboards as a filler for polymers. The studies on using of wastes produced in the processing of particleboards for filling high-density polyethylene (HDPE) were conducted by Chaharmahli et al. (2008). They examined the possibility of using sawdust obtained during sawing particleboards, and grinding pieces of particleboard as a filler. Although they used small particles they found that mechanical properties of WPCs composed from recycled particleboard and HDPE are comparable to those of conventional WPCs with wood flour. Gozdecki et al. (2010) showed that there is a possibility of using wastes generated in the production of particleboards as a filler for polymers. They used dust generated during sawing of particleboards and wastes produced during particleboard mat forming. They found that the use of wastes generated in the production of particleboards for filling polymers can be a good way of utilizing them. Yet, there are no investigations into a possible use of particleboards from post-consumer furniture as a filler in polymers. Post-consumer particleboards are frequently overlaid which can make their recycling difficult. Therefore, it is very important to search for such recycling methods that make it possible to use the whole of post-consumer particleboard along with their overlays, employing the most effective processing methods.

The objective of this study was to evaluate mechanical properties of WPCs made from post-consumer particleboard and two kinds of polymer.

2. MATERIALS AND METHODS

2.1. POLYMERS

Two kinds of virgin polymers were used in this study: polypropylene (PP) Moplen HP648T with a density of 0.90 g/cm^3 and a melt flow index of 53 g/10 min at 230 °C, and low-density polyethylene (PE) Malen E FABS, 23-DO22, with a density of 0.92 g/cm^3 and a melt flow index of 2 g/10 min at 230 °C. Both polymers were supplied by Basell Orlen Poliolefins (Poland).

2.2. WOOD MATERIALS

Four kinds of three-layer particleboards: virgin raw (VR), virgin overlaid (VO), post-consumer raw (PR) and post consumer overlaid (PO) were used to prepare wood filler. Table 1 shows the characteristics of these particleboards. VR and VO particleboards were supplied by Kronospan Szczecinek (Poland), PR and PO particleboards were obtained from about twenty-year-old post-consumer furniture. All particleboards were bonded with urea-formaldehyde resin. VO particleboard was overlaid with one layer of finishing papers impregnated with melamine-formaldehyde resin. The overlay of PO particleboard consisted of three layers of papers impregnated with the same resin.

Table 1: Particleboard characteristics.

Particleboard type	Density (kg/m^3)	Thickness (mm)	Overlay thickness (mm)
VR	649	18	-
VO	651	18	0.15
PR	706*	18*	-
PO	732	20	0.5

*After mechanical processing.

To obtain PR particleboard from PO particleboard, the overlays were mechanically separated. Particleboards were cut into small pieces and then milled by a laboratory mill. Obtained particles were screened by an analytical sieve shaker using sieves of 35 and 60 meshes. Particles smaller than 0.5 mm and larger than 4 mm were removed. Screened particles are shown in Figure 1. The fraction analysis of these particles is presented in Figure 2.

Figure 1: Particles of milled particleboards: a) VR, b) VO, c) PR and d) PO.

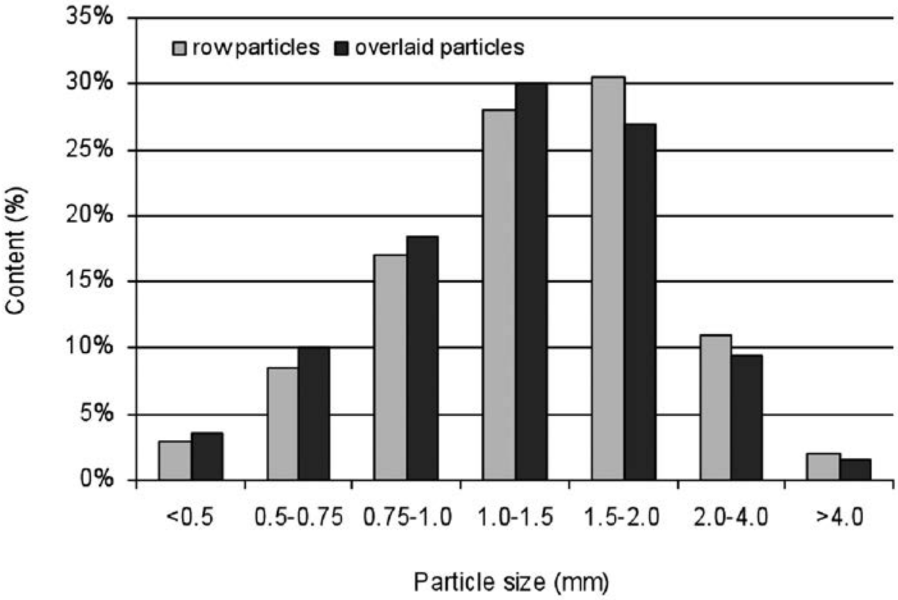

Figure 2: Fraction analysis of particles.

WPCs with typical wood flour (WF) were taken into account for comparison purposes. The softwood flour of a type of Lignocel® BK 40/90 (raw wood flour) was supplied by J. Rettenmaier & Sohne GmbH, Rosenberg, Germany.

2.3. EXPERIMENTAL DESIGN

Five types of WPCs with PP, including the control WPC with WF, and three types of WPCs with PE, including the control WPC with WF, were assumed (Table 2) using only one wood materials/polymer ratio of 40/60%.

Table 2: Experimental design.

WPC Type	Polymer Type	Source of Particles
PP-WF (control)	PP	WF
PP-VR	PP	VR
PP-VO	PP	VO
PP-PR	PP	PR
PP-PO	PP	PO
PP-WF (control)	PE	WF
PE-VO	PE	VO
PE-PO	PE	PO

2.4. PROCESSING

Particles from particleboards and WF were dried at 80 ºC in an air-circulation oven for 24 h before the mixing process to achieve less than 3% moisture content. Next, they were mixed with polymers. Test specimens were made by injection molding. The temperature profile was 120, 180, and 180 ºC at feed, zone 1, and zone 2, respectively. Injection pressure time and hold pressure time were 3 and 6 s, respectively. To minimize mechanical degradation of WP during molding, the diameter of the injection die was enlarged to 4.5 mm and the diameter of the sprue bush to 8 mm. Cross sections of the runner and the gate were 10×10 mm^2 and 6×6 mm^2, respectively.

Specimens were prepared according to EN ISO 527 and were then stored in controlled conditions (50% relative humidity and 20ºC) for two weeks prior to testing.

2.5. MECHANICAL PROPERTY TESTING

Mechanical properties of tested WPC were evaluated in relation to tensile, flexural, and impact properties. Tensile and flexural tests were performed according to EN ISO 527 and EN ISO 178, respectively. Span length in flexural test was 16 times the thickness of the specimen. Cross-head speed was 2 mm/min. Unnotched Charpy impact strength tests were conducted according to EN ISO 179. Ten replicates were run for each test. All tests were performed at a room temperature (20 ºC) and at constant relative humidity (50%).

The obtained data were statistically analyzed. The one-way ANOVA test was conducted to determine the significance of the effects of a kind of wood filler on WPC mechanical properties, and Tukey's test was applied to evaluate the statistical significance between mean values of the properties of different WPCs.

3. RESULTS AND DISCUSSION

Figure 3 shows the mean values of tensile modulus (Figure 3a) and strength (Figure 3c), flexural modulus (Figure 3b) and strength (Figure 3d), and unnotched impact strength (Figure 3e) of tested WPCs. Error bars represent one standard deviation based on ten specimens.

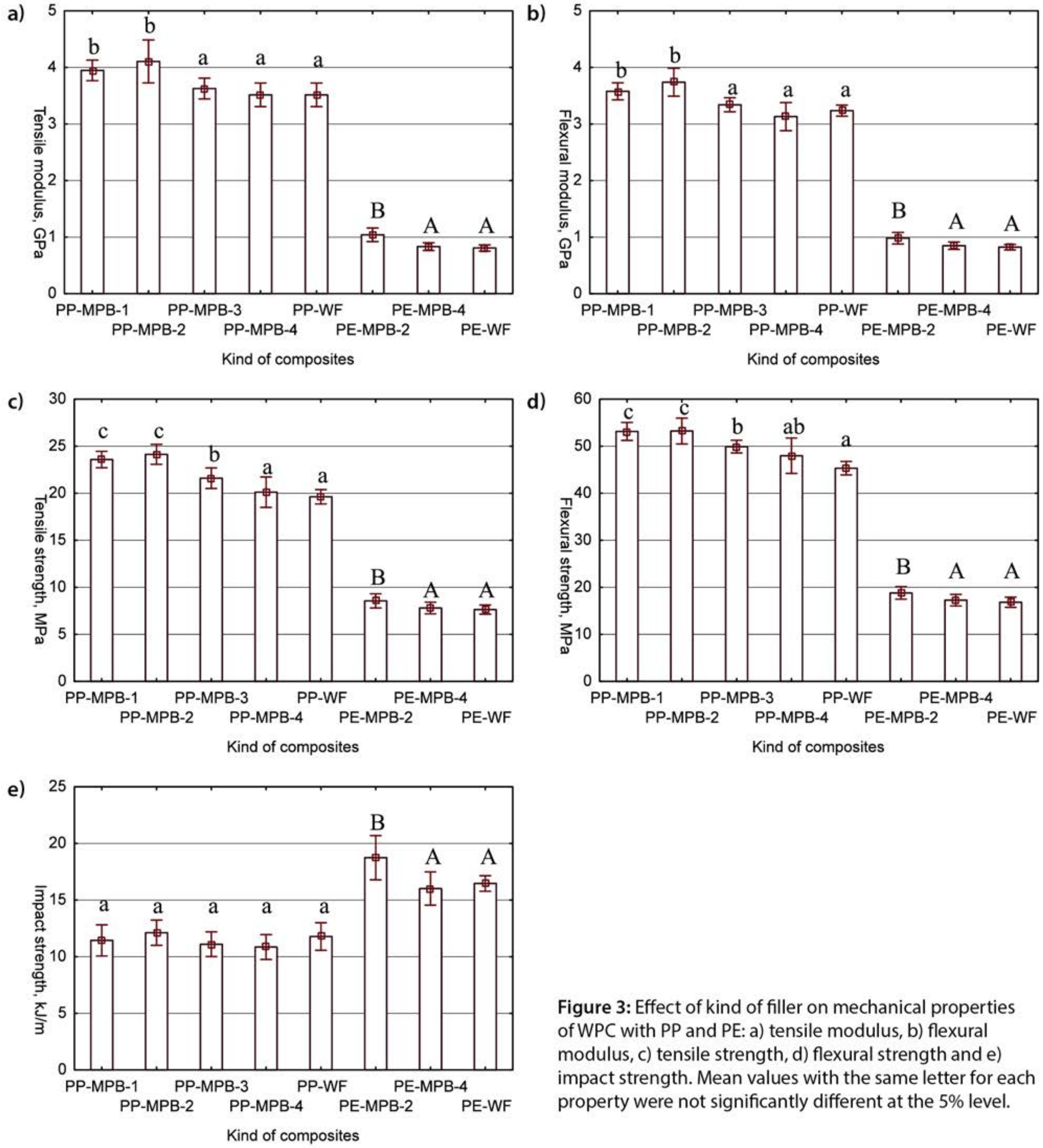

Figure 3: Effect of kind of filler on mechanical properties of WPC with PP and PE: a) tensile modulus, b) flexural modulus, c) tensile strength, d) flexural strength and e) impact strength. Mean values with the same letter for each property were not significantly different at the 5% level.

The results of the ANOVA test are shown in Table 3. All the determined properties of composites made from PE and the properties of composites made from PP, except for the impact strength, depended significantly on the WPC type.

Table 3: One-way ANOVA test on the effect of filler type on WPC mechanical properties (p-values).

Variable	Tensile Modulus	Tensile Strength	Flexural Modulus	Flexural Strength	Impact Strength
Type of WPCs with PP	<0.0001*	<0.0001*	<0.0001*	<0.0001*	0.1352*ns
Type of WPCs with PE	<0.0001*	<0.0001*	<0.0069*	<0.0028*	<0.0005*

*Denotes significance at 0.01; ns-non significant at 0.05.

The mechanical properties of WPCs containing PP and particles from virgin particleboard made from raw (PP-VR) and overlaid (PP-VO) particleboards did not differ significantly. Similarly, differences between properties of WPCs with PP and post-consumer raw (PP-PR) and overlaid (PP-PO) particleboards were not significant. Only the difference between the tensile strengths of PP-PR and PP-PO composites was statistically significant, but it was small – the tensile strength of PP-PO composite was smaller by 7%. In general, the mechanical properties of tested WPCs did not depend on the surface finish of particleboards used for manufacturing WPCs.

WPCs made from PP and post-consumer particleboards (PP-PR and PP-PO) generally had worse mechanical properties than those made from PP and virgin particleboard (PP-VR and PP-VO). The tensile modulus, tensile strength, flexural modulus, and flexural strength of WPCs made from PP and post-consumer particleboard were on average smaller by 11, 12, 11, and 8%, respectively. Only the impact strength of compared WPCs did not differ statistically. All properties of WPC containing PE and particles from post-consumer particleboard (PE-PO) were smaller than those of WPC containing PE and particles from virgin particleboard (PE-VO). The tensile modulus, tensile strength, flexural modulus, flexural strength, and impact strength of WPC made from PE and post-consumer particleboard were smaller by 19, 10, 11, 19, and 15%, respectively.

In general, the mechanical properties of WPCs made from post-consumer particleboard did not differ statistically from those of the control WPCs made from wood flour. The properties of WPCs made from PP and virgin particleboard were on average greater by 15% and the properties of WPC made from PE and virgin particleboard were on average greater by 16% than those of proper control WPCs. Better properties of WPCs made from milled particleboards in comparison with properties of WPCs made from wood flour were related to wood particle size. The particles of milled particleboard were much larger than those of wood flour. According to Chen et al. (2006) and Gozdecki et al. (2011, 2012) larger particles resulted in greater mechanical properties of WPCs.

As it was expected, the tensile and flexural properties of WPCs with PE were considerable smaller than those of WPCs with PP. Only the impact strength of WPCs with PE was greater than that of WPCs with PP.

4. CONCLUSIONS

Post-consumer, about twenty-year-old, particleboard was used for preparing two experimental WPCs with PP and PE as a matrix. Particles obtained by milling particleboard had a size from 0.5 to 4 mm. WPCs with 40% wood particles by weight were made by injection molding. The mechanical properties in tension and in bending, and the impact strength of these WPCs were comparable to those of typical WPCs with wood flour. It did not affect the WPC properties whether the particleboard was raw or overlaid. Post-consumer particleboards can be useful for manufacturing WPCs.

5. ACKNOWLEDGMENTS

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FOREST RESIDUES AS REINFORCING FILLERS IN THERMOPLASTIC COMPOSITES

ROGER M. ROWELL
PROFESSOR EMERITUS, BIOLOGICAL SYSTEMS ENGINEERING DEPARTMENT, UNIVERSITY OF WISCONSIN, MADISON, WI.
GUEST PROFESSOR, ECOBUILD, STOCKHOLM, SWEDEN

Keywords: Forest residues, thermoplastic composites, mechanical properties, moisture properties.

ABSTRACT

Composite materials employ two or more distinct, structurally complementary substances in order to produce structural or functional properties not present in any of the individual components. Faced with a decline in the quality of available saw timber and changing societal attitudes towards the use of forested lands, the wood products industry has created a vast array of composites to meet the structural needs of today's builders. One group of composites is composed of a biomass fraction and a thermoplastic. The bulk of the biomass used in these composites is wood. The wood utilized can come from forest residues. Both hardwood and softwood residues were reduced to small particles and fiber bundles using a hammer mill and blended in a twin screw mixer with either polyethylene or polypropylene with and without a compatibilizer. Mechanical and moisture sorption tests were conducted on extruded specimens showing the positive effect of the addition of a compatibilizer.

1. INTRODUCTION

Millions of tons of hardwood and softwood residues are generated each year from our forests from logging, removal of small diameter trees and up grading the forests (Figure 1).

Figure 1: Forest residues generated from forest operations.

Table 1 shows the inventory of logging residues in the United States by type and ownership from 2007 (Walsh, 2008). The inventory is broken down into softwood and hardwood residues. As the table shows, there is more hardwood residues in the US as compared to softwoods. This does not include mill residues, or residential discard or other industrial biomass waste streams.

Table 1: The inventory of logging residues in the United States by type and ownership (2007).

Quantities (million dry tons)

	National Forests	Other	Private Public	Total
Softwoods	0.95	1.71	25.14	27.81
Hardwoods	4.53	2.07	32.71	35.24
Total	5.48	3.78	57.85	63.05

There are many uses for forest residues and they all depend on availability and price. It can be left in the forest to add nutrients back to the soil, burned for energy, used as mulch, used as animal bedding, utilized in composites such as fiberboard or particleboard, and many other uses. One possible use is to add them as a component in thermoplastic composites.

Figure 2: Forest residues chipped and hammer milled into particles and fibers.

The forest residues are usually sorted depending on the application. For use as a component in thermoplastic composites, the residues are debarked and chipped. The chips are dried and hammer milled into particles, fiber bundles and fibers (Figure 2).

The advantages of using forest residues as a component in thermoplastic composites is that they are non-abrasive so mold life is extended (compared to glass and other abrasive inorganic fillers), a low cost, sustainable and recyclable additive, provide products with high specific properties, and high filling levels are possible. Since the fibers are flexible, sharp curvatures are possible which are not possible using glass fibers. The disadvantages of using a biomass resource is that they are biodegradable, moisture sensitive in processing and must be processed at temperatures under 200 °C (Caulfield et al., 2005).

The most common thermoplastics used in this technology are polyethylene (PE) and polypropylene (PP). They are readily available and have low softening and melting temperatures that are compatible with wood residues.

The birth of the wood-thermoplastic industry involved the interfacing of two industries that have historically known little about each other and have very different knowledge-bases, expertise, and perspectives (Caulfield et al., 2010). The forest products industry has greater experience and resources in the building products market and its production methods center around the typical wood processes; sawing, veneering, chipping, flaking and gluing. The plastics industry has knowledge of plastics processing, that centers around extrusion, compression-molding and injection-molding technologies.

Wood and thermoplastic are not the only components in wood-thermoplastic composites. These composites also contain additional materials that are added in small amounts to affect processing and performance (Jacobson et al., 1996). Although formulations are highly proprietary, additives such as coupling agents, light stabilizers, pigments, lubricants, fungicides, and foaming agents are all used to some extent.

Since the wood component of a wood-thermoplastic composite is hydrophilic and the plastic is hydrophobic, a compatibilizer is often used to improve interfacial bonding of the two different phases (Rowell et al., 1997). One of the most common compatibilizers used today is a maleic anhydride grafted polypropylene (MAPP) or maleic anhydride grafter polyethylene (MAPE). There are many different types of MAPP's and MAPE's differing in molecular weight and the degree of maleic anhydride substitution. One used most often had a number average molecular weight of 20,000, a weight average molecular weight of 40,000 and about had 6% by weight of maleic anhydride in the polymer.

This compatibilizer it thought to work by two different mechanisms. First, the anhydride reacts with a cell wall polymer hydroxyl group to form an ester bond the then the PP polymer attached to the anhydride intertangles into the PP or PE network in the melt.

The purpose of this research was to use hardwood and softwood residues in PE and PP thermoplastic composites and determine strength and moisture sorption properties.

2. EXPERIMENTAL

The two types of forest residue chips (mixed hardwoods and mixed softwoods) were processed in a hammer mill to fine particles and fiber bundles. These were dried at 105 °C overnight and then processed in a twin screw extruder with either polyethylene or polypropylene. The thermoplastics were first melted in the head of the twin screw extruder and then the wood was added in a side stuffer downstream of the melted plastic (Figure 3). A vapor release element is added just after the side stuffer to exhaust any moisture remaining in the wood. Two different levels of wood were used: 30 and 50% with and without a compatibilizer. The ribbon of blended wood and thermoplastic were water cooled after the extruder, cut into pellets and dried.

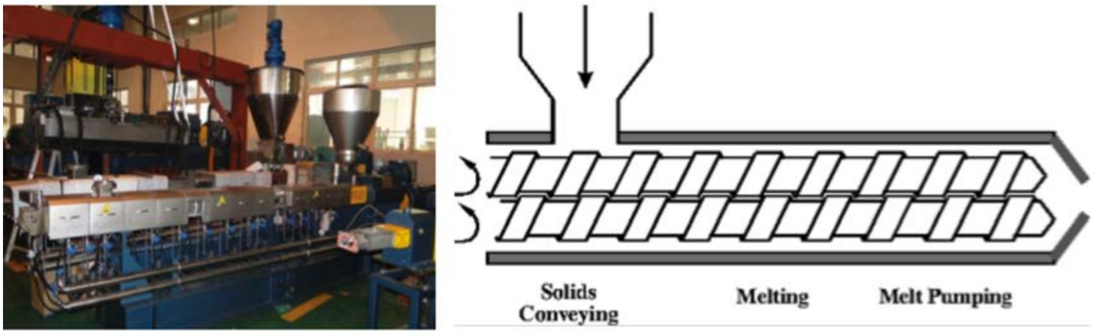

Figure 3: Twin screw extruder with side stuffer.

Test specimen were injection molded at 190 ºC using pressures varying from 2.75 MPa to 8.3 MPa depending on the constituents of the blend. Test specimen dimensions were according to the respective ASTM standards. The specimens were stored under controlled conditions (20 % relative humidity and 32 °C) for three days before testing. Tensile tests were conducted according to ASTM 638-90 and flexural testing using the ASTM 790-90 standard. The cross-head speed during the tension and flexural testing was 12.5 mm/min.

Separate samples were produced for moisture sorption tests. The specimens were placed in a 90% relative humidity chamber at 27 ºC for 200 days and the gain in weight due to moisture sorption measured every 25 days.

Results of ongoing outdoor tests on wood-thermoplastic composites area also presented.

3. RESULTS AND DISCUSSION

Table 2 shows the mechanical properties of hardwood-fiber polyethylene composites and Table 3 shows the mechanical properties of softwood-fiber polypropylene composites.

Table 2: Mechanical properties of hardwood-fiber polypropylene composites.

Specimen (%)	Flexural Strength (MPa)	Tensile Strength (MPa)
PP	27.9	26.2
PP/2MAPP	34.6	29.3
30H/70PP/0	49.5	29.3
30H/68PP/2MAPP	60.2	44.9
50H/50PP/0	50.2	28.4
50H/48PP/2MAPP	75.7	53.1

Table 1 shows that using the MAPP compatibilizer increases both flexural and tensile properties as compared to no compatibilizer.

Table 3: Mechanical properties of softwood-fiber polypropylene composites.

Specimen (%)	MOR (MPa)	MOE (MPa)
PP	31.9	1.60
30S/70PP/0	48.7	3.70
30S/68PP/2MAPE	52.5	3.76
50S/50PP/0	48.5	5.69
50S/48PP/2MAPE	51.9	5.73

Table 3 also shows an increase in properties with the addition of a compatibilizer but not as great as was seen in the hardwood-fiber polyethylene composites.

Table 4 shows the increase in moisture sorption of the hardwood-polypropylene composites. There is a very slow uptake in moisture even at the 50% fiber level. Adding the compatibilizer does decrease the moisture sorption as compared to non-compatibilized composites.

Table 4: Moisture sorption of hardwood-polypropylene composites – 90% RH, 27 °C

Hardwood/PP/ Weight Gain

MAPP (%)	25 D	50 D	75 D	100 D	150 D	200 D
<--%-->						
0/100/0	0	0	0	0	0.2	0.4
30/70/0	0.7	1.4	1.7	2.1	2.4	2.8
30/68/2	0.7	0.7	1.1	1.5	1.5	2.2
50/50/0	1.3	2.0	2.6	3.6	4.3	5.3
50/48/2	1.5	1.8	2.2	2.9	4.0	5.1

Several ongoing outdoor tests on wood-thermo plastic composites have shown warping problems due to heat expansion of the thermoplastic phase. Figure 4 shows a large deck in the Bahamas made of a wood-thermoplastic composite that has failed due to buckling in the hot sun.

Figure 4: Buckling of a wood thermoplastic composite in the Bahamas.

Figure 5 shows a guard rail in a state park in Oregon that has fungal fruiting bodies growing all over it. It has also warped due to heat.

Figure 5: Guard rail in Oregon with fungal fruiting bodies growing on it.

Figure 6 shows the result of a wood-thermoplastic sample that has been exposed to the sun for a year.

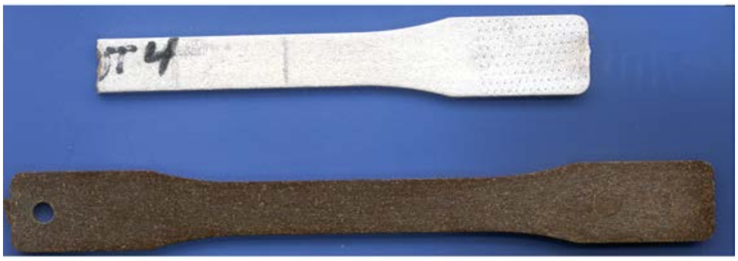

Figure 6: Wood-thermoplastic composite before (lower) and after (upper) one year exposed outdoors.

4. CONCLUSIONS

Forest residues reduced to particles or fiber bundles improve strength and stiffness as a component in thermoplastic composites. The use of a compatibilizer improves both mechanical properties and in reducing the extent of moisture pickup. But, there are still many problems to overcome in this technology including better resistance to warping, fungal attack and ultra violet energy.

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EUCALYPTUS SAWDUST AS A SUBSTRATE FOR CULTIVATION OF MEDICINAL MUSHROOM *GANODERMA LUCIDUM*

CECI SALES-CAMPOS[1], FABRÍCIO ROCHA VIEIRA[2], JOÃO PAULO FURLAN DE JESUS[2], NARA LAIANE CASAGRANDE DELBEM[3], MARLI TEIXEIRA DE ALMEIDA MINHONI[2] AND MEIRE CRISTINA NOGUEIRA DE ANDRADE[2]

[1]INSTITUTO NACIONAL DE PESQUISAS DA AMAZÔNIA – INPA/ COORDENAÇÃO DE TECNOLOGIA E INOVAÇÃO
AV. ANDRÉ ARAÚJO, 2936, ALEIXO. CEP 69083-000, MANAUS, AM - BRAZIL (CECI@INPA.GOV.BR)
[2]UNIVERSIDADE ESTADUAL PAULISTA – UNESP/FACULDADE DE CIÊNCIAS AGRONÔMICAS
RUA JOSÉ BARBOSA DE BARROS, 1780, FAZENDA LAGEADO. CEP 18610 307, BOTUCATU, SP – BRAZIL (MCNANDRADE@HOTMAIL.COM)
[3]UNIVERSIDADE ESTADUAL PAULISTA – UNESP/FACULDADE DE MEDICINA VETERINÁRIA E ZOOTECNIA
DISTRITO DE RUBIÃO JÚNIOR, S/N. CEP 186180 970, BOTUCATU, SP – BRAZIL (NARALAIANE@GMAIL.COM)

Keywords: *Eucalyptus*, mushrooms, *Ganoderma lucidum*, wood residues.

ABSTRACT

In order to prepare substrates for cultivation of mushrooms, biotechnological processes have been developed to search for ways of using lignocellulosic residues discarded in great amount in the environment. Thus, the objective of this paper was to evaluate the viability of the use of eucalyptus sawdust in cultivation of *Ganoderma lucidum*, measured by Biological Efficiency (BE) and Loss of Organic Matter (LOM). The experimental design was totally randomized in a 2 x 12 factorial scheme, corresponding to 2 *G. lucidum* strains and 12 kinds of cultivation substrates. The following formulations (on a dry basis) were used to prepare the substrates, with an addition of 4 % of lime and 60 % of water: S1 – 78 % of eucalyptus sawdust + 18 % of wheat bran; S2 – 96 % of bean straw; S3 – 58 % of eucalyptus sawdust + 38 % of Tifton straw; S4 – 58 % of eucalyptus sawdust + 38 % of bean straw; S5 – 58 % of eucalyptus sawdust + 38 % of brachiaria straw; S6 – 58 % of eucalyptus sawdust + 38 % of oat straw; S7 – 58 % of eucalyptus sawdust + 19 % of Tifton straw + 19 % of bean straw; S8 – 58 % of eucalyptus sawdust + 19 % of Tifton straw + 19 % of brachiaria straw; S9 – 58 % of eucalyptus sawdust + 19 % of wheat straw + 19 % of oat straw; S10 – 58 % of eucalyptus sawdust + 19 % of bean straw + 19 % of brachiaria straw; S11 – 58 % of eucalyptus sawdust + 19 % of bean straw + 19 % of oat straw; S12 – 58 % of eucalyptus sawdust + 19 % of brachiaria straw + 19 % of oat straw. We verified that: the highest BE averages were obtained with the substrates S8 (8.2 %) and S9 (7.2 %); the highest LOM averages were observed with the substrates S7 (42.6 %) and S1 (44.5 %). Therefore, the use of eucalyptus sawdust for cultivation of *G. lucidum* is viable, with reduction of its discard in the environment.

1. **INTRODUCTION**

The use of forest and agroindustry residues, such as sawdust, straws, leaves, barks, bagasses and brans, in the production of mushrooms aims at diminishing the environmental impacts caused by these residues and generate products of added value from low or no cost subproducts (Eira, 2000). Thus, biotechnological processes have been developed to search for methods of using such residues for cultivation of mushrooms (Bernabé-González et al., 2006; Nyochembeng et al., 2008).

Eucalyptus wood has also been used successfully in cultivation of edible mushrooms, mainly in composts with sawdust as a substrate, even though most of the forests are destined to the production of wood for “traditional use” (cellulose, paper, charcoal, firewood and fiberboards).

Growing of several mushroom species, including *Ganoderma lucidum*, has occurred in solid cultures using grass, cereal grains, sawdust or wood as a substrate, with variable cultivation time according to strain, cultivation substrate and biotic and abiotic factors (Urben, 2004).

Basidyomycete *G. lucidum* (Fr.) Karst belongs to the *Ganodermataceae* family and is very popular in Asian countries due to its multiple biological activities (Urben, 2004). Its cultivation has increased in China, Taiwan, Korea, Thailand and Vietnam. The world production of *Ganoderma* was approximately 4,300 tons in 1997 and China contributed with 3,000 tons (Jong and Birmingham, 1992).

Although several countries show an increasing interest in the production of *G. lucidum*, most of research works published in scientific periodicals are related to the nutraceutical and medicinal properties of *G. lucidum* and very little is said about its cultivation technology. Thus, analyzing the potential of the eucalyptus residue (sawdust) in the cultivation of *G. lucidum* is a way to promote the use of this material, which is commonly discarded in the environment, for the production of food with high added value (mushrooms). Therefore, the objective of the present work was to evaluate the viability of the use of eucalyptus sawdust for cultivation of *G. lucidum*.

2. MATERIALS AND METHODS

The primary matrixes of *G. lucidum* strains (GLM-09/01 and GLM-10/02) were prepared at the Laboratory of Edible Fungi Cultivation of the Coordination of Technology and Innovation of the National Institute for Amazon Research (INPA), Manaus, Amazonas, Brazil.

The cultivation was carried out at the Mushrooms Module of the College of Agronomic Sciences of the São Paulo State University (UNESP), Botucatu, São Paulo, Brazil, under controlled temperature conditions (25 ± 2 ºC) and relative humidity (80 ± 5%).

The experimental design was totally randomized in 2 x 12 factorial scheme, corresponding to 2 *G. lucidum* strains and 12 types of cultivation substrates, totalizing 24 treatments, with 11 repetitions each (substrate block – 1 kg), totalizing 264 experimental units.

The following formulations (on a dry basis), each added of 4 % of lime and 60 % of water, were used for the preparation of the substrates: **S1** - 78 % of eucalyptus sawdust + 18 % of wheat bran; **S2** - 96 % of bean straw; **S3** - 58 % of eucalyptus sawdust + 38 % of tifton; **S4 -** 58 % of eucalyptus sawdust + 38 % of bean straw; **S5** - 58 % of eucalyptus sawdust + 38 % of brachiaria straw; **S6** - 58 % of eucalyptus sawdust + 38 % of oat straw; **S7** - 58 % of eucalyptus sawdust + 19 % of tifton straw + 19 % of bean straw; **S8** - 58 % of eucalyptus sawdust + 19 % of tifton straw + 19 % of brachiaria straw; **S9** - 58 % of eucalyptus sawdust + 19 % of wheat straw + 19 % of oat straw; **S10** - 58 % of eucalyptus sawdust + 19 % of bean straw + 19 % of brachiaria straw; **S11** - 58 % of eucalyptus sawdust + 19 % of bean straw + 19 % of oat straw; **S12** - 58 % of eucalyptus sawdust + 19 % of brachiaria straw + 19% of oat straw.

After preparation, the substrates were submitted to sterilization under 121 ºC for 4 hours, followed by inoculation after cooling, at room temperature in aseptic conditions, by using a laminar flow chamber.

The mycelial colonization phase occurred during 20 days at 25 ºC. Next, the blocks were placed inside the Dalsem Mushroom chamber for production in 60 days, under controlled conditions of temperature (25 ± 2 ºC) and relative humidity (80 ± 5 %).

Data were submitted to variance analysis. The averages were compared by the Tukey test (5 %) using the SISVAR 4.2 software, developed by the Department of Exact Sciences of the Lavras Federal University (UFLA), Lavras, Minas Gerais, Brazil.

2.1. LOSS OF ORGANIC MATTER

This evaluation was performed according to Rajarathnam and Bano (1989) and Sturion (1994). The decomposition of the substrate by the fungus during cultivation was evaluated by means of the loss of organic matter (LOM), which is calculated by the difference between the dry mass of the initial substrate and the dry mass of the residual (post-harvest) substrate. LOM was evaluated as expressed by the following formula:

$$\text{LOM (\%)} = \frac{\text{Dry mass of the initial substrate (g) - Dry mass of the residual substrate (g)}}{\text{Dry mass of the initial substrate (g)}} \times 100$$

2.2. BIOLOGICAL EFFICIENCY

Yield was expressed by the biological efficiency (BE), which represents the conversion percentage of the substrate in fungal biomass (mushrooms).

$$\text{BE (\%)} = \frac{\text{Total fresh mass of mushrooms (g)}}{\text{Dry mass of the initial substrate (g)}} \times 100$$

3. RESULTS AND DISCUSSION

F values obtained in the variance analysis of the biological efficiency (BE) and loss of organic matter (LOM) data are presented in Table 1. A significant effect of the interaction between strain and substrate was observed.

Table 1. F values obtained in the variance analysis of the biological efficiency (BE) and loss of organic matter (LOM) in the cultivation of GLM-10/02 and GLM-09/01 strains of *Ganoderma lucidum* in different substrates.

Source of variation	BE	LOM
Strain (St)	0.131^{ns}	1.488*
Substrate (Su)	23.535**	20.872**
St x Su	3.904**	7.688**
CV%	28.35	12.72

3.1. BIOLOGICAL EFFICIENCY – BE

By comparing the BE averages of the substrates in the GLM -10/02 strain (Table 2), we found that the best average (8.2 %) was obtained with the substrate S8 (58 % of eucalyptus sawdust + 19 % of tifton straw + 19 % of brachiaria straw). However, it was not statistically different from substrates S2 and S9, with averages of 7.0 % and 6.2%, respectively (Table 2). The best BE average (7.2 %) for the GLM-09/01 strain was obtained with the substrate S9 (58 % of eucalyptus sawdust + 19 % of wheat straw + 19 % of oat straw) (Table 2). However, it was not different from substrates S2, S3, S4, S5, S7, S8 and S10. Similar results were obtained by Soto-Velazco et al. (2002), who cultivated *G. lucidum* in crushed maguey tequila (CMT) combined with 5 % (wet weight basis) of peanut shell (PS) or 5 % of cotton waste (CW) and found that the biological efficiencies obtained were 5.06 % for CMT alone and 7.84 % and 8.46 % for CMT +PS and CMT +CS, respectively.

By observing the BE averages of each substrate inoculated with the different strains of *G. lucidum*, we found out that only the substrates S3 and S8, among all the substrates tested, gave different averages between the strains GLM-09/01 and GLM-10/02 (Table 2).

3.2. LOSS OF ORGANIC MATTER – LOM

By observing LOM averages of the substrates in the strain GLM-10/02 (Table 2), we found out that the substrate S7 (58 % of eucalyptus sawdust + 19 % of tifton straw +19 % of bean straw) gave the highest average. However, it was not different from the substrates S1, S3, S5 and S8. The higher LOM average for the strain GLM-09/01 was provided by the substrate S1 (78 % of eucalyptus sawdust + 18 % of wheat bran). Nevertheless, it was statistically similar to the averages obtained with the substrates S1, S3, S8 and S12.

By analyzing LOM averages of the substrates inoculated with the two *G. lucidum* strains, we found out that only the substrates S2, S5, S7 and S12 gave different averages among themselves (Table 2).

Table 2. Biological efficiency and loss of organic matter of different substrates during the cultivation of the GLM-10/02 and GLM-09/01 strains of *Ganoderma lucidum* at 25 °C.

Substrates**	Strains			
	GLM-10/02		**GLM-09/01**	
	Biological efficiency (%)			
S1	1.5	Ae*	1.9	Ae
S2	7.0	Aab	6.0	Aab
S3	4.5	Bcd	6.7	Aab
S4	5.4	Abcd	6.0	Aab
S5	5.1	Abcd	5.1	Aabcd
S6	2.1	Ae	2.9	Ade
S7	5.2	Abcd	5.9	Aab
S8	8.2	Aa	5.1	Babcd
S9	6.2	Aabc	7.2	Aa
S10	5.5	Abcd	5.4	Aabc
S11	3.3	Ade	3.4	Acde
S12	5.5	Abcd	4.6	Abcd
	Loss of organic matter (%)			
S1	42.1	Aab	44.5	Aa
S2	32.6	Acd	28.3	Bef
S3	40.9	Aab	40.2	Aabc
S4	33.3	Acd	29.8	Aef
S5	37.6	Aabc	31.9	Bef
S6	29.2	Ade	30.0	Aef
S7	42.6	Aa	33.1	Bdef
S8	40.8	Aab	41.2	Aab
S9	30.2	Ade	27.3	Af
S10	35.6	Abcd	33.5	Acdef
S11	32.9	Acd	35.0	Abcde
S12	25.3	Be	39.5	Aabcd

*Averages followed by same lowercase letters in column and uppercase letters in line are not statistically different among themselves (Tukey. 5 %).

Substrates: S1 = 78 % of eucalyptus sawdust + 18 % of wheat bran; **S2**= 96 % of bean straw; **S3**= 58 % of eucalyptus sawdust + 38 % of tifton straw; S4= 58 % of eucalyptus sawdust +38 % of bean straw; **S5**= 58 % of eucalyptus sawdust + 38 % of brachiaria straw; **S6**= 58 % of eucalyptus sawdust + 38 % of oat straw; **S7**= 58 % of eucalyptus sawdust + 19 % of tifton straw +19 % of bean straw; **S8**= 58 % of eucalyptus sawdust + 19 % of tifton straw + 19 % of brachiaria straw; **S9**= 58 % of eucalyptus sawdust + 19 % of wheat straw + 19 % of oat straw; **S10**= 58 % of eucalyptus sawdust + 19 % of bean straw + 19 % of brachiaria straw; **S11**= 58 % of eucalyptus sawdust + 19 % of bean straw + 19 % of oat straw; **S12**= 58 % of eucalyptus sawdust + 19 % of brachiaria straw + 19 % of oat straw.

Into all substrates 4 % of lime and 60 % of water were added.

A high LOM average does not always mean a satisfactory BE. According to Zadrazil (1978), and Rajarathnam and Bano (1989), LOM occurs due to CO_2 and H_2O losses during the metabolism of the microorganisms and not only in function of the removal of materials for the construction of the basidiomata. In the present research, we verified that the substrate S2 is one of the substrates with the lowest LOM averages, even though it is among the ones which provided the best BE averages.

4. CONCLUSIONS

- The most appropriate substrate for cultivation of the GLM-10/02 strain of *G. lucidum* was S8 (58 % of eucalyptus sawdust + 19 % of tifton straw + 19 % of brachiaria straw) and the most promising substrate for cultivation of the GLM-09/01 strain was S9 (58 % of eucalyptus sawdust + 19 % of wheat straw + 19 % of oat straw).

- The highest losses of organic matter occurred in the composts S7 (58 % of eucalyptus sawdust + 19 % of tifton straw +19 % of bean straw) and S1 (78 % of eucalyptus sawdust + 18 % of wheat bran) for the strains GLM-10/02 and GLM-09/01, respectively.

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6. SUPPORT

Universidade Estadual Paulista (UNESP), Faculdade de Ciências Agronômicas (FCA), Coordenadoria de Saúde, Segurança do Trabalhador e Sustentabilidade Ambiental (CSTSA), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Instituto Nacional de Pesquisas da Amazônia (INPA), Governo do Estado do Amazonas, Fundação de Amparo à Pesquisa do Estado do Amazonas (FAPEAM), Secretaria de Estado de Ciência e Tecnologia (SECT), Instituto Nacional de Ciência e Tecnologia (INCT) - Madeiras da Amazônia.

CORK SORBENTS FOR AQUATIC OIL SPILLS CLEAN UP

ANA FONSECA*, MARIA JOÃO GUERREIRO, ISABEL ABREU
FACULDADE DE CIÊNCIA E TECNOLOGIA
UNIVERSIDADE FERNANDO PESSOA, PORTO, PORTUGAL
* CORRESPONDING AUTHOR: TEL: +351-225071300 FAX: +351-22508269
AFONSECA@UFP.EDU.PT

Keywords: cork, polypropylene, cotton, sorbents, oil spill, oil sorption

ABSTRACT

Oil spills may happen due to simple dumping of crude from tankers up to major environmental catastrophes, and may contribute to severe environmental impacts and economic losses. Fast and efficient removal of oil from the aquatic environment is desirable. The use of sorbents is considered one of the most efficient techniques in oil and polycyclic aromatic hydrocarbons removal from water, especially due to their lower costs. However, sorbents should be employed with caution to minimize secondary environmental problems, particularly when using synthetic sorbent material. In this work, the response of a heat treated cork sorbent was analyzed and compared with two other commercial sorbents. Cotton fiber showed a better performance in both sorption rate and sorption capacity, but worse results regarding oil loss after compression and floatability in water. Heat treated cork presented a better floatability and a better retention capacity than the other two sorbents. These results suggest that the use of heat treated cork as a sorbent has potential for oil removal in aquatic environments with the advantage of being a natural and ecological product.

1. **INTRODUCTION**

Oil spills may happen due to simple illegal dumping of crude from tankers up to major environmental catastrophes, like the recent Gulf of Mexico disaster that spilled over 750,000 cubic meters of oil. Illegal oil discharges incidents in Europe occur at an average number of 3,000 per year (EEA, 2010).

Oil spills contribute to major environmental impacts, killing birds, dolphins, imparting genetic mutations on shrimps and crabs, among other things, and may even be toxic to humans (Aguillera et al., 2010). Economic losses are also significant, hurting the fishing, tourism and oil industry (EEA, 2010; Karan et al., 2011). Therefore, fast and efficient removal of oil from the aquatic environment is desirable.

There are several approaches to cleaning oil spills. One approach is the use of physical methods that will contain the spill and then remove the oil from the water surface either by skimming or by using adequate sorbents. Another one is the use of chemical methods, like using dispersants to break up the oil and speed up natural degradation, and still the use of solidifiers or *in situ* burning (Karan et al., 2011). Biological methods are also used, introducing bacteria and other microorganisms to promote biodegradation of oil.

Sorbents are insoluble materials that recover liquids through absorption, adsorption, or both, and that should be both oleophilic (oil attracting) and hydrophobic (water repellent) (EPA, 2012; Adebajo et al., 2003). Retention over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent are also important factors for oil sorption success (Teas et al., 2001; Adebajo et al., 2003).

Absorbents retain liquid through their molecular structure by swelling of the material, whereas adsorbents attract the oil to the surface of the material. Once sorbed, removal of oil by removal of the sorbent is easier (Adebajo et al., 2003). The use of sorbents is considered one of the most efficient techniques in oil and polycyclic aromatic hydrocarbons (PAHs) removal from water, especially due to their lower costs. However, sorbents should be employed with caution to minimize secondary environmental problems, particularly when using synthetic sorbent material (ITOPF, 2012).

Sorbents may be natural or synthetic. Natural sorbents may also be organic or inorganic (EPA, 2012; ITOPF, 2012). Natural organic sorbents include cotton and cork, whereas polyethylene is a synthetic sorbent. Natural organic sorbents can adsorb up to 15 times their weight and are being used for oil spill cleanup (EPA, 2012; Adebajo and Frost, 2004). However, some organic sorbents tend to also adsorb water and sink (EPA, 2012), therefore floatability tests are also important to evaluate sorbent performance. Floatability is an important issue, especially when using skirt booms with ballast.

High porosity materials, like most natural organic sorbents, have higher initial oil pickup but might have poor retention capacity (Wei et al., 2003). Nonetheless, natural organic sorbents have the advantage of biodegradability and cost-effectiveness in comparison to the synthetic polymeric fibres (Abdullah et al., 2010; Karan et al., 2011; Adebajo and Frost, 2004). Low cost materials for hydrocarbon removal (e.g. cork) have been searched for in recent years and studies are being carried out for removal performance (Olivella et al., 2011).

Cork is a natural and renewable raw material obtained from the bark of the cork oak (*Quercus suber L.*). A new product based on cork has been developed for oil spill absorption purposes, and has recently been introduced in the market with the trade name CORKSORB®. This product is based on cork previously treated with heat and pressure, in order to improve its hydrophobic behaviour and absorption capacity. The use of heat treated cork in aquatic oil spills cleanup is recent, and the available scientific information regarding its performance is still scarce.

The objective of this study is to analyze and compare the response of a heat treated cork sorbent with two other commercial sorbents – melt-blown polypropylene and cotton fiber, representing synthetic and natural sorbents, respectively. Sorption and retention capacities, and floatability, were evaluated over time.

2. **MATERIAL AND METHODS**

Three commercial booms with different sorbents were used in this study – CORKSORB® (heat treated cork); ECOSORB R® (melt-blown polypropylene); and ECOSORB® (cotton fiber), with densities 65.8 kg/m^3, 65.5 kg/m^3, and 52.4 kg/m^3 respectively. All booms were cylindrical 3.0 m long and with a diameter of 0.18 m for both ECOSORB R® and ECOSORB®, and 0.20 m for CORKSORB®. The booms of cork and polypropylene had a non-woven fabric between the sorbent and the outer sleeve. In the cotton fiber boom the sorbent was directly in contact with the outer sleeve.

2.1. MEASUREMENT OF OIL SORPTION RATE

Sorption of oil was simulated in nine beakers (three replicates for each sorbent), filled with a 0.09 m layer of sorbent material extracted from the booms, and maintaining boom density. The top of the beakers with cork and polypropylene were covered with the fabric materials used in the respective booms. The beakers with cotton fiber were covered with fishing thread with the only purpose of preventing sorbent to fall from the beaker. The beakers were placed top-down on a metallic grid immersed in crude oil (Arabian Light 110) in a stationary condition. Specifications of the crude oil used in experiments are shown in Table 1.

Figure 1 shows the experimental set-up. At given times the beakers were removed from the oil, drained for 20 s and wiped to remove excess oil from the beakers' outer glass, and their weight was monitored. Oil sorption was calculated as grams of oil sorbed per gram of sorbent for times up to 8 days and at a constant temperature of 20 ºC.

Table 1: Specifications for Arabian Light 110 crude oil (data provided by the supplier of the oil sample).

Property (units)	
Specific gravity at 15 ºC	0.8605
API gravity (º)	32.8
Kinematic viscosity at 20 ºC (m^2/s)	11.24×10^{-6}
Kinematic viscosity at 40 ºC (m^2/s)	6.11×10^{-6}
Sulfur content (%wt)	1.89
Pour point (ºC)	-57
Acidity (mg KOH/g)	0.05

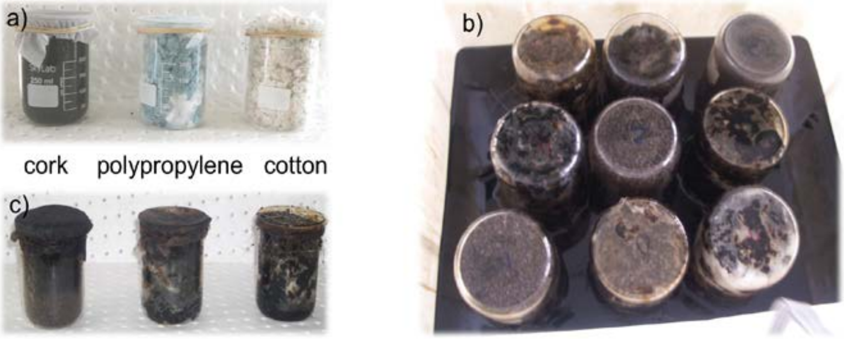

Figure 1: Experimental set-up for the oil sorption capacity determination of heat treated cork, melt-blown polypropylene, and cotton fiber: a) initial stage, b) during experiment; c) after 8 days.

2.2. MEASUREMENT OF RETENTION CAPACITY AFTER COMPRESSION

Three replicates of each sorbent from oil sorption experiments were put together at the end of the sorption experiments, and each sorbent was submitted during 1 min to a 2,000 $N.m^{-2}$ compression test. In order to evaluate retention capacity each sorbent was weighted before and after compression.

2.3. MEASUREMENT OF THE FLOATABILITY OF THE BOOMS

Two measuring tapes were placed around the perimeter of each boom, at 1 m distance from the boom's end on both sides. The distance between the measuring tapes in the same boom was also 1 m. The booms were then placed in water, and their floatability was evaluated by measurement of the submersed perimeter in each tape during a 42 days experiment. Figure 2 shows the experimental set-up for this essay.

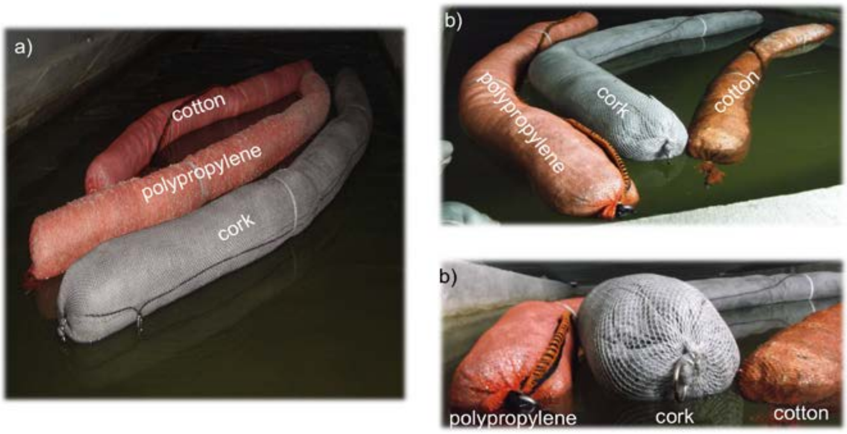

Figure 2: Floatability essays for booms of heat treated cork, melt-blown polypropylene and cotton fiber: a) initial stage; b) 34 days later.

3. RESULTS AND DISCUSSION

Figure 3 shows the global results for the oil sorption experiments. All three sorbents tested showed similar behavior: the initial rate of sorption is higher, in an intermediate phase the sorption rate lowers until the process reaches a steady-state phase where no further sorption occurs. Table 2 shows the results obtained for the sorption capacity at a steady-state for each sorbent. It is important to refer that these results do not represent maximum oil sorption capacities, since it was observed that the material on the top of the beakers was clearly dryer than the material closer to the oil surface. Therefore this steady-state stage was achieved without total saturation of the sorbents.

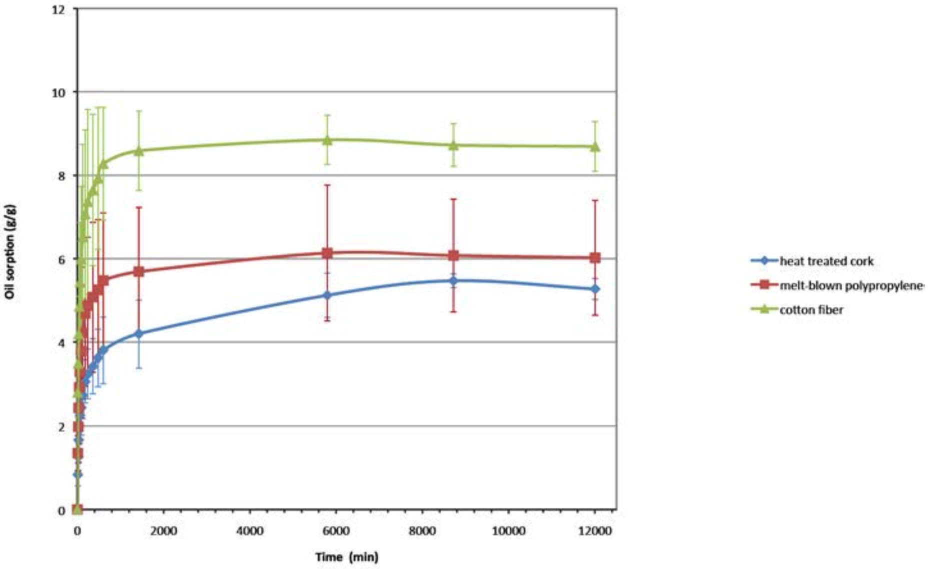

Figure 3: Oil sorption results (dots and error bars represent, respectively, mean value and two standard deviations of the three samples).

Table 2: Maximum amount of oil sorbed in the oil sorption experiments.

sorbent	Maximum oil sorbed	
	g oil / g sorbent	g oil / cm^3 sorbent
heat treated cork	5.3 ± 0.4	0.35 ± 0.03
melt-blown polypropylene	6 ± 1	0.40 ± 0.08
cotton fiber	8.8 ± 0.5	0.46 ± 0.03

The results for the initial stage of the experiments are shown in more detail in Figure 4. It can be seen that the initial rate of oil sorption is higher for cotton fiber.

It is important to refer that these results were obtained under static conditions, and therefore in a real aquatic oil spill cleanup situation, the rate of oil sorption is expected to be higher due to convection processes.

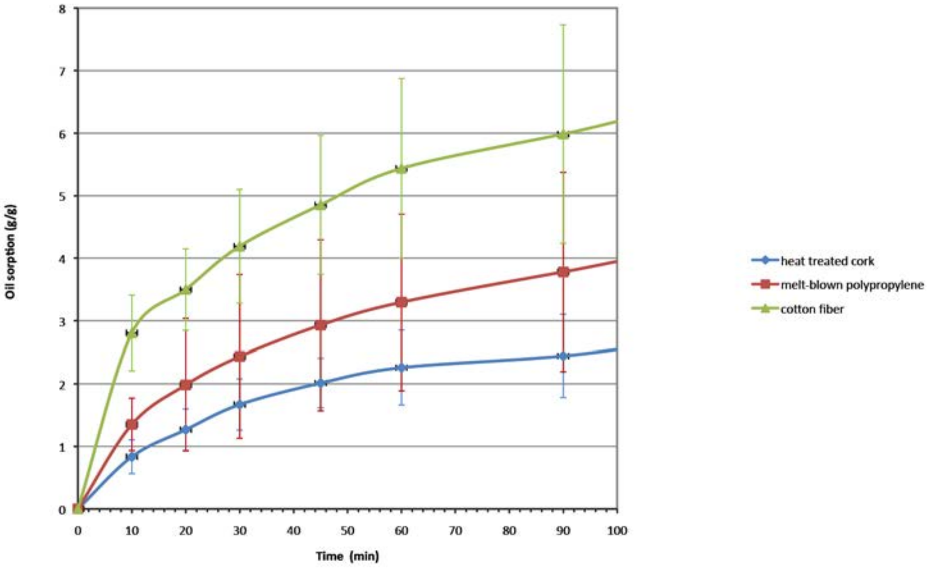

Figure 4: Oil sorption results for the initial stage of the experiments (dots and error bars represent, respectively, mean value and two standard deviations of the three samples).

Regarding the retention capacity of the three sorbents, the results obtained in our experiments are shown in Table 3. The results show that cotton fiber exhibits poor performance regarding retention capacity, loosing around 8 % of the oil previously absorbed, when compressed at 2,000 N.m^{-2}. The retention capacity is an important property of sorbents since after the oil spill clean-up with booms, these have to be manipulated for removal from the water and proper disposal, and during these operations the booms are exposed to compression forces. Heat treated cork showed the best results in this test.

Table 3: Oil loss from sorbent after compression.

Heat treated cork	Melt-blown polypropylene	Cotton fiber
0.2%	2.7%	7.9%

Regarding the floatability of the booms, Figure 2b and Figure 5 show the results obtained in this experiment. It was observed that the heat treated cork boom also had the best performance in this test, since at least 80 % of the boom remained above the water level during the entire experiment. Melt-blown polypropylene partially sank during the initial 8 days, but remained approximately stable below 35 % of volume immersed for the rest of the experiment. The cotton fiber boom showed a higher tendency to sink, with 70 % of its volume submersed after 42 days.

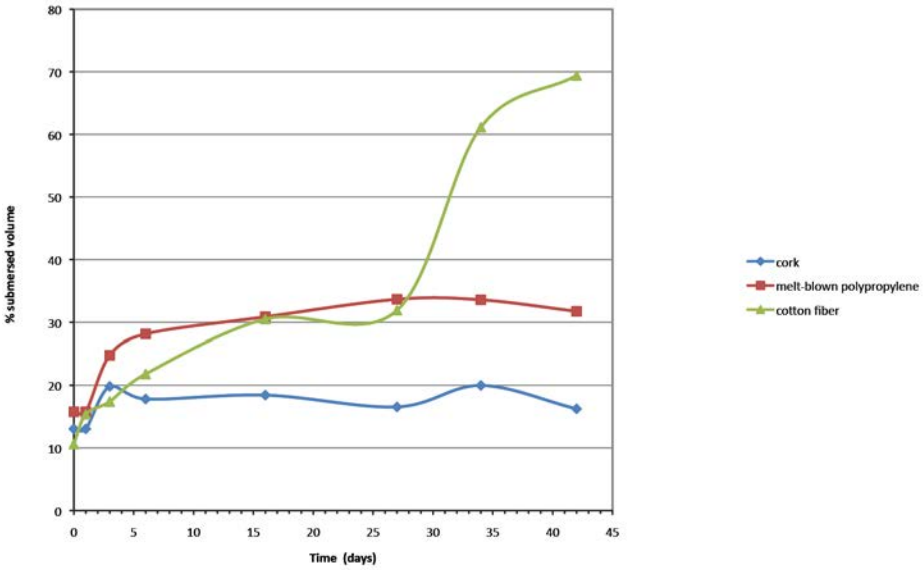

Figure 5: Floatability essays – percentage volume of submersed boom over time.

4. **CONCLUSIONS**

Regarding the oil sorption experiments, our results show that cotton fiber has a better performance than the other two sorbents, both in sorption rate and in sorption capacity. However, cotton fiber has shown to have worse results regarding oil loss after compression and floatability in water. Heat treated cork presented a better floatability and a better retention capacity after saturation than the other two sorbents. These results suggest that the use of heat treated cork as a sorbent has a potential for oil removal in aquatic environments with the advantage of being a natural and ecological product.

5. **AKNOWLEDGEMENTS**

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05. ADHESIVE ISSUES AND WOOD ADVANCED MATERIALS

CURING OF LIQUEFIED WOOD DURING WOOD BONDING

ALEŠ UGOVŠEK*, MILAN SERNEK
DEPARTMENT OF WOOD SCIENCE AND TECHNOLOGY, BIOTECHNICAL FACULTY, UNIVERSITY OF LJUBLJANA, ROZNA DOLINA, C. VIII/34, 1001 LJUBLJANA, SLOVENIA
* CORRESPONDING AUTHOR: M SORA D.D., TRG SVOBODE 2, 4226 ŽIRI, SLOVENIA
TEL: +386 40 471 410; ALES.UGOVSEK@GMAIL.COM

Keywords: adhesive, curing, dielectric analysis, differential scanning calorimetry, liquefied wood, rheometry.

ABSTRACT

For a long time now, the majority of wood and wood-based composites have been bonded with synthetic adhesives, which are based on non-renewable petrochemicals. Due to the availability of newly developed and patented procedures for the production of polymers from renewable sources, natural based adhesives represent a contemporary alternative. Animal hides and bones, blood, soy, tannins and lignin are just some of natural materials that are suitable for the production of adhesives. Additionally, liquefied wood is a novel natural-based material that has the potential to be used as an adhesive for wood bonding. To ensure optimal conditions during the bonding of wood with liquefied wood in a hot press, it is of great importance to understand the curing process of the liquefied wood. In this study, black poplar wood (*Populus nigra* L.) (25%), ethylene glycol (75%) as a solvent, and sulphuric acid as a catalyst, were used in the process of liquefaction. Using an additional procedure, the solvent content of the liquefied wood was reduced to one-third of its initial value. Wood lamellas were bonded with liquefied wood at six different press temperatures (150 – 200 °C). Dielectric analysis was used for in-situ measurements of the curing of the liquefied wood during the bonding. It was found that the curing started after a temperature of 100 °C was reached in the bond, which is correlated to water evaporation or diffusion. Rheological measurements using wood and aluminium plates were performed under dynamic temperature conditions in order to evaluate the effect of the wood surface on the curing of the liquefied wood. It was observed that the curing of the liquefied wood was affected by the wood surface as the curing started at lower temperatures compared to aluminium surfaces. Differential scanning calorimetry was used to evaluate the curing of the liquefied wood. It was found that the curing of liquefied wood can be divided in two parts: the initial elimination of water and solvent, and then crosslinking of the liquefied wood. The results of this study contribute to the understanding of the curing of liquefied wood, and demonstrate the potential for using liquefied wood as an adhesive for wood bonding.

1. INTRODUCTION

Nowadays, bonding of wood mainly bases on the use of synthetic adhesives that are prepared by the reaction of formaldehyde with various chemicals such as urea, melamine, phenol, resorcinol, or combinations of these. Due to the potential carcinogenicity of formaldehyde and due to the fact that mentioned chemicals are based on non-renewable oil based derivatives, a great number of researches was done to produce adhesives from alternative materials. Renewable natural-based products are an alternative and liquefied wood (LW) is one of them. So far LW has been most extensively investigated for the production of carbon fibres (Ma and Zhao, 2010), various synthetic resins (Wei et al., 2004; Pan et al., 2009; Kishi et al., 2011), polyurethane foams (Alma and Shiraishi, 1998), polyester derivatives (Kunaver et al., 2010a), films (Budija et al., 2009), and adhesives. LW has been used as a part of adhesive mixtures or synthesized resins for wood bonding (Maldas et al., 1997; Antonović et al., 2010; Kunaver et al., 2010b; Ugovšek et al., 2010; Wu and Lee, 2011), whereas the use of LW for wood bonding as an independent component has been investigated to a lesser extent (Ugovšek et al., 2011; Ugovšek and Sernek, 2013). In latter case, the understanding of LW curing is of importance since there is no additional polymer to affect the curing reaction.

During liquefaction the basic wood components (i.e. cellulose, lignin, and hemicelluloses) are degraded into smaller molecules and further recondensation between depolymerised compounds might occur (i.e. curing or crosslinking) (Kobayashi et al., 2004; Pan et al., 2007; Zhang et al., 2012). The curing process of LW can be monitored by differential scanning calorimetry (DSC), which is one of the most widely used thermal analysis techniques for studying polymeric materials (Menczel and Prime, 2009). With DSC the physical transitions and chemical reactions which occur during the curing of LW can be determined. Because the conditions in the process of wood bonding differ from these in metal pan used in DSC, chemical and physical aspects are important, due to the possible effect of the wood surface that is being bonded. A very convenient method for continuous "in situ" measurements of the curing of the adhesive during the wood bonding is dielectric analysis (DEA). Dielectric cure monitoring is sensitive to the mobility of ions and the rotational mobility of dipoles on the polymer molecule in the presence of an electric field. Using a thin (~0.1 mm) and durable remote dielectric sensor placed in an adhesive located between bonded lamellas makes it possible to monitor the curing process of adhesives (Sernek and Kamke, 2007). Finally, in order to obtain a mechanical aspect of the curing of LW, rheometry is a useful method with which various rheological parameters (storage and loss modulus, viscosity) can be determined (Malkin and Kulichikhin, 1991).

The aim of this study was to elucidate the curing process of LW during the bonding of wood using DSC, DEA and rheometry.

2. MATERIALS AND METHODS

2.1. PREPARATION OF LIQUEFIED WOOD (LW)

Sawdust of black poplar (*Populus nigra* L.) was liquefied according to a procedure reported by Ugovšek et al. (2011). Prior to the liquefaction process, the sawdust was dried in a laboratory oven (103 °C, 24 h). A mass ratio of 1:3 of black poplar and ethylene glycol (EG) as solvent was used for liquefaction. Sulphuric acid (3 % based on the EG mass) was added as a catalyst. Liquefaction was performed for a period of 120 minutes in a 1000 mL three-neck glass reactor, which was immersed in an oil bath that was preheated to 180 °C and equipped with a mechanical stirrer. After liquefaction, the reactor was immersed in cold water to quench the reaction. The emerging reaction solution was then diluted with a mixture of 1,4-dioxane and water (4/1, v/v), and filtered through filter disks (Sartorius filter disks, grade 388) to remove the insoluble parts of the LW. 1,4-dioxane and water were first evaporated using a rotary evaporator (Büchi, Rotavapor R-210) at 55 °C, and at reduced pressure (reducing from 100 to 1 kPa) using a vacuum pump (Vaccubrand, PC 3003 Vario). In the second evaporation step EG was partly removed at 120 °C and 1 kPa in order to achieve a final wood:EG mass ratio of approximately 1:1. This final product (LW with a wood:EG mass ratio of about 1:1) was used for all further analysis.

2.2. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC measurements were performed with a high-pressure differential scanning calorimeter - HP DSC 1 (Mettler Toledo). With DSC, energy needed to maintain the same temperature between the reference and sample is measured (Figure 1). 30 µl platinum crucibles were used for the curing of LW at a heating rate of 10 °C/min. A dynamic nitrogen atmosphere with a flow rate of 50 ml/min at normal pressure (100 kPa), was used.

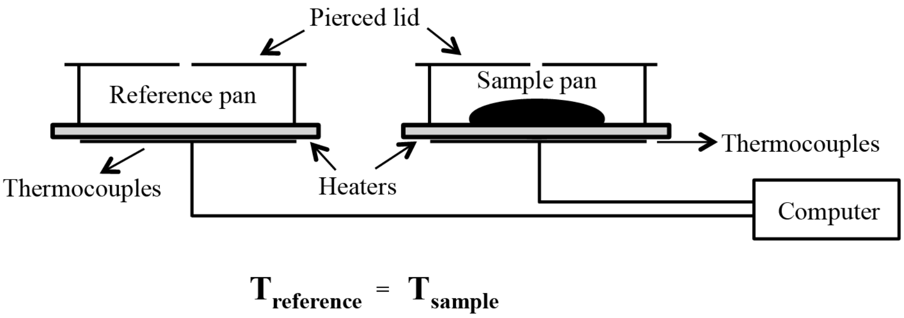

Figure 1: Principle of DSC measurement: computer monitors the temperature and regulates heat flow in order to maintain equilibrium between the temperature of reference ($T_{reference}$) and the temperature of sample (T_{sample}) at specific conditions.

2.3. DIELECTRIC ANALYSIS (DEA)

DEA was performed during the bonding of 5 mm thick beech wood (*Fagus sylvatica* L.) lamellas with LW. The lamellas were bonded in a conventional hot-press with a specific press pressure of 0.6 MPa at different press temperatures (150, 160, 170, 180, 190 and 200 °C). Fringe field sensor with an interdigitated design (IDEX, Netzsch 066S) was positioned in the bondline between the two lamellas and controlled by a precision LCR meter (Agilent 4285A), which operated at the frequency of 100 kHz. The bondline temperature was recorded by a type J thermocouple connected to a Data acquisition/Switch unit (Agilent 34970A). Both the LCR meter and the Data acquisition/Switch unit were connected to a computer equipped with Agilent VEE Pro 7.0 software (Figure 2).

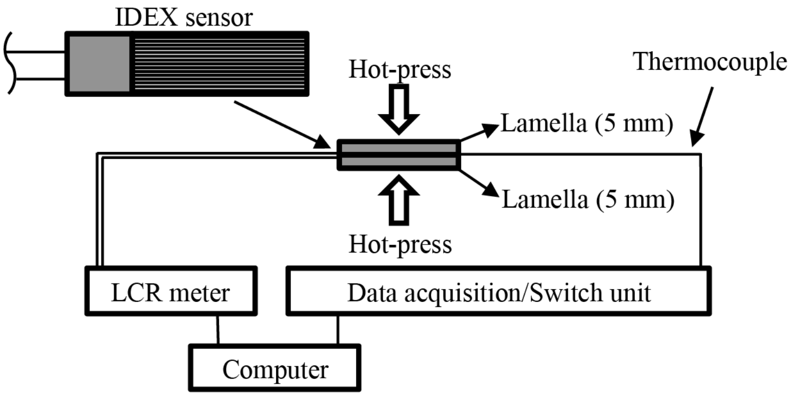

Figure 2: Experimental test configuration for LW cure monitoring by DEA during the bonding of 5 mm thick beech wood (*Fagus sylvatica* L.) lamellas.

2.4. RHEOLOGICAL OSCILLATORY TESTS

Rheological measurements of LW during curing were performed using a stress control rheometer ARES G2 (TA Instruments). Disposable aluminium and beech wood (*Fagus sylvatica* L.) plates with a diameter of 25 mm were used for the oscillation tests. Aluminium-aluminium, aluminium-wood and wood-wood plate combinations were used to evaluate the influence of the substrate on the curing of the LW which was applied between the plates (Figure 3). A gap of 0.3 mm between the plates was used. The wood plates were conditioned in a standard climate (20 ± 2 °C, relative humidity 65 ± 5%) prior to the tests. All tests were performed at a frequency of 10 rad/s, a strain of 1.0%, and a heating rate of 10 °C/min.

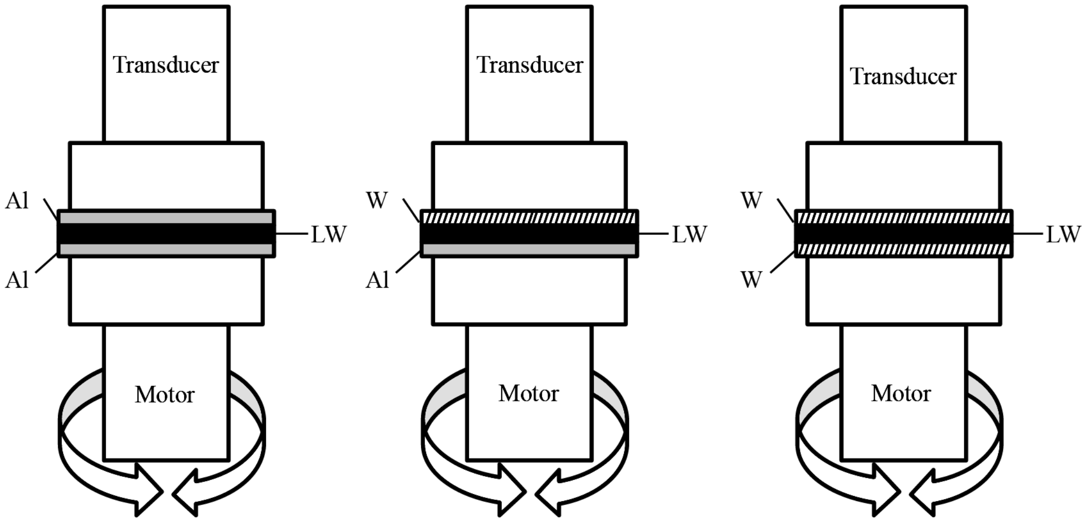

Figure 3: Rheological oscillatory test configuration for LW cure monitoring. LW was applied between two aluminium (Al) plates, between Al and wood (W) plates, or between two W plates. Shear strain was applied by motor which was oscillating; torque was measured independently by the transducer.

3. **RESULTS AND DISCUSSION**

The curing process of LW monitored by DSC under dynamic temperature conditions is presented in Figure 4. Endothermic signals – peaks with minimum (representing e.g. evaporation or melting of specific material) and exothermic signals – peaks with maximum (correlated to e.g. crosslinking or crystallization of specific material) are normally part of DSC thermogram. In the case of LW, two endothermic signals up to 200 °C and one exothermic signal at temperatures above 200 °C could be observed.

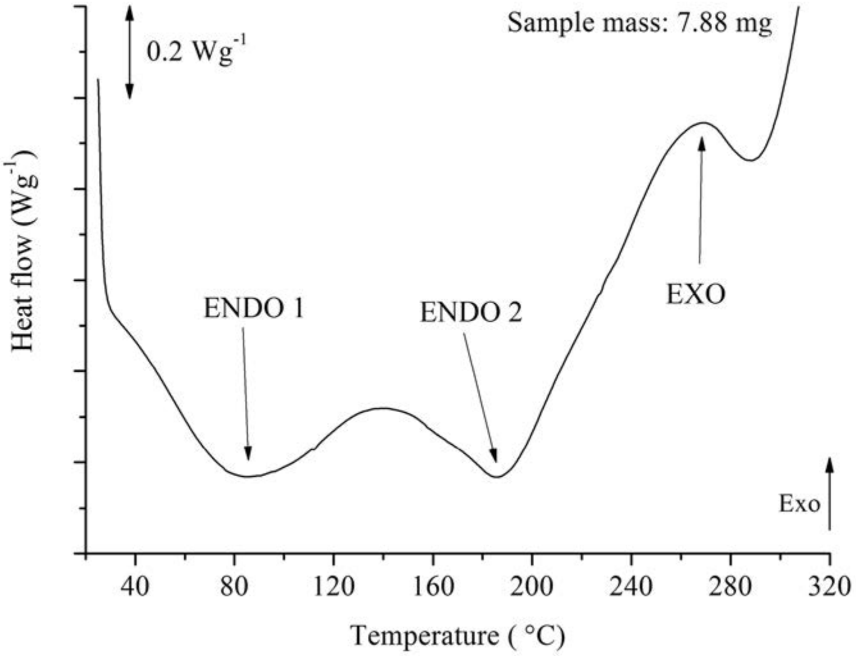

Figure 4: Physical transitions and chemical changes taking place during the curing of LW at dynamic temperature conditions monitored by DSC.

First endothermic signal (ENDO 1) is correlated to the evaporation of water, whereas second endothermic signal (ENDO 2) represents evaporation of EG. An increase in the heat flow between ENDO 1 and ENDO 2 is not correlated to the chemical reaction as it is a part of the baseline of the EG evaporation and does not represent an exothermic signal. The only exothermic signal (EXO) was observed on the temperature range from around 180 °C to 290 °C and is correlated to the curing of LW. Based on these results it could be interpreted that the curing process of LW consist of initial physical phase (i.e. evaporation of water and EG) and following chemical phase (i.e. curing).

Later finding is of importance as during the bonding of wood, water and EG could be beside evaporation eliminated out of LW also by means of diffusion in wood. For that reason, curing process was monitored during the bonding of beech wood lamellas using DEA (Figure 5).

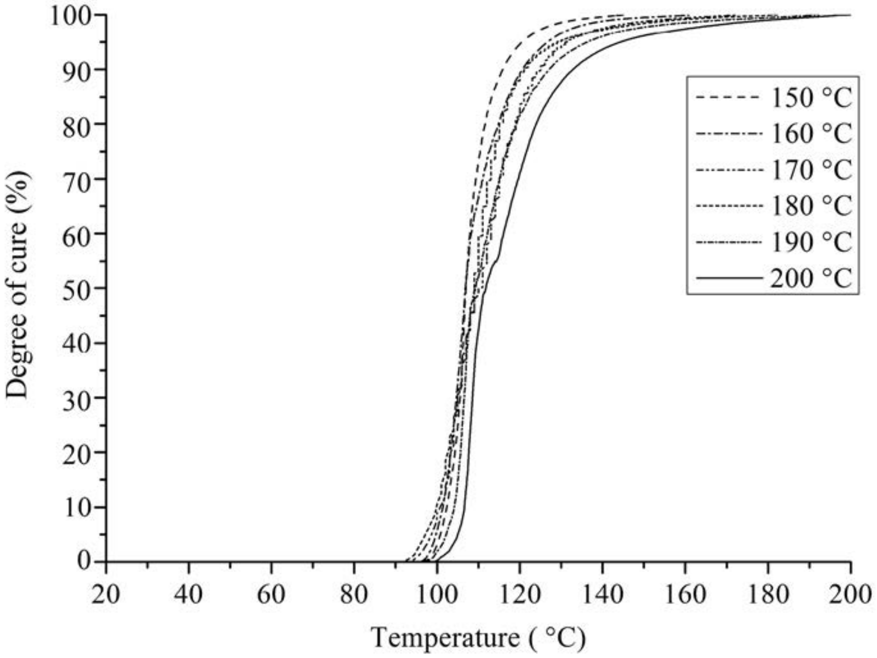

Figure 5: Influence of the temperature of the bondline on the degree of cure of LW during the bonding of 5 mm thick beech wood (*Fagus sylvatica* L.) lamellas monitored by DEA

The degree of conversion, or the degree of cure (α), as a function of bond line temperature (T) was calculated on the basis of the equation used by Sernek and Kamke (2007). Equation bases on the maximum (G_{max}) and minimum conductance (G_{min}), and conductance at specific temperature (G_T):

$$\alpha(\mathrm{T}) = \frac{G_{max} - G_T}{G_{max} - G_{min}} \quad (1)$$

At all press T, α started to increase at the temperature around 100 °C which is correlated to the intensive water diffusion/evaporation from the LW. After this temperature, degree of cure increased drastically and reached its maximum at highest temperature. At this point it should be noted that 100% degree of cure is not necessarily correlated to the actual totally cured state, but is calculated from obtained data at specific press temperature. However, it is evident that water (and also EG) elimination is an important moment at curing process of LW during the wood bonding and is followed by curing or bond line formation. Finally, the effect of substrate being bonded on the curing process of LW was evaluated with rheological oscillatory tests by means of change of storage modulus as a function of temperature (Figure 6).

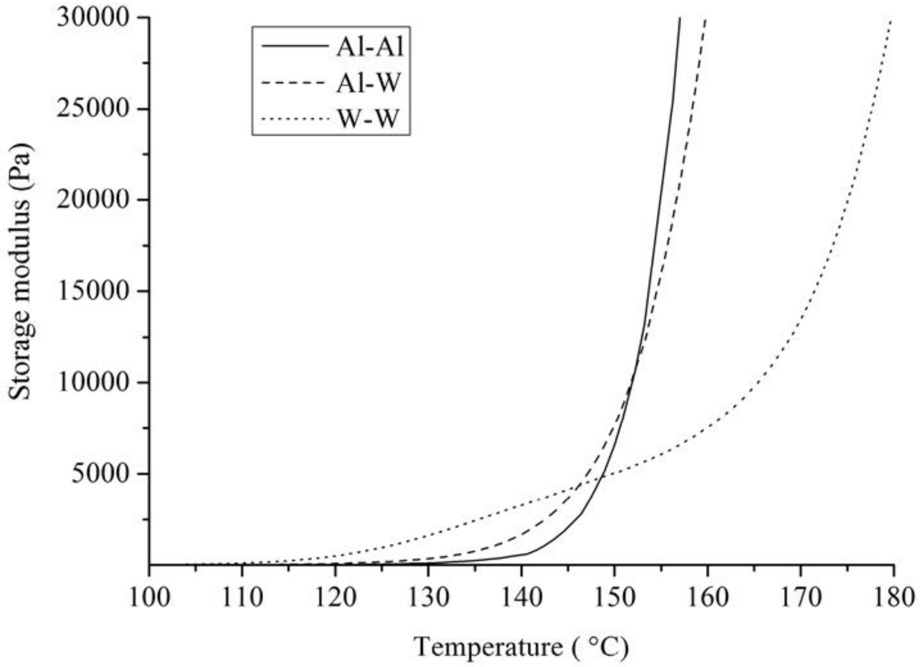

Figure 6: The effect of different substrates (aluminium –Al and wood – W) on the curing process of LW between oscillating plates, presented by means of storage modulus as a function of temperature.

Use of plates of different materials (i.e. alluminium and wood) helped to ascertain that LW placed between two wooden plates (W-W) started to cure at lower temperatures (around 110 °C) compared to LW placed betwen aluminium and wooden plates (Al-W) (around 120 °C), and two aluminum plates (Al-Al) (around 130 °C). These temperatures are correlated to water and EG elimination, and thus to the increased resistance of the material to flow. Additonaly it can be observed that further curing was the most intensive between aluminum discs due to better heat conductance of alluminium compared to wood and consequently more intensive heating of LW applied between plates. Hovewer, it could be ascertained that due to the porosity of wood as a substrate, the elimination of water and EG was the quickest and the bonding process started at lower temperatures.

4. CONCLUSIONS

Sawdust of black poplar (*Populus nigra* L.) was liquefied at 180 °C for 120 minutes using ethylene glycol (EG) as a solvent and sulphuric acid as a catalyst. With further procedure, 2/3 of initial EG was removed from liquefied wood (LW) and such LW was used for further analysis and wood bonding. Differential scanning calorimetry (DSC), dielectric analysis (DEA) and rheological oscillatory tests were used to elucidate the curing of LW during the wood bonding. It was found that LW curing process consist of water and EG elimination in the initial stage, and is followed by actual curing of LW. When LW was applied between wooden lamellas for the purpose of wood bonding, the start of bonding process was shifted to lower temperatures due to more efficient elimination of water and EG by means of diffusion into the porous wood structure. The curing of LW between wooden substrate started at around 20 °C lower temperatures than the curing of LW between non-porous aluminium. For this reason, further studies to elucidate the crosslinking reactions and to analyse the bondline structure are needed further on.

5. ACKNOWLEDGEMENTS

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ORGANOSOLV LIGNIN IN PHENOL-FORMALDEHYDE RESINS - EFFECT OF MOLECULAR WEIGHT AND LIGNIN METHYLOLATION

ALEXANDER STUECKER [1], JACOB PODSCHUN[2], MARTINA HEITMANN[2], RALPH LEHNEN [1]

[1] TI, THÜNEN INSTITUTE OF WOOD RESEARCH, LEUSCHNERSTR. 91B, 21031 HAMBURG, GERMANY
[2] UNIVERSITY OF HAMBURG, DEPARTMENT OF WOOD SCIENCE, CHEMICAL WOOD TECHNOLOGY LEUSCHNERSTR. 91B, 21031 HAMBURG

ABSTRACT

Softwood kraft lignin (KL), lignosulfonate (LS) and hardwood organosolv lignins (OL) from ethanol-water pulping were characterized by functional group analysis and molecular weight distribution. The properties of lignin-phenol-formaldehyde resins (LPF), synthesized with these lignins, were evaluated and the wood bonding effectiveness was tested in an Automated Bonding Evaluation System (ABES). All resins formulated were used as binders for particleboard production and compared to a pure phenol-formaldehyde (PF) resin. The results of the high molecular weight organosolv lignin indicate a higher potential for application in wood adhesives. In contrast, methylolation of the low molecular weight lignin seems to be more effective for improvement of wood bonding effectiveness and board properties.

1. INTRODUCTION

In a joint German project including universities, research institutes and chemical companies, ethanol-water pulping has been adapted for the conversion of beech wood into platform chemicals, such as ethanol and lactic acid (Puls et al., 2009; Michels and Wagemann, 2010). Organosolv lignins, co-generated during biomass fractionation can be used as a base material for the development of value-added products (Doherty et al., 2011). In order to reduce resin costs there have been many attempts to replace phenol with lignin in PF resins (Danielson and Simonson, 1998; Cetin and Özmen, 2002; El Mansouri et al., 2007; Wanget al., 2009). To improve the adhesive properties towards industrially acceptable products it is important to understand the effects of lignin properties on curing characteristics of the resin (El Mansouri and Salvado, 2006; Tejadoet al., 2007). It is commonly considered that relevant requirements seem to be a high amount of free phenolic hydroxyl groups with numerous free reactive ring positions, a high content of coumaryl (H-unit) and guaiacyl (G-unit) units and a molar mass which is low enough to keep the binder viscosity in the desired range but high enough to favour resin polymerization (Gosselink et al., 2010). However, still many questions remain unresolved. For example, most of the research results support the utilization of high molecular weight lignin fractions for the synthesis of modified PF-resins (Tejado et al., 2007; Lange et al., 1983). In contrast, Lei et al. (2008) found that in some cases low molecular mass lignins appeared to give better strength results of LPF-bonded particleboards. Experiments by El Mansouri et al. (2007) revealed that low molecular mass lignin showed better results than the higher molar mass lignin due to an increased proportion of reactive ring positions. In the present study two organosolv lignins with molecular weights between 2,100 and 4,100 g/mol were analyzed and utilized in resin syntheses in order to determine the effects of lignin molecular weight on the characteristics of lignin-phenol-formaldehyde resins. The lignins were compared to kraft lignin (Curan 100) and a high molecular weight lignosulfonate (LS). The introduction of hydroxymethyl groups is one of the most studied modification approach to improve the reactivity of lignins (Hu et al., 2011). Organosolv lignins were modified by methylolation to determine the influence of molecular weight on the reactivity of the lignins. The wood bonding effectiveness of the adhesive systems were analyzed in an Automated Bonding Evaluation System (ABES) and by particleboard testing. All resin formulations were compared to a pure PF resin.

2. EXPERIMENTAL

2.1. LIGNIN ISOLATION

The *kraft lignin (KL)* used was the commercially available product Curan 100 from Borregard LignoTech. The *lignosulfonate (LS)* used was recovered from bleachery waste water of the acid magnesium bisulphate process. The lignins were used without further purification. *Organosolv lignins (OL)* of different molecular weight were recovered after ethanol/water pulping of beech wood. The lignins (M_w 2,100 g/mol and 4,100 g/mol) originated from pulping performed at 170 °C for 90 min with 0.9 % H_2SO_4 (based on dry wood) for the low molecular weight lignin and 0.5 % H_2SO_4 (based on dry wood) for the high molecular weight lignin. The lignins were isolated after water-induced precipitation by filtration with Satorius Stedium filter discs (grade 1288, particle retention 12 – 15 µm).

2.2. LIGNIN CHARACTERIZATION

Methoxyl group content was determined according to the Vieböck and Schwappach method (Vieböck and Schwappach, 1930). Carbohydrate content, ash content and molar mass were determined as previously described (Ringena et al., 2006). For the determination of the glass transition temperature (T_g), 30 mg lignin was placed in an aluminum pan. The sample material was well densified to assure a good thermal transfer between sample and crucible. The measurements were carried out with a Mettler Toledo DSC 821^e system between 25 °C and 200 °C and a heating rate of 10 °C/min. *NMR spectroscopy* was performed in a Varian Mercury 400 MHz spectrometer. ^{31}P-NMR analysis was performed after phosphitylation with 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) accumulating 256 scans at 25 °C with a pulse angle of 45° and a relaxation delay of 20 s. Cholesterol was used as internal standard.

2.3. METHYLOLATION

80 g of each organosolv lignin was dissolved in 660 g distilled water and 20 g of a 30 % NaOH solution while heating to 60 °C. 36.8 g formaldehyde solution (37 %) was added and the mixture was continuously stirred by a magnetic stirrer at 60 °C for 8 hours. Methylolated lignins were directly used for resin formulation. The amount of formaldehyde and NaOH used for methylolation were taken into account to keep the molar ratios F/P and NaOH/P during resin synthesis constant. The high molecular weight lignin derivative was isolated by precipitation in dilute acetic acid (30 %). Due to the high solubility of low molecular weight lignin derivatives, precipitation procedures with stronger acids have to be investigated.

2.4. RESIN SYNTHESIS

The lignins were directly used as replacement for phenol during resin synthesis (LPF-resins). In all resins the phenol substitution level was 20 % (w/w). The PF and the LPF resins were synthesized with a formaldehyde to phenol molar ratio of 2 and sodium hydroxide to phenol molar ratio of 0.4. In general, the syntheses were continued until the viscosity reached 400 mPa·s - 500 mPa·s and then stopped by rapid cooling and by final addition of NaOH. Prior to application to wood, a hardener solution (K_2CO_3, 3 % solid content based on resin) was added.

2.5. ADHESIVE STRENGTH

The Automated Bonding Evaluation System (ABES) developed by Humphrey (1999) was used to test the bonding quality of the resins. Small lap-shear bonds pressed under controlled conditions of temperature and load were pulled after a range of curing times to determine the shear strength. The wood veneers (*Acer saccharum* Marsh.) were stored at 20 °C and 65 % relative humidity (RH). Average wood density was

625 kg/m^2. Specimens were prepared with a thickness of 0.6 mm (± 0.05 mm) and 20 mm by 117 mm. 11.2 µl of the adhesive was applied with an electronic pipette. The specimens were tested after bond-forming times ranging from 5 s to 420 s at 105 °C. Five replications were conducted for each data point.

2.6. PARTICLEBOARD MANUFACTURING

Commercial softwood core layer particles were provided by Rauch Holzwerkstoffe (Freudenberg am Main, Germany). The particles were prepared by screening with 5 mm mesh size and drying to about 2 % moisture content. The resins were diluted with additional water and hardener to achieve about 12 % moisture content of resinated particles. Blending took place in a rotary drum at atmospheric pressure. Resins were delivered by a pressurized air atomizing nozzle. Air and liquid pressure was set at 210 kPa and 70 kPa respectively. The resins were applied at 8 % solid content based on oven dry wood. The blended particles were dispersed by hand into a frame measuring 600 cm by 400 cm. The target density was 700 kg/m^3. The mats were hot-pressed at 220 °C for 240 seconds to obtain the final board thickness of 16 mm. The panels were conditioned at 20 °C and 65 % RH for 7 days before cutting and testing. Two panels were prepared for each type of resin.

2.7. PARTICLEBOARD TESTING

Particleboard testing included dry internal bond (dry IB, according to EN 319 (1993)), internal bond after two hours of boiling (wet IB, according to EN 1087-1 (1995)) and determination of the formaldehyde content (according to EN 120 (1992)). After conditioning, the panels were cut, in each case eight test specimens for dry IB and eight test specimens for wet IB. The test samples were weighed and measured for density determination. From each panel 110 g of particleboard were taken for formaldehyde analysis. For the determination of the formaldehyde value a correction factor was applied according to Jan and Deppe (1990).

3. RESULTS AND DISCUSSION

3.1. PROPERTIES OF LIGNINS

The purity of the organosolv lignins is very high (Table1). The ash content is at maximum 0.1 % and the carbohydrate impurities are on a low level between 0.99 % and 4.5 %. In contrast, kraft lignin (KL) and lignosulfonate (LS) show a significantly higher ash content of 5.8 % and 19.2 %, respectively. The lignins were further characterized by size exclusion chromatography (SEC), methoxyl group determination and thermal analysis. The kraft lignin shows high average molecular weight and polydispersity. The lignosulfonate shows the highest average molecular weight and a small polydispersity. The high molecular weight is probably due to condensation reactions during acid pulping conditions. Among the organosolv lignins, the low molecular weight lignin (OL_L) shows the lowest polydispersity, while the high molecular weight organosolv lignin (OL_H) exhibits a larger range of molecular weights. After methylolation of OL_H ($M\text{-}OL_H$) the molecular weight almost doubled from 4,100 to 8,100 g/mol while the polydispersity decreases slightly. The increase in molecular weight can probably be ascribed to condensation reactions of low molecular weight lignin fragments after attachment of formaldehyde via Lederer-Manasse- or Tollens-reaction to form methylol groups (Marton et al., 1966; Wooten et al., 1988).

Table 1. Molecular weight, dispersity and composition of kraft and organosolv lignins.

Lignin	M_w	D	OMe	Sulfur	CH[1]	Ash	T_g[2]	Pulping		
	(g/mol)	M_w/M_n	(%)	(%)	(%)	(%)	(°C)	T (°C)	t (min)	H_2SO_4 (%)
OL_L	2.100	2.3	23.4	0.09	0.99	0.1	143	170	90	0.9
OL_H	4.100	4.1	21.2	0.04	4.48	0.1	141	170	90	0.5
$M\text{-}OL_H$	8.100	3.7	22.0	0.03	n.d	0.1	113	170	90	0.5
KL	10.600	5.7	10.9	2.00	1.50	5.8	169	SW-Kraft pulping		
LS	57.000	3.0	7.8	2.94	0.34	19.2	n.d	HW/SW-Sulfite pulping		

[1] Carbohydrates (CH) [2] Glass transition temperature (T_g)

Surprisingly, the glass transition temperature (T_g) is not straightly correlated to the molecular weight. OL_L and OL_H differ considerably in terms of M_w, but show only slightly different glass transition temperatures of 143° C and 141 °C, respectively. The T_g may be affected by molecular side groups, branches or attractive forces between molecules. High molecular weight organosolv lignin shows slightly lower methoxyl content compared to OL_L which may be due to a lower number of syringyl units inherent to these lignins. Consequently, these products should be particularly suitable for cross-linking reactions in LPF-resins.

The T_g of the methylolated OL (M-OL_H) is surprisingly lower compared to the basic lignin although an increase in M_W is detectable. The derivatisation is probably linked to a reduction of intermolecular association between the lignin molecules. A similar effect can be observed after acetylation of lignins (Lisperguer et al. 2009).

In contrast, the main chains of kraft lignin seem to have higher rigidities as indicated by T_g of 169 °C.

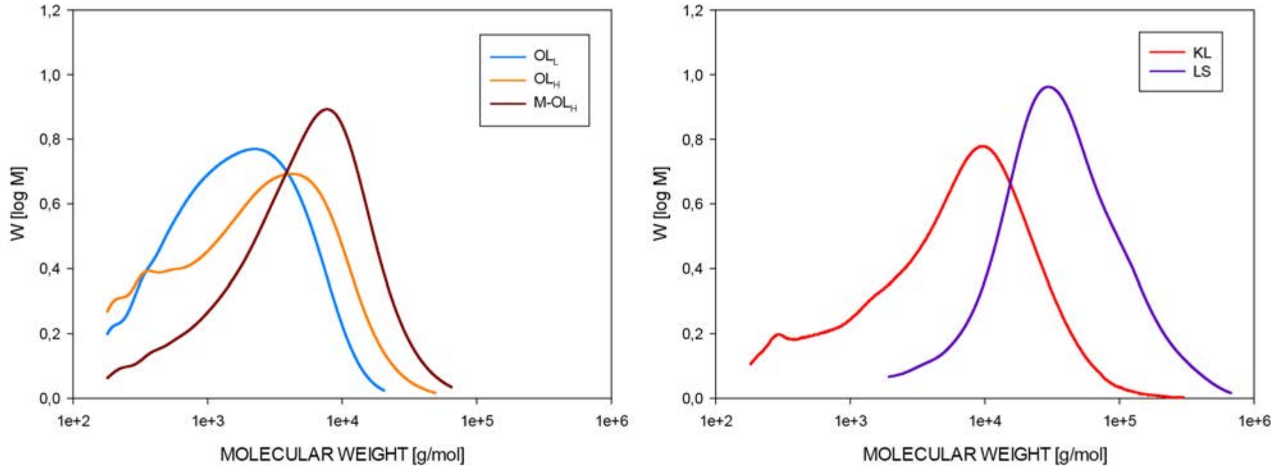

Figure 1: Molecular weight distribution of the analyzed lignins.

Figure 2 shows the ^{31}P NMR spectra of OL_H and of the methylolated version (M-OL_H). Peak assignment was done according to Granata and Argyropoulos (1995). The derivatisation leads to a decrease of the guaiacyl peak (δ = 138.3 ppm - 140.9 ppm). At the same time, the signals for the syringyl units (δ = 141.4 ppm - 144.2 ppm) and aliphatic hydroxyl groups (δ = 145.5 ppm - 149.5 ppm) increase. This effect indicates the successful methylolation. Due to methylolation, the signal at δ = 135.3 ppm - 140.9 ppm shifts lowfield and is overlapped by the signal for syringyl units. Argyropolous (1995) found similar results investigating the effect of Mannich reaction on ^{31}P NMR spectra of softwood kraft lignin.

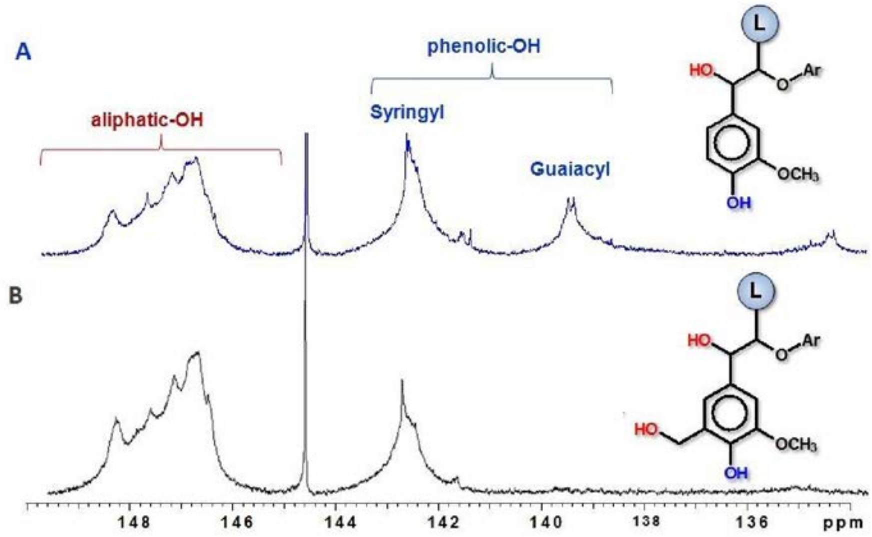

Figure 2: ^{31}P NMR spectra of high molecular weight organosolv lignin (A) and methylolated high molecular weight organosolv lignin (B).

The concentrations of the various functional groups in the lignins are shown in Figure 3. Calculation was done according to Argyropoulos et al. (2009). OL$_H$ is characterized by a high amount of aliphatic OH compared to aromatic OH (Figure 3). The derivatisation with formaldehyde leads to an increase of aliphatic OH due to the addition of methylol groups to the lignin molecule. The aromatic OH content of the OL-products increases with decreasing molecular weight. At the same time aliphatic group content of OL$_L$ is lower due to the more severe pulping conditions. The aromatic OH content in kraft lignin was substantially higher compared to organosolv lignins. All lignins contain a relatively low level of condensed hydroxyl groups with less than 0.5 mmol/g. ^{31}P NMR of lignosulfonate is more complex, due to its hydrophilicity.

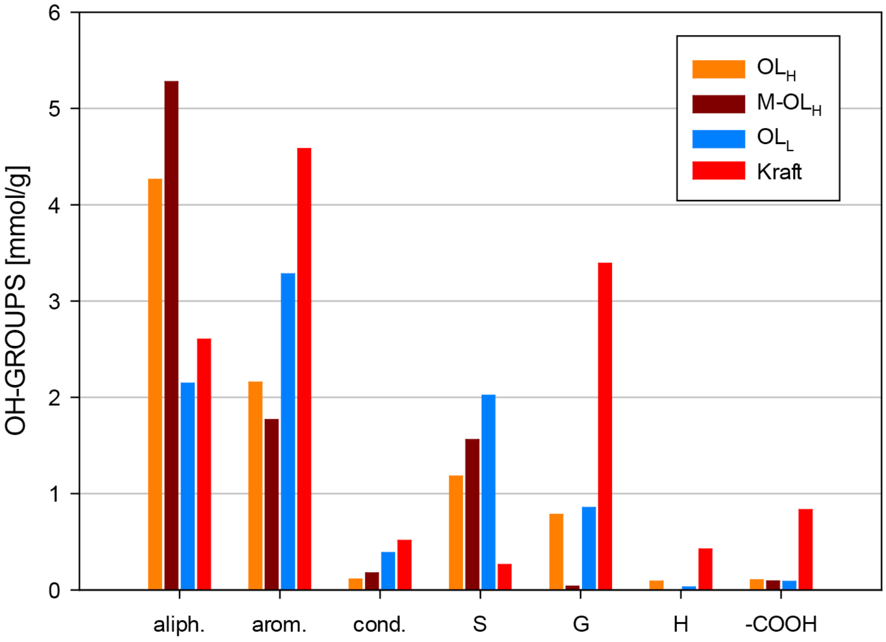

Figure 3: Hydroxyl groups of kraft and organosolv lignins calculated from ^{31}P NMR spectra.

3.2. PROPERTIES OF PF AND LPF-RESINS

For all resins phenol substitution level was 20 % (w/w). To promote the formation of crosslinking between lignin and the phenolic polymer the resins were formulated with the lignin fraction charged simultaneously with phenol and formaldehyde. Thus, a narrow viscosity range between 400 mPa·s and 560 mPa·s can be reached. It is evident that all LPF resins showed a longer gel time compared to the neat PF resin (Table 2). On the other hand, it is obvious that for unmodified organosolv lignins an increasing molecular weight caused a significant reduction of the gel time. While M-OL_H shows higher gel-time, gel-time of M-OL_L decreased from 33 minutes to roughly 27 minutes. Obviously, the methylolation of lignins with varying molecular weights influences the gelation behaviour of the resins in different ways. Both resins showed a slightly higher B-time. The low molecular weight lignin seems to be more suitable for chemical modification with formaldehyde.

All resins show very low levels of free formaldehyde content which is considered to be acceptable in industry.

Table 2: Composition and properties of PF and LPF resin formulations.

Resin	Solids	Viscosity	pH	NaOH	Gel-time	B-time	free HCHO
	[%]	[mPa·s]		[%]	[min:ss]	[min:ss]	[%]
PF	47.0	580	14	10.7	20:00	00:36	0.12
OL_H	44.2	522	14	9.4	24:30	01:03	0.18
M-OL_H	46.5	430	14	9.4	27:24	01:09	0.14
OL_L	46.8	400	14	10.2	33:00	01:01	0.10
M-OL_L	45.8	470	13.9	9.7	26:56	01:23	0.14
LS	46.7	466	13.8	10.2	37:00	00:56	0.15
KL	45.3	446	13.5	10.3	30:30	00:47	0.15

3.3. EVALUATION OF WOOD BONDING EFFECTIVENESS

To test the adhesive performance, shear strength measurements of bonded veneers were performed using the ABES-system. The shear strength development curves are shown in Figure 4. The development of the bonding rate is relatively well defined for all types of resins. The initial stage shows a rapid nearly linear increase of shear strength versus pressing time. Furthermore, a decreasing bonding rate is resumed which reached a typical maximum shear strength level for each resin. The PF standard shows a rapid initial increase of bond strength indicating a high reactivity. Compared to that, all LPF resins show a considerable slower gelation behavior. The final bond strengths reached after a pressing time of 420 s indicated differences in the bonding ability. High quality bonds were produced by the PF resin.

Among the organosolv lignins, high molecular weight lignin shows better performance. The strength development is faster and maximum shear strength is higher (3.0 N/mm^2) compared to low molecular weight lignin (2.7 N/mm^2). Methylolation of OL_H leads to a slight increase in maximum shear strength, but no difference in strength development speed. Although molecular weight increases during methylolation and more functional groups are incorporated, the effect on maximum shear strength is only marginal. However, methylolation of OL_L results in enhanced bonding effectiveness. M-OL_L is characterized by accelerated strength development and higher maximum shear strength, comparable to OL_H. These findings are consistent with the results from the resin characterization (Table 2).

Lignosulfonate shows the slowest strength development. This was not surprising, since this resin showed already the longest gel-time of all LPF-resins (Table 2). The final shear strength after 420 s pressing time is roughly on the same level compared to OL_L (2.6 N/mm²).

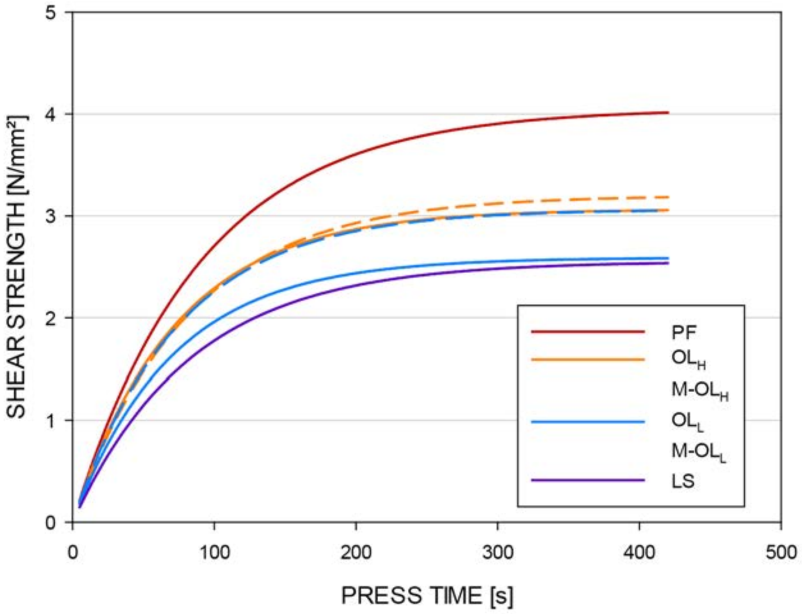

Figure 4. Shear strength development of different lignin/PF-resins determined by ABES (pressing temperature 105 °C).

3.4. PARTICLEBOARD QUALITY

Particleboard quality was characterized by dry internal bond, wet internal bond and formaldehyde content. The results for dry internal bond are summarized in Figure 5. The substitution of phenol by pure unmodified lignin leads to lower IB compared to the PF reference. The use of high molecular weight organosolv lignin results in particleboards with IB around 0.76 N/mm². So, these boards exceed the requirements of type P7 (requirements for heavy duty load-bearing boards for use in humid conditions) specified by the standard DIN EN 312:2010-12 (2010). Using organosolv lignin with low molecular weight, panels show 37 % lower IB (0.48 N/mm²). In conclusion, the molecular weight of lignin seems to have an influence on the dry mechanical properties of the particleboards. Methylolation of the organosolv lignins leads to a strong increase of the dry IB. In both cases, OL_H and OL_L, the chemical modification of the lignin results in better board performances, whereas the effect is stronger for low molecular weight OL. The IB rises to 1.21 N/mm² (M-OL_H) and 1.41 N/mm² (M-OL_L), respectively and exceed the performance of the PF-bonded particleboards. Using kraft lignin as substitute in LPF-resins, results for dry IB were slightly lower compared to OL_H. This is surprising since the kraft lignin shows more aromatic OH and hence is more suitable as a substitute for phenol in LPF resins (Figure 3). The results for the lignosulfonate were also unexpected. Although impurities of the lignin is quite high and gel time as well as ABES results indicate a less reactive lignosulfonate modified PF resin, particleboard bonded with this system show promising IB properties.

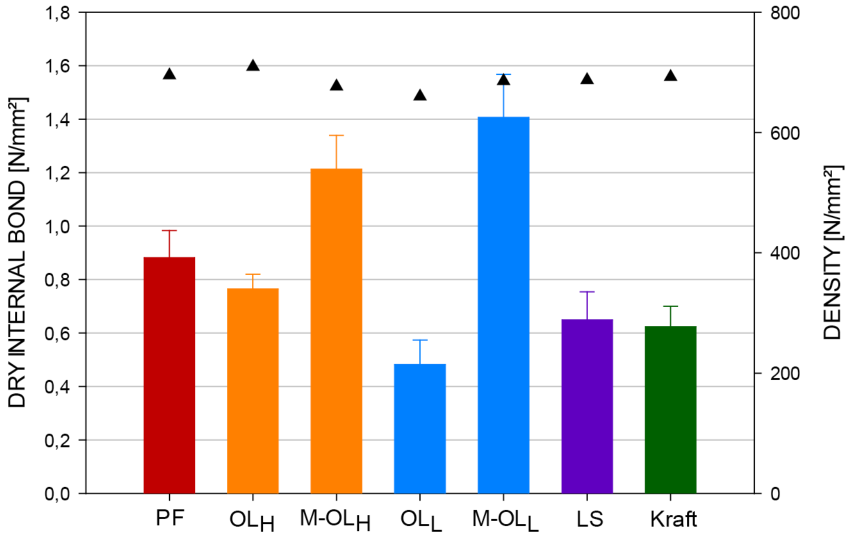

Figure 5: Effect of lignin type and methylolation on dry internal bond (--- requirements for particleboard type P7).

The wet internal bond is the most important characteristic for panels with application in humid conditions. As shown in Figure 6, an effect of molecular weight differences between OL_H and OL_L is difficult to ascertain. Both performances are on a similar level, 0.18 N/mm² (OL_H) and 0.17 N/mm² (OL_L), respectively. Methylolation leads only in the case of OL_L to better particleboard properties. The wet IB increases to 0.22 N/mm² and just misses the standard requirements of type P7. In case of OL_H, methylolation has no effect on the improvement of wet IB (M-OL_H = 0.18 N/mm²). Therefore, the increase in dry IB of M-OL_H cannot be ascribed to an improved incorporation of lignin into the phenol-formaldehyde network due to methylolation. Reasons for the high dry IB are not clear. ^{31}P NMR indicates an increase in the amount of aliphatic hydroxyl groups (Figure 3). Hence, it might be taken into account that secondary interactions, such as hydrogen bonding, results in an improved interaction between wood substrate and resin. In case of OL_L, methylolation leads to an improvement of the wet IB and an improved lignin-phenol-formaldehyde network can be assumed. But the great increase in dry IB has to be ascribed in parts again to other factors which have to be investigated in further studies. Resins prepared with kraft lignin and lignosulfonate showed good results for LPF-bonded particleboards. The performance of these boards were on a comparable level (≈ 0.21 N/mm²) and slightly lower as the methylolated OL_L.

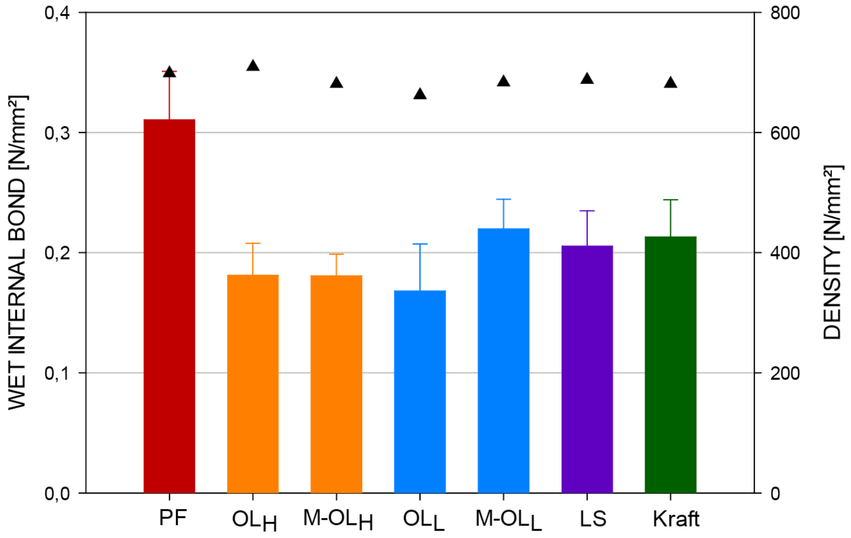

Figure 6: Effect of lignin type and methylolation on wet internal bond (--- requirements for particleboard type P7).

A crucial current topic is the emission from wood-based panels, especially formaldehyde. Therefore, the perforator values of all tested particleboards were determined by the perforator method. The results are shown in Figure 7. In general, phenol replacement by lignin leads not to an increase in formaldehyde content. The particleboards prepared with LPF-resins show very low perforator values, satisfying the standard requirements of the strictest emission class E1 (6.5 mg HCHO/100 g oven dry board).

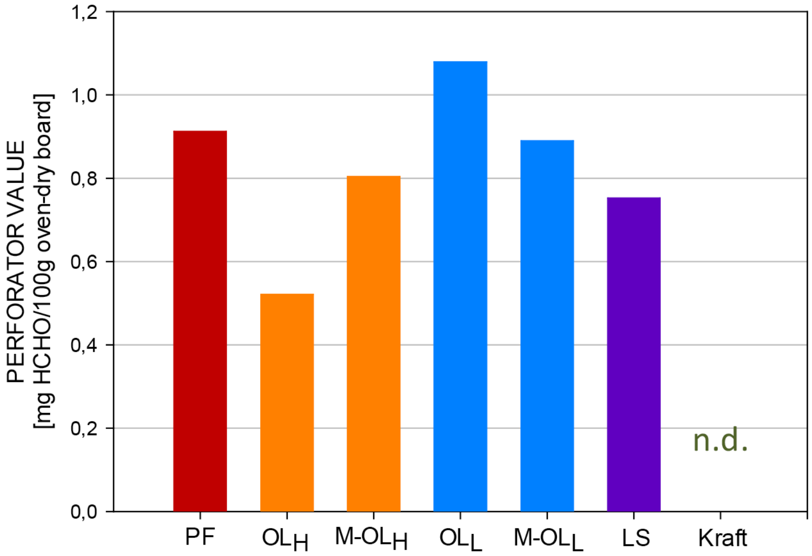

Figure 7: Formaldehyde content of the panels.

4. CONCLUSIONS

Characterization of hardwood organosolv lignins from ethanol-water pulping has been performed and compared to softwood Kraft and hard-/softwood lignosulfonate recovered from bleachery waste water. Lignosulfonate showed the highest molecular weight and the highest level of impurities. Kraft lignin showed also a high molecular weight and the highest level of free ring positions and phenolic OH groups compared to organosolv lignin. Methylolation of organosolv lignin leads to an increase in molecular weight. However, aliphatic OH groups increase, while aromatic OH groups decreases slightly. Lignin-based phenol formaldehyde resins revealed short gel time, if high molecular weight organosolv lignin is used. Methylolation of organosolv lignin led to a change in vitrification behavior. Evaluation of wood bonding effectiveness with ABES showed an inhibitory effect of lignin on resin cure. All LPF resins show lower reactivity compared to neat PF resin. Particleboard testing revealed that for organosolv lignin-based PF resins the high molecular weight lignin is more suitable to achieve good board performance. However, board results also show that methylolation of lignin is more effective if low molecular weight organosolv lignin was used. The perforator values of all particleboards were on a very low level satisfying the standard requirements of emission class E1.

5. ACKNOWLEDGEMENTS

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INTERNATIONAL STANDARDS FOR TESTING FORMALDEHYDE EMISSION IN WOOD-BASED PANELS

NUNO COSTA[1,2,3], JOÃO PEREIRA[1,2], JOÃO FERRA[3], PAULO CRUZ[3], JORGE MARTINS[1,4],
FERNÃO MAGALHÃES[1], ADÉLIO MENDES[1] AND LUÍSA CARVALHO[1,4,*]
[1]LEPAE – FACULDADE DE ENGENHARIA, UNIVERSIDADE DO PORTO – PORTO, PORTUGAL
[2]ASSOCIAÇÃO REDE DE COMPETÊNCIAS EM POLÍMEROS – PORTO, PORTUGAL
[3]EURORESINAS – INDÚSTRIAS QUÍMICAS, S.A. – SINES, PORTUGAL
[4]DEMAD – INSTITUTO POLITÉCNICO DE VISEU – VISEU, PORTUGAL
*CORRESPONDING AUTHOR: LHCARVALHO@DEMAD.ESTV.IPV.PT

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ABSTRACT

Formaldehyde is a common organic compound, with formula HCHO and is widely used as a raw-material in several industrial applications, including wood adhesives, such as urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF) and phenol-formaldehyde (PF) resins. Since the reclassification of formaldehyde as "carcinogenic to humans" by IARC (International Agency for Research on Cancer) in 2004, regulation authorities from several countries, as well as the market itself, were compelled to adopt new strategies to reduce formaldehyde emission from wood-based panels.

The evaluation and classification of formaldehyde emission from wood-based panels are not uniform all over the world. Europe, USA and Japan were pioneers in the development of testing techniques and on the establishment of their own standard methods for evaluation of formaldehyde emission, as well as in the development of classification standards according to emission limits from wood-based products.

There is no universal method and the existing methods have their own advantages and disadvantages. The different testing conditions affect the resulting data, so it is not possible to compare data from different testing methods. The existence of numerous determination and quantification standards and classes results in some misperception about which is the best method and how to relate the values between different methods.

In this paper, different methods of formaldehyde evaluation from wood-based panels are evaluated including testing conditions, equipment needed and time.

1. INTRODUCTION

Formaldehyde is a common organic compound, with formula HCHO. It is the simplest aldehyde, and at room temperature it is a colorless gas with a pungent odor and is also called methanal and methylaldehyde. In solution is called formalin or formol, while in solid state polymerize in the form of paraformaldehyde $(CH_2O)_n$ or trioxane $(CH_2O)_3$ (Morrison and Boyd, 1981). It is widely used in chemical industry as raw-material.

Formaldehyde is toxic by inhalation, ingestion and skin absorption (Blair et al., 1986), causing nasal and eye irritation at higher concentrations. The first considerations about indoor air quality and formaldehyde emissions happened in the end of 1970s, during the energetic crisis due to the building insulation. Building insulation leads to the reduction of air exchange between indoor and outdoor, leading to the accumulation of air pollutants in interior places. “Sick Building Syndrome” (SBS) and “Building Related Illness” (BRI) terminologies becomes usual since then (EPA, 1989).

Until recently, formaldehyde was classified by the *World Health Organization* (WHO) as “probably carcinogenic to humans” (Group 2A). In 2004, the *International Agency for Research on Cancer* (IARC), of WHO, recommended the reclassification to “carcinogenic to humans” (Group 1), being this recommendation finally published in 2006 (IARC, 2006). As a consequence, various authorities and institutions have been concerned about formaldehyde as an indoor priority pollutant and new regulations have emerged considering increasingly lower exposure limits. Within European Union, formaldehyde is currently classified as 3-R40 substance (“limited evidence of carcinogenic effect”), but the classification has been reviewed under the new regulation for chemicals *Registration, Evaluation, Authorization and Restrictions of Chemicals* (REACH). For this purpose, FormaCare (2010) (formaldehyde sector group of the European Chemical Industry Council) established a REACH taskforce to facilitate the creation of a consortium allowing European formaldehyde manufacturers to work together as a unified group for their REACH compliance activities.

Determination of formaldehyde emission in wood-based products can be performed by several methods and standards, which basically emerged in Europe, United States and Japan. Each method measures a slightly different emission characteristic and frequently produces results in different and non-interchangeable units, causing confusion among government regulators, consumers and industry personnel (Athanassiadou and Ohlmeyer, 2009). Furthermore, the formaldehyde emission values in 70s and 80s were substantially higher, being necessary to adapt and improve the existing methods for the current emission ranges. Lately, new test methods have been proposed in order to comply with the new requirements: higher accuracy, lower detection limits, faster and reliable.

Facing to the new guidelines and emission standards, wood panels manufacturers made a substantial effort to develop and provide products with low formaldehyde emission. Looking back, the release of formaldehyde from wood based panels has been decreased in the last decades (FormaCare, 2010).

According to Merchant Research & Consulting Ltd. (Anonymous, 2011), approximately 66% of the total demand on the global formaldehyde market is consumed in the production of wood adhesives, namely urea–, melamine- and phenol-formaldehyde resins. In 2008, according to SRI Consulting (Anonymous, 2009), formaldehyde based adhesives consumed around 63% of the world demand, showing that, despite the concern about formaldehyde issues, wood-based panels market does not intend to replace this type of adhesives. Nevertheless, the increase of formaldehyde market on wood-based panels market is only possible due to the development of new resins and formaldehyde scavengers, reducing formaldehyde emissions at levels close or even lower those of natural wood (Schafer and Roffael, 2000). On the other hand, due to the shortage of wood raw materials, wood-based panels producers have been forced to increase the incorporation of recycled wood, which seems to lead to an increase of formaldehyde emission (Martins et al., 2007), that might be due to the excess of free formaldehyde that was present in the past resins and remained in wood subtract.

Despite the concern about formaldehyde issues in the last years, there is a lack of information, as well as some controversy, about the different testing methods and product classification of wood-based panels according to the different international standard methods. In this paper it is discussed in detail the widely adopted methods for formaldehyde emission analysis: perforator, chamber and gas analysis method as well as the different product classes according to formaldehyde emission.

2. TESTING METHODS

Formaldehyde release from wood-based panels in service is caused, not only by residual formaldehyde trapped as gas in the structure of subtract, along with formaldehyde dissolved in water present in the interior of board (moisture), but is also essentially due to the hydrolysis (reversibility of reactions) of weaker formaldehyde bonds, namely methylol groups, acetals and hemiacetals, as well as methylene ether bridges (Dunky, 1998). Formaldehyde release is affected by internal and external factors. Internal factors include the type of wood and resin employed, operating conditions and parameters during panel pressing as well as panel age. External factors are related to the place in which panels are located, such as room temperature, air exchange rate, as well as the total panel area in relation to the total volume of the room (Athanassiadou and Ohlmeyer, 2009).

Test methods for determination of formaldehyde emission should take into account the factors listed above, in order to be reliable and give reproducible values. Existing methods can be divided into two main principles: measurable emission (really emitted amount of formaldehyde under the test conditions) and the emittable potential of formaldehyde in the panel (maximum emittable formaldehyde under conditioning at forceful conditions) (Dunky, 2004).

Table 1 summarizes the most important test methods and related standards for the determination of formaldehyde from wood-based panels.

Table 1: Test methods and standards for determination of formaldehyde from wood based panels (adapted from Athanassiadou and Ohlmeyer, 2009).

Test Method	Standard, Standard Draft or Method Name
Chamber	ASTM E 1333, ASTM D 6007, EN 717-1, JIS A 1901, JIS A 1911, ISO 12460-1, ISO 12460-2
Gas analysis	EN 717-2, ISO 12460-3
Flask method	EN 717-3, method AWPA
Desiccator	ASTM D 5582, ISO 12460-4, JIS A 1460, JAS MAFF 235, JAS 233, AS/NZS 4266-16
Perforator	EN 120, ISO 12460-5
Other	Field and Laboratory Emission Cell "FLEC", Dynamic Microchamber "DMC"

2.1. REAL EMISSION

2.1.1. CHAMBER METHOD

The quantification of the real formaldehyde emission of a product under typical indoor conditions in real-life and over defined time scales requires the use of a climate-controlled chamber. American standard ASTM E 1333 presents a large chamber that simulates the conditions of a typical living room with 22 m^3 (minimum size) at controlled temperature of (25 ± 1) ºC and relative humidity (RH) of (50 ± 4) %. ASTM D 6007 standard presents a smaller chamber (0.02 to 1 m^3) and the specimens remain in the operating chamber until a steady state formaldehyde concentration is reached. *Californian Air Resources Boards* (CARB) approved regulations that require the use of these chambers for the qualifying tests, increasing the importance of these methods. *International Organization for Standardization* (ISO) present as reference method the standard ISO 12460-1 (1 m^3) and a derived method (ISO 12460-2).

European Committee for Standardization (CEN) approved EN 717-1 as standard for chamber method, allowing three volume options: > 12 m^3, 1 m^3 and 225 L. Operating conditions are slightly different from the

American standard: temperature of (23 ± 1) ºC and RH of (45 ± 3) % and 1/hr. of air exchange rate (the double of the American standard), being the time analysis at least ten days. In Figure 1 is shown an apparatus of a chamber with 1 m^3.

Figure 1: Apparatus of a chamber method (EN 717-1), including the chamber and air source (left) and collecting system (right).

For production control, the board selected should immediately cut up after cooling and test pieces stored hermetically sealed at room temperature. The formaldehyde determination should be carried out not more than 72 hours after sampling. Formaldehyde concentration is determined by drawing air from the outlet of the chamber through two gas washing bottles containing water, which absorbs the formaldehyde (right side of Figure 1). Concentration of formaldehyde in the chamber atmosphere is calculated from the concentration in water in the gas washing bottles and the volume of the sampled air, expressed in [mg.m^3]. Sampling is periodically continued until the formaldehyde concentration in the chamber reaches the steady-state, which requires at least 10 days (EN 717-1). Each of the standards specifies a different method for determining when a steady-state condition is achieved. However, all accept a change in formaldehyde emission of less than 5 % over a given period as representing a quasi-steady-state condition. In addition, all the standards propose that the test is stopped after 28 days, even if the steady-state condition is not reached (Irle, 2011).

2.1.2. GAS ANALYSIS METHOD

Gas analysis (EN 717-2) is a derived test that determines formaldehyde release at accelerated conditions during 4 hours. In this method, a test piece with dimensions of 400 mm x 50 mm x board thickness with edge sealed is placed in a closed chamber at (60 ± 0.5) ºC with an air flow of (60 ± 3) L.hr^{-1}. with a RH below 3% under a overpressure of 1000 to 1200 Pa. Collecting system is similar to the apparatus used in the chamber method (EN 717-1), where formaldehyde released from test piece is continually drawn from the chamber and passes though gas washing bottles containing water. Formaldehyde is determined at hourly intervals, up to 4 hours. Every hour, air is automatically led into one of a series of pairs of washing bottles and at the end of each test, formaldehyde release is calculated from the formaldehyde concentration in water, the sampling time and exposed area of the test piece, expressed in [mg.m^{-2}.hr^{-1}]. Final value is computed considering the four individual results. Figure 2 shows an apparatus of a gas analysis method.

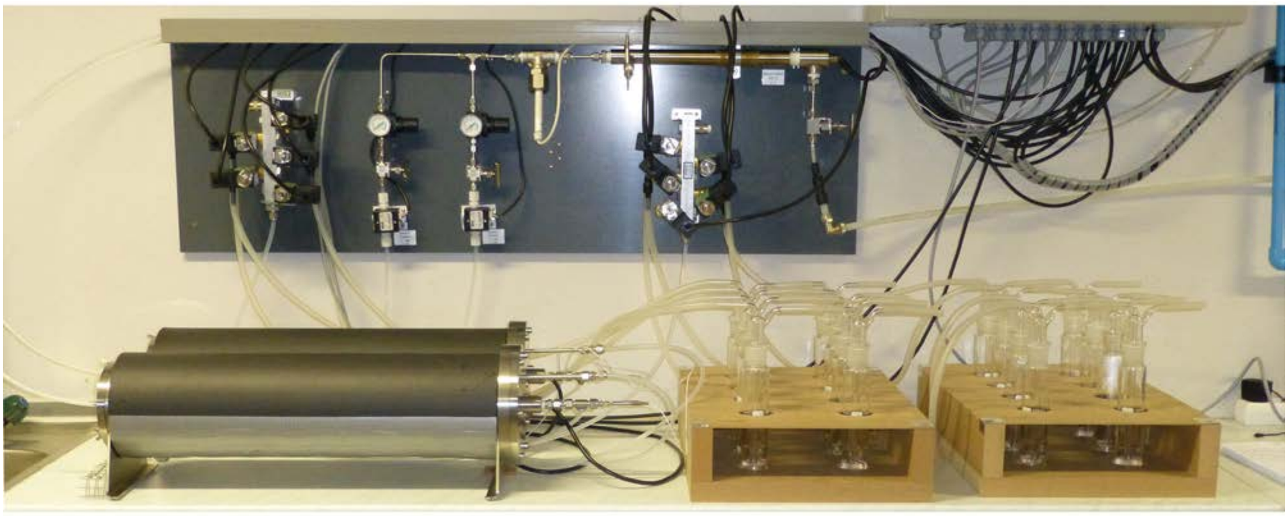

Figure 2: Apparatus of gas analysis method, according to the standard EN 717-2 (two closed chambers at left and corresponding collecting systems at right).

Despite a short time of analysis, gas analysis tests involve a high investment in equipment. EN 13986 standard indicates this method for faced and coated, overlaid or veneered wood-based panels.

2.1.3. DESICCATOR METHOD

Desiccator method is commonly used in Japan, and is defined in the Japanese standard JIS A 1460 and is one of the most economical methods. The test pieces are cut into rectangles of 150 mm x 50 mm and the number of testing pieces needed is dependent of their thickness (total surface area, including faces, sides and ends, should be the closest to 1800 cm^2). Testing samples are attached to a metal holder and placed on a stainless steel wire net above a crystallizing dish containing water. Time analysis is 24 hours at (20 ± 1) °C in a desiccator with 240 mm nominal diameter and the emitted formaldehyde is absorbed by the water in the crystallizing dish and emission results are expressed in [$mg.L^{-1}$].

The drawback of the desiccator method is the conditioning under defined conditions of temperature (20 ± 2) °C and RH (65 ± 5) % until reach a constant mass, which can take one week.

Figure 3: Apparatus of desiccator testing, according to JIS A 1460 (on left, an open desiccator with test pieces and an example of a test running, at right).

2.2. POTENTIAL EMISSION

2.2.1. PERFORATOR METHOD

Perforator method (EN 120) measures the formaldehyde content of wood-based panels that is possible to emit under forceful conditions.

While a test by chamber method may take several days until samples attain the formaldehyde equilibrium concentration, perforator method is a quicker and expeditious method, being indicated to a daily factory production control. This test is the most popular for measuring formaldehyde content in particleboard (PB) and medium density fiberboard (MDF) in Europe and worldwide, with less acceptance in North America.

Formaldehyde is extracted from test pieces (110 g of 25 x 25 mm testing samples) by boiling toluene during two hours, being formaldehyde collected in water by liquid-liquid (toluene-water) extraction in a perforator (glass equipment shown in Figure 4). Results are expressed in [mg/100 g oven dry board (o.d.b.)]. Perforator values for PB, Oriented Strand Board (OSB) and MDF shall be applied to moisture content of 6.5%, taken as reference, although moisture content between 3 and 9 % could be corrected by the Jann and Deppe (1990) equation that is based in the assumption that PB and MDF change their perforator values to the same extent regardless whether increasing or decreasing the moisture content in the reported range. However, this correction factor is contestable as it depends on other factors rather than the moisture content, such as molar ratio, chemical modification or any other added additives to resin (Roffael et al., 2010; Roffael and Johnsson, 2012). The accuracy of this method has been much discussed for values bellow 4 mg/100 g oven dry board.

The drawback of this method is the environmental impact of the toluene emission and residues.

Figure 4: Perforator equipment used in EN 120 (lower image shows the boiling of test samples in toluene, and upper image shows collecting of resulting formaldehyde dissolved in water.

3. QUANTIFICATION OF FORMALDEHYDE IN WATER SAMPLES

All the reported methods above adopted water to trap emitted formaldehyde due to the good ability of water to absorb formaldehyde. The formaldehyde retained in water is afterwards evaluated by analytical methods. The most used are the derivatization methods, being the acetylacetone and chromotropic acid methods generally adopted.

European methods for evaluation of formaldehyde emission adopted the photometrical method (by UV/Vis spectrometry) using the acetylacetone method. This method is based in the Hantzsch reaction which involves the cyclization of 2,4-pentadione, ammonium acetate and formaldehyde to form dihydropyridine 3,5 diacetyl-1,4-dihydrolutidine (DDL), which presents a maximum absorbance at 412 nm. The molecule also exhibits fluorescence and by means of it, it can be determined, using a fluorimetric spectrophotometer, at a wavelength of emission of 510 nm.

ASTM standards adopted the chromotropic acid method. In presence of concentrated sulfuric acid, chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) reacts with formaldehyde to give a red-violet hydroxydiphenylmethan derivative. In the second step of the reaction, a quinoid oxidation product is formed with atmospheric oxygen. The absorption maximum at 580 nm is used for UV/Vis detection (Salthammer et al., 2010).

4. EMISSION LIMITS FOR WOOD-BASED PANELS

Standards of formaldehyde testing methods usually do not mention any classification of wood based panels according to the results of formaldehyde emission or release. This classification is established in the specification standards of each product. The harmonized European standard EN 13986 (Wood-based panels for use in construction) classifies formaldehyde emission into two classes: E1 and E2 (see Table 2). Internal discussion within the European wood-based panel associations, lead EPF (European Panel Federation) to launch its own formaldehyde standards EPF-S, that corresponds to a perforator value below 4 mg/100 g oven dry board for PB and 5 mg/100 g oven dry board for MFD (thickness > 8 mm). Driven by IKEA (IOSMAT 0003), an equivalent class with half E1 formaldehyde emission limits was also introduced: the so-called E0 (or E0.5), despite it has not yet been recognized officially by CEN (Carvalho et al., 2012). Recently, the members of EPF agree to only produce E1 class.

In Japan, more strict limits are defined in standards JIS A 5908 and 5905, by descending order F**, F*** and F****. The F** is more or less equivalent to European E1 class, while the F*** and F*** are much lower, being the last one close to the emission of solid untreated wood, between 0.5 and 2.0 mg/100 g (Athanassiadou and Ohlmeyer, 2009).

Table 2: Overview of actual upper limits of formaldehyde emission (PB – Particleboard, MDF – Medium Density Fibreboard, PW – Plywood, OSB – Oriented Strand Board, LVL – Laminated Veneer Lumber) (adapted from Athanassiadou and Ohlmeyer (2009)).

Region	Standard	Test Method	Board Class	Board Type	Limit Value
Europe	EN 13986	ENV 717-1	E2	PB, OSB and MDF (unfaced)	> 0.124 mg.m^{-3} air
		EN120			$8 <$ mg/100 g o.d.b. ≤ 30
		ENV 717-1		PW, SWP and LVL (unfaced), PW, PB, OSB, MDF, LVL (and others) overlaid	< 0.124 mg.m^{-3} air
		EN 717-2			$3.5 <$ mg.m^{-2}.h^{-1}
		ENV 717-1	E1	PB, OSB and MDF (unfaced)	≤ 0.124 mg.m^{-3} air
		EN 120			≤ 8 mg/100 g o.d.b.
		ENV 717-1		PW, SWP and LVL (unfaced), PW, PB, OSB, MDF, LVL (and others) overlaid	≤ 0.124 mg.m^{-3} air
		EN 717-2			≤ 3.5 mg.m^{-2}.h^{-1}
Japan	JIS A 5908 & 5905	JIS A 1460	F**		≤ 1.5 mg.L^{-1}
			F***		≤ 0.5 mg.L^{-1}
			F****		≤ 0.3 mg.L^{-1}
USA	ANSI A208.1 & 2	ASTM E 1333		PB, MDF	≤ 0.3 ppm
				PW	≤ 0.2 ppm
	CARB	ASTM E 1333	Phase 1	PB	≤ 0.18 ppm
				MDF	≤ 0.21 ppm
			Phase 2	PB	≤ 0.09 ppm
				MDF	≤ 0.11 ppm

In the United States, ANSI A208.1 & 2 refer the limits of formaldehyde emission presented in Table 2. More recently, CARB established more stringent formaldehyde limits for wood-based panels, being nowadays as reference on wood-based panels market. Phase 1 limits are roughly equivalent to E1 (and F**) class while Phase 2 limits are similar to F***. CARB regulation states that, beyond the compliance of those emission limits, wood-based panels and finishing goods for sale or used in California must also be certified by CARB approved third party certification laboratory, unless they are approved Ultra Low Emission Formaldehyde (ULEF) or Na Added Formaldehyde (NAF) products. NAF and ULEF products must demonstrate a 90% or better compliance with a 0.04 ppm (ASTM E 1333) limit.

Different authors have attempted to establish correlations between formaldehyde testing methods (desiccator, perforator and chamber). Due to the different operating conditions used in each method, it is not possible to direct a relation, although it can be found approximate correlations in literature (Risholm-Sundman et al., 2007; Que and Furuno, 2007; Park et al., 2011; Costa et al., 2011; Pereira et al., 2012). In the very low region of emission, there is a poor correlation between corrected perforator values and the emission of boards (Roffael and Johnsson, 2012; Costa et al., 2012). In Table 3 it is presented a relationship between the limits of the different methods, some of them based on correlations.

Table 3: Relationship between different methods and standards limits
([a]Values obtained by correlation; adapted from Harmon (2008)).

Method	Japan		Europe	IKEA	USA	
	F***	F****	E1	E0.5	CARB P1	CARB P2
EN 120 [mg / 100 g o.d.b.]	≤ 4.5[a]	≤ 2.7[a]	≤ 8.0	≤ 4.0	≤ 11.3[a]	≤ 5.6[a]
EN 717-1 [$mg.m^{-3}$ air]	≤ 0.054[a]	≤ 0.034[a]	≤ 0.124	≤ 0.050	≤ 0.176[a]	≤ 0.088[a]
ASTM E 1333 [ppm]	≤ 0.055[a]	≤ 0.035[a]	≤ 0.127[a]	≤ 0.051[a]	≤ 0.180	≤ 0.090
JIS A 1460 [$mg.L^{-1}$]	≤ 0.5	≤ 0.3	≤ 0.9[a]	≤ 0.4[a]	≤ 1.3[a]	≤ 0.6[a]

5. NEW CHALLENGES ON WOOD-BASED PANEL EMISSIONS

Current regulations compelled wood-based panels industry to meet air emission standards. Until now, no limit values for the upper limit concentration of Volatile Organic Compounds (VOC) emitted from wood and wood-based panels have been taken under official regulation in Europe. This circumstance led to that the main efforts on emission reductions were centered only on formaldehyde issues. New synthesis protocols has been developed, as well as new scavengers were studied, allowing to reach formaldehyde emission from wood-based panels at the same as the solid wood level (Costa et al., 2012) without loss of board's mechanical properties. However, on VOC issues there is still the need for more studies on development of cost-effective scavengers to reduce VOC emission.

French regulation on VOC emission from construction products published on May 25th 2011 regards a mandatory labeling of construction products installed indoors, floor and wall coverings, paints and lacquers with their emission classes based on emission testing. Emission classes are C, B, A and A+, being the latest the one with lowest emission. This labeling includes a maximum for TVOC and for each of the organic compounds, namely formaldehyde, acetaldehyde, toluene, tetrachloroethylene, xylene, 1,2,4-trimethylbenzene, 1,4-dichlorobenzene, ethylbenzene, 2-butoxyethanol and styrene. Despite there is not any maximum emission limit, the lowest emission class (A+) is very restrictive and the major part of the existing wood based products actually on market does not fulfill these requirements.

6. CONCLUSIONS

There is no formaldehyde emission method that stands out, presenting all of them advantages and drawbacks. Chamber method is the closest to the in-use conditions and allows samples at higher dimensions, but presents longer time analysis and expensive equipment. Gas analysis is not time consuming and is easy to operate, but requires expensive equipment. Although desiccator method exhibits inexpensive equipment, trials last 24 hours, it requires a temperature controlled room and the need to previous conditioning that could take one week. Perforator method is the fastest and has the lowest implementation costs, despite the toluene residues and their lower accuracy for lower values.

The existence of many standards for testing and classifying of formaldehyde emission levels increases producers costs, forcing companies to obtain numerous certifications to operate on different markets, as well as it increases the complexity of the quality control procedures and could mislead the market.

The development of a universal test method and corresponding classification standard is imperative.

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DETERMINATION OF FORMALDEHYDE/ MELAMINE MOLAR RATIO IN AMINO RESINS BY NEAR-INFRARED SPECTROSCOPY

ANA HENRIQUES[1], NÁDIA T. PAIVA[1,2,3], NUNO COSTA[1,2,3], JOÃO M. FERRA[2], PAULO CRUZ[2], JORGE MARTINS[1,4], FERNÃO D. MAGALHÃES[1], LUÍSA CARVALHO[1,4,*]

[1] LEPAE, CHEMICAL ENGINEERING DEPARTMENT, FACULTY OF ENGINEERING, UNIVERSITY OF PORTO, RUA DR. ROBERTO FRIAS, 4200-465, PORTO, PORTUGAL
[2] EURORESINAS – INDÚSTRIAS QUÍMICAS, S.A., 7520-195 SINES, PORTUGAL
[3] ARCP – ASSOCIATION POLYMER COMPETENCE NETWORK, RUA DR. ROBERTO FRIAS, 4200-465 PORTO, PORTUGAL
[4] DEMAD – DEPARTMENT OF WOOD ENGINEERING, POLYTECHNIC INSTITUTE OF VISEU, CAMPUS POLITÉCNICO DE REPESES, 3504-510 VISEU, PORTUGAL

*CORRESPONDING AUTHOR: LHORA@FE.UP.PT

Keywords: Melamine-urea-formaldehyde resins, spectroscopy, chemometrics.

ABSTRACT

Melamine-urea-formaldehyde (MUF) resin production has increased in the last years motivated by the current concerns about the effects of formaldehyde on human health and to improve the physical properties of wood panels. Thereby, new processes for MUF synthesis have been developed. All such formulations are susceptible to possible operation error, which can significantly influence the characteristics of the final product. It is therefore crucial for industry to determine the formaldehyde/melamine (F/M) molar ratio of the product using near infrared (NIR) spectroscopy.The use of iPLS (interval Partial Least Squares) enabled to recognize the most interesting spectral ranges for analysis (4400-4800 cm^{-1}). Applying this method, it is possible to measure the error in the dosage of raw materials, determining in a more accurate and expedite method the F/M molar ratio in resins.

1. **INTRODUCTION**

Melamine-urea-formaldehyde (MUF) resin production has increased in the last years motivated by the current concerns about the effects of formaldehyde on human health since MUF resins are characterized by a low rate of formaldehyde emission (Tohmura et al., 2001) and to improve the physical properties of wood panels (Pizzi et al., 2003).

In industry, generally, the reaction control is based on indirect and inaccurate measurements of the synthesis progress, such as viscosity, pH, and water tolerance. Moreover, there is also the possibility of measurement errors in the dosage of raw materials. It is therefore important to implement more accurate and expedite methods for determining the formaldehyde/melamine (F/M) molar ratio of the synthesized product. In this way, the occurrences of higher rations than specified (which would penalize formaldehyde emissions) can be corrected.

The objective of our work was to develop a calibration method for determine the F/M molar ratio, based on measurement of FT-NIR spectra acquired by an optical fibre. Recently, the capabilities of FT-NIR spectroscopy have been exploited in several industries including: pharmaceutical (Ciurczak, 1987), biomedical (Ellis et al., 2006), petrochemical (Macho et al., 2002), (Paradkar et al., 2002) and polymer synthesis (Minopoulou et al., 2003).

In the particular case of UF resin synthesis, NIR spectroscopy has been used for the analysis of intermediates and to check the conformity of raw materials (Dessipri et al., 2003). Kasprzyk and co-workers (Kasprzyk et al., 2001) used the technique for qualitative and quantitative analysis of liquid MUF resins, particularly for the determination of melamine content.

Generally, NIR spectroscopy is used in combination with multivariate techniques, such as principal components analysis (PCA) and principal least-squares regression (PLSR) methods (Rodriguez-Saona et al., 2001).

To improve the capabilities of PLS modeling, a technique called iPLS (interval least squares regression), in which data are subdivided into nonoverlapping sections. Cross-validation is performed for each of these models and the interval which provides the lowest model root-mean-square error of cross-validation (RMSECV) is selected (Xiaobo et al., 2010).

In NIR, it is important to take into account not only the selection of the frequency window, but also of the preprocessing method, since they can minimize the influence of several factors such as background noise, baseline drift and light-scattering (Pizarro et al., 2004).

The main objective of this study was to develop a method to determine formaldehyde/melamine molar ratios in MUF resins.

2. **MATERIALS AND METHODS**

2.1. LABORATORY RESIN SYNTHESIS

All resins were produced in a 2.5 L round bottom flask, equipped with thermometer, mechanical stirrer and condenser. The temperature was controlled manually using a heating mantle. The pH was measured off-line using a pH meter. MUF resins were produced using the so-called single-stage process described in literature (Kamoun et al., 2000, Hse et al., 2008, Tohmura et al., 2001).

Solid urea is added manually at constant flow rate to an alkaline environment formaldehyde solution, promoting a methylolation reaction.

To initiate the reaction, the mixture was heated and maintained at 80 - 90 °C. At 30 minutes reaction time, melamine was added (16, 14 and 10 %) and the polymer was condensed until the desired viscosity (~500 cP).

In the third stage the pH was adjusted to a slightly basic value. The final amount of urea added should be sufficient for the formaldehyde/urea molar ratio to reach values of 2.0 to 1.5 at the end of this step.

A total of 216 lab-synthesized resin samples were used for calibration. 162 lab-synthesized resins were used for test validation.

2.2. FT-NIR ANALYSIS

NIR transmission spectra were collected on a Bruker (www.bruker.de) Zaffiro FT-NIR process-spectrometer with a TE-InGaAs detector and spectral range between 12,000 and 4,000 cm^{-1}. Spectra for each resin were collected with a spectral resolution of 8 cm^{-1} in triplicate at a zero filling factor of 2, each representing an average of 32 scans.

The reference spectrum was acquired in air, to prevent any impurities on the surface of the probe.

2.3. CHEMOMETRICS

The spectral manipulations were performed using OPUS quant 2 software package by Bruker.

To develop the statistical model, the influence of various regions was analyzed using iPLS with 20 intervals, where the error estimation parameter adopted was the root mean square error of cross validation (RMSECV):

$$\boldsymbol{RMSECV} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n}} \tag{1}$$

In RMSECV, y_i is the actual value of F/M, is the PLS predicted value, and n is the total number of test samples (Li et al., 2006).

The standard error of prediction (SEP) and the standard error of calibration (SEC) were adopted as error estimation parameters for both calibration and validation procedures (Czarnik-Matusewicz et al., 2006):

$$\mathbf{SEP} = \left\{\sum_{i=1}^{n_m} (m_i - \hat{m}_i)^2/n_m\right\}^{1/2} \tag{2}$$

$$\mathbf{SEC} = \left\{\sum_{i=1}^{n_t} (t_i - \hat{t}_i)^2/(n_t - h - 1)\right\}^{1/2} \tag{3}$$

In SEP, is the reference value of molar ratio F/U, is the PLS predicted value, and is the total number of test samples. In SEC, is the reference molar ratio F/U, is the predicted PLS value, is the total number of training samples, and h is the number of PLS factors (ranging from 1 to 10).

The quality of calibration is usually determined by the accuracy in the prediition of new unknown samples (Czarnik-Matusewicz and Pilorz, 2006).

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF FT-NIR SPECTRA

Figure 1 represents the iPLS model using the calibration samples. The interval with the lowest RMSECV is obtained for wavenumbers between 4400 and 4800 cm^{-1} (darker grey bar in the Figure 1).

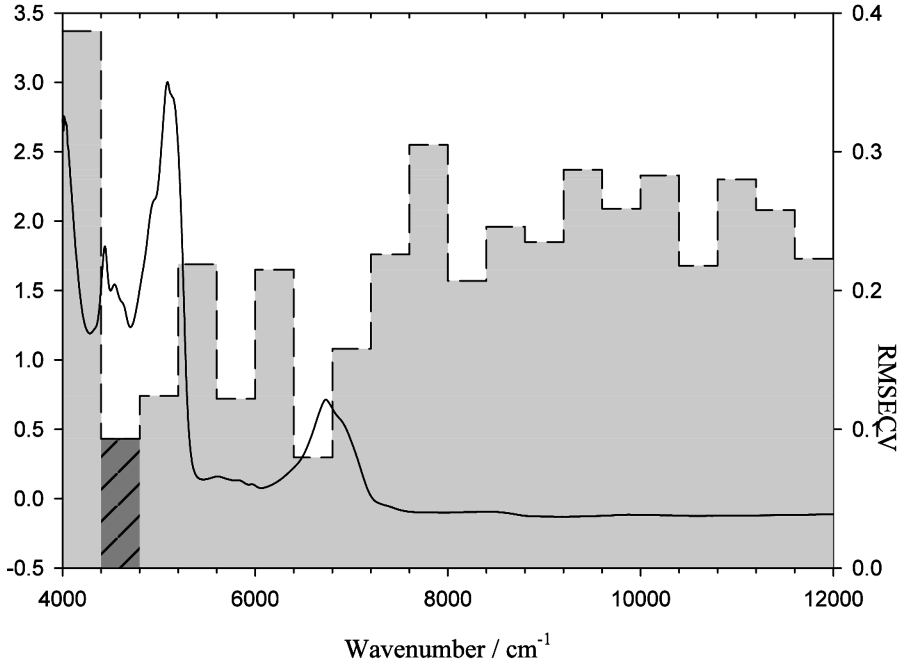

Figure 1: Average NIR spectrum of MUF resin (line) and RMSECV values for iPLS model on 20 wavenumber intervals (bars).

To increase the amount of information available to the model, an additional test was done. This test consists in combining the range of 4,400-4,800 cm^{-1} with other ranges available. The results are shown in Figure 2. The model that combines the intervals 4,400-4,800 and 6,800-7,200 cm^{-1} (darker grey bar in Figure 2) gave a RMSECV value slightly lower than the one obtained before considering only the 4,400-4,800 cm^{-1} interval.

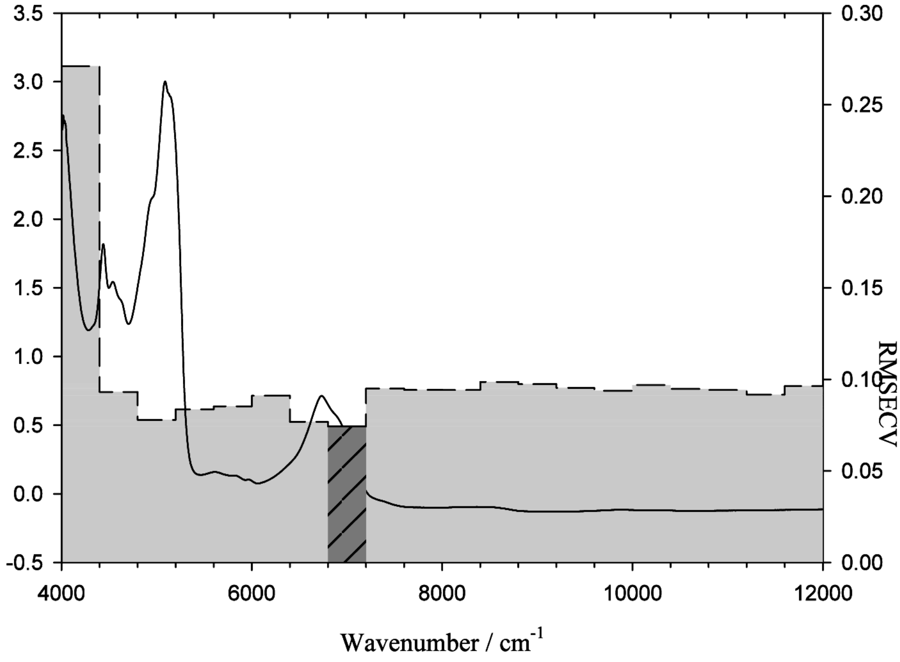

Figure 2: Average NIR spectrum of MUF resin (line) and RMSECV values for iPLS model on 20 wavenumber intervals (bars).

However, these regions include the peaks associated to the presence of water (Eddy et al., 2001), so only the wavenumbers between 4,400 and 4,800 cm^{-1} will be used. This region, as described by Kasprzy et al. (2001), is associated with vibration bands from starch and amino groups, vibrations from methylol hydroxyl groups and CH vibration bands.

The possibility of using different preprocessing's was also studied. Table 1 shows the statistical parameters of all preprocessing methods for the wavenumbers between 4,400 and 4,800 cm^{-1}. The R^2_{cal} and R^2_{val} correlation values were used to quantify the predictability of each method (Büning-Pfaue, 2003). The general goal was to obtain low values of standard error of calibration (SEC) and standard error of prediction (SEP) and high values of R^2_{cal} and R^2_{val} (Conzen, 2006). The results indicate that the model developed using the first derivative as preprocessing yields the lowest values of SEP and SEC and the highest values of R^2_{cal} and R^2_{val}.

Table 1: Summary of PLS –R model results.

Preprocessing method	**Calibration**		**Validation**	
	R^2	**SEC**	**R^2**	**SEP**
No spectral preprocessing	97.77	0.0931	95.94	0.255
Constant offset elimination	97.60	0.0968	95.23	0.276
Straight line subtraction	97.57	0.0972	96.66	0.231
Vector normalization	96.78	0.112	90.27	0.395
Min-max normalization	96.95	0.109	90.67	0.386
Multiplicative scattering correction	96.80	0.112	92.13	0.355
Internal standard	97.73	0.094	96.67	0.231
First derivative	**98.24**	**0.0828**	**98.64**	**0.147**
Second derivative	97.17	0.105	97.78	0.189
First derivative + Straight line subtraction	97.18	0.105	97.36	0.206
First derivative + Vector normalization	96.75	0.112	95.16	0.278
First derivative+ Multiplicative scattering correction	97.05	0.107	94.98	0.284

4. CONCLUSION

For the selected property (F/M molar ratio), spectral region 4,400-4,800 cm^{-1} was identified by iPLS as providing the best results for implementation of calibration methods.

For the spectral region, different preprocessing methods were tested, resulting in different calibration models. Some methods gave high correlation values, validating their applicability.

Once an appropriate model is developed and validated, the NIR technique may lead to a fast and accurate tool for F/M molar ratio process control in industrially synthesized MUF resins.

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STUDY OF THE CURE OF AMINORESINS WITH VERY LOW FORMALDEHYDE EMISSIONS

NÁDIA T. PAIVA[1,2,3], JOÃO FERRA[3], PAULO CRUZ[3], JORGE MARTINS[1,4],
FERNÃO MAGALHÃES[1] AND LUÍSA CARVALHO[1,4,*]
[1]LABORATORY OF PROCESS, ENVIRONMENTAL AND ENERGY ENGINEERING (FEUP), PORTO, PORTUGAL
[2]ASSOCIATION NETWORK FOR COMPETENCE IN POLYMER, PORTO, PORTUGAL
[3]EUROESINAS – INDUSTRIAS QUÍMICAS, S.A., PORTUGAL
[4]DEPARTMENT OF WOOD ENGINEERING, POLYTECHNIC OF VISEU, VISEU, PORTUGAL

*CORRESPONDING AUTHOR: TEL: +351 232 480565; FAX: +351 232 424651; LHCARVALHO@DEMAD.ESTV.IPV.PT

Keywords: MUF resins, hardener, ABES, curing time.

ABSTRACT

The main objective of this work was to study the influence of temperature and hardener on melamine-urea-formaldehyde (MUF) resin curing as well as the development of a mathematical model to describe the adhesive bond strength. The effect of two different compounds as resin hardeners (ammonium sulphate and ammonium bisulphite) was assessed, as well as the possibility of using ABES equipment for the resin gel time determination. The results of the curing studies of MUF resin with low formaldehyde emissions performed with ABES technique are presented. Comparing the two hardeners in study it is possible to say that despite the fact that ammonium bisulphite is essentially a formaldehyde scavenger, this compound can also to be used as hardener for this type of resins. Between the two hardeners used in this study, the results are very similar, but the best gel time results are obtained for the ammonium sulphate. A comparison between the results for the resin gel time obtained using ABES and conventional methods is also presented which allowed to conclude that ABES can be used as gel time determination equipment for MUF resins.

1. INTRODUCTION

Aminoresins are the most widely used adhesives for wood-based panels (WBP). These are thermosetting polymers that, before curing, are made of an aqueous solution/dispersion of unreacted monomers, linear or branched oligomeric and polymeric molecules (Dunky, 1998). They are obtained by condensation of aldehydes with compounds containing amino groups and their commercial success is mostly due to high reactivity, good performance and low cost. However, hydrolytic degradation of covalent bonds in the cured resin causes a significant weakening of mechanical strength and is a source of formaldehyde emissions. The main strategy to reduce the formaldehyde emission of aminoresins has been the change on its formulation by decreasing the molar ratio of formaldehyde to urea. However the reduction weakens the mechanical properties of particleboard and moreover it increases the time required for hardening under the action of current hardeners (latent acids) (Pizzi and Mittal, 2003). Hence, it is necessary to optimize the synthesis of urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF) resins, by changing their synthesis process. There are, in the literature, several possibilities to optimize the UF/MUF resins production described by several researchers. New processes for the synthesis of these resins have been studied and developed in order to produce resin with better physico-mechanical properties and lower formaldehyde emissions (Williams, 1983; Paiva et al., 2012). These can be summarized into two main classes: the strongly acid and the alkaline-acid processes. The details of these processes pathways have been described elsewhere by Ferra et al. (2012). The understanding of adhesive curing behaviour and its dependence on temperature and chemical conversion is an important starting point for the establishment of new ways for the board production and prediction of the properties of cured bondlines (Ferra et al., 2011). So, one of the most important aspects is the study of the resin gel time, which influences the pressing time and hence the productivity.

In industry, the methods used for determining resin gel time are not representative of reality, since they are very inaccurate and operator-sensitive. Other advanced characterization equipment, such as Differential Scanning Calorimetry (DSC) allows the identification of the onset temperature, curing rate, heat of reaction and kinetic parameters. However, it does not assess the strength of bonds formed within the resin, neither its interaction with wood. While DSC monitors the "chemical cure", ABES (Automatic Bonding Evaluation System) (Costa et al., 2012), TMA (Thermo Mechanical Analysis) and DMTA (Dynamic Mechanical Thermal Analysis) allow for the evaluation of the bonding strength development (Dunky, 2001).

ABES equipment, developed by Philip Humphrey (Humphrey, 1993), was designed to allow studying the dynamic cure process in wood-based panels production. This technique enables the characterization of different catalysts, adhesives and their affinity for wood, as well as the effects of the different cure temperatures and pressing times on bond shear strength. This equipment can be used with different supports such as wood, paper or cork (Martins et al., 2012; Ferra et al., 2012). For all the ABES analysis the most important parameters to take into account are the platen temperatures, resin spread rate and pressing time. The maximum force required to cause the failure of the system (adhesive + support) is measured. For different times it is possible to measure the adhesive shear strength and then the characteristic curve of the resin can be obtained for different temperatures plotting the shear strength as a function of time.

In this work, two different chemicals, ammonium sulphate and ammonium bisulphite, are used for the resin cure and tested with ABES equipment. In order to simplify the analysis a mathematical model was developed and fitted to all the experimental data. This model allows the characterization of the performance of new hardeners.

2. MATERIALS AND METHODS

2.1. RESIN PREPARATION

Resins were synthesized according to the so-called alkaline-acid process, which consists of three steps: a methylolation step at alkaline conditions, a condensation step at acidic conditions, and an addition of the so-called final urea (Ferra, 2012).

2.2. RESIN PROPERTIES DETERMINATION

Resin gel time was determined by measuring the reactivity of the resin sample at 100 ºC, after addition of curing catalyst. (20 ºC, 65% RH)

2.3. ABES ANALYSIS

Beech veneers were previously conditioned at given relative humidity (RH) and temperature conditions (20 ºC, 65% RH), in order to stabilize them and attain equilibrium moisture content (EMC) between 8 and 11 % (dry basis). Subsequently, the veneers were cut into strips using a pneumatically driven precision sample-cutting device supplied by Adhesive Evaluation System Inc (Corvallis, Oregon). Each veneer strip had 0.5 mm thickness, 20 mm wide and 117 mm in length, stored at 20 ºC and 65 % RH. Adherent pairs were mounted in the system (Figure 1) with an overlapping area of 100 mm^2 (20 x 5 mm). The amount of adhesive system used for each test was 15 µL. Three different temperatures (85, 95 and 105 ºC) were considered with press times between 25 and 400 seconds. For each temperature it was possible to obtain the characteristic curve by plotting the shear strength in function of time.

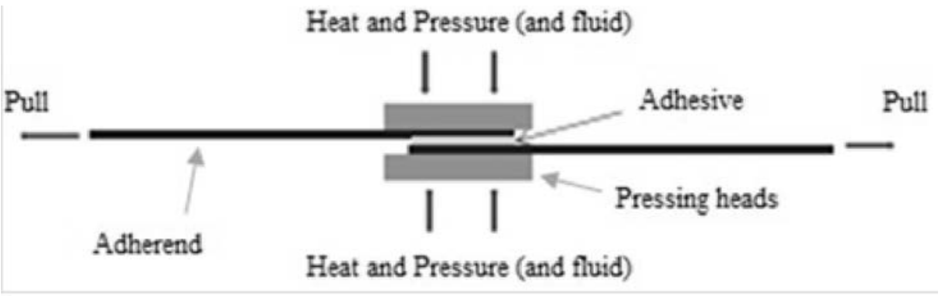

Figure 1: Conceptual representation of the bond forming and test geometry (adapted from Humphrey, 2009).

3. RESULTS AND DISCUSSION

In this study, a MUF resin with low formaldehyde emissions was used to test two different hardeners for UF/MUF resins: ammonium sulphate and ammonium bisulphite. Ammonium sulphate, which is a latent hardener usually used in the adhesive preparation for the board production, reacts with formaldehyde forming sulphuric acid promoting an acidic environment, essential for the cure reaction (Equation 1) (Dunky, 2001). On the other hand, ammonium bisulphite, which is usually used as a formaldehyde scavenger, dissociates in to ammonium and sulphite ions (Equation 2). The sulphite ion will react with sodium ion, decreasing the pH of the solution creating an acidic environment crucial for resin cure (Equation 3).

$$2(NH_4)_2SO_4 + 6HCOH \leftrightarrow 2H_2SO_4 + 6H_2O + (CH_2)_6N_4 \qquad (1$$

$$(NH_4)\,HSO_3 \leftrightarrow NH_4^+ + HSO_3^- \qquad (2$$

$$HSO_3^- + Na^+ + HCOH \leftrightarrow NaSO_3HCH_2 \qquad (3$$

To determine the ideal amount of hardener used in resin cure, gel time tests were carried out using hardener dosages between 1 and 6 % (Figure 2). The expected gel time values of this type of resins with low formaldehyde emission are usually between 75 and 90 seconds. Taking into account that increasing the amount of hardener used results in an increased production cost of wood-based panels, it was established that the amount of hardener to be used, in the ABES analysis, would be 3%. Therefore, for all the ABES tests, the following conditions were used: 3 % of hardener, glue joint area of 100 mm^2, pressing time between 25 and 400 seconds and test temperature between 85 and 105 °C.

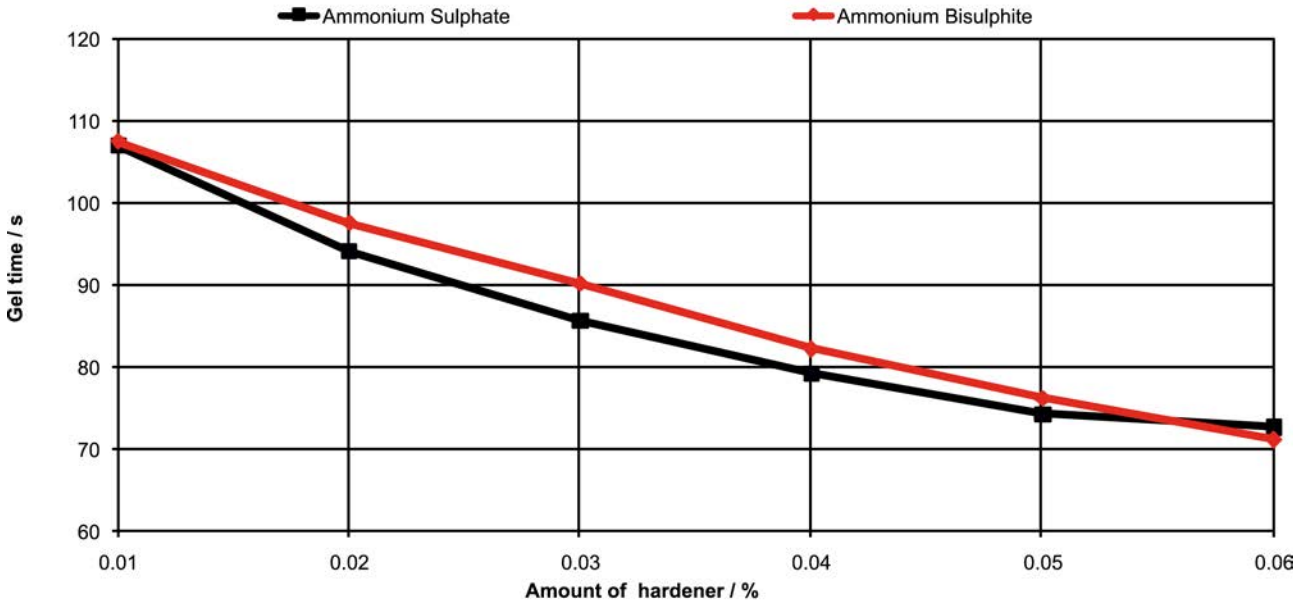

Figure 2. Gel time variation with the amount of hardener.

Figures 3 and 4 show the results obtained with ABES for the different hardeners at different temperatures. In the horizontal axis it is represented the curing time, while in the vertical axis it is represented the shear strength of the glue joint after curing.

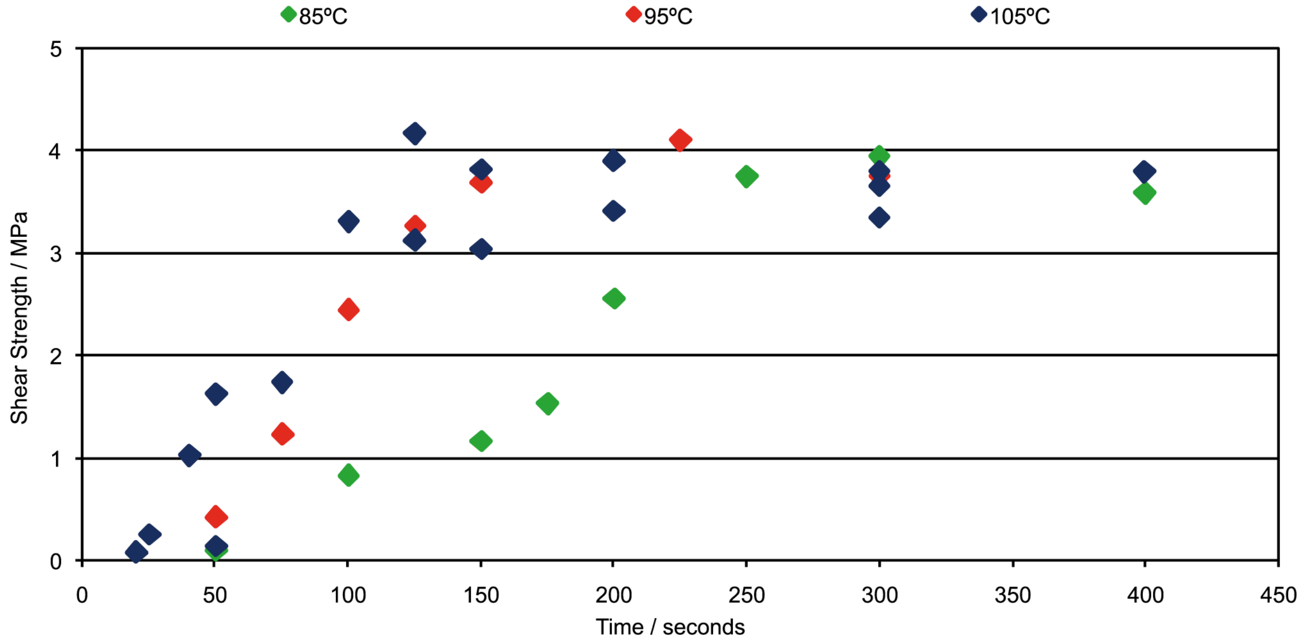

Figure 3: Experimental data obtained in the ABES tests with ammonium sulphate to different temperatures.

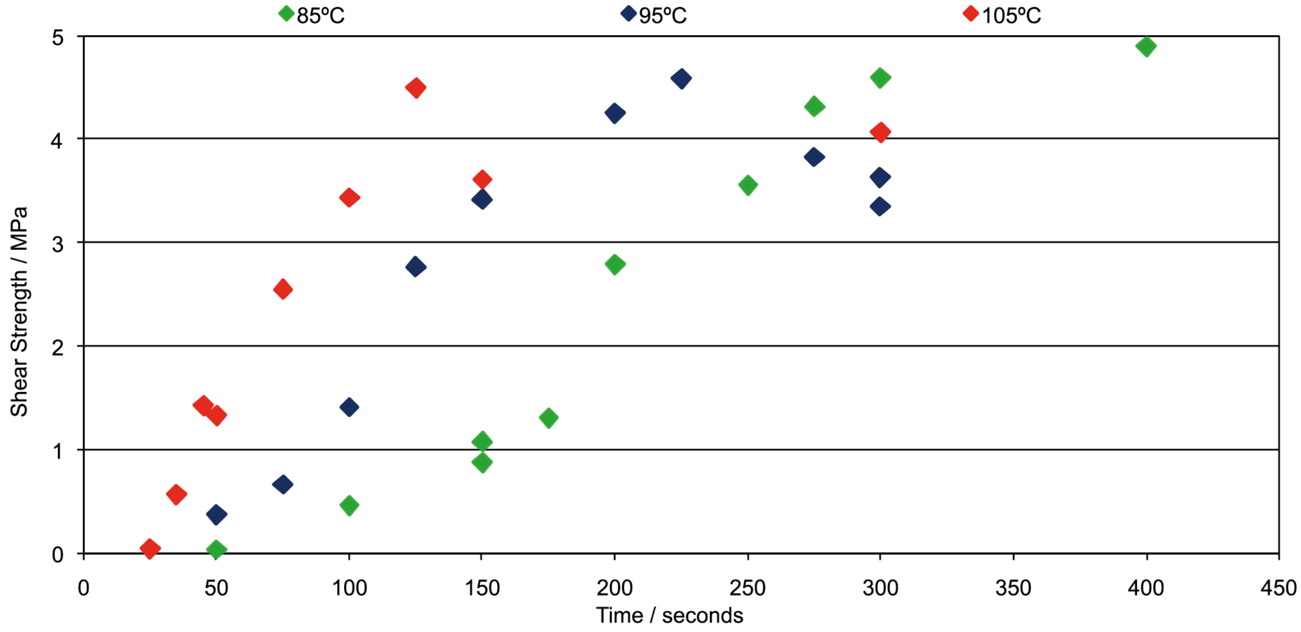

Figure 4: Experimental data obtained in the ABES tests with ammonium bisulphite to different temperatures.

From these figures it is possible to identify two distinct phases in the experimental results. Initially, resin cure progresses leading to an increase in shear strength along the pressing time. In a second phase, the shear strength value stabilizes at values close to 4 or 5 MPa. For higher pressing times there is a decrease in the maximum shear strength, which can be associated to thermal degradation of the glue joint and/or degradation of wood itself.

In order to describe the experimental data, a mathematical model relating shear strength, **τ**, with pressing time, *t*, was developed based on a function of three parameters as shown in Equation 4.

$$? = \frac{?_{\text{máx}}}{1 + \mathrm{A}}\left[\mathrm{A} + \tanh\left(\frac{t - t_0}{?}\right)\right] \quad \text{in which} \quad \mathrm{A} = \tanh\left(\frac{t_0}{?}\right) \qquad (4$$

The three model parameters are: $\tau_{máx}$ (maximum shear strength), to (resin gel time) and λ (model time constant). These three model variables aim at describing the phenomena involved during the adhesive curing reaction. In this equation *t* is the test time and τ is the shear strength obtained at a given time.

Figures 5 and 6 show the model fitting to the experimental data obtained in the ABES tests with both hardeners. The maximum shear strength is higher for the tests made with ammonium bisulphite, which values are around 4.5 MPa (near to 5 MPa for 85 ºC). On the other hand for the test made with ammonium sulphate, the maximum shear strength is around 4 MPa for the temperatures tested. Ammonium sulphate shows a higher curing rate when compared with ammonium bisulphite, for the same temperature, except for 85 ºC where the cure is faster using ammonium bisulphite as hardener.

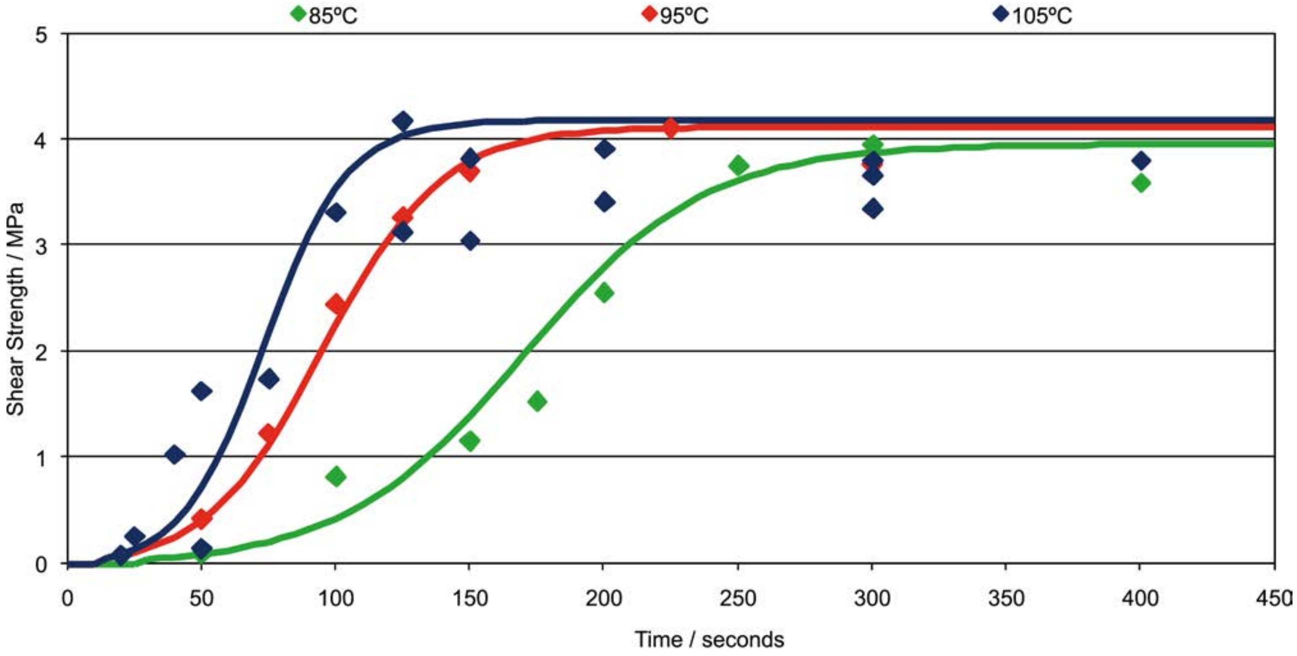

Figure 5: Model fitting to the experimental data obtained in the ABES tests with ammonium sulphate for different temperatures.

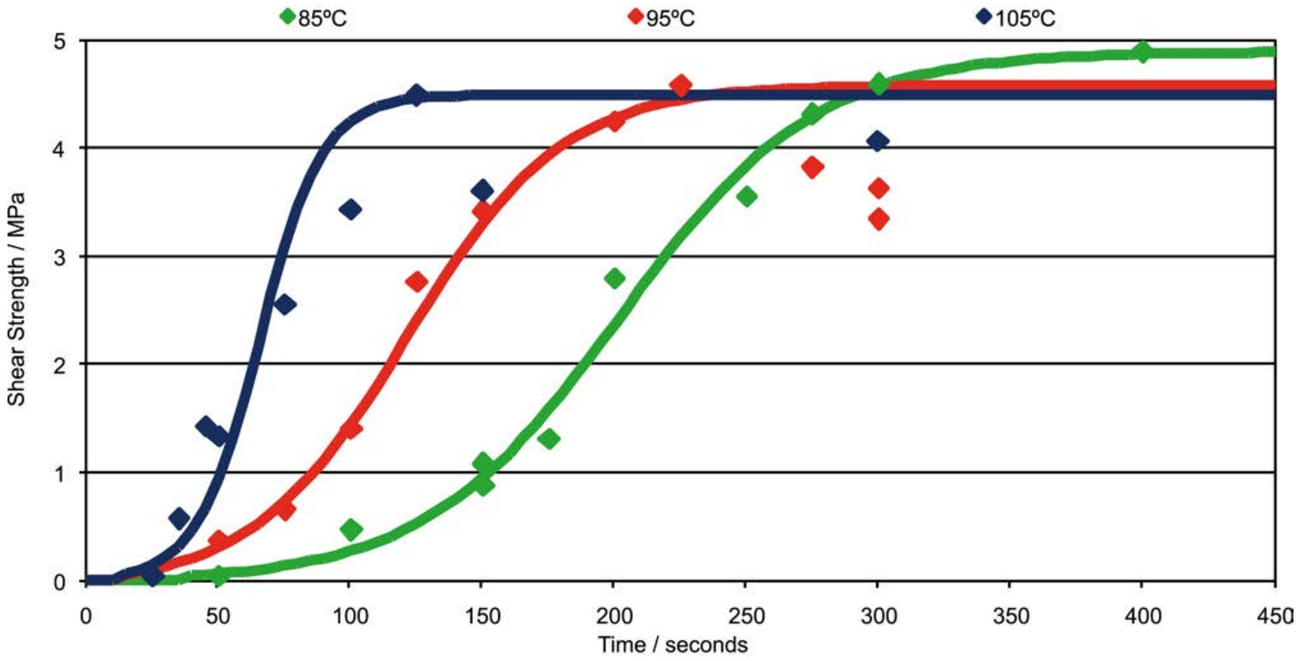

Figure 6: Model fitting to the experimental data obtained in the ABES tests with ammonium bisulphite for different temperatures.

Table 1 shows the parameter values of the resin cure model, $\tau_{máx}$ and t_0, as well as the determination coefficient for the different hardeners and temperatures.

Table 1: Fitted parameters of the resin cure model ($\tau_{máx}$: maximum shear strength; t_0: resin gel time and R^2: determination coefficient).

Hardener	Ammonium Sulphate			Ammonium Bisulphite		
Temperature	85	95	105	85	95	105
τ_{max}	3.968	4.128	4.193	4.921	4.610	4.521
t_o	169.9	95.6	73.7	201.9	121.5	65.8
R^2	0.970	0.998	0.865	0.990	0.995	0.941

$\tau_{máx}$ is independent of temperature but the results show that it is slightly higher for the tests made with ammonium bisulphite. On the other hand, t_0 is a function of the temperature and catalyst used. As expected, the resin gel time decreases with temperature increase and is higher for the test made with ammonium bisulphite, except for the trial carried out at 85 ºC.

The resin gel times at 100 ºC computed from the ABES model were compared to the values obtained by the conventional procedure (described in the Materials and Methods section). Table 2 presents these results which are very similar for both methods and hardeners, but the best gel time results are obtained for the ammonium sulphate.

Table 2: Gel time comparison between the two hardeners for the two methods.

Hardener/Method	Conventional Method	ABES Method
Ammonium Sulphate	86	86
Ammonium Bisulphite	90	89

Comparing the two hardeners in study we can say that, despite the fact that ammonium bisulphate is essentially used as a formaldehyde scavenger, this compound can be used as hardener for this type of resins.

4. CONCLUSIONS

With this work it was possible to show that ABES (Automatic Bonding Evaluation System) is a technique useful for the evaluation of the joint glued with UF and MUF and it is possible to use simple mathematical models for this evaluation. With ABES analysis it was possible to conclude that this technique allows the curing characterization of adhesives with different hardeners and different temperatures (ammonium sulphate and ammonium bisulphite). Despite the fact that ammonium bisulphite is essentially used as a formaldehyde scavenger, this chemical shows a good performance as hardener for this type of resins. Between the two hardeners used in this study, the results are very similar, but the best gel time results are obtained for the ammonium sulphate.

A mathematical model with three parameters ($\tau_{máx}$: maximum shear strength; t_0: resin gel time and λ: model time constant) was developed to describe the results. Different test temperatures, between 85 and 105 ºC, and curing times, between 25 and 400 seconds, were considered and, for all the temperatures, higher determination coefficients were obtained. The values, for the resin gel time, obtained by ABES equipment are similar to the ones obtained with the conventional method.

5. ACKNOWLEDGEMENTS

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DEVELOPMENT OF A NOVEL WOOD BASED PANEL FOR USE IN INTERNAL DOOR MANUFACTURE

DENNIS JONES[1,*], FINN ENGLUND[1], MARIELLE HENRIKSSON[1,2], KRISTOFFER SEGERHOLM[1,2], STACY TREY[1,2], MAGDALENA STERLEY[1], RUNE ZIETHEN[1], SERGIO GONZALES[3] AND LUIS SEGUI[3]

[1]SP TRÄ, SP TECHNICAL RESEARCH INSTITUTE OF SWEDEN, BOX 5609, SE 114 86 STOCKHOLM, SWEDEN
[2]ROYAL INSTITUTE OF TECHNOLOGY (KTH), SE 100 44 STOCKHOLM, SWEDEN
[3]TECNOLOGÍAS AVANZADAS ISPIRALIA (ITAV), CALLE ESTRADA 10B, MADRID 28034, SPAIN.

* CORRESPONDING AUTHOR: TEL: +46 10 516 6209; FAX: +46 33 135502; DENNIS.JONES@SP.SE

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ABSTRACT

There is a growing need for doors with enhanced performance in terms of security, acoustics and fire performance in public buildings such as schools and hospitals. In order to achieve this, it is necessary to develop alternatives to solid timber door systems. The Silentwood project, funded through the EU Framework 7 programme aims to develop and validate a novel, price-competitive, certifiable exterior wooden-based door with enhanced acoustic performance to attend the growing demand and comply with increasingly stringent building legislations for residential, educational and sanitary premises. This paper describes the development of biocomposite systems for use in conjunction with insulation materials such as natural fibre and inorganic fillers. Work describes the two modes of assessment undertaken in the project to date, whereby results from computer simulation models are compared against actual laboratory based results. Results from early composite manufacturing are hereby reported, as well as methods for the manufacturing of full door systems.

1. **INTRODUCTION**

Awareness on the impact of noise on health and quality of life has steeply grown in most advanced world in the last 10 years. Today the World Health Organization (WHO) acknowledges that noise seriously harms human health and interferes with people's daily activities at school, at work, at home and during leisure time (Niemann and Maschke, 2004). In fact, according to Green Paper on Future Noise Policy (European Commission, 1996) nearly 20 percent of the EU's population (close to 80 million people; basically the population leaving in urban areas) suffer from noise levels that scientists and health experts consider to be harmful, where most people become annoyed, sleep is disturbed and adverse health effects are to be feared. In particular, a study commissioned by the WHO to the Berlin Centre of Public Health (Ising and Kruppa, 2004), confirms health risks at chronically noise induced sleep disturbances on a degenerative level, which represent significantly elevated relative risks in the cardiovascular system, the respiratory system, and the musculoskeletal system as well as with depression. Similar conclusions on working and educational environments have been reached by the European Risk Observatory under the European Agency for Safety and Health at Work (OSHA, 1999).

In the light of these findings, the European Union has increased the pressure for decreasing noise exposure by reducing noise in the reception point, through insulating building elements (mainly doors, windows, walls and floors). At the 1998 International Conference in Building Acoustics, held as part of COST Action E5 ("Timber Frame Building Systems") in Dublin, Ireland, it was agreed that countries would very largely benefit from the existence of a common European Regulation on building acoustics. All indications are that this will be arriving shortly.

In order to investigate options for door manufacturing with improved noise reduction properties, a European Seventh Framework (FP7) project was established, bringing together partners from Spain, Sweden, Slovenia, Poland and Italy. The aim of "Silentwood" was to develop and validate *a novel, price-competitive, certifiable wooden-based panels with enhanced acoustic performance* for applications on doors and wall panels, to attend the growing demand and comply with increasingly stringent building legislations *for dwelling, sanitation and educational premises*. It will also cope with the broadest range of dimensional, aesthetic and architectonic variables and applicable world-wide standards (i.e. in relation to thermal insulation, fire-proofing and mechanical properties). It will be based on an innovative multilayered structure containing new noise reduction materials and internal noise attenuating topography and properties.

The aim of Silentwood is to allow the target SME associates (members of participating SME-AGs) to comply with existing building regulations at European level while increasing their long-term competitive margin and, at the same time, to open a new door for panel manufacturers to new market opportunities that can help them face their current critical situation. This project has also the goal of contributing to the foundation of a common European regulation on building acoustics. Among key considerations within this work are:

- Sound reduction index of 45 dB
- Weight limit of 60 kg per door
- Thickness 45 mm maximum
- Incorporate biobased materials
- Be cost competitive, preferably between 200-300 EUR

1.1. NATURAL FIBRES

In order to achieve the manufacturing goals outlined above, it was necessary to assess a wide range of materials, with particular emphasis on natural materials, and especially wood and plant fibres for the use of composite materials and insulation materials.

Among the key advantages to using natural fibres within composites and insulation-based products are:

- A known high acoustic performance
- The presence of low to zero toxins. This makes the use of natural fibres relatively easy to reuse/dispose, with demonstrable health benefits throughout their whole life cycle
- The potential of offering some degree of thermal mass, especially in combination with other materials (in the manufacture of multi-layered systems)
- The use and installation of natural insulation can reduce the need for protective clothing and masks, making it more comfortable for installers and others coming into contact with it
- Renewable materials are recognised for their carbon storage capacity throughout their usable lifespan
- The materials are known to be robust in handling, transportation and onsite construction
- They are known to be vapour permeable, and work well in combination with other low-environmental impact materials

There are of course a range of limitations that need to be considered, especially in terms of natural fibres within internal door units:

- There are only a limited number of natural fibre product manufacturers at present
- Currently the market price for natural fibre based insulation is higher than oil- or mineral-based competitors – typically around double the cost per unit volume (though this is expected to reduce as demand, manufacturing bases and supply increase)
- In the case of wall insulation systems, the use of natural fibres usually requires thicker wall cross-sections. This has not been proven in the case of internal door units, where the thermal performance demand is not as great as external wall units.
- Limited number of cases of application

Wood and plant fibres represent highly complex organic matrices comprising three main components; cellulose, hemicellulose and lignin, along with a small percentage of smaller extractable compounds. Examples of some chemical compositions have been previously tabulated (Rowell et al., 1997), which was a modification of a previous table (Rowell et al., 1991).

The use of wood fibres can offer several advantages compared to synthetic fibres such as glass and carbon fibres. Even though higher priced than mineral fibre, wood fibres are relatively inexpensive, though costs are expected to increase slightly as demand for wood fibres increases from new market areas (such as bio-fuel). The main attraction to the use of wood fibres is that they are derived from renewable (and more importantly sustainable) resources and are biodegradable. Another key advantage when it comes to their processing is that they are less abrasive than conventionally-used synthetic fibres to the equipment used in the manufacturing processes. This results in lower effects due to 'wear and tear' and replacement of expensive equipment.

Among the fibres considered were wood fibres (both softwood and hardwood), hemp, flax and sheep's wool. The thermal properties from natural fibres (Sutton and Black, 2011) demonstrate their beneficial use in products such as doors and other building products (Table 1).

Table 1: Thermal performance of fibres.

Type of material	Typical thermal conductivity (W/(m.K)
Natural organic materials	
Wood fibre	0.038 – 0.050
Paper (cellulose)	0.035 – 0.040
Hemp	0.038 – 0.040
Wool	0.038 – 0.040
Flax	0.038 – 0.040
Cork	0.038 – 0.070
Inorganic materials	
Mineral (rock) fibre	0.032 – 0.044
Glass fibre	0.038 – 0.041
Synthetic materials	
Extruded polystyrene	0.033 – 0.035
Expanded polystyrene	0.037 – 0.038
Polyurethane / polyisocyanurate	0.023 – 0.026

1.2. DOOR REQUIREMENTS

The required performance of an internal door will depend specifically upon its intended use. For example, standard single leaf doors used in domestic houses will require far lower performance compared to those in public buildings when it comes to such factors as:

- Acoustics
- Fire Performance
- Thermal insulation
- Security

Within this project, the objective is to achieve realistic door designs capable of meeting a sound reduction level of 45dB, adequate fire performance for use in public buildings, thermal insulation performance equivalent to a U value of 3.0 W/(m·K) (when separating a heated and unheated area), whilst being lightweight to allow ease of opening and minimise stress failure on hinges and hardware. Ideally the doors will be expected to last for a minimum of 20 years in service. Many of the considerations are similar to those outlined in a technical specification laid down by the UK Department for Children, Schools and Families (Flint et al., 2008). In terms of acoustic performance, improving the sound reduction levels from 25 dB to 45 dB results in the following characteristics:

- 25 dB: speech at normal level is heard and understood outside the room
- 30 dB: speech at normal level can be heard faintly outside the room and the speech can be overheard
- 35 dB: speech at normal level cannot be understood outside the room, but speech at the high level can be heard and partly overheard outside the room
- 40 dB: speech cannot be overheard, but loud shouts or screams can be heard faintly
- 45 dB: speech cannot be overheard; shouts or screams are not heard as well.

The performance of a door is also affected by the frequency of the noise being transmitted, whereby performance can be controlled by the relative stiffness of the material or its damping effects at either ends of the frequency spectrum (Figure 1, Bies and Hansen, 2009).

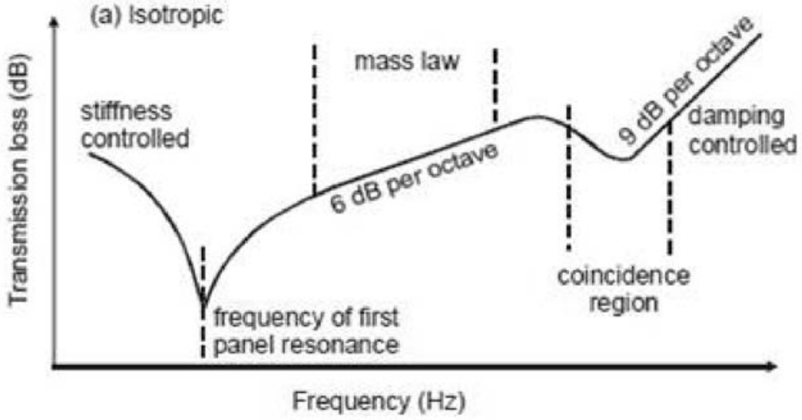

Figure 1: Effect of frequency on transmission loss (Bies and Hansen, 2009).

2. MATERIALS AND METHODS

Based on a preliminary evaluation of characteristic properties of natural fibres, resin systems and fillers, a range of materials were selected for the manufacture of composite panels. Composites with both thermoplastics and thermosets have been prepared and evaluated experimentally. The thermoplastic composites were prepared either by extrusion into profiles or boards, or by injection moulding. The thermosets were prepared by vacuum infusion or hand layup.

One thermoplastic matrix, polypropylene (PP), was experimentally evaluated. The PPs used were Moplen HF500N from LyondellBasell, BE170MO from Borealis, and Innovene 400-GA05. They were all very similar, with slight variations (mainly the Melt Flow Index), which did not appreciably affect the final properties of the products. Talc was used as additive in some of the thermoplastic composite systems. For the experimental evaluation Luzenac 2 and Luzenac ST60 from Imerys Talc were combined at a 1:1 mixing rate.

Composites with two different thermoset matrices, one polyester and one epoxy, were also experimentally evaluated. The polyester resin was Hydrex 200 M-800 with the hardener Norpol Peroxide 1 from Reichhold, Norway. 1 % - 1.5 % hardener was used in the present study. The epoxy was EcoPoxy ER500 resin with hardener EH750 from EcoPoxy systems, Rhode Island, USA. A mixing ratio of 2:1 (resin:hardener) was used. The pot life is 2.5-3.5 hours at 25 °C and it is fully cured after 72 hours according to the manufacturer. In the present study the manufactured composites were post cured at 60 °C for approximately 18 hours.

For the thermoplastic composites short fibres were used, i.e. a wood component with shorter length than the wood tracheid itself. The type of wood used with PP systems was either Scots pine (*Pinus sylvestris*) (in the first three examples) or beech (*Fagus sylvatica*) (in the fourth example). For the thermoset systems, fibre mats with thermo-mechanical pulp-type fibres were supplied from SCA (Luna wave with a surface weight of 250 g/m^2) and Feeling Wood (Feeling wood insulation boards). Long flax fibres were also combined with the thermosets. Insulation boards from Isolina were used as fibre mats.

The following composite systems were prepared and evaluated experimentally:

2.1. THERMOPLASTIC COMPOSITES

PP/wood fibre: Extruded high wood content composite profiles with 70 % and 80 % Scots pine fibres, PP grade: Moplen HF500N (supplied by LyondellBasell)

PP/wood fibre: Injection moulded composite with 0, 10, 30, and 50 % Scots pine fibres, PP grade: BE170MO (supplied by Borealis)

PP/wood fibre/talc: Injection moulded composite with talc and wood. As in experiments using PP from Borealis, but with the addition of 5, 10, 15, and 20 % talc (Luzenac 2 and Luzenac ST60, supplied by Imerys)

PP/wood fibre: Extruded composite panels with 20, 40, and 50 % beech fibres. This system was manufactured in a commercial scale process at Isokon, Slovenia. The panels were approximately 1 m wide and 2 m long, PP grade: Innovene 400-GA05

PP/Flax fibre: Flax fibre-polypropylene composite, (a) PP/Flax fibre– tape woven mats in 0/90 direction (a prototype composite system). Hot pressed at a temperature of 190 °C by SP, Borås, Sweden. (b) , PP/Flax fibre– 4x4 hopsack weave (commercially available from Composites Evolution, UK, sold under the brand name Biotex), composites made up from 6 layers hot pressed together at 190 °C at Swedspan, Hultsfred, Sweden

2.2. THERMOSET COMPOSITES:

Polyester: Polyester composites (Hydrex 200 M-800 with the hardener Norpol Peroxide 1 (1-1.5%) from Reichhold, Norway, combined with (a): Isolina insulation boards (Särkisalmi, Finland), (b) Luna wave (cellulose fibre mats with thermo-mechanical pulp-type fibres supplied by SCA, Sweden using vacuum infusion, and (c) Luna wave using hand layup

Epoxy: Epoxy composites (EcoPoxy ER500 resin with hardener EH750 from EcoPoxy systems, Rhode Island, USA. A mixing ratio of 2:1 (resin:hardener) was used. The pot life is typically 2.5-3.5 hours at 25 °C and it is fully cured after 72 hours according to the manufacturer. In the present study the manufactured composites were post cured at 60 °C for approximately 18 hours) combined with (a) Isolina (vacuum infusion), Feeling wood insulation boards (vacuum infusion), (c) Luna wave (vacuum infusion), and (d) Luna wave (hand layup)

2.3. DYNAMIC MECHANICAL EVALUATION

The composites have been evaluated by flexural vibration according to a resonance curve method (ISO 6721-3) to determine dynamic stiffness and loss factor. Specimen dimensions were 5 x 10 x 180 mm^3 and the frequency region of interest was 100 Hz - 3000 Hz.

3. RESULTS AND DISCUSSION

PP/wood fibre/talc system is presented in Figure 2, showing the cross-section of the injection moulded composite with talc. The wood fibre content is up to 40 % wood, and it is observed that in comparison to the same system without talc, that this system has well distributed fibres even with the inclusion of talc. Both larger dimensioned structures, including filled cell lumens can be observed to the left and smaller wood and talc fibres are observed to the right in the cross section. Surface damage through the frictional drawing of a microtome blade over the sample was avoided through the use of UV-laser ablation.

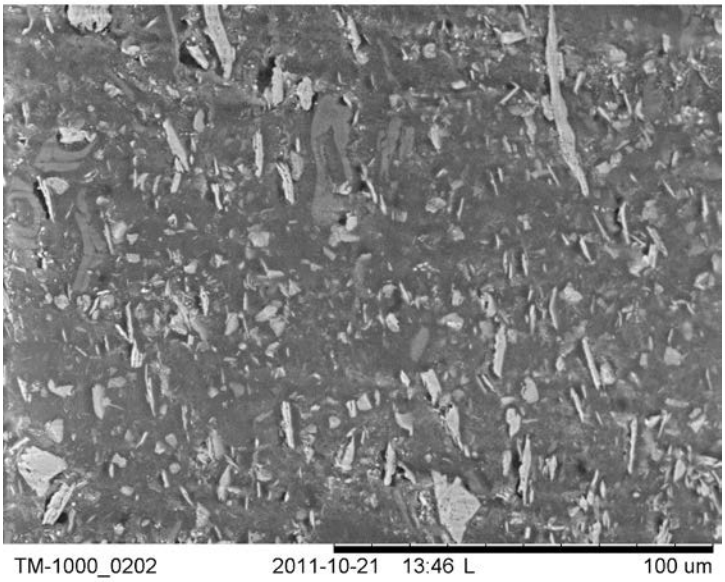

Figure 2: Cross-section of PP/wood fibre/talc with 30 % softwood, PP, and talc.

Parallel studies were undertaken, which allowed comparison of results from Finite Element Modelling (FEM) with experimental data. The numerical inputs into FEM allowed for the development of a theoretical 3D distributional profile of fibres within the resin matrix (Figure 3).

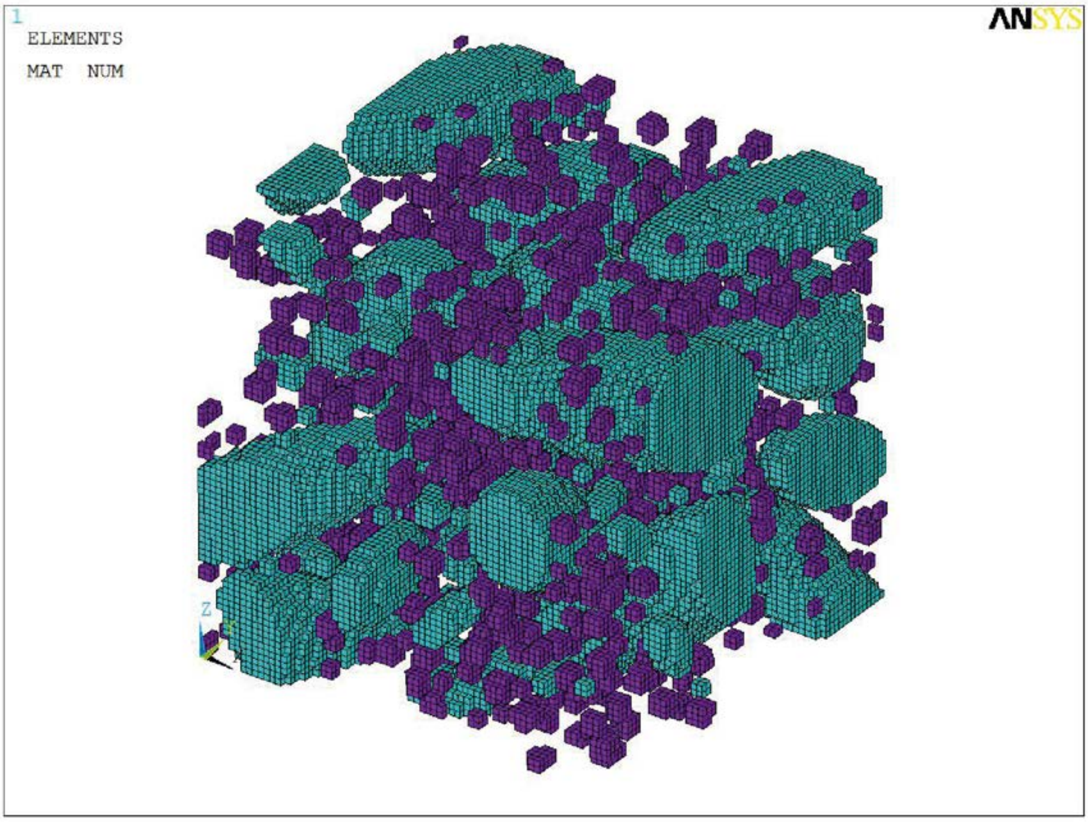

Figure 3: FEM simulation for distribution of 60 % PP/ 30 % Wood flour/ 10 % Talc.

Based on the FEM distribution of materials within the composite matrix, it is possible to establish theoretical profiles for density (Figure 4, left), Storage modulus (Figure 5, left) and Loss factor (Figure 6, left). These theoretical values could then be compared to experimentally determined values for equivalent compositions (Figures 4-6, right). There appears to be fairly good correlation between the modelled results and experimentally derived values. The experimental loss factor values indicated that the PP and polyester systems were much lower than the model predicted they would be. While the epoxy systems loss factor values were slightly higher than the model predicted.

The experimental densities of the PP combined with wood and talc proved to be much higher at around 1,350 kg/m^3 than the model predicted, while the PP with only wood flour was only slightly higher than expected. The epoxy systems at high wood contents around 55 % had lower expected densities along with the polyester systems. The higher densities than expected were the epoxy systems at 10 % - 30 % wood contents.

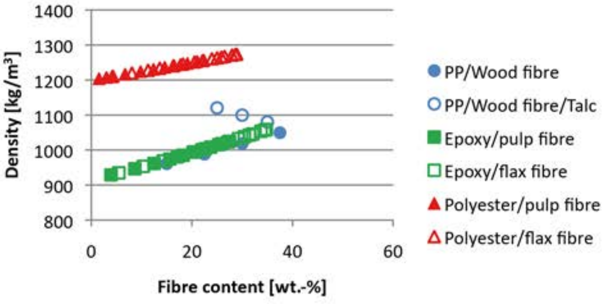

Figure 4 (left): Theoretical determination of composite density from simulation.

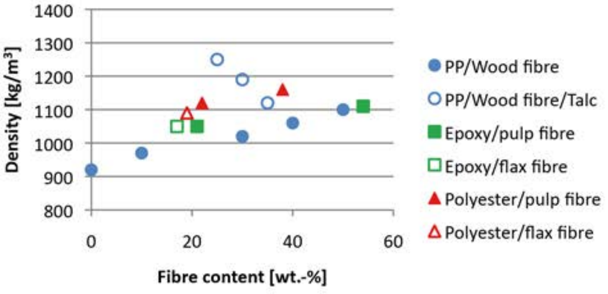

Figure 4 (right): Experimental determination of composite density.

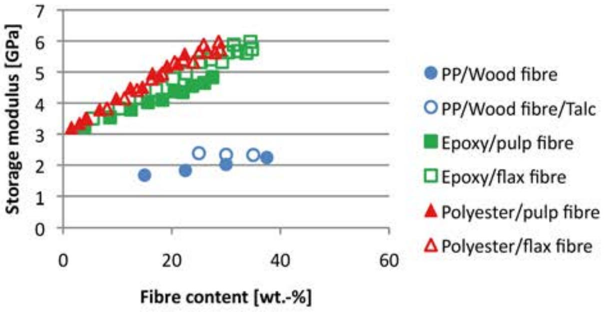

Figure 5 (left): Theoretical determination of elastic modulus from simulation.

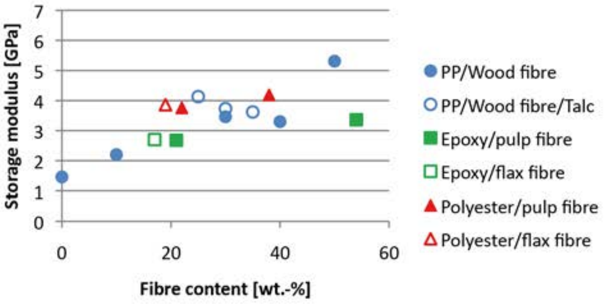

Figure 5 (right): Experimental determination of elastic modulus.

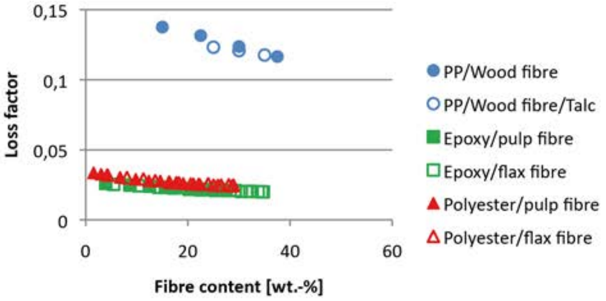

Figure 6 (left): Theoretical determination of loss factor from simulation.

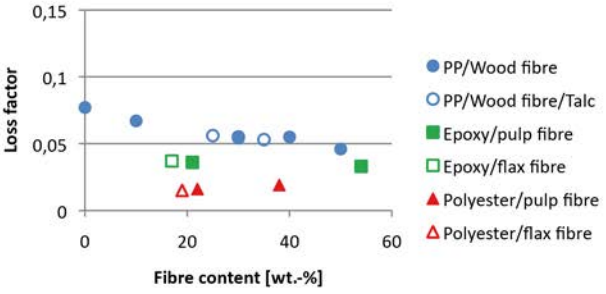

Figure 6 (right): Experimental determination of loss factor.

Some points can be raised based on the results from the experimental and modelling work:

- Results obtained with injection moulded PP/wood fibre system, corresponded fairly well to the numerical simulation results.
- All the composites are anisotropic and are stronger and stiffer in the longitudinal direction of the reinforcing component (wood, flax).
- The loss factor is connected to the stiffness of the material, the thermoplastic composites with wood fibres showed much higher loss factor compared to the thermoset composites.
- For the long fibre composite systems, lack of accounting for a fibre intersection in the simulation model and occurrence of these intersections in the produced composites could produce a source of error between experimental and numerical results. Additionally, tortuosity and fibre length could affect results. For thermosets, finite element simulations consider a computational cell much smaller than the actual fibre length (due to an important scale difference between fibre radius and fibre length) resulting into a consideration of an effective fibre length longer than the actual one; thus numerical predicted results

could yield in a higher elastic modulus as those given in experiments. Due to this, the higher the fibre content, the greater the diversion of the experimental values for storage modulus, and loss factor from those obtained by simulation.

- For the case of composites containing talc, there exists an uncertainty in the elastic modulus value (a value of $E = 90$ GPa was considered in the simulation). Due to this, the numerical results may result in less stiff composites, since the assumed modulus of talc may be smaller than the actual one.

4. PRELIMINARY DOOR MANUFACTURE

Based on the results obtained to date, full-size composite panels of dimension 2.2 m by 1.2 m were manufactured and used in prototype doors, following a potential proprietary design. Actual acoustic testing of these early prototype doors led to a sound reduction of 45 dB, so meeting one of the key criteria in the programme. It is hoped that as manufacturers become more acquainted with the new design, further improvements may be achieved.

5. CONCLUSIONS

Project partners have to date demonstrated the potential of wood and plant fibres for use in both the manufacture of composites and use as naturally derived insulation material for innovative internal door designs for use in a range of public buildings, such as schools. Material combinations have been assessed by both computer simulation (using Finite Element Modelling) and experimental determination from manufactured composites. Based on the encouraging results achieved, a range of components were manufactured in dimensions suitable for incorporation in full-size door manufacture. Preliminary results of a proprietary design suggest that sound reductions of as much as 45 dB can be achieved. Work is continuing to further develop and improve the design and manufacture of doors.

6. ACKNOWLEDGEMENTS

The authors would like to thank the involvement, interest and expertise of all project partners who have helped contribute to the development and delivery of this project and to the EU Seventh Framework Programme for their funding of this work, under grant agreement number 234639-2.

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THE SILVER NANO PARTICLE FORMATION ON AR PLASMA TREATED PINE WOOD

S. DAHLE[1,2], L. WEGEWITZ[1,3], W. VIÖL[2] AND W. MAUS-FRIEDRICHS[1,3,*]

[1] INSTITUT FÜR ENERGIEFORSCHUNG UND PHYSIKALISCHE TECHNOLOGIEN, TECHNISCHE UNIVERSITÄT CLAUSTHAL, LEIBNIZSTRASSE 4, 38678 CLAUSTHAL-ZELLERFELD, GERMANY
[2] HOCHSCHULE FÜR ANGEWANDTE WISSENSCHAFT UND KUNST, FAKULTÄT FÜR NATURWISSENSCHAFTEN UND TECHNIK, VON-OSSIETZKY-STRASSE 99, 37085 GÖTTINGEN, GERMANY
[3] CLAUSTHALER ZENTRUM FÜR MATERIALTECHNIK, TECHNISCHE UNIVERSITÄT CLAUSTHAL, LEIBNIZSTRASSE 4, 38678 CLAUSTHAL-ZELLERFELD, GERMANY

* CORRESPONDING AUTHOR: W.MAUS-FRIEDRICHS@PE.TU-CLAUSTHAL.DE

Keywords: Silver, Nano Particle, Pine Wood, Metastable Induced Electron Spectroscopy, Ultraviolet Photoelectron Spectroscopy, X-Ray Photoelectron Spectroscopy, Atomic Force Microscopy, Adsorption.

ABSTRACT

We have employed Metastable Induced Electron Spectroscopy, Ultraviolet Photoelectron Spectroscopy, X-ray Photoelectron Spectroscopy and Atomic Force Microscopy to investigate the adsorption behavior of silver on Ar plasma treated pine wood chips. The plasma treatment of wood surfaces in argon leads to a hydrophobization of the surfaces by the detachment of hydroxide groups and the formation of inter-carbon double bonds. Thus, this may be useful for an improved wetting of the wood surfaces with nonpolar solvents. The silver deposition on the other hand is intended to produce biocidal properties for an application towards wood preservation. For dependable interpretation of the results gained, different model systems were examined previously. Accordingly to previously published results for some of these precursors, we find the formation of metallic nano particles on the adsorption of silver for the model systems as well as for the pine wood samples. It was found that these particles most probably are formed as recently as the surface gets exposed to water or air.

1. INTRODUCTION

The use of silver in functionalization applications like corrosion protection, RF shielding, reflective coatings, and many more is very well established up to now. Especially silver nano particle coatings drastically increased in attention, due to their additional functions. For instance, silver nanoparticles are known to enhance the efficiency of organic light emitting devices (Yang et al., 2009), whereas silver films on TiO_2 nano particles enhance photocatalytic reaction rates (Chuang and Chen, 2009; Kato et al., 2005). One of the most common applications of silver particles is the functionalization of surfaces because of their antibacterial properties (Ilic et al., 2010; Lok et al., 2006). This may be useful especially on wood surfaces to preserve them from aging through attack of microorganisms by other means than lacquering or impregnation. The relevance of surface modifications of wood by means of laser or plasma technology increased substantially in the past few years. Low-temperature radio frequency plasma treatment was found to enhance the durability of nano particle coatings. Therefore, a combined method of plasma-treatment and metal nano particle coating may be quite interesting for industrial applications regarding economical aspects as well as an improvement of functionality. The combination of both surface treatments is possible in numerous ways, e.g. by using a plasma-jet with precursor gases.

The presented investigation is part of a research project concerning the interaction of metals (Ag, Ti) with wood surfaces. On basis of the results obtained here we will come closer to understand such complex systems as wood. Furthermore, the reactions with atmospheric gases as well as typical volatile organic compounds are investigated, with perspective to future applications. One particular aim of the project is to understand the influence of plasma treatments on the given metal functionalizations, to be able to fabricate the functional films out of a plasma treatment and thus combine both features in one processing step.

To understand the interaction behavior of Ag with wood surfaces, several molecular precursors are used to resemble the organic groups of lignin and cellulose. For lignin, these precursors are sinapyl alcohol and coniferyl alcohol as two main monolignols from which lignin gets synthesized. Since these two are derived from cinnamyl alcohol (also known as phenylallyl alcohol), we also use this less complex molecule as main lignin precursor for our investigations presented here (Klarhöfer et al., 2007, Klarhöfer et al., 2008, Klarhöfer et al., 2010). The effect of plasma treatment on the presented molecules has been studied previously (Klarhöfer, 2009). This study extends our recent investigations on the adsorption of silver on cinnamyl alcohol, which have been found to form chemically inert nano particles (Dahle et al., 2012).

2. EXPERIMENTAL DETAILS

An ultra high vacuum (UHV) apparatus with a base pressure of 5×10^{-11} hPa, which has been described in detail previously (Klarhöfer et al., 2008; Maus-Friedrichs et al., 1991; Ochs et al., 1996; Ochs et al., 1998; Krischok et al., 2001), is used to carry out the experiments. All measurements were performed at room temperature.

Electron spectroscopy is performed using a hemispherical analyzer (Leybold EA 10) in combination with a source for metastable helium atoms (mainly He* $^3S_1$) and ultraviolet photons (HeI line). A commercial non-monochromatic X-ray source (Fisons XR3E2-324) is utilized for XPS.

During XPS, X-ray photons hit the surface under an angle of 80° to the surface normal, illuminating a spot of several mm in diameter. For all measurements presented here, the Al K_α line with a photon energy of 1486.6 eV is used. Electrons are recorded by the hemispherical analyzer with an energy resolution of 1.1 eV for detail spectra and 2.2 eV for survey spectra, respectively, under an angle of 10° to the surface normal. All XPS spectra are displayed as a function of binding energy with respect to the Fermi level.

For quantitative XPS analysis, photoelectron peak areas are calculated via mathematical fitting with Gauss-type profiles using OriginPro 7G including the PFM fitting module, which applies Levenberg-Marquardt algorithms to achieve the best agreement between experimental data and fit. To optimize our fitting procedure, Voigt profiles have been applied to various oxidic and metallic systems but for most systems the Lorentzian contribution converges to 0. Therefore all XPS peaks are fitted with Gaussian shapes. Photoelectric cross sections as previously calculated (see Scofield, 1976) with asymmetry factors (Powell and Jablonski, 2010a), taking into account asymmetry parameters (Reilman et al., 1976; Jablonski, 1995) as well as inelastic mean free paths from the NIST database (Powell and Jablonski, 2010b; using the database of Tanuma, Powell and Penn for elementary contributions and the TPP-2M equation for molecules) and the energy dependent transmission function of our hemispherical analyzer are taken into account when calculating the stoichiometries.

MIES and UPS are performed applying a cold cathode gas discharge via a two-stage pumping system. A time-of-flight technique is employed to separate electrons emitted by He* (MIES) from those caused by HeI (UPS) interaction with the surface. The combined He*/HeI beam strikes the sample surface under an angle of 45° to the surface normal and illuminates a spot of approximately 2 mm in diameter. The spectra are recorded simultaneously by the hemispherical analyzer with an energy resolution of 220 meV under normal emission within 140 seconds.

MIES is an extremely surface sensitive technique probing solely the outermost layer of the sample, because the He^* atoms interact with the surface typically 0.3 to 0.5 nm in front of it. This may occur via a number of different mechanisms depending on surface electronic structure and work function, as is described in detail elsewhere (Ertl and Küppers, 1985; Harada et al., 1997; Morgner, 2000). Only the processes relevant for the spectra presented here shall be discussed shortly:

During Auger Deexcitation (AD), an electron from the sample fills the 1s orbital of the impinging He*. Simultaneously, the He 2s electron is emitted carrying the excess energy. The resulting spectra reflect the Surface Density of States (SDOS) directly. AD-MIES and UPS can be compared and allow a distinction between surface and bulk effects. AD takes place for all organic systems shown here.

On pure and partly oxidized metal surfaces with a work function beyond about 3.5 eV like silver surfaces, Auger Neutralization (AN) occurs as long as the surface shows metallic behavior. As a result the impinging He* atom is ionized in the vicinity of the surface by resonant transfer (RT) of its 2s electron into unoccupied metallic surface states. Afterwards, the remaining He^+ ion is neutralized by a surface electron thus emitting a second surface electron carrying the excess energy. The observed electron spectrum is rather structureless and originates from a self convolution of the surface density of states (SDOS).

A combined UPS (HeI, HeII) source (Omicron HIS 13 VUV source) emitting photons at 21.2 and 40.8 eV excitation energy is utilized for UPS (HeII) measurements. All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi level, thus being able to compare MIES and UPS spectra more easily. Obviously, the binding energy scale is only valid for the AD process. Nevertheless, all spectra including structures originating in the AN process have also been displayed in this particular manner. The surface work function can be determined from the high binding energy onset of the MIES or the UPS spectra with an accuracy of ± 0.1 eV.

The surface topography of the untreated and silver covered pine wood veneer is determined by Atomic Force Microscopy (AFM) using a Veeco Dimension 3100 SPM. All measurements are performed in Tapping Mode with Al-coated silicon cantilevers (NSC15, Micromasch). The typical resonant frequencies of this series are about 325 kHz, typical spring constants are in the range of 40 N/m. The radius of the tip curvature is less than 10 nm. The pictures are recorded with line-scan frequencies of 0.5 – 1.0 Hz. SPIP (Image Metrology A/S) is used for post-processing and depiction of the images. The post-processing procedure includes plane correction, de-spiking and subsequent Gaussian filtering according to ISO 16610-61.

The experiments on cinnamyl alcohol were carried out on inert Au(111) substrates. These substrates were cleaned prior to the experiments by Ar-sputtering at 4 kV for 20 min and subsequent heating up to 1000 K. The Ag reference was prepared by adsorption on a Si(100) substrate, which was preliminary cleaned by flashing up to 1400 K.

Silver (Sigma-Aldrich, 99%) was evaporated with a commercial UHV evaporator (Omicron EFM3) onto the samples. On a clean Si(100) target metallic silver films grow at a rate of 0.23 nm min^{-1} at room temperature when evaporated with an Ag^+ ion flux of 1 μA at the fluxmeter of the EFM3. This flux is a degree for the number of Ag atoms moving toward the sample per second. The film growth rate for Ag has been estimated from the Si 2p peak attenuation in XPS.

Cinnamyl alcohol (Sigma-Aldrich Co., > 97.0%) was evaporated in a directly connected preparation chamber (base pressure < 10^{-9} hPa) using a temperature controlled evaporator (Kentax TCE-BS). During all experiments cinnamyl alcohol has been evaporated at 40 °C for 5 min, leading to a film with a thickness of about 1.8 nm estimated from the Au 4f peak attenuation in XPS (Klarhöfer et. al., 2008).

Pine wood veneer with a thickness of about 0.7 mm was cut into pieces of approximately 10 x 10 mm^2 before being introduced into the high vacuum transfer chamber. No additional treatments were carried out prior to experiments.

Plasma treatments have been carried out employing a dielectric barrier discharge. The plasma source is mounted to the preparation chamber mentioned above and has been described elsewhere (Wegewitz et al., 2011). An alternating high voltage pulse generator with a pulse duration of t_p = 0.6 **μ**s and a pulse repetition rate of 10 kHz is connected to the dielectric isolated electrode, while the sample forms the grounded counter electrode. The discharge gap is set to about d = 1 mm. During the plasma treatment, a voltage of U = 11 kV (peak) is measured. The high voltage supply delivers a power of P = 2 W. The increase of the sample temperature during the plasma treatment does not exceed 10 K (Kogelschatz, 2003).

Ar (Linde Gas, 99.999%), O_2 (Linde Gas, 99.995%), and H_2O (de-ionized) are offered via backfilling the chamber using a backable leak valve. The gas line is evacuated and can be heated in order to ensure cleanness. A quadrupole mass spectrometer (Balzers QMG311 equipped with a Balzers QMA 140) is used to monitor the partial pressure of the reactive gases simultaneously during all MIES and UPS measurements. Additionally, a differentially pumped quadrupol mass spectrometer system (Balzers QMG 422) with a linear motion feed for positioning the faceplate right in front of the sample is used for detection of possible reaction products during the decomposition process.

3. **RESULTS AND DISCUSSION**

The investigations presented in this section start with the interaction of silver with Ar plasma treated cinnamyl alcohol and the influence of water adsorption afterwards. Cinnamyl alcohol serves as model system for lignin. The natural precursors of lignin, coniferyl alcohol and sinapyl alcohol are derived from the smaller cinnamyl alcohol and act as model systems, too. In this manner, the interpretation of the results can be done discussing influences on the single atom groups inside the lignin. In the same manner, glucose and cellobiose serve as model systems for cellulose. From all of these model systems, the results on wood should be properly understandable (Klarhöfer, 2009).

3.1. INTERACTION OF SILVER WITH CINNAMYL ALCOHOL

Figure 1 shows the MIES (left) and UPS HeI (right) spectra of cinnamyl alcohol on Au(111) as prepared (black lines) and after Ar plasma treatment (green lines), adjacenct silver adsorption (red lines) and subsequent water dosage (blue lines). The spectra of cinnamyl alcohol resembles very well the known structures $1e_{1g}$ (p) at around 4.4 eV, $3e_{2g}$ (sCH) and $1a_{2u}$ (p) at 7.0 eV, $3e_{1u}$ (sCH), $1b_{2u}$ (sCC) and $2b_{1u}$ (sCH) from 8.5 to 10.5 eV and $3a_{1g}$ (sCH) at 11.7 eV (Dahle et al., 2012; Klarhöfer, 2009). After Ar plasma treatment, especially those groups correlated to the attached OH group got diminished, thus pointing out the reducing effect of the Ar plasma treatment (Klarhöfer, 2009; Ochs et al., 1996). The subsequent silver adsorption decreases the intensities of the cinnamyl alcohol without changing the peak distribution. The surplus structures after silver adsorption resemble the known valence band spectrum of metallic silver (Ochs et al., 1996). Thus, the silver seems to adsorb on top of the cinnamyl alcohol film without further interaction.

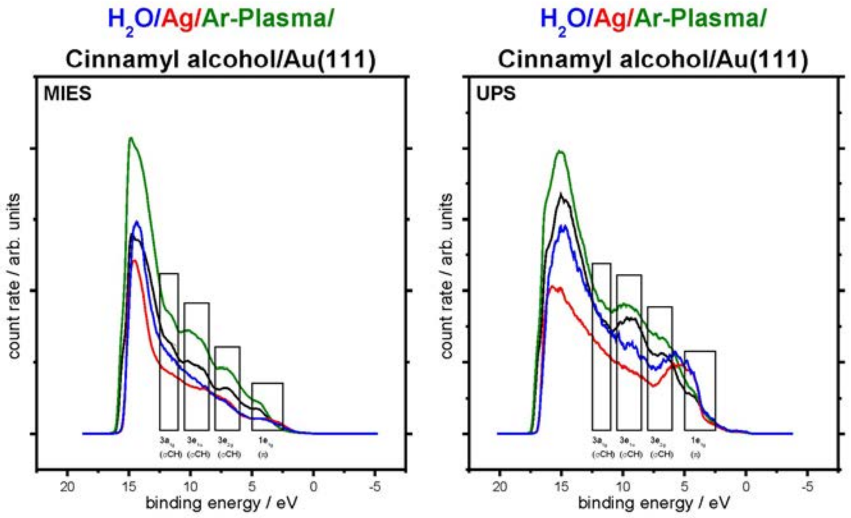

Figure 1: MIES (left) and UPS (right) spectra of cinnamyl alcohol on Au(111) as prepared (black lines) and after Ar plasma treatment (green lines), adjacent silver adsorption (red lines) and subsequent water dosage (blue lines).

Figure 2 depicts the XPS spectra of the Au 4f (left), the C 1s (middle) and the Ag 3d region (right) of cinnamyl alcohol on Au(111) as prepared (black lines and squares) and after Ar plasma treatment (green lines and circles), adjacenct silver adsorption (red lines and triangles) and subsequent exposure to 1660 L of water (blue lines and hollow diamonds). The background signal was subtracted from each spectrum for better comparability, no further modification on the originally recorded data was made.

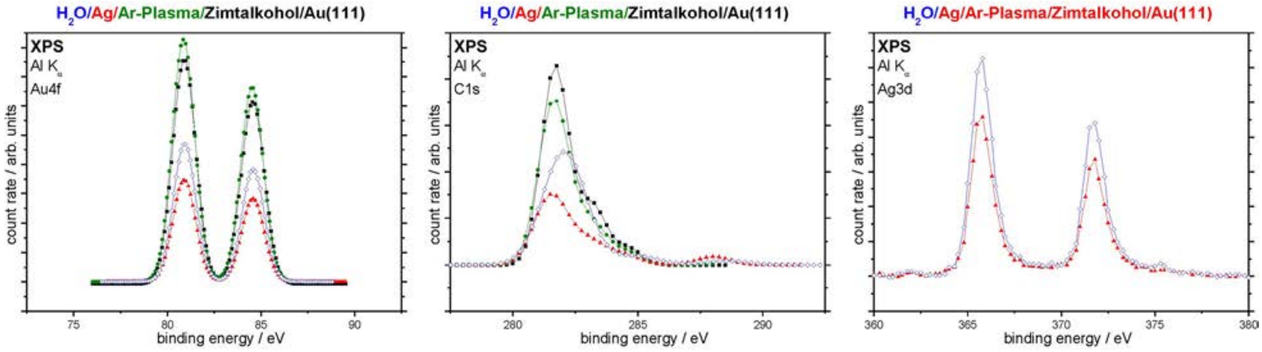

Figure 2: XPS spectra of cinnamyl alcohol on Au(111) as prepared (black lines) and after Ar plasma treatment (green lines), adjacent silver adsorption (red lines) and subsequent water dosage (blue lines).

The increase of the Au 4f intensity together with a decrease of the overall C 1s intensity on Ar plasma treatment indicates a slight thinning of the cinnamyl alcohol film. The parts of the C 1s at higher binding energies, corresponding to C-O and C=O bonds seem to decrease slightly stronger than the maximum at the low binding energy side, corresponding to C-C bonds. This indicates a reduction of the surface, which can only include the detachment of the OH group (Klarhöfer, 2009; Klarhöfer et al., 2010). During the adsorption of silver both the C 1s and Au 4f intensity decrease similarly. The only significant change in shape is the appearance of a peak at the high binding energy side of the C 1s structure corresponding to plasmon loss processes and indicating the presence of metallic bands nearby. The Ag 3d peaks resemble very well the shape for metallic silver (Ochs et al., 1996). Thus, the silver seems to cover the cinnamyl alcohol film without chemical interactions. The adsorption of 1660 L of water leads to an increase of the overall intensity of all three, the Au 4f, C 1s and Ag 3d structures. Thus, the adsorbed water must increase the substitutional electron delivery during the measurement. Nevertheless, the C-O and C=O fractions at the high binding energy side of the C 1s increase much more than the C-C fraction at the low binding energy side. Thus, the cinnamyl alcohol seems to get drastically oxidized during water adsorption, while the gold substrate and the silver covering remain unaffected. This oxidizing behaviour has not been found during additional experiments concerning the water adsorption on (a) cinnamyl alcohol on Au(111) without silver covering and on (b) cinnamyl alcohol on a closed silver film. These experiments are not shown here due to their extensive discussion, but will be shown in upcoming publications. These results give evidence that the adsorption sites of the silver atoms have to be of great importance for the reaction of the cinnamyl alcohol.

Figure 3 shows QMS spectra recorded with the differentially pumped mass spectrometer described in sect. 2 during the exposure of a silver covered cinnamyl alcohol film to water. The partial pressures of OH (true to scale), C_2H_3OH (sevenfold magnification), HCO (hundredfold magnification) and O_2 (fortyfold magnification) are depicted representatively for four different kinds of progressions found among the various molecules desorbed from the surface during exposure to water. The partial pressure of OH increases in terms of an exponential convergence, since it is produced mainly due to fracturing of the dosed water in the mass spectrometer. Thereagainst, the oxygen from the residual gas gets consumed in terms of an exponential decay. The partial pressure of C_2H_3OH shows a maximum at 1000 s, corresponding to 260 L, thus indicating a first stage of the reaction. Thereagainst, HCO partial pressure shows a plateau at the maximum of the C_2H_3OH partial pressure and afterwards continues until reaching its maximum at 1500 s, corresponding 390 L. These four progresses seem to indicate a decomposition of the cinnamyl alcohol towards short-chained alcohols and aldehydes.

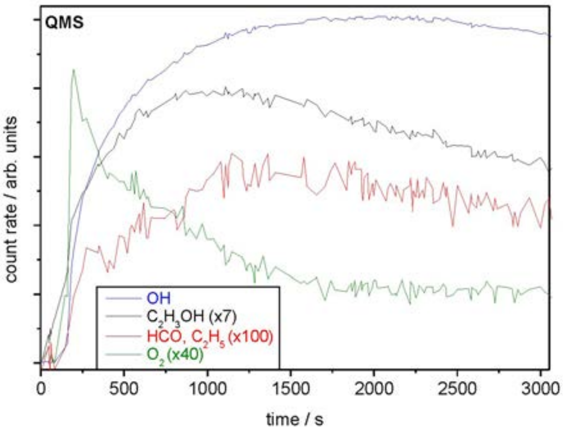

Figure 3: QMS peak evolution of the desorbed molecules from cinnamyl alcohol on Au(111) after silver adsorption during water dosage.

Figure 4 holds the AFM image of a 500 x 500 nm^2 region on the silver covered cinnamyl alcohol taken at atmospheric air. Thus, the sample was exposed to huge amounts of oxygen and water prior to the AFM measurement due to the experimental setup. The image includes an atmospheric aerosol adsorbed at the left margin and depicts the coverage of the gold surface with small regular structures, indicating the formation of silver nano particles at a mean diameter of 13 nm and a standard deviation of 5 nm (Ochs et al., 1996).

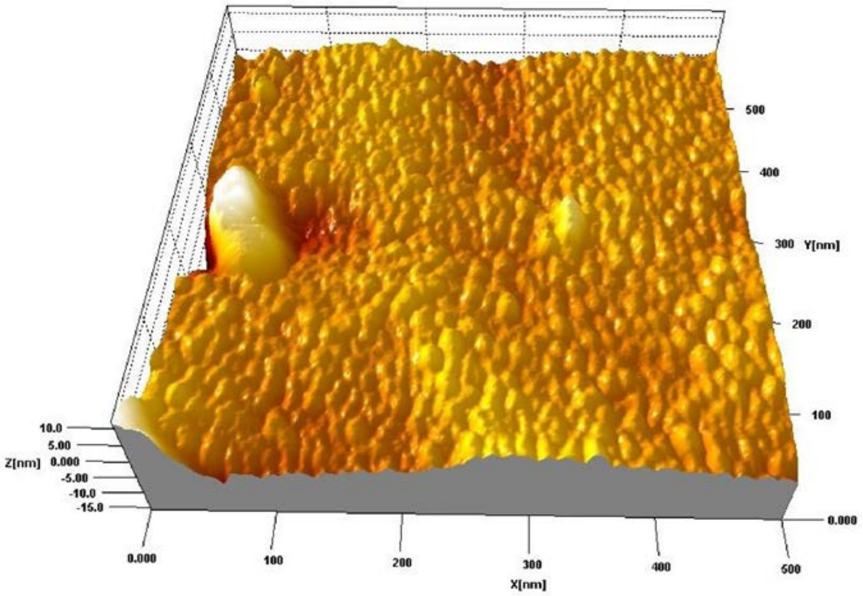

Figure 4: AFM image of cinnamyl alcohol on Au(111) after silver adsorption and subsequent water dosage (Dahle et al. 2012).

These findings were basically reproduced for coniferyl alcohol, sinapyl alcohol and lignin. Therefore, the corresponding spectra and results are not shown in detail. Since lignin is one main substance of content of wood and is known to cover the cellulose fibres, we proceed the discussion with our results on the adsorption of silver on pine wood samples and the influence of subsequent water dosage or exposure to air, respectively.

3.2. INTERACTION OF SILVER WITH PINE WOOD

Figure 5 shows the MIES (left), UPS HeI (middle) and UPS HeII (right) spectra of pine wood as introduced into the UHV chamber (black lines) and after silver adsorption (red lines). The MIES and UPS HeI spectra of the freshly introduced pine wood sample resemble mostly the lignin spectra from the literature (Klarhöfer et. al., 2010). Thereagainst, the UPS HeII spectrum appears rather structureless. The HeI part of the spectrum (at higher binding energies of the recorded data, not shown) is exactly alike the one from the combined MIES and UPS measurements, hence a problem with the analyzer or recording can be excluded. On the contrary, this effect may originate in a much lower cross section for photons at 40.8 eV than for those at 21.2 eV.

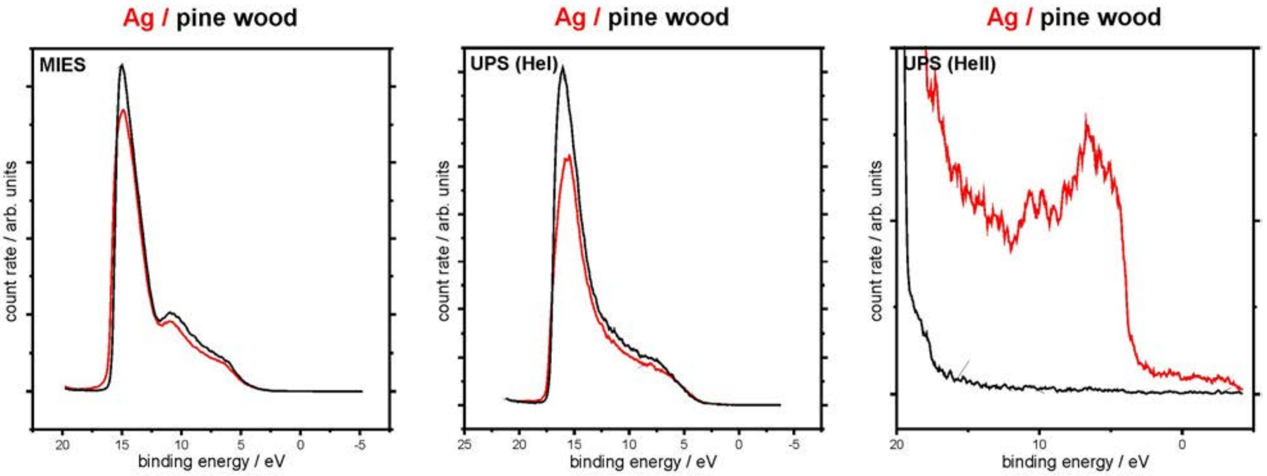

Figure 5: MIES (left), UPS HeI (middle) and UPS HeII (right) spectra of pine wood as prepared (black lines) and after silver adsorption (red lines).

Regarding the spectra after silver adsorption, the MIES and UPS HeI spectra have not changed very much beside a slight decrease of the secondary electron peak. The UPS HeII spectrum clearly shows the valence band states of metallic silver. This indicates that the impinging silver atoms get adsorbed closely beneath the surface, while no strong interaction with the surrounding lignin takes place.

Figure 6 shows XPS spectra of the C 1s (left), the O 1s (middle) and the Ag 3d (right) region of a pine wood sample freshly introduced into the UHV chamber (black lines and squares) as well as after silver adsorption (red lines and triangles). The comparison of these spectra shows a clear decrease of the intensity of the C 1s structure with an unchanged shape. Thereagainst, the O 1s structure gets diminished, too, but is shifted slightly towards higher binding energies. This might indicate some interaction with the adsorbed silver or the presence of some surplus water adsorbed on the sample. The Ag 3d structure is significantly broadened compared to a pure silver film (Ochs et al., 1996). This may be due to inhomogeneous charging effects as well as it could originate in chemical interactions of at least some of the silver atoms with the substrate.

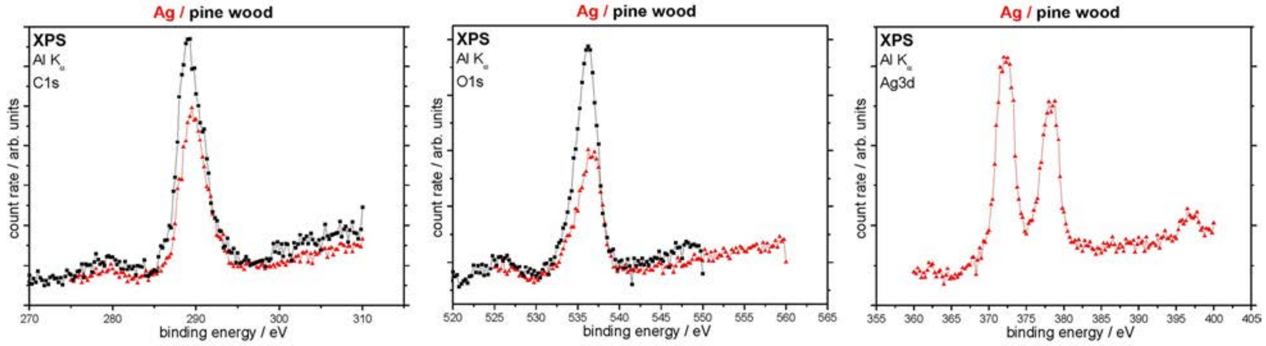

Figure 6: XPS spectra of pine wood as prepared (black lines) and after silver adsorption (red lines).

Figure 7 holds the AFM images of a pine wood veneer chip before (left) and after (right) silver adsorption. Both images were measured with the same parameter setup and underwent the same postprocessing as described in sect. 2. Both images exhibit deep rifts between wide plateau-shaped ridges. The surface of these ridges is unsteadily and rough for the untreated pine wood, while the ridges appear much more smoothly after the silver adsorption. Furthermore, it seems to be fully covered by quite regular humps in the size of 33.6 ± 6.7 nm, just as it was the case for the silver covered cinnamyl alcohol.

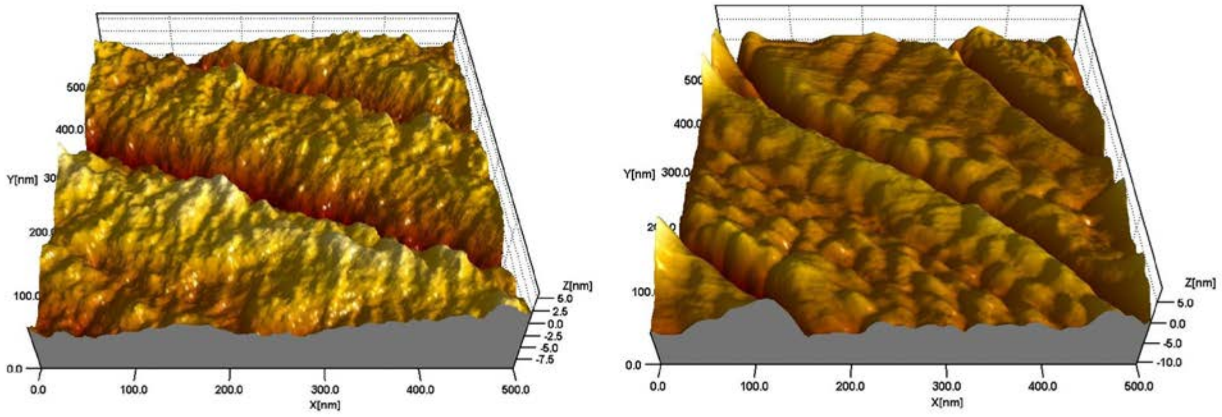

Figure 7: AFM images of pine wood veneer before (left) and after (right) silver adsorption.

4. CONCLUSION

The interaction of silver with cinnamyl alcohol films as well as pine wood samples and the influence of subsequent water dosage, e.g. by air contact has been discussed. It has been shown that silver adsorbs on top of a cinnamyl alcohol film but occupies subsurface positions for the pine wood samples. In both cases, no chemical interaction could be detected directly after silver adsorption. The subsequent exposure to water vapour led to an oxidation of both, the cinnamyl alcohol film as well as the pine wood sample. During this oxidation, the desorption of various molecules from the surfaces was detected, e.g. short-chained alcohols and aldehydes, while the underlying process seemed to include two stages. After contact to atmospheric air, both systems that underwent the silver deposition were fully covered in nano particles.

5. ACKNOWLEDGEMENTS

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SYNTHESIS AND CHARACTERIZATION OF CARBONIZED CELLULOSE FOR ECO FUEL CELLS

TOSHIMITSU HATA[1,*], RYOHEI ASAKURA[1], YOSHIHARU UCHIMOTO[2],
ROLAND BENOIT[3], SYLVIE BONNAMY[3], PAUL BRONSVELD[4]

[1] RESEARCH INSTITUTE FOR SUSTAINABLE HUMANOSPHERE, KYOTO UNIVERSITY, UJI, JAPAN.
[2] DEPARTMENT OF INTERDISCIPLINARY ENVIRONMENT, KYOTO UNIVERSITY, KYOTO, JAPAN.
[3] CRMD, CNRS-UNIVERSITÉ OF ORLEANS, ORLEANS, FRANCE.
[4] DEPARTMENT OF APPLIED PHYSICS, UNIVERSITY OF GRONINGEN, GRONINGEN, THE NETHERLANDS.

* CORRESPONDING AUTHOR: FAX: +81 774383664; HATA@RISH.KYOTO-U.AC.JP

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ABSTRACT

The development of sustainable and environment-friendly energy systems is necessary. The polymer electrolyte fuel cell (PEFC) has been recognized as an energy-converting device of high efficiency, with low operating temperature and environmental impact. In PEFC, platinum applied as a catalytic electrode is an extremely expensive precious metal. One solution is to use nitrogen-doped carbon as cathode material in order to develop low-cost non-platinum catalyst. In this study optimum synthesis conditions and characterization of carbonized cellulose prepared from cellulose acetoacetate (CAA) and melamine were realized in order to optimize the electrochemical performance of fuel cells. Metal-loaded CAA mixed with melamine as nitrogen source was carbonized at 600 and 900 ºC under N_2 atmosphere. Surface chemistry of N-doped carbonized cellulose was investigated using X-ray photoelectron spectroscopy (XPS). The microtexture of the carbons was characterized by transmission electron microscopy (TEM). According to a theory the ORR activity of the N-doped carbonized CAA materials improve with the increase of atomic ratio of quaternary nitrogen. The development of well graphitized particles and the grafting of nitrogen groups on carbon particles may have important effects on the improvement of electrochemical performance.

1. INTRODUCTION

Research and development of environment-friendly energy is conducted worldwide. Fuel cells are significantly more energy efficient and cleaner than combustion-based power generation technology. Especially, polymer electrolyte fuel cells (PEFC) has been recognized as an energy-converting device of high efficiency, low operating temperature, and low environmental impact (Bashyam and Zelenay, 2006; Costamagna and Srinivasan, 2001). As Pt, which is an extremely expensive precious metal, has been used as a catalytic electrode in PEFC for its high activity with respect to the oxygen reduction reaction (ORR) (Maldonado and Stevenson, 2004), the development of low-cost non-platinum catalysts is desired. In answer to this, nitrogen doped carbon materials have been studied as possible cathode material with efficient oxygen reduction reaction (ORR) activity.

We have used carbon material derived from cellulose, from a renewable biomass source, as a raw material (Xie et al., 2009) prepared by loading it with Co and mixing it with melamine as a nitrogen source. Cellulose acetoacetate (CAA) was introduced with the metal ion of Co. Characteristics of carbon materials are derived from raw material such as CO-metal loaded phtalocyanine and aerogel (Ozaki et al., 2010; Fu et al., 2005; Bron et al., 2002; Jasinski, 1964). The objective of the present study was to investigate the chemical composition and structure of carbonized cellulose prepared from cellulose acetoacetate (CAA) and melamine as a function of the carbonization temperature.

2. **EXPERIMENT**

2.1. SAMPLE PREPARATION

Cellulose acetoacetate (CAA) was prepared from microcrystalline cellulose with diketene (Edgar et al., 1995; Clemens, 1986). CAA was soaked in 0.2 M aqueous solution of cobalt (II) chloride to introduce metal ions. And then chelation of metal ions such as Co^{2+} was conducted from acetylaceton through Enol. The carbon precursor was prepared by mixing cellulose with melamine with a ratio of 75wt% melamine to metal loaded cellulose. The carbon precursor was heated up to the carbonization temperature under a nitrogen gas flow at the rate of 20 °C/min and was kept for 15 min at the carbonization temperature in the range from 600 to 900 °C (Omori, 2000). Finally, the carbonized samples were pulverized by using mortar and pestle.

2.2. CHARACTERIZATION

Surface chemical states of carbonized samples were investigated using X-ray photoelectron spectroscopy (XPS) with a Mg anode at 15kV. The microstructure of the carbons was determined by transmission electron microscopy (TEM). The transmission electron microscope was a JEOL 2010F operated at an acceleration voltage of 200 kV. The specific surface area and pore volume were determined by N_2 measurement at the temperature of liquid nitrogen with a BET apparatus.

3. **RESULTS AND DISCUSSION**

3.1. STRUCTURE OF CARBONS

Cellulose samples loaded with Co (CoCAA) and carbonized in the range from 600 to 900 °C were observed by TEM (JEOL 2010F at 200 kV) to clarify how the carbonization temperature affects the morphology of the resulting carbon. Figure 1 shows TEM images of CoCAA carbonized at 600 °C (a) and 900 °C (b). A nanoshell-like structure with a size of 10 to 20 nm was observed in carbonized CoCAA. The surface of the nanoshells seemed quite disordered, which could be instrumental in the edge exposure of carbon. With the increase of the carbonization temperature, the amount of amorphous carbon was reduced, and graphitic micro fibrils became more pronounced.

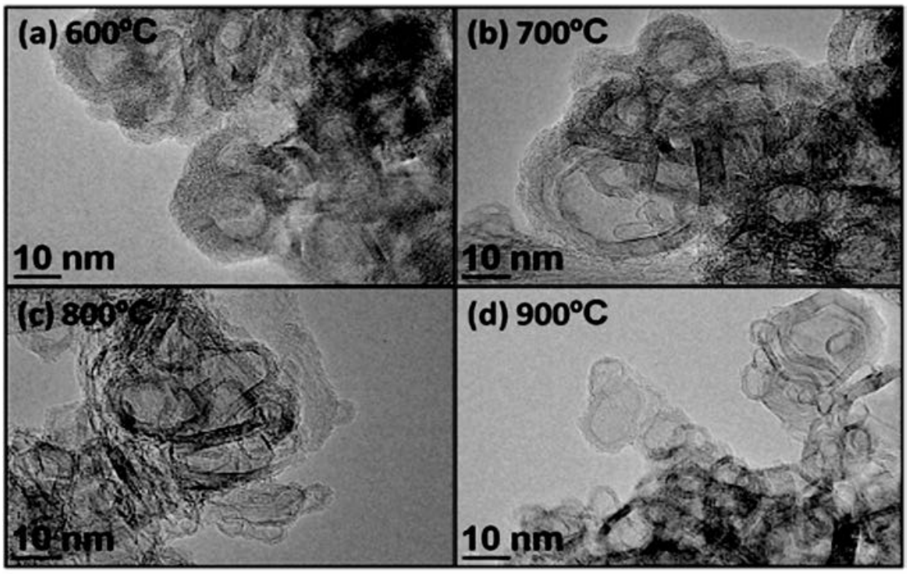


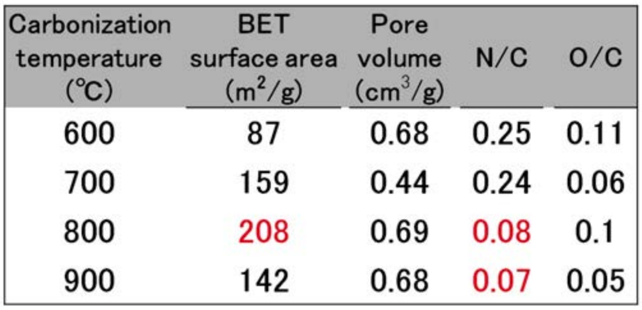
Figure 1: TEM images of CoCAA carbonized at 600 °C (a), 700 °C (b), 800 °C (c), and 900 °C (d).

The specific surface area and pore volume were determined by N_2 measurement at the temperature of liquid nitrogen with a BET apparatus and are summarized in Table 1. The surface area of the carbonized CoCAA sample was about 100-200 m^2/g over the range from 600 to 900 °C. The CoCAA sample carbonized at 800 °C had the greatest surface area in this study. The gap between the nanoshells and/or the voids in the nanoshells could be detected as mesopores (Nabae et al., 2010). One should keep in mind that besides nitrogen content also porosity might contribute positively to the proper working as catalytic material.

3.2. SURFACE CHEMISTRY OF CARBONS

The surface chemical composition and binding states in the samples were investigated by XPS. The data are listed in Table 1 and N1s spectra are given in Figure 2. N/C ratios diminished quite abruptly with increasing carbonization temperature from 700 to 800 °C. On the other hand, the effect of the carbonization temperature on the O/C ratios was less outspoken, as can be read from Table 1.

Table 1: Results of the various characterizations of carbonized cellulose prepared from cellulose acetoacetate (CAA) and melamine.



Carbonization temperature (°C)	BET surface area (m^2/g)	Pore volume (cm^3/g)	N/C	O/C
600	87	0.68	0.25	0.11
700	159	0.44	0.24	0.06
800	208	0.69	0.08	0.1
900	142	0.68	0.07	0.05

In Figure 2 the evolution of the two main N1s-peaks are shown as function of the carbonization temperature. With the increase of the carbonization temperature, the quaternary nitrogen peak became more pronounced, in principle, out of four specific chemical oxidation states; pyridinic (398.6eV), pyrolitic (400.5eV), quaternary (401.3eV) and pyridinic (402-405eV) (Pels et al., 1995; Raymundo-Piñero et al., 2002). One of the two experimental peaks is pyridinic and the other quaternary. Considering the N/C ratio in Table 1 and the N1s spectra in Figure 2, the conclusion must be that surplus nitrogen is removed above 700 °C and graphitic nitrogen is generated. N-doped carbonized cellulose can efficiently be synthesized by balancing the properties based on the hypothesis where quaternary nitrogen (BE: 401.2±0.2 eV) shows the maximum effect to get catalysts with higher potential.

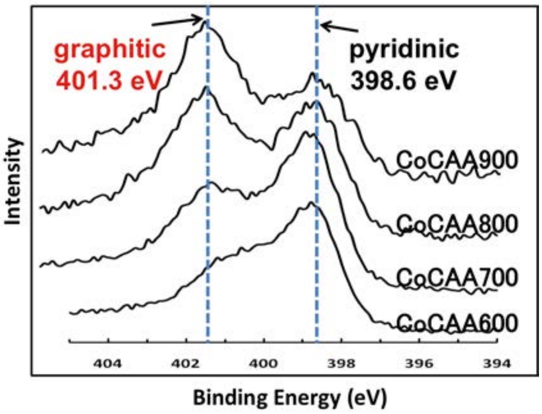


Figure 2: N1s XPS spectra for CoCAA. The XXX notation in figure label CoCAA XXX show carbonization temperature.

4. CONCLUSION

Well graphitized and nitrogen groups grafted carbon particles were successfully developed. The structure and surface chemistry of nitrogen doped carbonized cellulose may give important information for the use as a low-cost catalytic cathode in PEFC without Pt, which will be shown from the measurement and analysis of Cyclic Voltammetry (CV) in our future study.

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