FEASIBILITY OF INCORPORATING TREATED LIGNIN AND CELLULOSE NANOFIBER IN FIBERBOARDS MADE FROM CORN STALK AND RICE STRAW

Dyna Theng

Universitat de Girona

Feasibility of incorporating treated lignin and cellulose nanofiber in fiberboards made from corn stalk and rice straw

DOCTORAL THESIS

Dyna Theng

2017

DOCTORAL THESIS

Feasibility of incorporating treated lignin and cellulose nanofiber in fiberboards made from corn stalk and rice straw

Dyna Theng

2017

DOCTORATE IN TECHNOLOGY

Supervised by:

Dr. Gerard Arbat Pujolràs

Dr. Marc Delgado-Aguilar

Memory presented to obtain the Title of Doctor of Philosophy by the University of Girona

Universitat de Girona

Dr. Gerard Arbat Pujolràs and Dr. Marc Delgado-Aguilar, professors at the Department of Chemical and Agricultural Engineering and Food Technology of the University of Girona,

DECLARE:

That the thesis entitled "Feasibility of incorporating treated lignin and cellulose nanofiber in fiberboards made from corn stalk and rice straw" presented by Dyna Theng has been completed under our supervision.

For all intents and purposes, we hereby sign this document.

Signature,

Dr. Gerard Arbat Pujolràs Dr. Marc Delgado-Aguilar

Girona, April 26th 2017

ACKNOWLEDGEMENTS

Firstly, I would like to acknowledge the sources of my scholarship (the Erasmus Mundus Techno II project and Erasmus^{+} KA107 project), for the financial support provided during my doctoral program. I would like to thank Prof. Dr. Emili Garcia-Berthou, coordinator of the Erasmus Mundus Techno II project, and Prof. Dr. Sovan Lek, coordinator of the Erasmus^{+} KA107 project, for giving me the chance to get the scholarship for my PhD studies. Thanks also to Prof. Dr. Bunthan Ngo, rector of the Royal University of Agriculture (RUA) in Cambodia, Prof. Dr. Mom Seng, vice-rector of RUA, Mr. Kouch Theng, vice-dean of the Faculty of Veterinary Medicine, RUA, and Dr. John Schiller, senior fellow at the University of Queensland, Australia, for their encouragement and support to me in my endeavor to obtain the scholarship for my PhD studies. I would also like to acknowledge the Ministry of Agriculture, Forestry and Fisheries, Cambodia, for giving me permission to pursue my PhD studies.

I would like to express my sincere appreciation to my supervisor, Dr. Gerard Arbat Pujolràs, and co-supervisor, Dr. Marc Delgado-Aguilar, for their valuable guidance and advice. They have inspired and motivated me greatly and have made a tremendous contribution to this project.

Special thanks to Dr. Pere Mutjé Pujol, director of the LEPAMAP research group, Dr. Philippe Evon, research engineer of Laboratoratoire de Chimie Agro-industrielle (LCA), INPT, France, and Dr. Carlos Vaca-Garcia, Head Officer of International Relations of INP-ENSIACET, for providing me with the opportunity to join these research groups and for arranging my access to laboratory facilities. Thanks also to Ms. Ana María Jiménez Serna, Mr. Joan Pere López, Mr. Laurent Labonne, LCA and LEPAMAP's members, and all my friends for their great assistance to me in my laboratory work.

I also want to thank to my wife, Pisey Vong, for her patience during her pregnancy and for taking care of our baby son, Pisoth Sreng Vong. Both of you are the driving force of my life and the inspiration to be a better person every day. I love you!

Last, but not least, I acknowledge my beloved father, Mr. Lysreng Uon, my mother, Mrs. Leav Hak, my mother-in-law, Mrs. Rein Tum, together with other family members and relatives, for their care, understanding, encouragement, blessing, prayers and love. Special thanks to my mother-in-law and my wife's nephew and niece, Mr. Rithy Phalla and Miss. Vechdy Phalla, for their help in looking after my wife and son during the period of my studies.

PUBLISHED AND SUBMITTED PAPERS

The present PhD thesis is based on the following publications and submitted papers.

Paper I. Theng, D., Arbat, G., Delgado-Aguilar, M., Vilaseca, F., Ngo, B., Mutjé, P. 2015. All-lignocellulosic fiberboard from corn biomass and cellulose nanofibers. *Ind. Crops Prod.*, 76, pp 166-173. DOI: 10.1016/j.indcrop.2015.06.046
Journal Impact Factor 2015: 3.449

Paper II. Theng, D., El Mansouri, N., Arbat, G., Ngo, B., Delgado-Aguilar, M., Pelach, M., Fullana-i-Palmer, P., Mutje, P. 2017. Fiberboards made from corn stalk thermomechanical pulp and kraft lignin as green adhesive. *BioResour.*, 12, 2379-2393. DOI: 10.15376/biores.12.2.2379-2393
Journal Impact Factor 2015: 1.334

Submitted articles

Paper III. Theng, D., Arbat, G., Delgado-Aguilar, M., Ngo, B., Labonne, L., Evon, P., Mutjé, P. 2017. Comparison between Two Different Pretreatment Technologies of Rice Straw Fibers Prior to Fiberboard Manufacturing: Twin-screw Extrusion and Digestion plus Defibration. Manuscript submitted to *Ind. Crops Prod.*
Journal Impact Factor 2015: 3.449

Summary of my contribution to the papers included in this PhD thesis:

In all papers, I have participated in the experimental planning, designed and performed all the experimental work, and written the initial version of every manuscript.

Conference contributions

1. Dyna Theng, Gerard Arbat, Bunthan Ngo, Fabioloa, Vilaseca, Jorge Alberto Velásquez, Neus Pellicier, Pere Mutjé. 2014. Feasibility of incoporating treated NFC in all lignocellulosic materials made from corn stalk biomass. *Oral presentation - The VIII IberoAmerican Congress on Pulp and Paper Research*, Medellin, Colombia.
2. Dyna Theng, Gerard Arbat, Quim Tarrés, Marc Delgado-Aguilar, Fabiola Vilaseca, Bunthan Ngo, Pere Mutjé. 2014. Lignocellulosic medium density fiberboards without synthetic adhesives: properties enhancement through the addition of cellulose nanofibers. *Poster presentation - COST Action FP1205 Seminar on "Ongoing modification of cellulose nanofibres and their potential applications"*, Madrid, Spain.
3. Dyna Theng, Gerard Arbat, Marc Delgado-Aguilar, Fabiola Vilaseca, Bunthan Ngo, Pere Mutjé. 2015. Using cellulose nanofibres to reinforce binderless fibreboard made from rice straw biomass. *Poster presentation - COST Action FP1205 seminar on "Advances in cellulose processing and applications –research goes to industry"* Joint Working Groups & Management Committee meetings, Iasi, Romania
4. Dyna Theng, Gerard Arbat, Marc Delgado-Aguilar, Fabiola Vilaseca, Bunthan Ngo, Pere Mutjé. 2015. Feasibility of incorporating treated cellulose nanofiber in all-lignocellulsic fiberboards made from rice straw biomass. Poster presentation – 3rd International Symposium on Green Chemistry, La Rochelle, France.
5. Dyna Theng, Gerard Arbat, Marc Delgado-Aguilar, Quim Tarrés, Bunthan Ngo, Pere Mutjé. 2015. All-lignocellulosic fiberboard made from rice straw fibers with natural binders. Poster presentation – 1st International workshop on biorefinery of lignocellulosic materials, Córdoba, Spain.
6. Dyna Theng, Gerard Arbat, Marc Delgado-Aguilar, Quim Tarrés, Bunthan Ngo, Pere Mutjé. 2015. All-lignocellulosic fiberboard made from rice straw thermomechanical pulp with Eucalyptus cellulose nanofiber reinforcement. Oral presentation - 2nd National Conference on Agriculture and Rural Development, Phnom Penh, Cambodia.

LIST OF ABBREVIATIONS

ADF	Acid detergent fiber
CC	Carboxylic content
CCo	Cooling cost
CD	Cationic demand
CNF	Cellulose nanofibers
CS-TMP	Corn stalk thermo-mechanical pulp
CTMP	Chemi-thermo-mechanical pulping
DMA	Dynamic mechanical analysis
DP	Degree of polymerization
dTGA	Derivative thermogravimetry analysis
E	Extrudate
HCo	Heating cost
IB	Internal bonding strength
IS	Impact strength
kN	Kilonewton
kW	Kilowatt
L_W/D	Length/diameter aspect ratio
L/S	Liquid/solid ratio
MCo	Mechanical cost
Min	Minute
MOE	Modulus of elasticity
MOR	Modulus of rupture
MPa	Megapascal
NDF	Neutral detergent fiber
PC	Production cost
RMP	Refiner mechanical pulping
RS-TMP	Rice straw thermo-mechanical pulp
SEM	Scanning electron microscopy
SGW	Stone groundwood
SME	Specific mechanical energy
STE	Specific thermal energy
TEMPO	Tetramethyl-piperidine-l-oxyl radical
TGA	Thermogravimetric analysis

TMP	Thermo-mechanical pulping
TPC	Total production cost
TRS	Total reduced sulfur
TS	Thickness swelling
WA	Water absorption
WRV	Water retention value
YN	Yield of nanofibrillation

LIST OF TABLES

LIST OF FIGURES

TABLE OF CONTENTS

ABSTRACT

Cellulose-based materials can be found in a huge variety of daily-life products such as paper, cardboard boxes, fiberboards and furniture, among others. Cellulosic resources are interesting due to their abundance, renewability, good mechanical properties and, in addition, their biodegradable character. However, the world natural fiber demand is increasing day by day, while forested lands have a finite capacity to supply the cellulosic resources. While several industries, such as papermaking, is implementing resources saving strategies (i.e. recycling and lower basis weights), there are some that have not adopted this commitment yet. In the same extent, there is the need to look for alternative raw materials, such as waste, side streams or others. Exemplarily, fiberboards manufacturing industries are still using fresh wood resources as raw material and, in addition, they provide the cohesion to the wood particles (or chips) through the addition of synthetic adhesives based on urea/phenol-formaldehyde.

Agricultural waste is of particularly interest due to abundant, cheap, widely available worldwide and renewable material. It represents a good option for wood sources substitution because of their similar in chemical and physical characteristics. In this sense, the present Doctoral Thesis studies the possibility of substituting wood sources by crop residues and replacing synthetic binders by natural adhesives in fiberboard production. Corn and rice biomass were selected to be used as raw materials, followed by thermo-mechanical pulping (TMP) pretreatment, which not includes any chemical. Fiberboards made of corn TMP without any binder presented lower mechanical properties than commercial ones (which contain synthetic binder), while rice presented properties of the same magnitude. In terms of physical properties, lower water absorption and thickness swelling were found for the fiberboards made of agricultural wastes than for the commercial one, clearly showing an advantage of using such raw materials.

Both physical and mechanical properties were then improved through the addition of cellulose nanofibers (CNF), prepared by TEMPO-mediated oxidation, and lignin, extracted from industrial black liquor, as natural binders. In this case, both rice and corn fiberboards presented improved mechanical and physical behavior, being better than commercial fiberboards in all cases (regardless the raw material and the natural binder).

Finally, with the purpose of exploring further the possibilities of these raw materials, another method of thermo-mechanical treatment using a pilot scale twin-screw extruder was tested on rice straw. Some parameters such as energy consumption, production cost, and fibers' characteristics were studied to compare these two technologies. The pilot scale twin-screw

extruder could produce thermo-mechanical fibers with similar characteristics to that of pulping, leading to fiberboards with similar characteristics.

Overall, the present Doctoral Thesis shows a more sustainable and effective way of producing cellulose-based fiberboards without the aid of any synthetic binder, contributing thus to both technical and environmental aspects of fiberboard manufacturing.

RESUMEN

Los materiales en base a celulosa se pueden encontrar en una gran variedad de productos corrientes, tales como papel, cajas de cartón, paneles de fibras, muebles, además de muchas otras. Estos recursos celulósicos son interesantes por su abundancia, renovabilidad, buenas propiedades mecánicas, además de su carácter biodegradable. Por otra parte, la demanda mundial de fibras naturales está aumentando día a día, mientras que los bosques naturales tienen una capacidad finita para suministrar estos recursos celulósicos. Si bien varios tipos de industrias, como la papelera, están implementando estrategias de ahorro de recursos (como son el reciclaje y la utilización de gramajes más bajos), no todos han adoptado este compromiso. Así pues existe la necesidad de buscar materias primas alternativas, tales como residuos celulósicos, materiales reciclados u otros. Sin embargo aún hoy muchos fabricantes de paneles de fibras siguen utilizando maderas naturales como materia prima, además de utilizar adhesivos sintéticos a base de urea/fenol-formaldehído.

Los residuos agrícolas tienen particular interés por ser un material abundante, barato, ampliamente disponible a nivel mundial y renovable. Representan una buena opción para la sustitución de la madera ya que presentan características químicas y físicas similares. En este sentido, la presente Tesis Doctoral estudia la posibilidad de sustituir la madera por los residuos de los cultivos, y los adhesivos sintéticos por aglomerantes naturales, en la producción de tableros de fibras. Para este fin se seleccionó biomasa de maíz y arroz, que recibieron un tratamiento previo consistente en la elaboración de pasta termomecánica (TMP), sin incluir ningún producto químico. Los paneles de fibras hechas de maíz TMP sin aglutinante presentan propiedades mecánicas inferiores a la de los paneles comerciales (que contienen aglomerante sintético), mientras que en el caso del arroz presentan propiedades de la misma magnitud. En términos de propiedades físicas, absorción de agua y consecuente aumento del grosor se constató que los paneles de fibras procedentes de residuos agrícolas presentan mejores propiedades que los paneles comerciales.

Las propiedades físicas y mecánicas mejoraron con la adición de aglutinantes naturales como las nanofibras de celulosa (CNF), preparadas por oxidación TEMPO, y la adición de lignina, extraída de licor negro industrial. En este caso, los paneles de fibra de arroz y maíz presentan un mejor comportamiento mecánico y físico que los paneles de fibras comerciales en todos los casos (sin tener en cuenta la materia prima y el aglutinante natural utilizados).

Finalmente, con el propósito de explorar más a fondo las posibilidades de los paneles naturales, se aplicó otro método de tratamiento termomecánico usando una extrusora de doble husillo a escala piloto, que se probó con paja de arroz. Se estudiaron algunos parámetros como el consumo de energía, los costes de producción y las características de las fibras para comparar estas

dos tecnologías. La extrusora de doble husillo pudo producir fibras termomecánicas con características similares a la de fabricación de pasta, dando lugar a placas de fibras con características similares.

En general, la presente Tesis Doctoral muestra una forma más sostenible y eficaz de producir paneles de fibras a base de celulosa sin la ayuda de ningún aglomerante sintético, lo que contribuye a la mejora técnica y reducir el impacto ambiental del proceso de fabricación de paneles de fibras.

RESUM

Els materials en base a cel·lulosa es poden trobar en una gran varietat de productes corrents, com ara paper, caixes de cartró, panells de fibres, mobles, a més de moltes altres. Aquests recursos cel·lulòsics són interessants per la seva abundància, són renovables, bones propietats mecàniques, a més del seu caràcter biodegradable. Per altra banda, la demanda mundial de fibres naturals està augmentant dia a dia, mentre que el boscos naturals tenen una capacitat finita per subministrar aquests recursos cel·lulòsics. Si bé diverses indústries, com la paperera, estan implementant estratègies d'estalvi de recursos (com són el reciclatge i la utilització de gramatges més baixos), no tots han adoptat aquest compromís. Així doncs hi ha la necessitat de buscar matèries primeres alternatives, com ara residus cel·lulòsics, materials reciclats o altres. Mentrestant encara molts fabricants de panells de fibres segueixen utilitzant fustes naturals com a matèria primera, a més d'utilitzar adhesius sintètics a base d'urea/fenol-formaldehid.

Els residus agrícoles tenen particular interès per ser un material abundant, barat, àmpliament disponible a nivell mundial i renovable. Representen una bona opció per a la substitució de de la fusta ja que presenten característiques químiques i físiques similars. En aquest sentit, la present Tesi Doctoral estudia la possibilitat de substituir la fusta pels residus dels cultius, i els adhesius sintètics per aglomerants naturals, en la producció de taulers de fibres. Per aquest fi es va seleccionar biomassa de blat de moro i arròs que van rebre un tractament previ consistent en l'elaboració de pasta termomecànica (TMP), sense incloure cap producte químic. Els panells de fibres fetes de blat de moro TMP sense cap aglutinant presenten propietats mecàniques inferiors a la dels panells comercials (que contenen lligant sintètic), mentre que en el cas de l'arròs presenten propietats de la mateixa magnitud. En termes de propietats físiques, absorció d'aigua i conseqüent augment del gruix es va constatar que els panells de fibres procedents de residus agrícoles presenten millors propietats que els panells comercials.

Les propietats físiques i mecàniques van millorar-se amb l'addició d'aglutinants naturals com les nanofibres de cel·lulosa (CNF), preparades per oxidació TEMPO, i l'adició de lignina, extreta de licor negre industrial. En aquest cas, els panells de fibra d'arròs i blat de moro presenten un millor comportament mecànic i físic que els panells de fibres comercials en tots els casos (sense tenir en compte la matèria primera i l'aglutinant natural utilitzats).

Finalment, amb el propòsit d'explorar més a fons les possibilitats dels panells naturals es va realitzar un altre mètode de tractament termomecànic fent servir una extrusora de doble cargol a escala pilot, que es va provar amb palla d'arròs. Es van estudiar alguns paràmetres com el consum d'energia, els costos de producció i les característiques de les fibres per comparar aquestes dues

tecnologies. L'extrusora de doble cargol a escala pilot va produir fibres termomecàniques amb característiques similars a la de fabricació de pasta, donant lloc a panells de fibres amb característiques similars.

En general, la present Tesi Doctoral mostra una forma més sostenible i eficaç de produir panells de fibres a base de cel·lulosa sense l'ajuda de cap lligant sintètic, el que contribueix a la millora tècnica i reduir l'impacte ambiental del procés de fabricació de panells de fibres.

GENERAL INTRODUCTION

Cellulosic sources

Natural fibers

Fiberboards

1 GENERAL INTRODUCTION

1.1 Cellulosic sources

Natural fibers are interesting due to several aspects such as renewability, availability, biodegradability, recyclability, light weight, and high mechanical properties (Sanjay et a., 2016) . Cell walls of plants consist mainly of three organic compounds, i.e. cellulose, hemicellulose, and lignin. Cellulose is the most abundant polymer on the earth, and presents in a wide variety of living species including plants, animals, and some bacteria (Chen, 2014). However, the world natural fiber demand is increasing day by day, while the world forested lands have a finite capacity to supply the cellulosic resources (Hubbe, 2014). In this sense, there is the need to look for alternative raw materials and/or to develop high performance cellulose-based materials.

Agricultural waste is of particularly interest due to abundant, cheap, widely available worldwide and renewable material (Searle & Malins, 2013). It represents a good option for wood sources substitution because of their similar in chemical (Table 1) and physical (Table 2) characteristics. Regarding the chemical compositions, all non-woods are characterized by a lower cellulose and lignin content than wood, but not so highly different. Crop fibers such as wheat straw, rice straw, and corn stalk have number of cellulose content (between 28 and 48%) closer to that of softwood (40-45%). However, they have higher pentosan or hemicellulose content and ash, particularly rice straw between 23-32% and 3.2-20%, respectively, compared to softwood at 7-14%, 1% for pentosan and ash content (Hurter, 2006).

Table 1. *Chemical compositions of some agricultural wastes compared to those of wood sources*

Fiber sources	Cellulose (%)	Lignin (%)	Pentosan (%)	Ash (%)	Silica (%)
Kenaf core	34	17.5	19.3	2.5	-
Sugarcane bagasse	32 - 44	19 - 24	27 – 32	1.5 - 5	0.7 - 3
Wheat straw	29 - 35	16 - 21	26 – 32	4 - 9	3 - 7
Rice straw	28 - 36	12 - 16	23 - 28	15 - 20	9 - 14
Corn stalk	48	16	28	3.2	-
Softwood	40 - 45	26 - 34	7 – 14	1	<1
Hardwood	38 - 49	23 - 30	19 – 26	1	<1

Source: Hurter (2006). The cellulose is defined as alpha cellulose.

Concerning the physical properties, softwoods are relatively uniform consisting of over 90% tracheid fibers and only 10% stubby ray cells and other fines. Hardwoods are more heterogenous and contain only about 50% tracheid fibers and a large number of vessel cells and ray cells. However, nonwoods have large differences in their physical characteristics, varying from 20 to about 175% (Table 2). Monocots such as cereal straws, sugarcane bagasse, and corn stalks

are more similar to hardwoods as the "fiber' fraction in the same order. Moreover, they are more heterogenous with a large proportion of very thin-walled cells, barrel-shaped parenchymous cells, and vessel and fine epidermal cells in a wide range of dimensions.

Table 2. *Mean of morphological properties of some crop residues and wood fibers.*

Sources of fibers	Length (mm)	Diameter (mm)	L/D aspect ratio
Kenaf core	600	30	20
Sugarcane bagasse	1700	20	85
Wheat straw	1480	13	110
Rice straw	1410	8	175
Corn stalk	1260	16	80
Softwood	3000	30	100
Hardwood	1250	25	50

Source: Hurter (2006)

Nevertheless, a main disadvantage of wood is that wood takes several years to grow to the pulpwood size, while nonwood plants are annual and seasonal crops (Hurter, 2006).

Within the group of agricultural wastes, corn, rice, and wheat biomass can be considered as the potential candidates for wood-base panel production in terms of its global production. Globally, the production of the cereals is increasing year by year since they are the main food crops for human and animals around the world. Figure 1 shows the evolution of the crops in the world during the decade 2005 to 2014 (FAOSTAT, 2017).

Corn (*Zea Mays, Poaceae* family) is a cereal crop, grown in various agro-ecological zones (Hoopen & Maïga, 2012). It is an important food for many people in Africa, Asia and Latin America (Yaning et al., 2012) and is also used in livestock feed (poultry, pigs, cattle) in the form of grains, feed milling or as fodder (Hoopen & Maïga, 2012). Cobs, leaves and stalks are important residues of corn processing and consumption, remaining after corn grains are collected. According to Sokhansanj, Turhollow, Cushman, and Cundiff (2002), the corn biomass is about 0.50 kg in every 1 kg of dry corn grain.

Rice (*Oriza Sativa L.*) is cultivated to feed more people and animals over a longer period than any other crop. As far back as 2500 B.C., rice has been documented in the history books as a source of food and for tradition as well (Thomas L., 1997). Rice straw is a by-product of rice crop with a straw to grain ratio of 1.4 (Kim & Dale, 2004). In terms of total production, rice is the second most important grain crop in the world after corn. The world annual rice production in

2014 was about 741 million tons (Figure 1), which gave an estimation of about 1,139 million tons of rice straw.

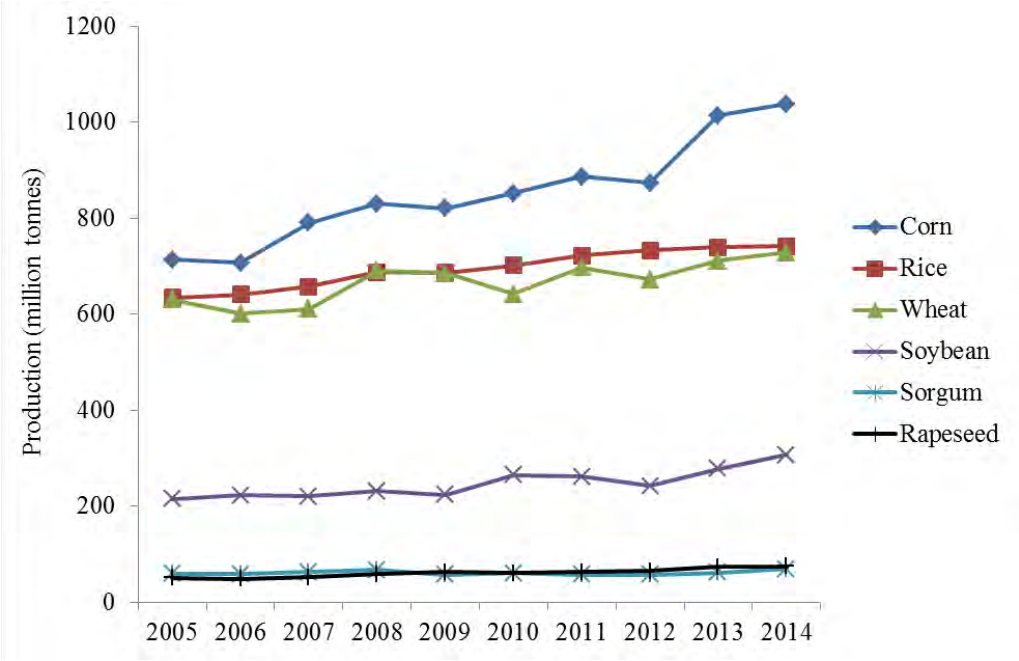


Figure 1. *Data of some crops production in the world during 2005-2014.*

However, a large part of these are used for cattle feed, for bioethanol production, or incorporated into the soil as an organic amendment (G. Chen et al., 2010; Flandez et al., 2012; Hong, Zhou, & Hong, 2015; Pinto et al., 2012; Randy & Lynn, 2013). Possible uses of these agricultural wastes are limited by its low bulk density, a slow degradation in the soil, the harboring stem diseases (the possible transmission of diseases to the future crop), and a high ash content which can be a problem for subsequent ethanol or energy production (Binod et al., 2010). Thus, open field burning is still a common practice, particularly in some developing regions of the world (Pang et al., 2012). For instance, according to Kanokkanjana and Garivait (2013), about 56 % of the total rice straw production was burned in Thailand in 2010. Since these residues are not efficiently managed after its exploitation and there is a lack of waste management, there is the need of looking for applications of such residues. Therefore, it would be necessary to find alternatives for the use of these crop residues.

1.2 Natural fibers

All plant fibers have the form of a heterogeneous complex of carbohydrate polymers. Cellulose and hemicelluloses are densely packed by layers of lignin, which protect them against enzymatic hydrolysis. Thus, a pretreatment step is necessary to break the lignin seal, until exposing cellulose and hemicelluloses for a subsequent enzymatic action or contributing to the biomass

defibration (Vandenbossche et al., 2016, 2015, 2014). Since each raw material present different chemical composition, versatility on process conditions is required. Recently, some pretreatment methods have been carried out to treat the fiber sources from agricultural wastes in order to obtain resources for their purposes. The different methods are chemical, mechanical, and thermo-mechanical pretreatment (Pelaez-Samaniego et al., 2013).

1.2.1 Pulping

Pulping is the process to free fibers in wood or plants from the lignin that binds these fibers together, and then to suspend the fibers in water into a slurry suitable for paper and/or fiberboard making (IETD, 2010; Suchsland & Woodson, 1987). The commercial processes are generally classified as mechanical, chemical or semi-chemical pulping (Kramer et al., 2009).

Chemical pulping has been used for years, using both woody and non-woody fibers (Wegener, 1992). There are two principal methods in this pulping process: alkaline (or kraft) and acidic (or sulfite) process. The chemical kraft pulping method is the most commonly use to dissolve lignin from wood to create a pulp for paper and board manufacturing (Sridach, 2010). The kraft pulping produces a stronger pulp, but it is feeling the pressure on environmental regulations on emission from the manufacturing plants of total reduced sulfur compound (TRS), sulfur dioxide, suspended solids, and waste water pollution (Barla, 2007).

Mechanical pulping is the oldest form of pulping, uses mechanical energy to weaken and separate fibers from wood through a grinding action. There are four main types of mechanical pulping (Kramer et al., 2009) as following:

- Stone groundwood (SGW) pulping: small logs are ground against artificial bonded stones made of silicon carbide or aluminum oxide grits. The process gives a high yield and short fibers. For paper making, the process needs to combine with expensive chemical fibers to be strong enough to pass through the paper machine and subsequent coating and printing processes.
- Refiner mechanical pulping (RMP): wood feedstock is ground between two grooved discs. The process keeps the high yield advantages of the SGW process, while producing somewhat longer fibers and greater strength. Another advantage of this process is being able to use wood feedstock such as wood scraps and sawdust from lumber mills other than logs.
- Thermo-mechanical pulping (TMP): wood chips are firstly steamed to soften them before being ground in the same manner as the RMP process. The TMP process generates the

highest grade mechanical pulp, but it is also a high energy intensity process due to its steaming. Nevertheless, TMP is the most common mechanical process in use today.

- Chemi-thermo-mechanical pulping (CTMP): this involves the application of chemicals to wood chips prior to refiner pulping. The chemical pre-treatment of wood chips allows for less destructive separation of fibers from the feedstock, resulting in longer fibers, higher fibers content, and little fines. The CTMP process also produces more flexible fibers (i.e. higher sheet density, burst strength, and tensile strength) with higher pulp brightness, compared to the TMP process.

Chemical pulping creates higher sheet strength than mechanical pulping (Kramer et al., 2009). However, the production yield was much lower, about 40-50% pulp, while the mechanical pulping yields is up to 97% (Brady & Dahlgren, 1998; IETD, 2010; Kramer et al., 2009).

According to Cotana et al. (2015), among all pretreatment by pulping methods, thermo-mechanical pulping (hydrothermal processing) is an interesting clean technology for the fractionation of lignocellulosic biomass. The main advantages, compared to chemical pretreatment, are that TMP does not use any solvent besides water. It reduces corrosion of equipment. In addition, the operational process is simple and economical. However, this pretreatment process still has some disadvantages including:

- Degradation part of the xylan fractionation to volatile compounds
- Incomplete disruption of the biomass bonds
- Formation of inhibitors that influences the following steps.

1.2.2 Steam explosion

Steam explosion technology was invented by Mason in 1926, which used to disintegrate the wood materials (Mason, 1926). It is one of the most effective way which is used in biological energy and panel production (Kabel et al., 2007; Luo et al., 2014; Zhang & Xue, 2015). Steam explosion is a very physicochemical treatment of raw materials that involves an instantaneous release of high steam pressure in a closed container (Yu et al., 2012). The principle of steam explosion pretreatment is using the high temperature and high pressure steam to process the plant fiber raw materials. It aims to make the degradation of hemicellulose, softening lignin, and decreasing literal connection strength between the fibers (Shao et al., 2008). After a period of high temperature and high pressure treatment, the steam released in a short time to achieve the effect of the chemical composition separation and the structural change (Vignon, Dupeyre, & Garcia-Jaldon, 1996).

In view of various pretreatment methods, steam explosion has been widely used in the pretreatment of lignocellulosic biomass, due to its advantages such as (i) high efficiency without pollution (no chemical are used except water), (ii) good yield of hemicellulsoes with low degraded by-products, (iii) equipment corrosion is minimum due to a mild pH of reaction media when compared to acid hydrolysis processes, (iv) stages of acid handling and acid recycling are avoided, and (v) disruption of the solid residues from bundles to individual fibers occurs due to explosion effect (Garrote, Dominguez, & Parajo, 1999; Stelte, 2013).

1.2.3 Extrusion

Extrusion is defined as an operation of creating objects of a fixed, cross-sectional profile by forcing them through a die of the desired cross-section. The extrusion process has been expanded as one of the physical continuous pretreatment methods. It is widely used in the snack food, feed, plastic, and composite industries (Zheng & Rehmann, 2014).

Extrusion is a novel and promising thermo-mechanical pretreatment method for biomass conversion because of the low cost, good monitoring of temperature and screw speed, high shear, and excellent processing ability. Twin-screw extruder is increasing favored because of the extended control of residence time distribution and mixing, and also superior heat and mass transfer capacity (Lin et al., 2013). The twin-screw extruder is based around screw elements' functions such as:

- Forward screw elements: transport bulk material with different pitches and lengths with the least degree of mixing and shearing effects;
- Kneading screw elements: exert a significant mixing and shearing effect with different stagger angles in combination with a weak forward conveying effect;
- Reverse screw elements: push the material backward, carried out extensive mixing and shearing effects (Rigal, 1996).

With different screw configurations, the twin-screw extruder can conduct diverse functions and processes in a single step such as transporting, heating, mixing, shearing, grinding, chemical reaction, drying and liquid-solid separation (Kartika, Pontalier, & Rigal, 2010).

Extrusion pretreatment has some advantages over the other pretreatments including lower production cost and better monitoring process (being able to control all variables) (Abe, Iwamoto, & Yano, 2007); no sugar degradation products (De Vrije et al., 2002) as this component can contribute to the self-bonding of fiberboards using hot pressing (Hashim e al., 2012, 2011a, 2011b; Tajuddin et a., 2016). According to Rizvi and Mulvaney (1992), the extrusion method also

provided good adaptability to different process modifications and high continuous inlet flow rate, leading to better productivity.

However, extrusion pretreatment technology also has some disadvantages such as stones or metallic materials in some substrates severely reduce the life time of the screws. This has a negative impact on the economics of the extrusion process. Another disadvantage is thermal-sensitive. In addition, establishing a parallel with papermaking, it is reasonable to assume that the ultimate strength of fiberboards made from extrudate probably lower than TMP. Indeed, in the paper industry, a higher specific surface and a decrease in the mineral content (cases of TMP compared to extrudates) should promote the compatibility of lignocellulosic fibers, leading to an increasing amount of bonds between fibers (i.e. higher relative bonded area) and thus to a higher fiberboard compaction (Page, 1969; Vilaseca et al., 2008).

1.3 Fiberboards

1.3.1 Definition of fiberboard

Fiberboard is a generic name for construction panels made of wood or vegetable fibers. Some are homogenous materials, while others are laminated sheets with fiber cores and surfaces of ground wood. The fiberboard panels are usually manufactured from different fibers such as jute, straw, sugarcane stalk, flax, hemp, grass, newspaper, and peanut shells; under names of Fir-tex, Homasote, Masonite, Beaver Board, Feltex, Nu-Wood, and Upson Board (Wilson, 2007). The fiberboards are commonly used in furniture industry, indoor and outdoor, insulation and soundproofing.

1.3.2 Fiberboard manufacturing process

Historic manufacturing process of fiberboards using various starting materials (pretreated fibers). However, pulping process that cooked or ground the wood or plant fibers is the most required one (Wilson, 2007). Two methods have been widely used in the fiberboard production:

- Wet process: involves the dispersion of cellulosic materials into water. Hydrogen bonds formation and thermosetting adhesive behavior of lignin are expected during heating and drying process. Accordingly, less or non-binder are needed. On contrary, a low density and limited strength of fiberboards, along with waste water pollution are the main disadvantage of this process (Zhang et al., 2015).
- Dry process: moisture content of the cellulosic materials is reduced through drying before combination with additives or resins. After distribution of mixture into mat, in undergoes prepress and hot pressing to finally produce fiberboards (Zhang et al., 2015).

The different feature between the wet and dry process fiberboard is that the wet process has a fibers' moisture content of more than 20%, whereas the dry process has a moisture content of fibers less than 20% at the forming stage (WPIF, TRADA, & TTF, 2014).

According to Zhang et al. (2015) and Lee & Hunt (2013) binderless fiberboard production has been patented using a wet process, while the industrial manufacture of this binder free fiberboard is mainly based on dry-forming process without resins addition.

1.3.3 Binders

In fiberboard manufacturing, the presence of adhesives either a synthetic or a natural is required to glue the wood particles together for obtaining a proper product in term of mechanical properties and dimensional stability (Kojima et al., 2016; Zhang et al., 2015).

1.3.3.1 Synthetic adhesives

Formaldehyde based resins such as phenol formaldehyde and urea-formaldehyde are common synthetic adhesives used in fiberboard production due to their low cost, high effectiveness, and desirable performance. However, the emission of formaldehyde from fiberboards gave rise to environmental and health trouble (Salthammer et al., 2010) as formaldehyde is a non-biodegradable constituent. Moreover, the cost of fiberboard products would increase due to extensive use of these adhesive (Kojima et al., 2016), approximately 60% of the total fiberboard production (Hashim et al., 2011). Recently, formaldehyde has been reclassified into carcinogenic category 1B according to labeling and packaging of substances and mixtures regulation in Europe (Regulation 605/2014).

1.3.3.2 Natural adhesives

A. Lignin

Lignin is a complex polymer that binds to cellulose fibers and hardens and strengthens the cell walls of plants. It is the second most abundant natural polymer after cellulose. The lignin is separated from wood during pulping and papermaking operations (Lora & Glasser, 2002).

Lignin structure varies following their isolation method and source of plants (Lora & Glasser, 2002). However, it can be rationalized as the polymerized product of the three basic phenylpropane monomers (monolignols): coumaryl alchohol, coniferyl alcohol, and sinapyl alcohol (Figure 2a). These three monolignols are the majority in the lignin polymer molecules. The proportion of different monomers in lignin varies depending on the different type of plant material. Several kinds of lignin such as kraft lignin and lignosulfonate, have been added for binderless fiberboard manufacture. They showed improvement on mechanical and dimensional

stability of the fiberboard product (Anglès et al., 2001; Mancera et al., 2012). In the production of binderless fiberboards, lignin plasticization and cross-linking reaction between lignin and furfural have been considered to be partially responsible for board adhesion. The lignin was melt and created a welding effect during the molding operation (Bouajila et al., 2005). Kraft lignin, which is the most common technical lignin, illustrates the different important linkages as shown in Figure 2b.

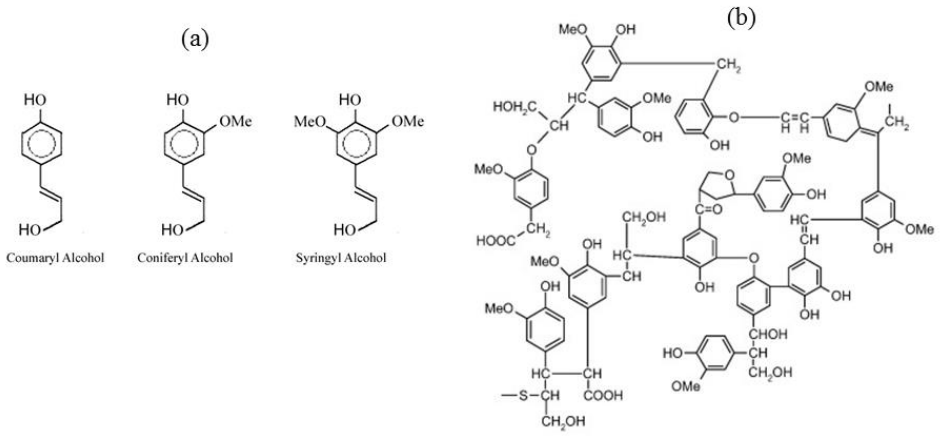


Figure 2. *Structure of monolignols lignin (a) and kraft lignin (b).*

Kraft lignin is generated during kraft pulping in alkaline medium, contacting a little number of aliphatic thiol groups that give the isolated product a characteristic of odor, especially during heat treatment. Kraft lignin is a dark-colored, water- and solvent- insoluble products that dissolve in alkali because of its high phenolic hydroxyl groups concentration (Lora & Glasser, 2002). Depending on the pH value to which the black liquor is acidified, a different composition and yield of the lignin is obtained (Norgren & Edlund, 2014).

The main source of lignin is readily available for use on a larger scale comes from spent pulping liquors and chemical liberation of wood fibers from the pulp and paper industries. According to (Norgren & Edlund, 2014) the global production of lignin-based materials and chemicals exceeds 50 million tons per year. However, it has not yet been converted into high-value products on a large-scale and today lignin is mainly used for energy recovery at the pulp mills. Just a small amount of it, approximately 2% is utilized in value-added and commercial products such as paper industries, medical, agriculture, fuel, chemical, concrete and cement, carbon fibers/nanotubes, board binder, dust controller, battery, cosmetics, foams, plastics, and heat (Ayyachamy et al., 2013).

Nevertheless, this trend is changing due to the increasing of interest in developing lignin-based products. Some of these high-value products include: green substitutes for fossil fuel, carbon

fibers, surfactants, polymer blends and composites; phenol replacement in phenol-formaldehyde resin; and green binders. Lignin could replace up to 50% of synthetic binders (i.e. phenolic based resins), although the effective use for it remains uncertain on industrial scale (Gosselink et al., 2011).

B. Cellulose nanofibers (CNF)

Cellulose nanofibers (CNF) are the smallest cellulose building elementary fibril made up of 36 cellulose chains. It has dimension between 5 and 50 nm in diameter, depending on cellulose source and preparation method, with several micrometers range in length (Thakur & Thakur, 2015). CNF has been regarded as a high-performance cellulose-based material (Sun et al., 2016). It consists of two linked D-glucose molecules with 1-4 β glycosidic bonds and composes of crystalline and amorphous regions (Figure 3). These repeating units (or called degree of polymerization, DP) vary depending on different types of fiber sources. CNF can be extracted from the cell wall of various raw materials such as softwood, hardwood, plants and other agricultural residues.

Fabrication of CNF composes mainly in disassembling the hierarchical structure of cellulose fibers. Recently, the CNF has been interesting by several researchers for application in various products (Delgado-Aguilar et al., 2015; Espinosa et al., 2016; Lay et al., 2016; Sun et al., 2016; Thakur & Thakur, 2015). Most of these studies have been performed mainly on bleached chemical pulps from woody plants, for instance eucalyptus and pine (Espinosa et al., 2016).

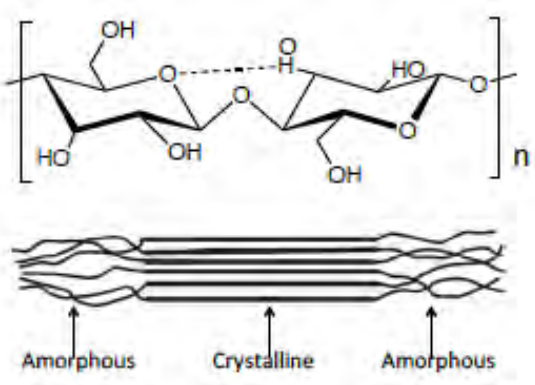


Figure 3. *Chemical structure of CNF (top) and their cellulose chains (bottom).*

The purpose of pretreatment is to obtain fiber less stiff and cohesive, which reduces energy consumption in mechanical disintegration process, particularly leading to the industrial scale production. This method makes the nanofibrillation easier, mainly by shortening and loosening the cell wall structure of the cellulose fibers and limiting the hydrogen bonds, or adds repulsive charge, and/or decreasing the DP or the amorphous link between individual CNF (Siró & Plackett, 2010).

There are mainly three pretreatments have been used to separate nanofibrils as following:

- Mechanical treatment: disintegration, refining, or PFI milling is used to reduce the cellulose raw material size and to open the structure for further separation (Henriksson et al., 2007).
- Enzymatic pretreatment: is often done using endoglucanase enzyme. The enzyme is used because it is not attack crystalline cellulose as easily as the other cellulosic enzymes (Henriksson et al., 2007).
- Chemical pretreatment: TEMPO-mediated oxidation (2,2,6,6-tetramethyl-piperidine-l-oxyl radical, carboxymethylation, and periodate-chlorite oxidation have been used to favor the nanofibers isolation (Oksman et al., 2014).

None of the existing methodologies for nanocellulose production has been successfully scaled up in terms of effectiveness and production costs. In this sense, there is an apparent need of developing optimized methodologies for nanocellulose production strongly addressed for the final application. Tailor-made nanostructured cellulose must be developed taking into account the differences on the chemical composition of the starting materials, production costs and the final requirements and applications.

CNF has been potentially applied in various functions and products based on its specific advantages (Table 3).

Table 3. *Properties and potential applications of cellulose nanofibers*

Properties of CNF	Potential applications
• Light weight material • Natural and renewable • Biodegradability • Biocompatibility • High strength and stiffness • High surface area and aspect ratio • High reactivity, barrier properties • Transparent and dimensional stability • Thermal stability (~ 200 °C)	• Composites (e.g. electronics, biosensors) • Construction and porous materials • Fiber web structures (e.g. paper and board) • Coatings • Functional additives (e.g. rheology modifier) • Functional surfaces • Environment and waste treatment • Energy, thermal insulation • Heavy metals and toxins detectors and removers • Textile

Source: Wei et al. (2014)

Among all these interesting and novel applications, nanocellulose can offer a wide range of functionalities, properties and environmental friendly solutions.

CNF has been used as an additive for papermaking slurries. Several recent publications confirm the improvement of paper's strength after addition of CNF as a bulk additive. The presence of CNF in the papermaking slurries boosts the formation of hydrogen bonds between fibers during paper formation, the main mechanism that dominates the increase of paper's strength. Besides, CNF promote reduction of porosity and increase of the density in the paper (Espinosa et al., 2016). However, the use of CNF technology in wood-based materials remains a limitation. In our understanding, there were two literatures found the use of CNF as a reinforcement of particleboard and fiberboard made from wood fibers (Cui et al., 2014; Kojima et al., 2016).

The application of wood fibers and the development of nanoscale cellulosic materials (e.g. cellulose nanofibrils, CNF) has also opened a new window of possibilities of reinforcement of polymer matrices. CNF can be designed with tailor-made properties such as surface chemistry (a variety of functional groups, with and without lignin) and morphology, from a range of natural fibers. This adds to the versatility of the material as an appropriate and environmentally sound component for bionanocomposite products with enhanced properties and functionality. However, the development has been limited by various aspects such as:

- Effective and cost effective production
- Appropriate surface modification for enhancing the interaction with polymer matrices; and
- Industrially feasible compounding strategies.

OBJECTIVES

Motivation of the study

General objective

Specific objectives

2 OBJECTIVES

2.1 Motivation of the study

Commercially, fiberboards are made of fresh wood resources and synthetic adhesives such as urea/phenol-formaldehyde. Although wood is widely available, natural resources must be used in a responsible way, trying to get the best out of the resources that Earth provides us. In my home country, Cambodia, rice and corn are abundant and the waste after their cultivation (straw and stalks, respectively) is merely left in the field, dumped or even burned. This practice could fall into disuse through the valorization of these wastes, contributing both to economic growth of rural areas and environment.

On the other hand, formaldehyde-based resins come from non-renewable resources and, in addition, they are not biodegradable. In this sense, alternative binders based on natural resources must be developed. One strong alternative is the use of high-performance cellulose-based materials, such is the case of cellulose nanofibers (CNF), which could provide cohesion to the laminates. Another alternative is to recover lignin from industrial black liquors, which are a side stream from pulp industry.

In 2013, I applied for an ERASMUS Mundus grant to develop my Doctoral Thesis in the field of natural fibers and therefore I was assigned to LEPAMAP research group, in the University of Girona. This group works on the use of natural fibers for several applications (i.e. papermaking, composites, fiberboard manufacturing and others) since the beginning of the Nineties and, in the last years, they have been intensively working on CNF.

Overall, the motivation of this study is to find greener alternatives to fiberboards manufacturing, improving at the same time their properties and giving a “new life” to those resources that nowadays are considered as waste. The success of this study would show a business opportunity for rural areas wide world, but specifically in my home country where resources are not well managed, and, at the same time, an opportunity to contribute to the environment.

2.2 General objective

The general objective of the study was to make fully bio-based and biodegradable fiberboards from two agricultural wastes, i.e. corn and rice biomass, with significantly better physical and mechanical properties than commercial fiberboards made from wood and synthetic adhesives.

2.3 Specific objectives

To accomplish the general objectives, several specific objectives were defined and they can be listed as follows:

i. To determine the suitability of rice and corn biomass to be used as raw materials for fiberboards manufacturing in terms of chemical composition compared to softwood and hardwood.
ii. To explore the optimum conditions (temperature, time and liquid/solid ratio) for thermomechanical pulp production in terms of production yield and mechanical properties of fiberboards.
iii. To study novel methodologies of pulp production at pilot scale using a twin-screw extruder.
iv. To assess the effect of the pulping and the extruding on the chemical composition of the raw materials and the morphology compared to softwood and hardwood.
v. To determine the viability of using extrusion and pulping in terms of production costs.
vi. To obtain fiberboards from corn and rice fibers through wet process methodology without synthetic adhesives.
vii. To explore the suitability of using cellulose nanofibers and lignin as natural adhesives for fiberboards.
viii. To significantly improve the mechanical (bending strength) and physical (water absorption and thickness swelling) properties through the incorporation of natural binders.
ix. To obtain fiberboards with significantly better properties (mechanical and physical) than those commercials.

MATERIALS AND METHODS

Materials

Equipment

Methods

3 MATERIALS AND METHODS

3.1 Materials

Corn biomass (paper I and II) was kindly supplied by La Tallada d'Empordà (Spain). The provided biomass was the whole plant of corn including cobs and silks. This biomass, properly screened, was used to produce thermo-mechanical pulp (TMP).

Rice straw (paper III) was provided by JCL AGRI (France). The rice straw was used to study on using different technologies, i.e. TMP preparation by digestion plus defibration at laboratory scale to compare with a commercial scale twin-screw extrusion.

Commercial bleached *Eucalyptus* pulp was used as raw material for cellulose nanofibers (CNF) preparation and was kindly supplied by Torraspapel S.A. (Spain). This pulp is typically used for printing/writing paper manufacturing. According to the supplier, the kappa number was lower than 0.6, leading to a brightness of 91.1 %.

Industrial black liquor (paper II) is a waste of pulp and paper factory, provided by Torraspapel S.A. (Zaragoza, Spain). The black liquor (in sticky glue-like form) had concentration of 64% and pH of about 12, stored in a plastic container, at room temperature. This black liquor was used to obtain lignin powder.

3.2 Equipment

3.2.1 Mills

Several mills were used in this Thesis for different purposes. A knives mill from Agrisma (Spain) (Figure 4a) was used to mill corn stalk and rice straw from the whole plant to be biomass particles, for the use in the TMP preparation by pulping in a laboratory scale digestion plus defibration. The knives mill was used and presented in Paper I and II. A hammer mill of Electra BC P (France) (Figure 4b) was used to mill rice straw from whole plant to be biomass particles for a pilot scale fibers preparation of extrusion method to compare with the digestion plus defibration pulping. The hammer mill was used and presented in Paper III. Finally, a Foss mill of Cyclotec 1093 (Denmark) (Figure 5) was used to grind the materials for chemical compositions, mineral and thermal properties analyses (Paper III).

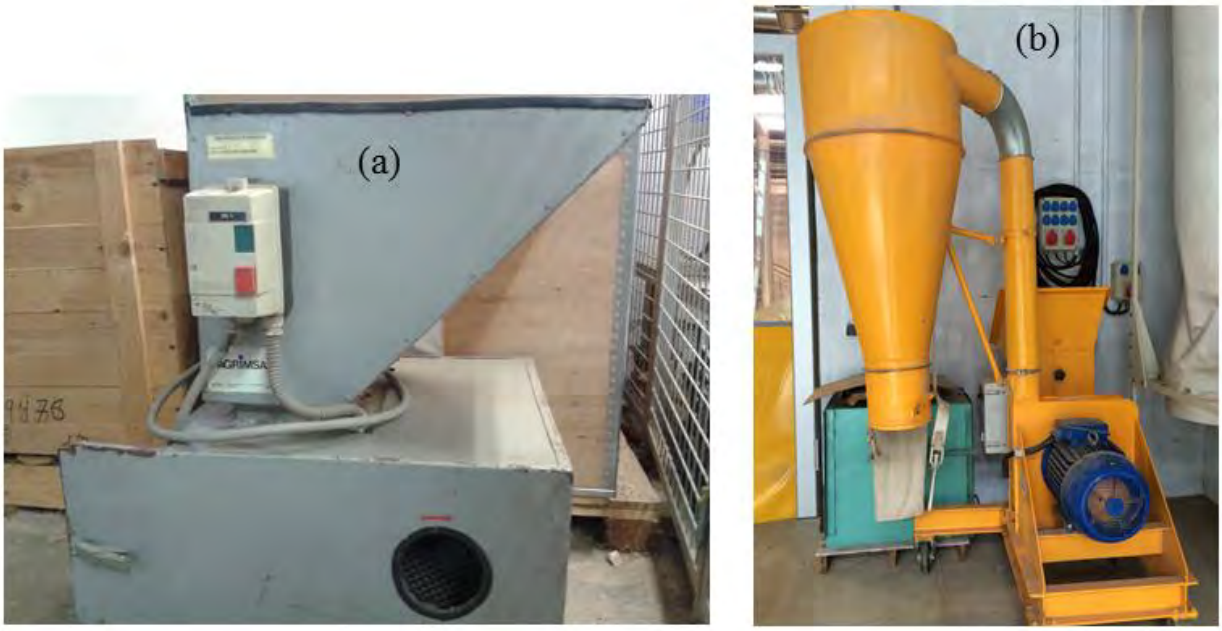


Figure 4. *Knives mill of Agrisma (a) and hammer mill of Electra (b).*

Figure 5. *Foss mill, Cyclotec 1093, Denmark.*

3.2.2 Rotary digester

The laboratory scale rotary digester was designed by LEPAMAP research group from the University of Girona and was used for TMP preparation (Paper I, II, and III). The digester had two heating resistances with a heating speed of 1 °C/min and a motor making the digester rotating vertically.

Figure 6. *Laboratory scale rotary digester.*

3.2.3 Sprout-Waldron defibrator

Sprout-Waldron defibrator 105-A (Austria) was used to defibrate the treated biomass, after the digestion step (Paper I, II, and III). The Sprout-Waldron defibrator was equipped with tap water and a filtrate bath. The tap water was applied by spraying on the input pulp and to maintain temperature and lubrication during all the processes.

Figure 7. *Sprout-Waldron defibrator 105-A (a) and its disc (b)*

3.2.4 Twin-screw extruder

A pilot-scale Clextral Evolum HT 53 (France) (Figure 8) co-penetrating and co-rotating twin-screw extruder was used to conduct fibers pretreatment by extrusion method. It is a continuous operating system. The extruder was equipped with a constant weight feeder from Coperion K-Tron SWB-300-N (Switzerland) (Figure 9a) in the first module and a piston pump

Clextral DKM Super K Camp 112/12 (France) (Figure 9b) at the end of module 3. Three different types of segmental screw elements (Figure 10) were used (Paper III).

Figure 8. *Twin-screw extruder.*

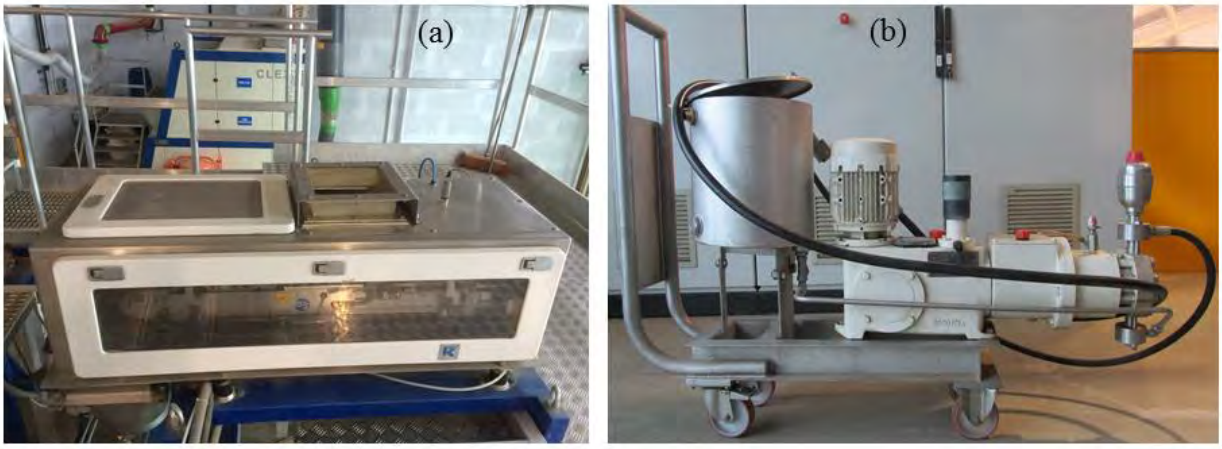


Figure 9. *Constant weight feeder (a) and piston pump (b).*

Figure 10. *Segmental screw elements: BL22-90° bilobe paddle-screws (a), reversed simple-thread (b), and conveying simple-thread screws (c).*

3.2.5 High-pressure homogenizer

A high-pressure homogenizer NS1001L PANDA 2K-GEA from Gea Niro Soavi (Italy) was used for obtaining cellulose nanofibers (Paper I).

Figure 11. *High pressure homogenizer.*

3.2.6 Pulper

A laboratory scale pulper (Spain) was used:

- To disperse *Eucalyptus* pulp with distilled water before the TEMPO-mediated oxidation process of CNF preparation (Paper I).
- To disperse the TMP with water and additives such as CNF and lignin in the fibers preparation step (Paper I and II).

Figure 12. *Laboratory scale pulper.*

3.2.7 Paper sheet former

A paper sheet former, Rapid Köthen ISP mod. 786 FH (Germany) was used to filtrate the fibers matrix and to form a web cake (Paper I and II).

Figure 13. *Paper sheet former.*

3.2.8 Hot press and mold

A laboratory scale hot press, lab-Econ 300 from Fontijne Grotnes B.V., the Netherland (Figure 14a) was used to press the fibers matrix of TMP and TMP with CNF or lignin to be fiberboard panels by wet process method. A laboratory scale mold (50 mm × 150 mm), designed by University of Girona was used to form the fiberboard shape (Figure 14b) (Paper I and II).

Figure 14. *Lab-Econ 300 hot press (a) and the molding box (b)*

3.2.9 MorFi compact analyzer

A MorFi compact analyzer from TechPap (France) was used to analyze the morphology of of TMP and extrudate fibers (i.e. weighted length, diameter, and fines element). Fines elements were defined as fibers with diameters under 75 μm (Paper I, II, and III).

Figure 15. *MorFi compact analyzer.*

3.2.10 Densi-Tap volumenometer

A Densi-Tap from Panasonic (Japan) was used to analyze tapped and apparent density of TMP and extrudate (Paper III).

Figure 16. *Densi-Tap volumenometer.*

3.2.11 TGA analyzer

A TGA-50 series instrument (Shimadzu, Japan) was used to analyze thermal properties or thermogravimetric analysis (TGA) of the crop residues, TMP, extrudate and lignin powder (Paper II and III).

Figure 17. *TGA analyzer.*

3.2.12 Spectrophotometer

A spectrophotometer (Konica Minota CR-410, Japan) was used to measure the color of the starting materials (crop residues, TMP and extrudate) and fiberboard specimens, using the CIE L*a*b* referential, which is widely employed for non-luminous objects, D65 illuminant, and the observer angle was 2 degree (Paper III).

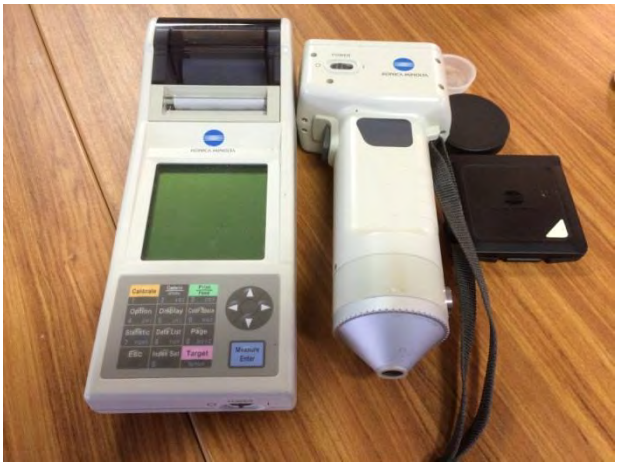


Figure 18. *Spectrophotometer.*

3.2.13 Mechanical of bending tester apparatus

A dynamometer of IDM Test (San Sebastian, Spain) with a 5000 N load cell (Figure 19) was used to analyze on mechanical properties of the fiberboard specimens including bending and internal bonding strength. The apparatus was connected with a computer using registration and data processing of Register III software program to estimate the energy-to-break for each specimen and the load deformation curve from zero to rupture. And for the bending test, the apparatus was

installed with a 3 points bending technique equipment (Figure 20a), while a sandwich clump (Figure 20b) was used to analyze the internal bonding strength (Paper I and II).

Figure 19. *Dynamometer mechanical tester apparatus.*

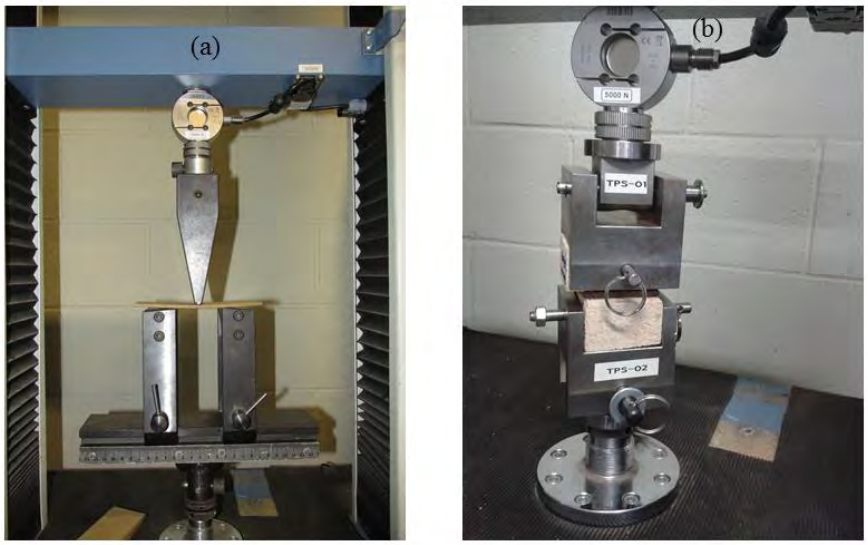


Figure 20. *Three points bending holder (a) and sandwich clumps (b).*

3.2.14 Impact tester

A CEAST impact tester, Resil 5,5" (Pianezza, Italy) was used to analyze the rigidity of the fiberboard on *Izod* impact strength without notch (Paper I and II).

Figure 21. *Resil 5.5" impact tester.*

3.3 Methods

3.3.1 Preparation of fibers for fiberboard manufacturing

There were two different fibers preparation methods: pulping and extrusion, carried out in this study. Figure 22 shows the flowchart of the fibers preparation from corn stalk (Paper I and II) and rice straw (Paper III) biomass using both technologies.

3.3.1.1 Pulping

The pulping was conducted using a laboratory scale rotary digester (Figure 6) and a Sprout-Waldron defibrator (Figure 7) to prepare thermo-mechanical pulp from grinded corn stalk and rice straw biomasses. In the pulping process, grinded corn stalk or rice straw biomasses were fed into the digester with distilled water at liquid/solid ratios ranging from 4 to 6, at the maximal biomass plus water mass (8 kg) per batch, previously heated to 80 °C. The severity of pulping at digestion stage such as temperature and time were conducted in trials previously to determine an optimum condition. The optimal condition was defined by the high production yield of TMP and the high mechanical strength on bending of fiberboard made from the TMP. The severities of digestion were in the range 140-180 °C and 15-30 min for the cooking temperature and duration, respectively. Then, the digested pulp was washed using tap water, filtered and analyzed its moisture content.

The mass of solid inlet and liquid inlet were calculated using equation (1) and (2), respectively.

$$m_w = \frac{m_d}{100 - \%MC_i} \times 100 \quad (1)$$

Where: m_w is the mass of humid inlet (kg); m_d is the mass of dry inlet (kg dry matter); and $\%MC_i$ is the moisture content of the inlet (%).

$$m_L = L/S \times m_d - (m_w - m_d) \quad (2)$$

Where: m_L is the mass of water inlet (kg); and L/S is the liquid/solid ratio, defined as the ratio of the water mass (including both liquid water and moisture inside rice straw) to the dry solid mass.

The production yield was calculated using equation (3).

$$\%\text{Yield} = \frac{m_p \times \frac{100-\%MC_p}{100}}{m_d} \times 100 \quad (3)$$

Where: m_P is the mass of digested pulp (kg) and $\%MC_p$ is the moisture content of pulp (%).

Lastly, the digested pulp was passed one time through the Sprout-Waldron defibrator with addition of spraying tap water, and filtered again to eliminate the excess of water. Finally, the thermo-mechanical pulp (TMP) is ready for fiberboard manufacturing. The TMP can be stored in a plastic bag at room temperature about one week period with moisture content around 20%, or dry in ventilated oven for a better conservation, or storage in refrigerator at 4 °C to avoid fermentation by bacteria and fungus.

3.3.1.2 Extrusion

The extrusion was conducted using a pilot-scale Clextral Evolum HT 53 (France) co-penetrating and co-rotating twin-screw extruder (Figure 8) with three different segmental screw elements (Figure 10). In the extrusion process, grinded rice straw was fed into the extruder inlet port using a constant weight feeder (Figure 9a), at a 15 kg/h wet matter inlet flow rate. Water was injected using a piston pump (Figure 9b) at the end of module 3. After water injection, two series of BL22-90° bilobe paddle-screws (2D in total length) were located in modules 5 to disperse intimately water inside the grinded rice straw. The CF1C reversed simple-thread screws with grooves (1.5D in total length) were positioned at the beginning of module 8 to give an intense shearing/mixing action to the liquid/solid mixture. The screw speed (SS) was fixed at 150 rpm and the set values for the barrel temperature were 25, 80, 110, 110, 110, 110, 110 and 100 °C at the level of modules 1 to 8, respectively. The experimental variable of this part of the study was the liquid/solid (L/S) ratio (i.e. Q_L/Q_S), ranging from 1.0 to 0.4. The extrusion pretreatment was presented in paper III.

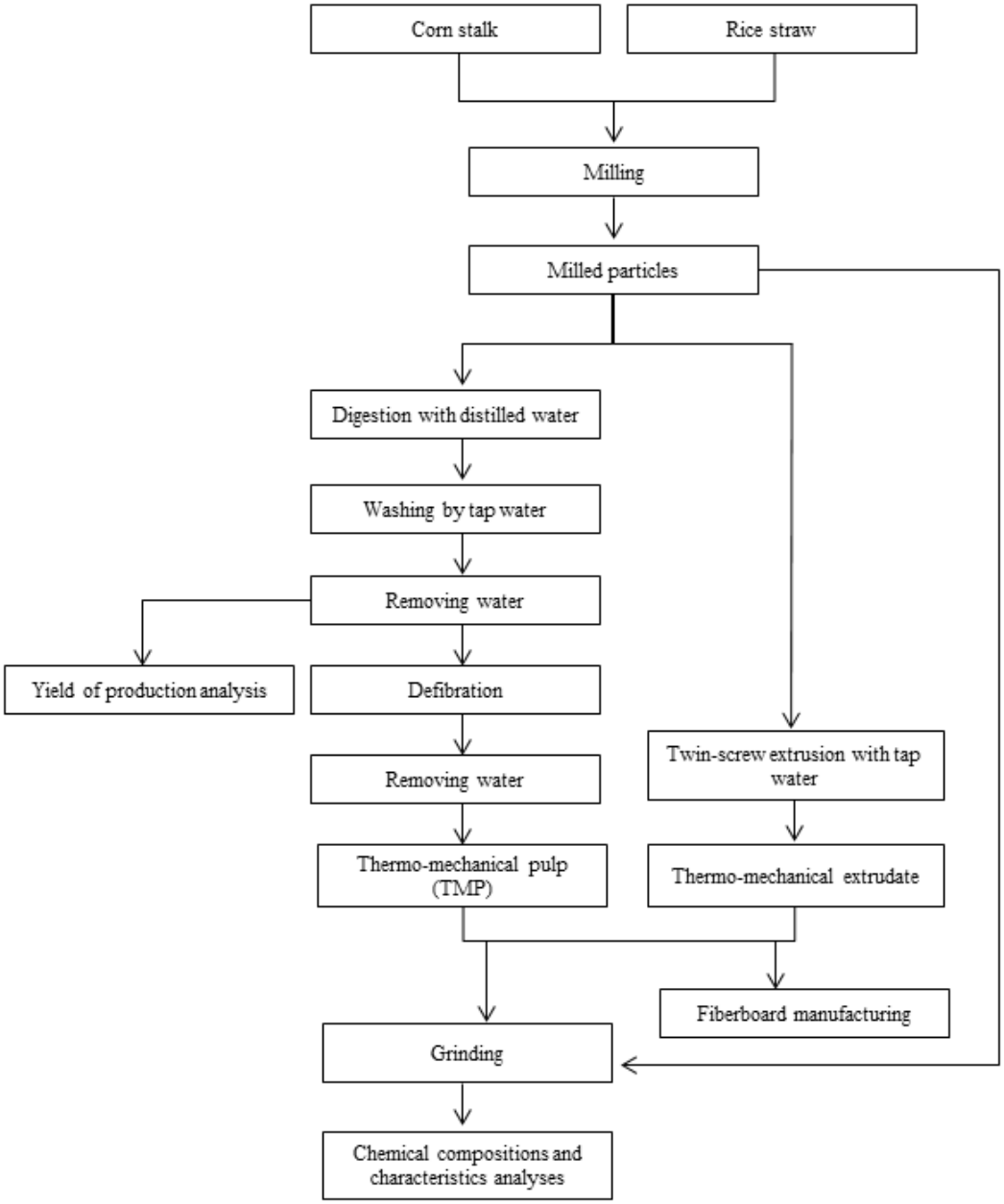


Figure 22. *Flowchart showing the fiber preparation for fiberboard manufacturing.*

3.3.2 Analytical methods

- **Chemical characterizations:** Regarding chemical compositions of crop residues, TMP, and extrudate were determined. Cellulose content was measured according to (Wise, Murphy, & D Adieco, 1946). Determination of ash, lignin and pentosans were done following TAPPI standard methods T211 om-93, T222 om-98 and T223 cm-01, respectively (Paper I and II). In paper III, the ash contents were determined according to the French standard NF V 03-322, while the three parietal constituents (cellulose, hemicelluloses, and lignin) was made using the ADF-NDF method of Van Soest and Wine (Van Soest & Wine, 1967; Van Soest PJ, 1968). An assessment of the water-soluble

components was made by measuring the mass loss of the test sample after 1 h in boiling water.

- **Morphological analysis:** The morphological analysis was carried out using a MorFi Compact analyzer equipped with a CCD video camera. About 30,000 fibers were analyzed by the software MorFi v9.2. Among other parameters, this software was able to calculate mean fiber length, mean diameter and fines percentage (fibers shorter than 76 μm). All characterizations were performed in duplicate (Paper I, II, and III).
- **Schopper-Riegler degree analysis:** The Schopper-Riegler degree of TMP was analyzed following ISO 5267-1 standard (Paper I and II).
- **Tapped and apparent densities analysis:** The tapped and apparent densities of TMP and extrudate were measured using the Densi-Tap volumenometer, Panasonic, Japan, fitted with a 250 mL graduated cylinder. Before compaction, apparent density was also measured. All measurements were conducted in duplicate (Paper III).
- **Thermogravimetric analysis:** The thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 analyzer. Dynamic analysis was conducted under air at a heating rate of 5 °C/min, from 25 to 800 °C. For all measurements, the mass of the test sample was around 8 mg. The weights of samples were measured as a function of temperature and stored. These data were later used to plot the percentage of undegraded sample (1 - D) (%) as a function of temperature,

$$D = \frac{W_0 - W}{W_0} \quad (4)$$

Where: W_0 and W are the weights at the starting point and during scanning (mg). All measurements were carried out in duplicate (Paper II and III).

- **Color analysis:** The color of the materials was measured using a spectrophotometer (Konica Minota CR-410, Japan) (Paper III). The color measurements were made using the CIE L*a*b* referential, which is widely employed for non-luminous objects. The illuminant was D65, and the observer angle was 2°. In the L*a*b* color space, L* is the lightness and it varies from 0 (black) to 100 (white), and a* and b* are the chromaticity coordinates: +a* is the red direction, -a* is the green direction, +b* is the yellow direction, and -b* is the blue direction. The center is achromatic (Konica Minolta Sensing, 2007). The measured L* color values were used to estimate the darkening of the pretreated fibers compared to its initial color. The color difference (ΔE*) was calculated by:

$$\Delta E^* = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2} \quad (5)$$

3.3.3 Preparation of cellulose nanofibers (CNF) and its properties characterizations

Cellulose nanofibers were produced from commercial bleach *Eucalyptus* pulp by means of TEMPO-mediated oxidation methodology for a 5 mmol concentration, as reported by (Alcalá et al., 2013; Alila et al., 2013; Besbes et al., 2011; González et al., 2013; González et al., 2014; Saito et al., 2007). The CNF preparation was accomplished by the fibrillation process, using a high-pressure homogenizer (NS1001L PANDA 2K-GEA). The equipment operated at 600 bar pressure and 60-70°C, repeated for 5 times to obtain a transparent gel-like product. Finally, the CNF pulp was stored in refrigerator at 4°C for use in the fiberboard manufacturing (Paper I).

The CNF pulp was analyzed its carboxylic content (CC), yield of nanofibrillation (YN), cationic demand (CD), water retention value (WRV), and degree of polymerization (DP). These properties are the important characteristics of the material for usage as an appropriate reinforcement additive to improve both mechanical and physical properties of the fiberboard manufacturing.

3.3.4 Preparation of lignin powder

Purified kraft lignin powder was prepared from commercial black liquor as described by (Lin, 1992). The commercial black liquor was first treated with hot water with stirring, and then acidified using 72% sulfuric acid to reduce the pH of the mixture to 2. The mixture was stored at room temperature during 24-48 hours to extract all lignin content. The solid lignin was washed with distilled water and filtered several times to remove residual sulfuric acid. To recover pure, powder-form lignin, the solution pH was increased to 6.0 by the addition of sodium hydroxide, and the lignin was subsequently dried in oven at 60 °C (Mancera et al., 2012). The dried lignin was crushed to obtain powder, stored in plastic bags at room temperature for use in the fiberboard manufacturing (Paper II).

3.3.5 Fiberboard manufacturing

The fiberboards were made using wet process. The flowchart of the whole process fiberboard manufacturing is shown in Figure 23. The first column depicts the fibers preparation, while the second one describes the step of molding and thermo-pressing (Paper I and II).

3.3.5.1 Fibers preparation

A hundred gram dry weight of TMP was in each web cake formation, depending on the target dimension of the fiberboard (3 mm × 50 mm × 150 mm of thickness, width, and length, respectively), with a calculation following the diameter of the circle web cake former (200 mm). The one web cake can be cut for two fiberboard specimens and the rest part can be benefit to make two more panels.

A. Neat fiberboard

The neat fiberboard was made from TMP of corn stalk or rice straw alone. Thus, the TMP was dispersed with only tap water using the disintegrator (Figure 14) until 80,000 revolutions before further steps until the web cake was formed by the paper sheet former (Figure 17).

B. Fiberboard with CNF or lignin addition

The TMP of corn stalk or rice straw was dispersed with CNF (0.5 - 10% dry weight) or lignin (5 - 29% dry weight) and tap water using the pulper until 80,000 revolutions. Then, the mixture was further stirred by a mechanical stirrer at 300 rpm during 20 min with addition of cationic starch and colloidal silica at 0.5% and 0.8%, respectively. Lastly, the mixture was filtered and formed a web cake by the paper sheet former.

3.3.5.2 Thermo-pressing

The pressing operation is an extremely critical step in fiberboard manufacturing, involving simultaneous application of heat and pressure. The pressing conditions of fiberboard making in the hot press reveal as following:

- Cut the web cake for the size of the molding box and introduce into the mold with covering the top and bottom surface by metallic net to protect sticky problem with the mold.
- Since the web cake is usually wet with moisture content around 90%, it is required to eliminate before the thermo-pressing. The removal of water can be done using the same thermal press with following conditions:
  - Introducing the mold with fibers matrix inside into the thermal press;
  - Heating and pressing at 75 ºC, 100 kN about 3 min;
  - Heating and pressing at 75 °C, 170 kN about 5 min;
  - Terminating the thermal pressing operation and collecting the released water; and
  - Drying at 150 °C, 100 kN during 60 min.
- The thermal pressing step can be carried out after the fibers matrix is dried. It was noticed that the fibers matrix is exploded when the moisture content remain in the matrix at thermal pressing stage. The thermal pressing was conducted with the following conditions:
  - Press at 230 ºC, 170 kN during 2 min
  - Stop and open the mold to breath during 1 min
  - Press at 230 °C, 170 kN during 5 min.

- Finally, the thermal press was cooling by tap water until the temperature 70 °C to open the mold and take out the fiberboard specimen. The fiberboard specimen was cooled at room temperature.

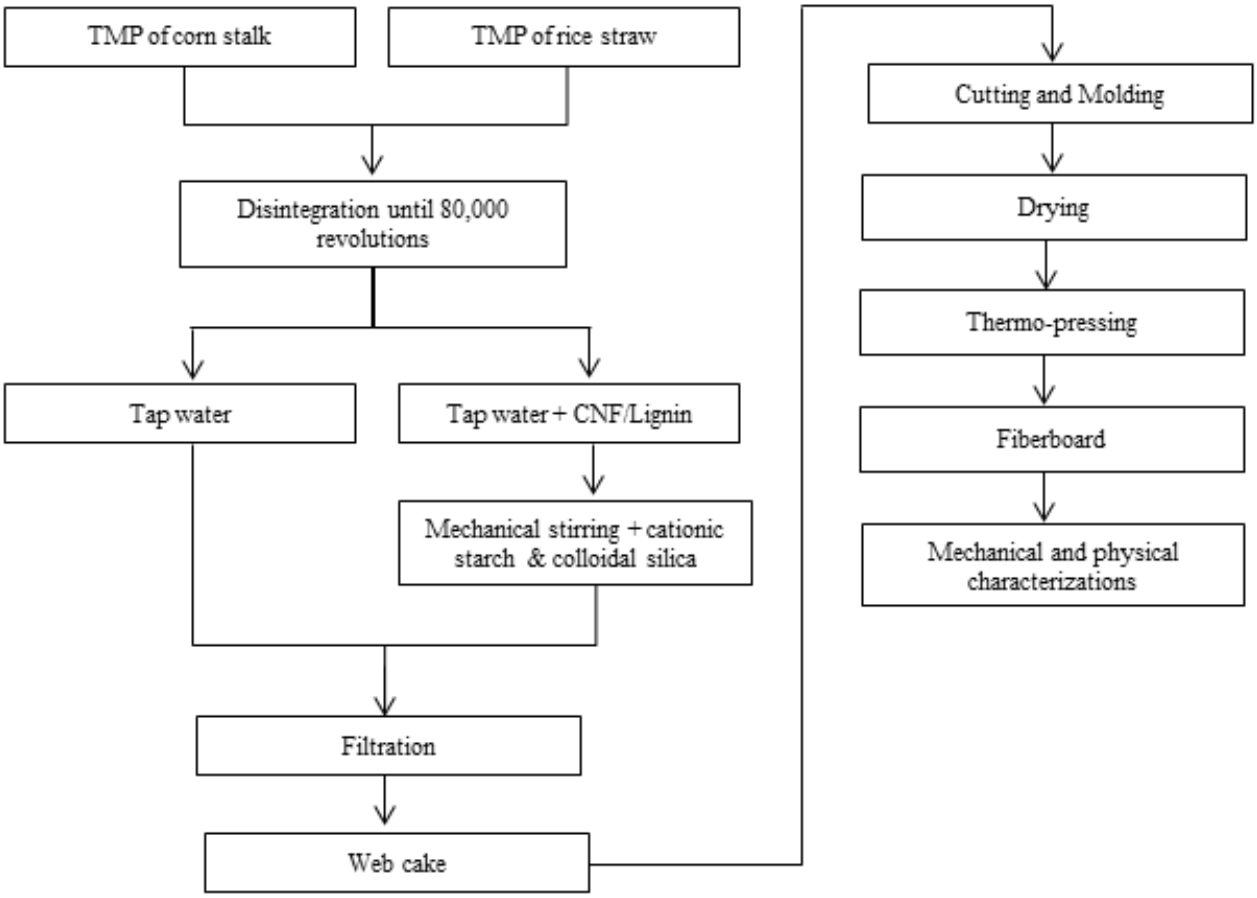


Figure 23. *Flowchart of the process followed to produce fiberboard.*

3.3.6 Fiberboard analysis (Paper I and II)

3.3.6.1 Mechanical analysis

- Density analysis: Density of the fiberboard was measured following the European standard (EN323, 1993).
- Bending strength properties: Modulus of rupture (MOR) and modulus of elasticity (MOE) were analyzed at the same time following the European standard (EN310, 1993).
- Internal bonding strength (IB) property: The IB was determined in accordance to the European standard (EN319, 1993).
- Impact strength (IS) property: *Izod* impact strength was tested following the American standard (ASTM-D256-10e1, 2010) without notch.
- Dynamic mechanical analysis (DMA): the DMA was performed using a DMA/SDTA861e instrument from Mettler Toledo, operating in a 3 point bending mode. The DMA provides

the real and imaginary parts of the dynamic stress modulus (the storage modulus E' and the loss modulus E", respectively). In this work, the complex modulus was given (E*= E'+i E''). The isochronal scans were recorded from 25 to 250 ºC at a heating rate of 5 ºC·min-1, at 1Hz of frequency and 15µm amplitude. Sample dimensions were 3 ×10 × 50 mm. A reducing force mode was engaged which adjusts the static force during the test to minimize creep. The DMA oven was under dry nitrogen flow in order to limit water sorption during experiments.

3.3.6.2 Dimensional stability analysis

Dimensional stability properties of fiberboard including: thickness swelling (TS) and water absorption (WA) was done at the same time by immersing the fiberboard specimen in distilled water during 24 h following the European standard (EN317, 1993).

3.3.6.3 Production cost analysis on fibers preparation

The production cost of fibers preparation using a batch pulping process (TMP using digestion plus defibration method) and a continuous process twin-screw extrusion (Paper III).

A. Production cost analysis for TMP preparation

The production cost analysis was focused on energy consumption, the main issue. Since the digester and the defibrator are in laboratory scale, an electric monitor was connected to them to measure the energy consumption for further production cost calculation. Then, the production cost of the TMP preparation was calculated using the following formula:

$$PC = P \times 0.08 \quad (6)$$

Where: *PC* is the specific production cost (€/kg dry matter) and *P* is the specific energy consumed by the motor of the digester and defibrator (kW h/kg dry matter).

The total production cost of the TMP preparation is defined as the sum of specific heating cost at digestion and specific mechanical cost at defibration :

$$TPC = PC_{di} + PC_{de} \quad (7)$$

Where: PC_{di} is the specific production cost of digestion (€/kg dry matter) and PC_{de} is the specific production cost of defibration (€/kg dry matter).

B. Production cost analysis for extrudate preparation

Twin-screw extrusion is a continuous process, thus the sampling was collected during 10 min with 10 min before each sampling to ensure the stabilization of the operating conditions. The

operating conditions, including in particular the feed rates of grinded rice straw and water, the temperature along the screw profile and the current feeding the motor, were recorded. Sample collection time was determined with a stopwatch. Mass of the extrudate was immediately weighed and measured the moisture content. All the recorded data was used for the production cost calculation.

The total production cost of the extrusion process is defined as the sum of three specific terms: mechanical cost (MCo), cooling cost (CCo), and heating cost (HCo).

The mechanical cost (€/kg dry matter) of the extrusion process was determined according to the following formulas:

$$\text{MCo} = \frac{SME}{1000} \times 0.08 \tag{8}$$

Where: *SME* is the specific mechanical energy consumed by the motor per unit weight of dried grinded rice straw (W h/kg dry matter). The *SME* was calculated according to the equation (9) mentioned below. The electrical energy cost was considered according current costs in Europe, which is of about 0.08 €/kW h assuming cogeneration in Spain and nuclear energy in France.

$$\text{SME} = \frac{\frac{454 \times I \times cos\varphi \times S_S}{S_{max}}}{Q_S} \tag{9}$$

Where: I is the current feeding the motor (A), $cos\ \varphi$ the theoretical yield of the twin-screw extruder motor (cos φ = 0.95), S_s the screw rotation speed (rpm), S_{max} the maximal screw rotation speed (S_{max} = 800 rpm), and Q_s is the inlet flow rate of dried grinded rice straw (kg dry matter/h).

The equation (10) mentioned below is used to calculate the cooling cost (€/kg dry matter) of the extrusion process.

$$\text{CCo} = \frac{SCE}{1000} \times 0.08 \tag{10}$$

Where: *SCE* is the specific cooling energy consumed per unit weight of dried grinded rice straw (W h/kg dry matter). The *SCE* was calculated using the equation (11) mentioned below.

$$\text{SCE} = \frac{m \times C_p \times |\Delta T|}{Q_S \times 3600} \tag{11}$$

Where: m is the inlet flow rate of cooling water (kg/h), C_p the calorific capacity of water (C_p = 4180 J/kg K), and $|\Delta T|$ is the difference in temperature between the inlet and the outlet of the cooling water circuit (K).

The heating cost (€/kg dry matter) was calculated using the following formula:

$$\text{HCo} = \frac{STE}{1000} \times 0.08 \quad (12)$$

Where: *STE* is the specific thermal energy consumed per unit weight of dried grinded rice straw (W h/kg dry matter). It was determined using the following formula:

$$\text{STE} = \frac{P \times 1000}{Q_S} \quad (13)$$

Where: *P* is the heating power. The heating power used in this calculation was the sum of the heating powers of all the heated modular zones along the twin-screw extruder barrel (i.e. modules 2 to 8). The control panel of the extruder was set to record the heating power as a percentage of the maximal value of the heating power available for all the heated modules every 5 seconds. In this study, the twin-screw extruder had seven heated modules, situated from zones 2 to 8, with a maximal value for the heating power of 5.0 kW, except in zone 5 where it was 3.4 kW. The heating power of each module was calculated using the equation (14).

$$\text{P}_{\text{module}} = \frac{M \times P_{max}}{100} \quad (14)$$

Where: *M* is the average percentage of the maximal value of the heating power during sampling (%), and P_{max} is the maximal value of the heating power available for the corresponding heated module (kW).

PUBLICATIONS

Paper I

Paper II

Paper III

4.1 Paper I

Title	All-lignocellulosic fiberboard from corn biomass and cellulose nanofibers
Authors	Dyna Theng, Gerard Arbat, Marc Delgado-Aguilar, Fabiola Vilaseca, Bunthan Ngo, Pere Mutjé
Journal	Industrial Crops and Products
Year	2015
Volume	76
Issue	-
Pages	166-173
Status	Published

https://doi.org/10.1016/j.indcrop.2015.06.046

Industrial Crops and Products 76 (2015) 166–173

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

All-lignocellulosic fiberboard from corn biomass and cellulose nanofibers

Dyna Theng[a,c], Gerard Arbat[b,*], Marc Delgado-Aguilar[a], Fabiola Vilaseca[a], Bunthan Ngo[c], Pere Mutjé[a]

[a] Grupo LEPAMAP, Departamento de Ingeniería Química, Universitat de Girona, Spain
[b] Departamento de Ingeniería Agraria y Tecnología Agroalimentaria, Universitat de Girona, Spain
[c] Royal University of Agriculture, Cambodia

ARTICLE INFO

Article history:
Received 6 February 2015
Received in revised form 18 June 2015
Accepted 20 June 2015
Available online 4 July 2015

Keywords:
Corn biomass
Binderless fiberboard
HDF
Cellulose nanofibers

ABSTRACT

In general, fiberboards are made of lignocellulosic fibers with synthetic adhesive to connect between fibers. Synthetic adhesives are usually non-biodegradable constituents and they cause health and environmental troubles. The present study aims to develop fiberboards from corn thermomechanical fibers reinforced with cellulose nanofibers. In this work, corn stalk biomass was used to produce high yield thermomechanical pulp (TMP) that was converted into binderless fiberboards. Cellulose nanofibers (CNF) were also added as reinforcing agent. The mechanical and physical properties of the resulting fiberboards were characterized and compared with commercial high density fiberboard (HDF) containing synthetic adhesives. Fiberboards with 0.5 wt% CNF showed modulus of rupture of 43 MPa, similar to that of commercial HDF. The highest mechanical performance was reached for fiberboards at 2 wt% of CNF, with modulus of rupture of 52 MPa. CNF was found to increase the resistance of the new all-lignocellulosic fiberboards when compared to the products made only with corn stalk fiber, and also when compared with commercial HDF.

1. Introduction

Fiberboards are fibrous panels made up of lignocellulosic materials joined together with a synthetic binder (American National Standard, 2002). Urea-formaldehyde or phenol-formaldehyde are common resins used in fiberboard manufacturing because they are less expensive compared with other adhesives. However, the formaldehyde emission is one of the most important disadvantages of these resins, since it can potentially cause health and pollution problems. Instead, binderless boards are wood-based composites consisting of particles of lignocellulosic material bonded together without any added resin. Recently, there is a growing request for binderless boards (El-Kassas and Mourad, 2013; Rokiah et al., 2009). In order to meet the market demand and environmental care, several studies have been done to convert fiberboards into binder-free fiberboards by using different methods such as thermotreatments (Anglès et al., 2001; Baskaran et al., 2012; Halvarsson et al., 2009; Huang et al., 2015; Mejía et al., 2014; Pan et al., 2010; Quintana et al., 2009; Rokiah et al., 2009; Saari et al., 2014 Wuzella et al., 2011); the replacement of urea formaldehyde by starch (Abbott et al., 2012); the addition of soybean protein (Ciannamea et al., 2010; Li et al., 2009); pretreating fibers with white-rot fungus (Wuzella et al., 2011); the addition of lignin (Anglès et al., 2001; Mancera et al., 2012; Mejía et al., 2014; Sun et al., 2014; Velásquez et al., 2003); and more lately, by adding of cellulose nanofibers (Cui et al., 2014).

The present study aims to develop fiberboards from thermomechanical fibers produced from corn biomass. Additionally, cellulose nanofibers will be incorporated to improve the mechanical efficiency of the corn fiberboards. Corn biomass will be treated by steaming in a rotary digester, and later mixed with eucalyptus cellulose nanofibers. The final purpose is to produce corn binder-free fiberboards with enhanced properties with respect to commercial fiberboard containing synthetic adhesives.

2. Materials and methods

2.1. Materials

The basic materials used in the research were corn biomass and bleached Kraft *Eucalyptus* pulp. Corn residues were collected from field at La Tallada d'Empordà, Spain, composed of about 12% humidity, kept at room temperature and used for the

* Corresponding author.
E-mail address: gerard.arbat@udg.edu (G. Arbat).

http://dx.doi.org/10.1016/j.indcrop.2015.06.046
0926-6690/

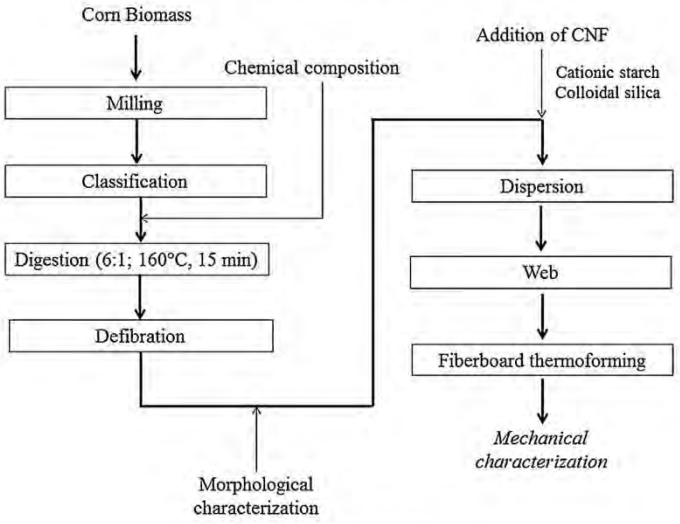


Fig. 1. Flowchart of the whole process.

fiberboard production. The bleached Kraft *Eucalyptus* pulp had a Kappa number <1, a Shopper-Riegler degree of 16 and the α-cellulose content was 76%, containing about 10% moisture content. This pulp was provided by La Montañanesa (Grupo Torraspapel, Zaragoza, Spain), stored at room temperature and used to prepare cellulose nanofibers (CNF). The reagents used to produce CNF were: 2,2,6,6-tetramethylpiperidine-l-oxyl radical (TEMPO), sodium bromide (NaBr), sodium hypochlorite solution (NaClO), and sodium hydroxide (NaOH). These were purchased from Sigma–Aldrich and used without further purification. Cationic starch and colloidal silica were provided by Torraspapel S.A. (Sarrià de Ter, Girona, Spain) and used as retention agents during the dispersion of corn fibers and CNF.

2.2. Methods

The flowchart of the general procedure is summarized in Fig. 1. The first column depicts the production of thermomechanical fibers from corn biomass, while the second one describes the addition of the CNF and the retention agents, and the formation of the fiberboard.

2.2.1. Preparation of corn thermomechanical pulp (TMP)

Integral corn biomass containing stalks, leaves and husk were chopped together using a knives mill from Agrisma (Torelló, Barcelona, Spain), equipped with a set of sieves with a 10 mm pathway. Then, 600 g (dry weight) of the corn chips were cooked in a rotary digester at 160 °C for 15 min, using liquor to fiber ratio 6:1. The pulp was washed with tap water, filtered and passed one time through a Sprout-Waldron refiner (model 105-A). The resulting TMP pulp was subjected to vacuum machine in order to remove the excess water until the moisture content reached about 85%, kept in a plastic bag and stored at room temperature for its use in the fiberboard production (Flandez et al., 2012; González et al., 2013).

2.2.2. Preparation of cellulose nanofibers (CNF)

Cellulose nanofibers were produced by means of TEMPO-mediated oxidation methodology, as reported by (Alcalá et al., 2013; Alila et al., 2013; Besbes et al., 2011; González et al., 2013, 2014; Saito et al., 2007). Firstly, a suspension 1.5 wt% of *Eucalyptus* pulp was disintegrated until 60,000 revolutions and filtered. Secondly, 15 g (dry weight) of *Eucalyptus* pulp was suspended in a solution containing TEMPO (0.24 g) and NaBr (1.5 g). The suspension was stirred to ensure good dispersion of all reagents. Six mmol of sodium hypochlorite solution (44.66 mL) followed by 1.5 M of sodium hydroxide (NaOH) were added to the suspension to keep the pH to about 10, stirring at 500 rpm and 60 °C during 2 h. The oxidation was finished when the pH of the solution was stable. Next, it was filtered and washed several times before the mechanical treatment. The fibrillation process was carried out by passing a 1–2 wt% fiber suspension through a high-pressure homogenizer (NS1001L PANDA 2K-GEA). The equipment operated at 600 bar pressure and 60–70 °C. The process was repeated for 5 times to obtain a transparent gel-like product. The gel-like cellulose nanofibers was stored in refrigerator at 4 °C for use as a natural reinforcement agent in the fiberboard production (González et al., 2014).

2.2.3. Characterization of the CNF

2.2.3.1. Carboxylic content. The content of COOH groups in oxidized fibers was calculated by conductimetry (Alcalá et al., 2013; Da Silva Perez et al., 2003; González et al., 2014). A dried sample (50–100 mg) was suspended in 15 mL of 0.01 M HCl solution. The fiber suspension was stirred for 10 min and then taken to a conductivity sensor; N_2 was bubbled into the suspension during the whole experiment. The titration was carried out by adding 0.1 mL of a 0.01 M NaOH solution to the suspension and then recording the conductivity in mS/cm; this process was repeated until observing a reduction, stabilization and increase in the conductivity. With these results, a titration curve was plotted and the volume of NaOH was finally calculated and applied in Eq. (1):

$$CC = 162(V_2 - V_1)c[(w\text{-}36(V_2 - V_1))c]^{-1} \quad (1)$$

where V_1 and V_2 are the equivalent volumes of added NaOH solution (L), c is the NaOH concentration (mol/L), and w is the weight of oven-dried sample (g). The results indicate the average mmols of —COOH groups per gram of CNF.

2.2.3.2. Yield of nanofibrillation. The yield of nanofibrillation was determined according to the methodology reported by González et al. (2014). A 0.2% suspension of CNF was centrifuged at

4500 rpm for 20 min. The centrifuging allowed the isolation of the nanofibrillated fraction (contained in the supernatant) from the non-fibrillated and partially fibrillated component retained in the sediment fraction which was recovered, weighed and oven-dried to constant weight at 90 °C. The yield of nanofibrillation was then calculated using Eq. (2):

$$\text{Yield\%} = [1\text{-(weight of dried sediment/weight of diluted sample (\%Sc))}]100 \quad (2)$$

where %Sc represents the solid content of the diluted gel sample.

2.2.3.3. Cationic demand (CD). The cationic demand gives an idea of the surface charge of the sample. The cationic demand of CNF was determined using a Mütek PCD 04 particle charge detector (Alcalá et al., 2013; González et al., 2014). First, 0.04 g of CNF (dried weight) were diluted in 1 L of distilled water and dispersed with a pulp disintegrator over 10 min at 3000 rpm. Afterwards, 10 mL were taken and mixed with 25 mL of cationic polymer polydiallyldimethyl ammonium chloride (polyDADMAC) for 5 min with magnetic stirring. The mixture was centrifuged in a Sigma Laborzentrifugen model 6K 15 for 90 min at 4000 rpm, and 10 mL of the supernatant were taken to be tested in the Mütek equipment. Anionic polymer (Pes–Na) was then added to the sample drop-by-drop using a pipette until the equipment reaches 0 mV. The volume of anionic polymer consumed was noted and used to calculate the cationic demand (eq/L, meq/L and μeq/L) using Eq. (3):

$$C_2 = \frac{C_1 V_1}{V_2} \quad (3)$$

where C_2 is the sample's concentration (g/L), C_1 = anionic polymer concentration (g/L), V_1 = used volume of the anionic polymer (g/L), V_2 = sample's volume (g/L).

2.2.3.4. Water retention value (WRV). The method used to determine WRV for CNF was based on TAPPI UM 256 (TAPPI, 2011). A determined volume of CNF gel was divided into 2 equal portions, which were centrifuged in a Sigma Laborzentrifugen model 6K15 at 2400 rpm for 30 min to eliminate non-bonded water. A nitrocellulose membrane with a pore diameter of 0.65 μm was used at the bottom of the centrifuge bottles to retain the CNF. Once centrifuged, only the CNF in contact with the membrane was removed, weighed and then dried at 105 ± 2 °C for 24 h in containers of previously measured weight. The average water retention value was then calculated using Eq. (4):

$$\text{WRV}(\%) = \frac{(W_w - \text{Wd})}{\text{Wd}} \times 100 \quad (4)$$

where W_w is the wet weight (g) and Wd is the dry weight (g).

2.2.3.5. Degree of polymerization (DP). In the present work the dissolution of pulp fibers in copper(II) ethylenediamine was made according to the standard UNE 57-039-92. The DP was calculated from the equation: $\eta = K \times M^a$, where η is the intrinsic viscosity and M the molecular mass. The constants K and a have been considered as 2.28 and 0.76, respectively (Henriksson et al., 2008).

2.2.4. Fiberboard preparation

A hundred grams dry-based of corn TMP with humidity about 85% plus CNF from 0 to 10 wt% were dispersed with water in a disintegrator until 80,000 revolutions. The CNF were dispersed starting from the CNF gel-like form. An amount of CNF gel was taken and subsequently diluted with distilled water. The diluted form of CNF was added to the fiber suspension until the target CNF amount was reached. After that, cationic starch and colloidal silica were introduced in amounts of 0.5 wt% and 0.8 wt%, respectively, stirring at 300 rpm for 20 min to ensure a good dispersion of all substances (Alcalá et al., 2013; González et al., 2013).

A Rapid-Köthen (model ISP mod. 786 FH) was used to form a fiber web. From this, a fiber cake was cut to the size of the forming box (50 mm × 150 mm) and introduced into the hot press machine (model Lab-Econ 300 from Fontijne Grotnes B.V., The Netherland). The fiberboard with about 3 mm thickness was obtained at 230 °C temperature and 170 kN of press force because after some preliminary tests this was accepted to be the optimum condition. There were three steps in the fiberboard pressing stage (Angles et al., 1999; Mancera et al., 2012): (i) press for 2 min at the working temperature and loaded; (ii) open the mold and allow it to breathe for 1 min; and (iii) press again for 5 more minutes.

2.2.5. Morphological and chemical characterization

The morphological analysis was carried out by using a MorFi Compact analyzer (TechPap), which is able to calculate the average length, average diameter and fines percentage, among other parameters. The Schopper–Riegler freeness was determined following ISO 5267-1 standard.

Regarding chemical composition, ash, lignin, pentosans and cellulose content of both corn biomass and TMP were determined. Cellulose content was measured according to Wise et al. (1946). Determination of ash, lignin and pentosans were done following TAPPI standard methods T211 om-93, T222 om-88 and T223 cm-84, respectively.

2.2.6. Mechanical characterization

Modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond strength (IB) were analyzed following European standards. A dynamometer from IDM Test (San Sebastian, Spain) with a load cell of 5 kN was used. EN 310:1993 standard was used for MOR (Eq. (5)) and MOE (Eq. (6)) characterization (samples' dimensions 50 × 150 mm). The IB (Eq. (7)) was determined according to EN 319:1993 (dimension of specimens was 50 × 50 mm). Registration and data processing was done by the Register III program.

Impact strength (IS) analysis was conducted according to ASTM D256 by using an Izod impact test apparatus model Resil 5,5. The sample dimensions were 50 × 13 × 3 mm.

$$\text{MOR}(\text{MPa}) = \frac{3F_{\max} l}{2bt^2} \quad (5)$$

$$\text{MOE}(\text{MPa}) = \frac{l^3 (F_2 - F_1)}{4bt^3 (a_2 - a_1)} \quad (6)$$

$$\text{IB}(\text{MPa}) = \frac{F_{\max}}{lb} \quad (7)$$

where $F_{\max}$ is the maximum load; l, b, and t are length, width, and thickness, $F_2 - F_1$ is the increment of load on the straight line portion of the load-deflection curve; and $a_2 - a_1$ is the increment of deflection at the mid-length of the test piece.

2.2.7. Physical analysis

The physical characterization was done by measuring the density (Eq. (8)), thickness swelling (TS) (Eq. (9)) and water absorption (WA) (Eq. (10)), according to EN 323:1993, EN 317:1993 and EN 382:1993, respectively. The dimensions of the specimens were 50 × 50 mm. The samples were immersed in distilled water and stored at 20 °C during 24 h.

$$\rho = \frac{m}{(b_1 b_2)} 10^6 \quad (8)$$

where m is the mass of the test piece, b_1 and b_2 are width and length, t is the thickness.

$$\text{TS} = \frac{(t_2 - t_1)}{t_1} \times 100 \quad (9)$$

Table 1
Chemical composition of corn stalk biomass and corn stalk pulp.

Materials	Ash (%)	Extractives (%)	Lignin (%)	Holocellulose (%)
Corn stalk biomass	3.2	3.1	16.0	77.7
Corn stalk pulp	2.4	3.3	15.7	80.1

where: t_1 is the thickness of the test piece before immersion and t_2 is the thickness of the test piece after immersion.

$$WA = \frac{(m_2 - m_1)}{m_1} \times 100 \quad (10)$$

where m_1 is the mass of the test piece before immersion and m_2 is the mass of the test piece after immersion.

2.2.8. DMA analysis

Dynamical mechanical analysis (DMA) was performed using a DMA/SDTA861e instrument from Mettler Toledo, operating in a 3 point bending mode. DMA provides the real and imaginary parts of the dynamic stress modulus (the storage modulus E′ and the loss modulus E″, respectively). In this work, the complex modulus was given ($E^* = E' + i\,E''$). The isochronal scans were recorded from 25 to 250 °C at a heating rate of 5 °C min^{-1}, at 1 Hz of frequency and 15 μm amplitude. Sample dimensions were 10 × 50 × 3 mm. A reducing force mode was engaged which adjusts the static force during the test to minimize creep. The DMA oven was under dry nitrogen flow in order to limit water sorption during experiments.

3. Results and discussion

3.1. Corn biomass composition

Corn biomass consists of stalk (60 wt%), leaves (25 wt%) and the rest of components forming the grain, except the cob. As reported by Byrd et al. (2006), the leaves and other components, usually discarded, have interesting properties due to their cellulose content, lignin and other chemical components. Other authors have also determined the chemical composition of corn stalk biomass (Won and Ahmed, 2004).

The chemical composition of the original corn biomass used in this study is shown in Table 1. The results are in agreement to those found in the literature (Akgül et al., 2010; Barbash et al., 2012; El-Tayeb et al., 2012; Flandez et al., 2012; Hess et al., 2002). The thermomechanical treatment of the biomass changes the initial chemical composition, by reducing the ash and lignin content and increasing the hollocellulose constituent. If TMP pulp is produced at higher temperature or pressure, the final production yield would be reduced. Based on the principle "from a residue, a minimum sub-residue", thermomechanical pulp (TMP) was selected to prepare fiberboards, as substitute of forest resources and to reduce the resulting waste (Flandez et al., 2012).

3.2. CNF characterization

In the present study, TEMPO-mediated cellulose nanofibers (CNF) were prepared according to the described procedure. The oxidized cellulose fibers showed a carboxylic content of 1006 μ eq/g (Table 2). The introduction of carboxylic groups in the cellulose chains produces swelling of the fibers in aqueous suspension (Da Silva Perez et al., 2003), due to the increase in its hydrophilic character (Saito et al., 2007). In addition, carboxylic groups also affect the degree of defibrillation; therefore pulps with higher carboxylic content require less passes through the homogenizer to achieve a good degree of microfibrillation (Alila et al., 2013; Benhamou et al., 2014; Besbes et al., 2011; Shinoda et al., 2012).

Table 2
Properties of TEMPO-oxidized CNF.

Sample	—COOH content (μ eq/g)	Yield (%)	Cationic demand (μ eq/g)	WRV (g/g)	DP
CNF	1006	>95	1460	8.3	352

The amount of COOH groups determines many of the properties expected for CNF suspensions (Besbes et al., 2011; Isogai et al., 2011). CNF with high COOH content have a lower degree of polymerization (DP) than untreated fibers. The DP is reduced because of side reactions that cleave the glycosidic bonds in the cellulose chain (Alila et al., 2013; Saito et al., 2009). This is more obvious in TEMPO-mediated oxidations performed under alkaline conditions like in the present study. CNF films made out of nanofibers with a high degree of polymerization will have better mechanical properties than films from CNF's with lower DP's (Henriksson et al., 2008). It is important to note that lower levels of polymerization are expected after passing the oxidized fibers through the homogenizer, since the shear forces inside the machine cut down fibers and further reduce their length (Benhamou et al., 2014; Shinoda et al., 2012). This facilitates delamination of the fibers and effective release of the microfibrils during the mechanical process. The yield of fibrillation was also very high, meaning that almost all the solid material was effectively nanosized. CNF with low COOH content results in a lower yield of fibrillation (Besbes et al., 2011).

The cationic demand (CD) is a methodology to determine the outer surface charge of fibers, usually applied to pulp suspensions (Klemm et al., 2011; Rouger and Mutjé, 1984). It represents the anionic nature of the fibers and has been traditionally used to determine the extent of fiber delamination of beaten papermaking pulps. High cationic demand is expected for CNF due to large fibrillation and the anionic nature of cellulosic materials suspended in water (Carrasco et al., 1996; Mutjé et al., 2006).

The water retention value (WRV) is a papermaking parameter commonly used to describe the internal fibrillation of fibers. Actually, WRV measures the water chemically bound to cellulose. A higher fibrillation degree allows larger amounts of moisture to bind to CNF through hydrogen bonds (Alcalá et al., 2013; González et al., 2014). In this study, the WRV was 8.3 g/g (Table 2) similar to other TEMPO-mediated oxidized fibers.

3.3. Characterization of corn TMP

Thermomechanical pulp was prepared from corn biomass according to the procedure detailed above. Table 3 shows the main morphological characteristics, the yield of production and the Schopper-Riegler degree of corn TMP.

Table 3
Yield and morphological analysis of corn TMP.

Yield (%)	L_w (μm)	D (μm)	Fines (%)	°SR
87	653	24	60	44

From the mean weighted length (L_w) and the diameter (D) of corn TMP fibers, the aspect ratio was about 27, which is remarkable considering that they come from steam and mechanical defibrillation treatments (Alila et al., 2013; Flandez et al., 2012). The aspect ratio is a parameter directly related to the mechanical performance of the fiberboard product (Dasgupta, 1994; González et al., 2013; Mendez et al., 2007). On the other hand, the Schopper-Riegler degree (44°SR) is relatively high but consistent with the content of fines (60%), also quite high (González et al., 2013). The production yield of corn TMP was roughly 87% (Table 3).

Compared to the initial corn biomass, the chemical composition of the TMP fibers was altered. The ash content decreased considerably (0.8%) as a result of the steam and defibrillation processes. The

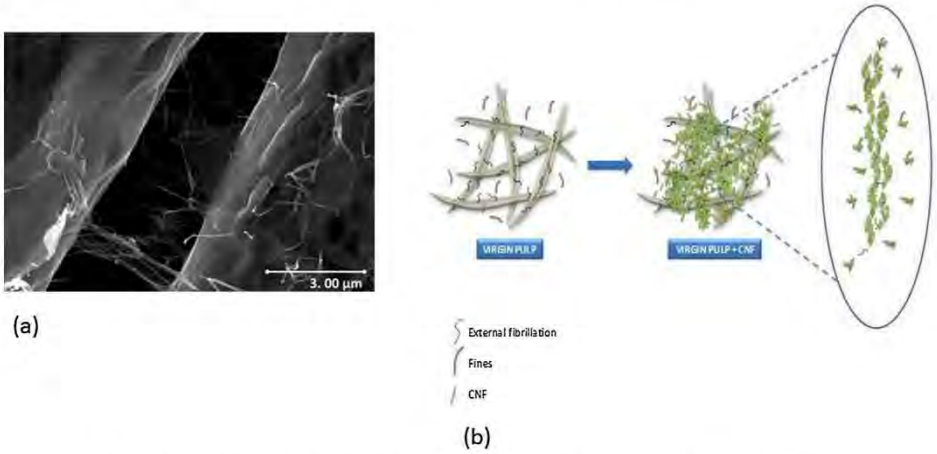


Fig. 2. SEM imaging of pulp slurry with CNF in bulk (a) and mechanism of strengthening of fiberboards with CNF (b).

extractives were not significantly affected, since they are soluble in organic solvents like ethanol–toluene (3.3%). Lignin has a small water-soluble fraction, which is reflected in the obtained TMP fibers with 15.7% lignin content. The holocellulose content increased up to 80% due to the elimination of the other chemical components (Flandez et al., 2012).

3.4. Mechanical characterization

The mechanical performance of fiberboard is usually expressed by the modulus of rupture (MOR) and the modulus of elasticity (MOE) (Teixeira and Moslemi, 2001). As shown in Fig. 3(a and b), the MOR and MOE of non-reinforced corn TMP fiberboard were about 30 MPa and 1874 MPa, respectively (Theng et al., 2014). This strength was somehow below the commercial HDF, but above other values found in the literature, such as for binderless fiberboard made of agricultural waste (Mancera et al., 2012), fibreboards of corn stalk and resin (Kargarfard and Jahan-Latibari, 2011), fibreboards made of corn stalk pretreated with white-rot fungus enzymes (Wu et al., 2011) or binderless fiberboards from banana bunch (Quintana et al., 2009).

MOR and MOE were enhanced by increasing the CNF content (Alcalá et al., 2013; Delgado-Aguilar et al., 2015; González et al., 2013). The highest value was obtained for the formulation at 8 wt% CNF, with MOR and MOE of 53 MPa and 5160 MPa, respectively. This improvement may be due to several factors such as the high intrinsic mechanical properties of CNF, their high specific surface that enlarges the number of feasible hydrogen bonds, the reduction of void spaces between fibers due to tension forces and CNF shrinkage, and the homogeneous distribution of the fibers (Alcalá et al., 2013; Delgado-Aguilar et al., 2015). The interaction between fibers and CNF can be seen in Fig. 2a, where CNF are linked between themselves and to the macrofibers by creating a network (Alcalá et al., 2013). It was observed that the modulus of rupture did not improve from the formulation of 2 wt% to 8 wt% of CNF (Theng et al., 2014). This might be due to a saturation phenomenon of CNF nanofibers on the surface of micro sized corn TMP fibres. Alternatively, maybe CNF were not fully dispersed during the preparation of fibreboards, indicating that more energy would be needed to obtain a better distribution of CNF and a more efficient interaction between CNF and the larger fibres (Alcalá et al., 2013). Moreover, it is worth to consider that if the pulp has a high content of fines elements or high external fibrillation, this saturation may appear at lower levels of CNF (Delgado-Aguilar et al., 2015). In the present work, the fines content was about 60%. Hypothetically if these fines were removed, the enhancement of mechanical properties provided by

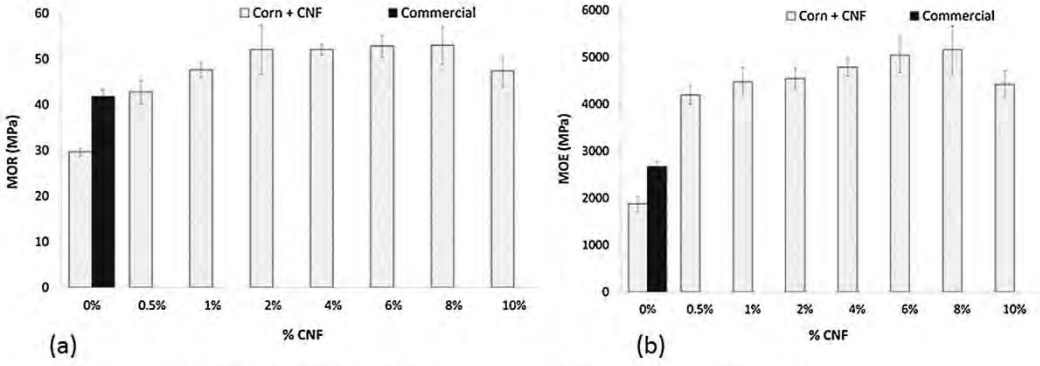


Fig. 3. MOR (a) and MOE (b) for different percentages of CNF. The vertical bars are the standard deviations.

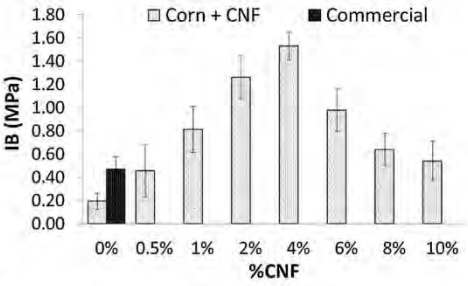


Fig. 4. Internal bond strength for different percentage of CNF. The vertical bars are the standard deviations.

CNF would be more significant and, consequently, the saturation level for CNF would also be superior. This result is in agreement with those obtained by Cui et al. (2014) on particleboard made of Pine (*Pinus pinaster* L.), where the board at 2 wt% of CNF was the strongest. In our study, while the modulus of rupture (MOR) was constant after 2 wt% of CNF, the modulus of elasticity (MOE) kept improving until 8 wt% of CNF. Both properties started declining at 10 wt% CNF content, showing an inefficient performance of the nano-reinforcement above this level. In Fig. 2b it is possible to distinguish the interaction between CNF and the microfibers, as well as the interaction of CNF with the fine elements (Alcalá et al., 2013; Delgado-Aguilar et al., 2015; Flandez et al., 2012; Theng et al., 2014).

The MOR and MOE values of this study (corn stalk fibreboards with CNF) were superior than some reported in earlier studies, like those from particleboards made of pine with CNF reinforcement (Cui et al., 2014) or with urea-formaldehyde (Buyuksari et al., 2010), or particleboards from rice husk and soybean protein (Ciannamea et al., 2010); and similar to those of fiberboards from agricultural waste with the addition of lignin (Mancera et al., 2012).

The internal bond (IB) refers to the bonding strength between fibers (Mancera et al., 2012). For this property, a similar trend was observed compared to the mechanical parameters mentioned above. The results, displayed in Fig. 4, show that the IB was improved with the addition of CNF. As reported by González et al. (2013), the high specific area of CNF helped to strengthen the bonding capacity of fibers. Fiberboards with only 1% of CNF showed the IB strength required in the standard specifications. The maximum IB strength was 1.53 MPa (Fig. 4), about 8 and 3 times superior than the fiberboard at 0 wt% CNF (0.19 MPa) and the commercial HDF (0.47 MPa), respectively. Additionally, this value was above than that of fiberboards with 20% of lignin (Mancera et al., 2012) and other values found in the literature (Halvarsson et al., 2009; Kargarfard and Jahan-Latibari, 2011; Quintana et al., 2009; Velásquez et al., 2003).

All binderless fiberboards from corn residues with CNF have densities somewhat higher than corn fiberboard without CNF (Table 4). The results displayed the same trend than in previous reports (Alcalá et al., 2013; Theng et al., 2014). According to the European standard EN 316:1999 (EN316, 1999), wet processed boards are classified as function of its density as high density fiberboard (HDF, density $\geq 900\,kg\,m^{-3}$), medium density fiberboards (MDF, density 400–900 $kg\,m^{-3}$), and low density fiberboard (LDF, density 230–400 $kg\,m^{-3}$). The densities measured in this study were above those of MDF, therefore they should be called high density fiberboard (HDF). The determination of the density allows the calculation of specific mechanical properties of corn fiberboards (Table 4). It is worth to notice that CNF fiberboards had similar specific strength with commercial HDF, but higher specific elasticity (Table 4). In this case, the addition of nanoreinforcement is needed to equalize or exceed the result of the market material. Table 4 also indicates the results of Izod impact strength. It was observed that the energy required to break CNF-corn fiberboard was higher than that of non-reinforced fiberboards. Although, the results recorded in this study were higher than those reported by some other researchers (Castro et al., 2012; Silva et al., 2011), the energy for crack propagation is still very low with respect to the market products. This is likely due because, in the commercial HDF, the formaldehyde-based resin show higher interface bonding strength than cellulose nanofibrils, and so higher energy to break (Castro et al., 2012).

Dynamic mechanical analysis (DMA) is a sensitive technique that characterizes the mechanical response of materials by monitoring property change with respect to the temperature and frequency of applied sinusoidal stress. This technique separates the dynamic response of materials into two distinct parts: an elastic part (E′) and a viscous component (E″). The complex modulus E* ($E^* = E' + iE''$) is defined as the instantaneous ratio of the in-phase or elastic response E′ (which is proportional to the recoverable or, stored energy) and viscous response E″ (which is proportional to the irrecoverable or, dissipated energy). DMA has been also used to analyze the structural and thermo-mechanical properties of thermosetting adhesives (Kumar et al., 2013). The DMA for commercial HDF and corn fiberboards was also performed. The complex modulus is depicted in Fig. 5. All fiberboards made from corn stalk biomass gave better results than the commercial product. Moreover, the incorporation of cellulose nanoreinforcement produced a superior complex modulus that increased with the CNF content (Alcalá et al., 2013; Besbes et al., 2011; Silva et al., 2011). In all cases, the stiffness decreased with increasing temperature (Kumar et al., 2013), as expected. However, while commercial and non-reinforced fiberboards show a constant decrease of rigidity with temperature, fiberboards reinforced with cellulose nanofibers exhibited some different tendency. Thus, the stiffness of the fiberboards show a diminish after 60–70 °C due to an increase of mobility and start softening of the lignin and low molecular weights compounds. Afterwards, between 100 and 120 °C the complex

Table 4
Results of mechanical properties of fiberboard – values in brackets are the standard deviations.

Fiberboard (+CNF)	ρ Kg/m^3	MOR/ρ MPa·m^3/Kg	MOE/ρ MPa·m^3/Kg	IB/ρ MPa·m^3/Kg	Impact kJ/m^2
Commercial	883 (19)	0.047	3.02	$5.32 \cdot 10^{-4}$	10.8 (0.2)
Corn TMP	917 (48)	0.032	2.04	$2.07 \cdot 10^{-4}$	3.2 (0.5)
Corn + 0.5%	1106 (14)	0.039	3.79	$5.06 \cdot 10^{-4}$	4.3 (0.6)
Corn + 1%	1110 (33)	0.043	4.03	$6.85 \cdot 10^{-4}$	4.4 (0.2)
Corn + 2%	1143 (31)	0.046	3.97	$1.10 \cdot 10^{-3}$	4.7 (0.6)
Corn + 4%	1100 (38)	0.047	4.35	$1.39 \cdot 10^{-3}$	5.6 (0.8)
Corn + 6%	1115 (26)	0.047	4.52	$8.79 \cdot 10^{-4}$	5.0 (0.5)
Corn + 8%	1129 (33)	0.047	4.57	$4.25 \cdot 10^{-4}$	4.8 (1.3)
Corn + 10%	1069 (40)	0.044	4.14	$5.05 \cdot 10^{-4}$	3.6 (0.5)

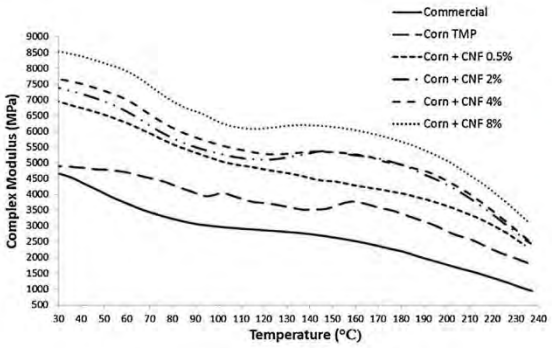


Fig. 5. Dynamic mechanical analysis of corn fiberboard.

modulus seems to stabilize and the slope decrease is very low. This preservation of the complex modulus, or even small stiffening in some formulation, may be caused by the release of water from the material that prevents the loss of rigidity of fiberboards (between 120 and 170 °C approx.) (Barbosa et al., 2010). Thereafter, above 190 °C, the complex modulus clearly diminished and the material began degradation (Alcalá et al., 2013) that is evident after 240 °C.

3.5. Physical characterization

Water absorption (WA) and thickness swelling (TS) are two important parameters when determining the physical characteristics of fiberboards (Mancera et al., 2012). Both parameters are shown in Fig. 6. All corn fiberboards, particularly those containing CNF, had lower percentage of water absorption and thickness swelling than the commercial fiberboard. The WA and TS of commercial HDF was 81% and 68%, respectively, while it was 50% and 35% for corn fiberboard. Between the fiberboards with and without CNF, interestingly, the presence of CNF diminished the water absorption value (Theng et al., 2014). One explanation can be that cellulose nanofibers bring to a more compact final structure that prevents the penetration of water into the fiberboard. Even if they are hydrophilic, cellulose nanofibers are quite compatible with the rest of the components of the fiberboard. Therefore, in a well distributed system, the interface between cellulose nanofibers and the corn microfibers is favorable and the final result may be a more compacted material that absorbs less water than the non-reinforced one. This occurs with just the addition of 0.5 wt% of CNF, and remains like this up to 8 wt% of nanofiber content. The obtained results were slightly higher than those reported in the literature by a number of authors (Kargarfard and Jahan-Latibari, 2011; Velásquez et al., 2003), similar to those of previous studies (Buyuksari et al., 2010; Quintana et al., 2009; Saari et al., 2014), but much lower values than those of (Baskaran et al., 2012; Ciannamea et al., 2010; Hashim et al., 2010; Mancera et al., 2012).

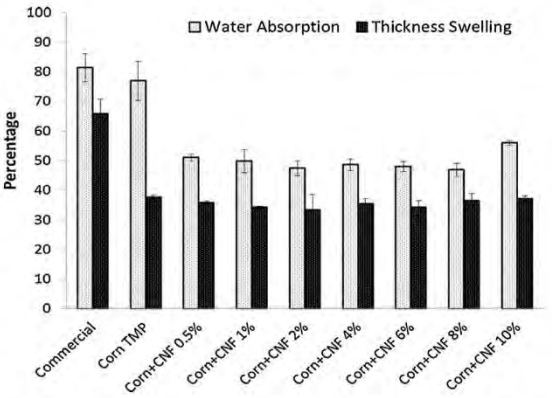


Fig. 6. Water absorption and thickness swelling values for the prepared corn fiberboard.

4. Conclusions

It can be concluded that the addition of CNF improved the mechanical and physical properties of corn fiberboard, although had a higher density when compared with non-reinforced fiberboard or the commercial HDF. The flexural strength increased linearly with increasing amount of CNF. An addition of only 0.5 wt% of eucalyptus cellulose nanofibers gave already higher strength than that of the commercial boards (76% of increase in MOR).

Non-wood fiberboards reinforced with CNF are good alternative to the commercial HDF, normally produced with synthetic resins and wood fibers.

Acknowledgements

The authors wish to thank Erasmus Mundus Techno II project for financial support. Special thanks are given to the Spanish Ministry for the financing through the project CTM2011-28506-C02-02.

References

Akgül, M., Güler, C., Çöpür, Y., 2010. Certain physical and mechanical properties of medium density fiberboards manufactured from blends of corn (*Zea mays indurata* Sturt.) stalks and pine (*Pinus nigra*) wood. Türk. J. Agric. For. 34, 197–206.

Alcalá, M., González, I., Boufi, S., Vilaseca, F., Mutjé, P., 2013. All-cellulose composites from unbleached hardwood kraft pulp reinforced with nanofibrillated cellulose. Cellulose 20 (6), 2909–2921.

Alila, S., Besbes, I., Vilar, M.R., Mutjé, P., Boufi, S., 2013. Non-woody plants as raw materials for production of microfibrillated cellulose (MFC): a comparative study. Ind. Crops Prod. 41, 250–259.

American National Standard A, 2002. Medium Density Fiberboard (MDF) for Interior Applications, Composite Panel Association, 18,922 Premiere Court. Gaitersburg, MD 20,879–1569, The United States of America.

Angles, M., Reguant, J., Montane, D., Ferrando, F., Farriol, X., Salvado, J., 1999. Binderless composites from pretreated residual softwood. J. Appl. Polym. Sci. 73 (12), 2485–2491.

Anglès, M.N., Ferrando, F., Farriol, X., Salvadó, J., 2001. Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition. Biomass Bioenergy 21, 211–224.

Barbash, V., Trembus, I., Nagorna, J., 2012. Pulp obtaining from corn stalks. Chem. Chem. Technol. 6 (1), 83–87.

Barbosa, V., Ramires, E.C., Razera, I.A.T., Frollini, E., 2010. Biobased composites from tannin-phenolic polymers reinforced with coir fibers. Ind. Crops Prod. 32 (3), 305–312.

Baskaran, M., Hashim, R., Said, N., Raffi, S.M., Balakrishnan, K., Sudesh, K., Sulaiman, O., Arai, T., Kosugi, A., Mori, Y., Sugimoto, T., Sato, M., 2012. Properties of binderless particleboard from oil palm trunk with addition of polyhydroxyalkanoates. Comp. Part B: Eng. 43 (3), 1109–1116.

Benhamou, K., Dufresne, A., Magnin, A., Mortha, G., Kaddami, H., 2014. Control of size and viscoelastic properties of nanofibrillated cellulose from palm tree by varying the TEMPO-mediated oxidation time. Carbohydr. Polym. 99, 74–83.

Besbes, I., Vilar, M.R., Boufi, S., 2011. Nanofibrillated cellulose from alfa, *Eucalyptus* and pine fibres: preparation, characteristics and reinforcing potential. Carbohydr. Polym. 86 (3), 1198–1206.

Buyuksari, U., Ayrilmis, N., Avci, E., Koc, E., 2010. Evaluation of the physical, mechanical properties and formaldehyde emission of particleboard manufactured from waste stone pine (*Pinus pinea* L.) cones. Bioresour. Technol. 101 (1), 255–259.

Byrd, M., Jameel, H., Johnson, W., 2006. Chemical and Pulping Characteristics of Corn Stalk fractions. Proceedings of New Technologies in Non-wood Fiber Pulping and Papermaking. Press of South China, University of Technology, Guangzhou.

Carrasco, F., Mutje, P., Pelach, M., 1996. Refining of bleached cellulosic pulps: characterization by application of the colloidal titration technique. Wood Sci. Technol. 30 (4), 227–236.

Castro, D.O., Ruvolo-Filho, A., Frollini, E., 2012. Materials prepared from biopolyethylene and curaua fibers: composites from biomass. Polym. Test. 31 (7), 880–888.
Ciannamea, E.M., Stefani, P.M., Ruseckaite, R.A., 2010. Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives. Bioresour. Technol. 101 (2), 818–825.
Cui, J., Lu, X., Zhou, X., Chrusciel, L., Deng, Y., Zhou, H., Zhu, S., Brosse, N., 2014. Enhancement of mechanical strength of particleboard using environmentally friendly pine (*Pinus pinaster* L.) tannin adhesives with cellulose nanofibers. Ann. For. Sci. 72 (1), 27–32.
Da Silva Perez, D., Montanari, S., Vignon, M.R., 2003. TEMPO-mediated oxidation of cellulose III. Biomacromolecules 4 (5), 1417–1425.
Dasgupta, S., 1994. Mechanism of paper tensile-strength development due to pulp beating. Tappi J. 77 (6), 158–166.
Delgado-Aguilar, M., González, I., Pèlach, M.A., De La Fuente, E., Negro, C., Mutjé, P., 2015. Improvement of deinked old newspaper/old magazine pulp suspensions by means of nanofibrillated cellulose addition. Cellulose, 1–14.
El-Kassas, A.M., Mourad, A.H.I., 2013. Novel fibers preparation technique for manufacturing of rice straw based fiberboards and their characterization. Mater. Des. 50, 757–765.
El-Tayeb, T., Abdelhafez, A., Ali, S., Ramadan, E., 2012. Effect of acid hydrolysis and fungal biotreatment on agro-industrial wastes for obtainment of free sugars for bioethanol production. Braz. J. Microbiol. 43 (4), 1523–1535.
EN216, 1999. Wood fiberboard: definition, classification and symbols. Eur. Comm. for Standardization, Bruss., Belgium, Central Secretariat: rue de Stassart 36, B-1050 Brussels.
Flandez, J., González, I., Resplandis, J.B., El Mansouri, N.-E., Vilaseca, F., Mutjé, P., 2012. Management of corn stalk waste as reinforcement for polypropylene injection moulded composites. Bioresource 7 (2), 1836–1849.
González, I., Alcalá, M., Arbat, G., Vilaseca, F., Mutjé, P., 2013. Suitability of rapeseed chemithermomechanical pulp as raw material in papermaking. Bioresource 8 (2), 1697–1708.
González, I., Alcalà, M., Chinga-Carrasco, G., Vilaseca, F., Boufi, S., Mutjé, P., 2014. From paper to nanopaper: evolution of mechanical and physical properties. Cellulose 21 (4), 2599–2609.
Halvarsson, S., Edlund, H., Norgren, M., 2009. Manufacture of non-resin wheat straw fibreboards. Ind. Crops Prod. 29 (2–3), 437–445.
Hashim, R., Saari, N., Sulaiman, O., Sugimoto, T., Hiziroglu, S., Sato, M., Tanaka, R., 2010. Effect of particle geometry on the properties of binderless particleboard manufactured from oil palm trunk. Mater. Des. 31 (9), 4251–4257.
Henriksson, M., Berglund, L.A., Isaksson, P., Lindstrom, T., Nishino, T., 2008. Cellulose nanopaper structures of high toughness. Biomacromolecules 9 (6), 1579–1585.
Hess, J., Olson, A., Jacobs, R., 2002. Wisconsin Corn Stover-Part 1: Chemical Composition. Proceedings of TAPPI 2002 Fall Technical Conference. TAPPI Press.
Huang, Y., Wei, X., Zhou, S., Liu, M., Tu, Y., Li, A., Chen, P., Wang, Y., Zhang, X., Tai, H., Peng, L., Xia, T., 2015. Steam explosion distinctively enhances biomass enzymatic saccharification of cotton stalks by largely reducing cellulose polymerization degree in *G. barbadense* and *G. hirsutum*. Bioresour. Technol. 181, 224–230.
Isogai, A., Saito, T., Fukuzumi, H., 2011. TEMPO-oxidized cellulose nanofibers. Nanoscale 3 (1), 71–85.
Kargarfard, A., Jahan-Latibari, A., 2011. The performance of corn and cotton stalks for medium density fiberboard production. Bioresource 6 (2), 1147–1157.
Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., Dorris, A., 2011. Nanocelluloses: a new family of nature-based materials. Angew. Chem. Int. Ed. 50 (24), 5438–5466.
Kumar, A., Gupta, A., Sharma, K.V., 2013. Thermal and mechanical properties of urea-formaldehyde (UF) resin combined with multiwalled carbon nanotubes (MWCNT) as nanofiller and fiberboards prepared by UF-MWCNT. Holzforsch 8 (4), 6231–6241.
Li, X., Li, Y., Zhong, Z., Wang, D., Ratto, J.A., Sheng, K., Sun, X.S., 2009. Mechanical and water soaking properties of medium density fiberboard with wood fiber and soybean protein adhesive. Bioresour. Technol. 100 (14), 3556–3562.
Mancera, C., El Mansouri, N.E., Pelach, M.A., Francesc, F., Salvado, J., 2012. Feasibility of incorporating treated lignins in fiberboards made from agricultural waste. Waste Manage. 32 (10), 1962–1967.
Mejía, E.H., Quintana, G.C., Ogunsile, B.O., 2014. Development of binderless fiberboards from steam-exploded and oxidized oil palm wastes. Bioresource 9 (2), 2922–2936.
Mendez, J., Vilaseca, F., Pelach, M., Lopez, J., Barbera, L., Turon, X., Girones, J., Mutje, P., 2007. Evaluation of the reinforcing effect of ground wood pulp in the preparation of polypropylene-based composites coupled with maleic anhydride grafted polypropylene. J. Appl. Polym. Sci. 105 (6), 3588–3596.
Mutjé, P., Pelach, M., García, J., Presta, S., Vilaseca, F., Jimenez, L., 2006. Comparison of cationic demand between olive wood organosolv pulp and eucaliptus kraft pulp. Process Biochem. 41 (7), 1602–1607.
Pan, M., Zhou, D., Ding, T., Zhou, X., 2010. Water resistance and some mechanical properties of rice straw fiberboards affected by thermal modification. Bioresource 5 (2), 758–769.
Quintana, G., Velásquez, J., Betancourt, S., Gañán, P., 2009. Binderless fiberboard from steam exploded banana bunch. Ind. Crops Prod. 29 (1), 60–66.
Rokiah, H., Othman, S., Norli, I., Mahamad Hakimi, I., Hasnah, M., Salmiah, U., 2009. Extractable formaldehyde from waste mediem density fiberboard. J. Trop. For. Sci. 21 (1), 25–33.
Rouger, J., Mutjé, P., 1984. Correlation between the cellulose fibres beating and the fixation of a soluble cationic polymer. Br. Polym. J. 16 (2), 83–86.
Saari, N., Hashim, R., Sulaiman, O., Hiziroglu, S., Sato, M., Sugimoto, T., 2014. Properties of steam treated binderless particleboard made from oil palm trunks. Comp. Part B: Eng. 56, 344–349.
Saito, T., Hirota, M., Tamura, N., Kimura, S., Fukuzumi, H., Heux, L., Isogai, A., 2009. Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. Biomacromolecules 10 (7), 1992–1996.
Saito, T., Kimura, S., Nishiyama, Y., Isogai, A., 2007. Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. Biomacromolecules 8, 2485–2491.
Shinoda, R., Saito, T., Okita, Y., Isogai, A., 2012. Relationship between length and degree of polymerization of TEMPO-oxidized cellulose nanofibrils. Biomacromolecules 13 (3), 842–849.
Silva, C.G., Benaducci, D., Frollini, E., 2011. Lyocell and cotton fibers as reinforcments for a thermoset polymer. Bioresource 7 (1), 78–98.
Sun, Y.-C., Lin, Z., Peng, W.-X., Yuan, T.-Q., Xu, F., Wu, Y.-Q., Yang, J., Wang, Y.-S., Sun, R.-C., 2014. Chemical changes of raw materials and manufactured binderless boards during hot pressing: lignin isolation and characterization. Bioresource 9 (1), 1055–1071.
TAPPI, U., 2011. Water retention value (WRV). TAPPI Test Method. Atlanta, GA, USA.
Teixeira, D.E., Moslemi, A., 2001. Assessing modulus of elasticity of wood-fiber cement (WFC) sheets using nondestructive evaluation (NDE). Bioresour. Technol. 79 (2), 193–198.
Theng, D., Arbat, G., Ngo, B., Vilaseca, F., Velasquez, J.A., Pellicer, N., Mutje, P., 2014. Feasibility of incorporating treated NFC in all lignocellulosic materials made from corn stalk biomass. in: The VIII IberoAm. Congr. on Pulp and Paper Res., (Eds.) J.A.V.J., G.C.Q.M., UPB, RIADICYP and PROVALOR. Medellín, Colombia.
Velásquez, J.A., Ferrando, F., Salvadó, J., 2003. Effects of kraft lignin addition in the production of binderless fiberboard from steam exploded *Miscanthus sinensis*. Ind. Crops Prod. 18 (1), 17–23.
Wise, L.E., Murphy, M., D'Addieco, A.A., 1946. A chlorite holocellulose, its fractionation and bearing on summative wood analysis and studies on the hemicelluloses. Pap. Trade J. 122 (2), 35–43.
Won, J.M., Ahmed, A., 2004. Corn stalk as a raw material for papermaking. In: In 58th Appita Annual Conference and Exhibition Incorporating the Pan Pacific Conference, Proceedings (p. 5), Appita Inc. Canberra, Australia.
Wu, J., Zhang, X., Wan, J., Ma, F., Tang, Y., Zhang, X., 2011. Production of fiberboard using corn stalk pretreated with white-rot fungus *Trametes hirsute* by hot pressing without adhesive. Bioresour. Technol. 102 (24), 11258–11261.
Wuzella, G., Mahendran, A.R., Bätge, T., Jury, S., Kandelbauer, A., 2011. Novel, binder-free fiber reinforced composites based on a renewable resource from the reed-like plant *Typha* sp. Ind. Crops Prod. 33 (3), 683–689.

4.2 Paper II

Title	**Fiberboards made from Corn Stalk Thermomechanical Pulp and Kraft Lignin as a Green Adhesive**
Authors	Dyna Theng, Nour-Eddine El Mansouri, Gerard Arbat, Bunthan Ngo, Marc Delgado-Aguilar, M. Àngels Pèlach, Pere Fullana-i-Palmer, and Pere Mutjé
Journal	BioResources
Year	2017
Volume	12
Issue	2
Pages	2379-2393
Status	Published

Fiberboards Made from Corn Stalk Thermomechanical Pulp and Kraft Lignin as a Green Adhesive

Dyna Theng,[a,d] Nour-Eddine El Mansouri,[b] Gerard Arbat,[c,*] Bunthan Ngo,[d] Marc Delgado-Aguilar,[a] M. Àngels Pèlach,[a] Pere Fullana-i-Palmer,[e] and Pere Mutjé [a]

The feasibility of incorporating purified kraft lignin, at different concentrations ranging from 5 to 29%, into fiberboards made from corn residues was studied. The lignin was obtained from black liquor, which is a residue of the paper industry. Corn stalk raw material and its thermomechanically produced fiber were characterized in terms of their chemical composition. The physical and mechanical properties of the resulting fiberboards were evaluated. The fiberboards produced following a wet process had good mechanical and water resistance properties that satisfied the requirements of the relevant standards. In addition, a Life Cycle Thinking (LCT) approach suggested that lignin-based fiberboards are environmentally preferable than those based on thermosetting resins.

Keywords: Corn residues; Thermomechanical pulp; Kraft lignin; Green adhesive; Mechanical properties; Life cycle thinking

Contact information: a: Laboratori d'Enginyeria Paperera i Materials Polimers (LEPAMAP), University of Girona, Girona, Spain; b: Laboratoire Interdisciplinaire de Recherche en Sciences et Techniques (LIRST), Université Sultan Moulay Slimane, Béni-Mellal, Morocco; c: Department of Chemical and Agricultural Engineering and Technology, University of Girona, Girona, Spain; d: Royal University of Agriculture, Phnom Penh, Cambodia; e: Escola Superior de Comerç Internacional (UPF), Barcelona, Spain;
**Corresponding author: gerard.arbat@udg.edu*

INTRODUCTION

Corn (*Zea mays*, Poaceae family) is a cereal crop, grown in various agro-ecological regions. Corn is an important food for many people in Africa, Asia, and Latin America (Yaning *et al.* 2012) and is also used in livestock feed (poultry, pigs, cattle) in the form of grains, feed milling, or as fodder (Escalante-Ten Hoopen and Maïga 2012). The global corn production increased from 729 to 1038 million tonnes (42.38% improvement) during the decade 2004 – 2014, which is higher than the relative increase of world population 12.89% (6.44 to 7.27 billion) for the same period (FAOSTAT 2016).

Cobs, leaves, and stalks are important residues of corn processing and consumption, remaining after corn grains are collected. Among these, corn stalks give an important proportion, amounting to 0.50 kg for every kg of dry corn grain produced (Sokhansanj *et al.* 2002). Among all agricultural wastes, corn stalk is an important lignocellulosic crop in terms of annual global production (Table 1). Currently, these residues have a number of limited application, *e.g.* (a) use of stalks as livestock feed and biofertilizer (Chen *et al.* 2010; Li *et al.* 2007; Duffy and Marchand 2013), as lignocellulosic fibers for pulp and paper making (Flandez *et al.* 2010) and ethanol production (Hong *et al.* 2015), (b) use of corn cobs as building materials and activated carbon (Cao *et al.* 2006; Pinto *et al.* 2012), (c) use of corn leaves as a feedstock for fermentable sugars and supplemental fiber for paper pulp (Donghai *et al.* 2006; Shinners and Binversie 2007). However, these residues are not efficiently managed; they are mainly burned in the field, particularly in developing parts of the world

(Pang *et al.* 2012). Since there is a lack of waste management, there is a need for applications of such residues.

Table 1. Annual Production of Agricultural Lignocellulosic Residues in 2014*

Lignocellulosic Residue	10^6 Tm/year
Cereals**	1,537
Corn	1,237
Rice	1,139
Soybean	481
Sorghum stalk***	252
Sugarcane	203
Rapeseed	123
Cotton Stalk***	68
Total:	5,040

*Elaborated from Smil 1999, (Smil 1999; Kim and Dale 2004; FAOSTAT 2016, and Leal *et al.* 2013)
**Includes wheat, barley, triticale, oat, and rye
***Cotton stalk and sorghum stalk production values were published in Hurter (2015)

Kraft lignin is a by-product of pulp mills generated during the kraft pulping of wood chips, which is the most common chemical pulping method. Currently, approximately 2% of the produced lignin is utilized in value-added and commercial products (paper industries, medical, agriculture, fuel, chemical, concrete and cement, carbon fibers/nanotubes, board binder, dust controller, battery, cosmetics, foams, plastics, and heat), while the rest is burned to generate energy and recover chemicals (Khitrin *et al.* 2012). However, this trend is changing due to the increasing interest in developing lignin-based products. Some of these high-value products include: green substitutes for fossil fuel, carbon fibers, surfactants, polymer blends, and composites; phenol replacement in phenol-formaldehyde resin; and green binders. For these two last applications, Anglès *et al.* (2001), Mancera *et al.* (2012); and Mejía *et al.* (2014) have reported several strategies to develop natural lignin-based adhesives for their use in panel products. Moreover, many recent patents have described the replacement of formaldehyde-based resins with industrial lignin but, for various reasons, they have not been implemented (Vishtal and Kraslawski 2011). It must be noticed that previous published references used the dry process to produce fiberboard, but there has been a lack of publications on the topic of the wet process at the laboratory scale, which has great interest at the industrial scale, as there are industries that follows this process.

Waste production has been an issue of concern within the European Union for many years, with a first Directive published in 1975 (EC 1975). The first adopted policies were "end-of-pipe" oriented, *i.e.*, introducing technologies to minimize the impact of waste after it was produced. Subsequent policies have improved on the preceding ones in terms of environmental impact and economic cost. In early 1997, the Council of the European Union confirmed the so-called waste management hierarchy in which waste prevention is the first priority of waste management, followed by re-use and material recycling; only after verifying those options are not feasible, waste is used for energy recovery (EC 1997). Burning without energy recovery and landfilling are the very last options of waste management. The life cycle approach is commonly used to verify that a given waste management option is better environmentally speaking than another one or to confirm the hierarchy for a specific case (Finnveden *et al.* 2005; Moberg *et al.* 2005; Hauschild and Barlaz 2009). To standardize the "green" product categorization, the European Commission has initiated the "Single Market for Green Products" (Klüppel 2005), based on a harmonized methodology for the calculation of the so-called "Product Environmental Footprints", which are, in fact, life cycle assessment

studies. Waste should not only be considered a problem but rather a valuable resource for industry (Zamagni 2012). Recently, circular economy principles have been strongly pushed into the European market. Turning Europe into a more circular economy means enhancing product recyclability, reducing the use of new raw materials and demonstrating that a new economy based on the preservation of the environment can help to achieve a minimum-waste production (Zaman 2015). Based on a life cycle thinking approach, the environmental pros and cons of the boards with added lignin were examined.

The present study aims to (1) develop fiberboards made from corn stalk thermomechanical fibers with reinforcement of kraft lignin as a natural binder using the wet process to produce fiberboards and (2) discuss life cycle aspects of the composite preparation and subsequent processes. Corn biomass will be treated by steaming in a rotary digester reactor without any chemical agent addition, while kraft lignin will be extracted from black liquor (residues of pulp and paper production) and dried to be a powder form, and later mixed both materials together with additional of water using a disintegrator. The final goal is to produce binder-free composite from corn stalk having enhanced properties with respect to commercial fiberboards that rely upon the usage of synthetic resin, and lastly to discuss the shelf life of this product based on pros and cons impact on environment.

EXPERIMENTAL

Materials

The basic materials used in the research were corn biomass and spent black liquor pulp. Corn residues (moisture content of 12%) were collected from a field at La Tallada d'Empordà, Girona, Spain, and stored at room temperature. The commercial spent black liquor pulp was supplied by Torraspapel S. A. Pulp and Paper Factory (Zaragoza, Spain), and had a pH of about 12. Sulfuric acid (H_2SO_4) at 72% concentration and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (Barcelona, Spain) and used as received. Cationic starch and colloidal silica were provided by Torraspapel S. A. (Sarrià de Ter, Girona, Spain) and were used as retention agents during the dispersion of both the corn fibers and the powdered purified kraft lignin.

Methods

Thermo-mechanical corn stalk fiber production

The preparation of thermomechanical fibers involves vaporization, followed by mechanical defibration. A suspension of corn stalks was submitted to steam-water treatment by keeping the suspension at 160 °C for 15 min in a reactor, at a water-to-solid ratio of 6:1 (liters of water per kg of solid). The obtained pulp was rinsed in cold water and then submitted to mechanical defibration in a Sprout-Waldron refiner (model 105-A, Andritz, Janesville, WI, USA), which was responsible for fiber individualization (Theng *et al.* 2015).

Lignin preparation

Purified kraft lignin powder was prepared from commercial black liquor, as described by Lin (1992). Commercial black liquor was first treated with hot water with stirring. The homogenized black liquor solution (pH 12) was acidified using 72% sulfuric acid with stirring. The solid lignin was recovered by precipitation after lowering the pH of the mixture to 2 and applying filtration. Solid lignin was washed with distilled water and filtered several times to remove residual sulfuric acid. To recover pure, powder-form lignin, the solution pH was increased to 6.0 by the addition of sodium hydroxide, and the lignin was subsequently

dried in an oven at 60 °C (Mancera *et al.* 2012). After drying at room temperature, lignin samples were stored in plastic bags for use as a natural green adhesive in corn stalk fiberboards.

Fiberboard production

Corn stalk pulp was passed through a Sprout-Waldron machine and subjected to a vacuum until the moisture content reached 20%. Using a disintegrator at 80,000 revolutions to ensure good dispersion, the pulp was mixed with lignin in different proportions (0, 5, 9, 13, 17, 21, 25, and 29%), followed by addition of the retention agents 0.5% cationic starch and 0.8% colloidal silica, and water. With the obtained mixture, a web was made using a paper sheet former of 20 cm diameter, which was then cut carefully to the same size of the molding box (150 mm in length and 50 mm in width). Boards were prepared with a target thickness of 3.0 mm. After the material was placed in the mold, it was hot-pressed in a three-stage cycle (Angles *et al.* 1999) consisting of: (1) pressing at the desired temperature (230 °C) and pressure (0.23 MPa) for a given period of time (2 min); (2) a breathing period or pressure relaxation for 1 min; and (3) pressing at the desired temperature and pressure for a given period of time (230 °C, 0.23 MPa, and 5 min). The experimental procedure is shown in Fig. 1.

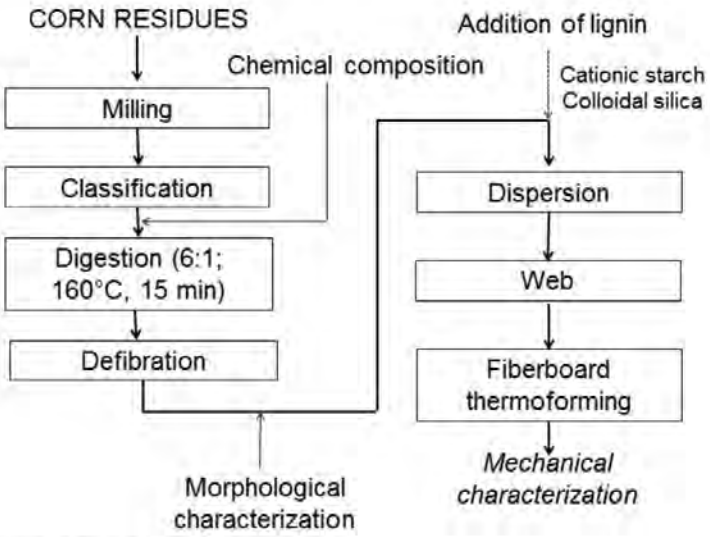


Fig. 1. Flow chart of the experimental procedure

Physical and mechanical characterization

The boards were characterized using European standards. The measured mechanical properties were impact strength (IS), modulus of elasticity (MOE), and modulus of rupture (MOR) (EN310 1993). Dimensional stability was characterized by thickness swelling (TS) (EN317 1993) and water absorption (WA) (EN382-1 1993). Additionally, the density of the boards was determined (BS-EN323 1993). Boards were conditioned at 20 °C and 65% relative humidity before any physical or mechanical tests were conducted, and the dimensions of the test pieces were determined by EN325 (1993).

Characterization of corn stalk materials and lignin adhesive

For corn stalk waste and corn stalk pulp, the ash contents were obtained gravimetrically after furnace calcinations for 3 h at 575 °C (ASTM D1102-84 2001). The corn stalk samples were milled and treated with 95% ethanol for 6 h in a Soxhlet apparatus to remove extractives. The Klason lignin was determined by the conventional method as the insoluble fraction after two-step acid hydrolysis (TAPPI T 222 Om-98 1985). Acid-soluble lignin was determined by applying the spectrophotometric method (TAPPI UM 250 1991). The cellulose and hemicellulose were determined as described by Wise *et al.* (1946) and TAPPI standard T223 cm-01 (2001), respectively.

Thermogravimetric analysis (TGA) of purified kraft lignin powder was measured using a TGA-50 series instrument (Shimadzu, Japan), with temperature up to 1000°C and maximum sample mass 1 g. The samples were heated from room temperature to 800 °C with a heating rate of 5 °C/min under an air atmosphere. Thermogravimetric analysis was conducted to measure if the temperature of the thermoforming would degrade lignin.

RESULTS AND DISCUSSION

Thermogravimetry of Purified Kraft Lignin

The TG curve of the lignin sample displayed the mass loss of polymeric materials *vs.* the temperature of thermal degradation (Fig. 2).

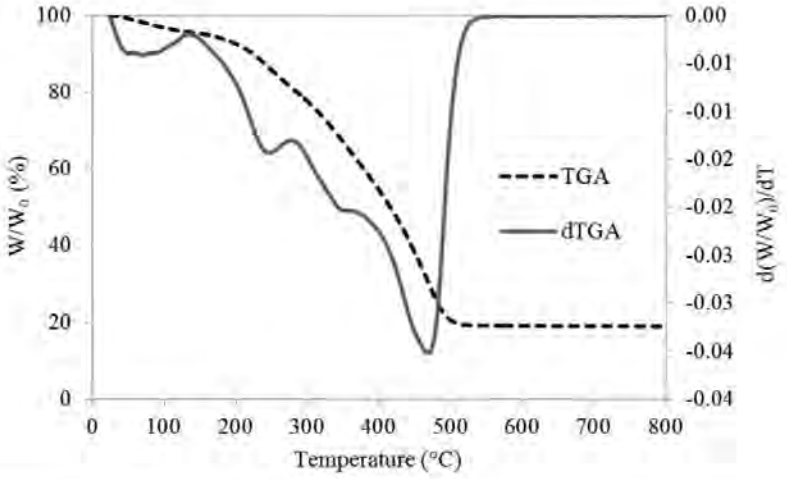


Fig. 2. Thermogravimetric analysis of kraft lignin

A first mass loss was observed at 100 ºC, concurring with water vaporization. Moisture content of the trial lignin powder was 3.73%, being of the same magnitude as the observed weight loss in the TGA curve at 100 ºC. Then, the thermal degradation of all lignin compounds took place at a stage between 200 ºC and 500 ºC (approximately 72% of mass loss). At this stage, all carbohydrate volatile components in the lignin sample were degraded. At higher temperature, there was no more weight loss, since the remaining mass corresponded to ash (about 19% of the total mass) by the end of the measurement. These

results are in accordance with a previous report showing that the degradation temperature of lignin began at around 200 °C, depending on the lignin origin (El Mansouri *et al.* 2011).

Figure 2 also indicates the mass loss rate as a DTGA (derivative thermogravimetry) curve, which is shown as a square dot line. The peak of this curve can be expressed as a single thermal decay temperature and used to compare its polymeric materials in term of thermal characteristics. This analysis illustrated that when the lignin sample was heated at about 450 °C, pyrolytic deprivation took place and the inter-unit linkage of the lignin structure became fragmented, with the release of monomeric phenols into vapor phase. The range of obtained maximum derivative thermogravimetric is in agreement with other previous findings (El-Saied and Nada 1993; Sun *et al.* 2000; Tejado *et al.* 2007; El Mansouri *et al.* 2011). The high temperature of lignin degradation allows applicable of blending it with other lignocellulosic materials and compress at quite high temperature to produce fiberboards without decomposed lignin.

Chemical Composition of Corn Stalk Raw Material and Pulp

Table 2 shows the chemical composition of corn stalk raw material and pulp.

Table 2. Chemical Analysis of Corn Stalk Raw Material and Pulp

Chemical Analysis	Corn Stalk	Corn Stalk Pulp
Ash Content (%)	3.20	0.80
Extractives (%)	3.10	1.05
Lignin Content (%)	16.00	17.24
Cellulose (%)	50.57	55.17
Hemicelluloses (%)	27.03	25.75
Holocelluloses (%)	77.60	80.92

Corn stalk contains more cellulose but has relatively low lignin content compared to commonly used wood fibers from pine and eucalyptus (Mancera *et al.* 2012), which suggests its suitability as an alternative for industrially manufactured fiberboards and papers. The corn stalk raw material was submitted to thermomechanical processing at 160 °C for 15 min; this procedure determined the final morphology and chemical composition of the obtained fibers. In this case, the fiber yield was about 87.1 wt./wt.%. Theng *et al.* (2015) indicated that thermomechanically processed corn fibers contain almost all the initial lignin, with the exception of the waxes and extractives removed during the steam treatment. The obtained pulp exhibited higher cellulose and lignin contents with lower hemicelluloses content.

Effects on Water Absorption and Thickness Swelling

Water absorption (WA) and thickness swelling (TS) are physical properties related to the dimensional stability of the fiberboards (Fig. 3). These properties demonstrate how the boards would behave if they were used under humid conditions, as physico-mechanical properties of lignocellulosic materials always are strongly related to the water content. Lower values of water absorption and thickness swelling mean higher dimensional stability, resulting in a better performance when fiberboards are submitted to any strain. Establishing a parallelism with papermaking, fiberboards with less relative bonded area (RBA) are more likely to retain water due to the availability of hydroxyl groups on the fiber surface. In addition, fiberboards with a higher RBA have more inter-fiber bonds per volume unit, leading to higher physico-mechanical properties (Page 1969).

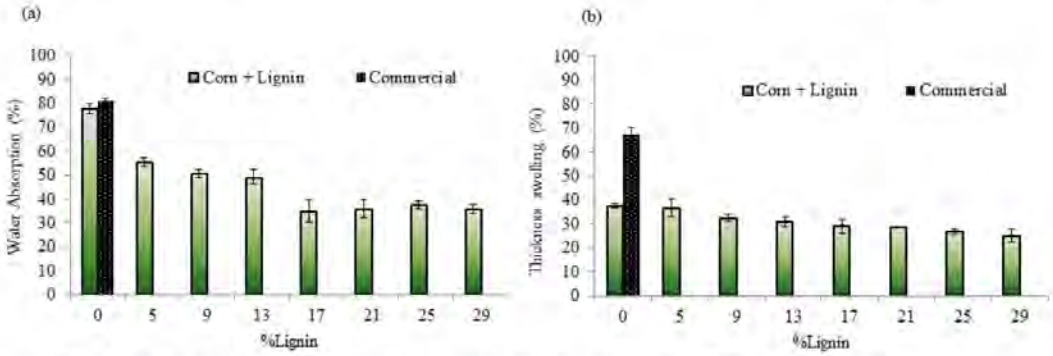


Fig. 3. (a) Mean water absorption (WA) and (b) thickness swelling (TS) of fiberboards

As shown in Fig. 3(a), increasing amounts of kraft lignin decreased the water absorption values of the fiberboards. Specifically, the addition of 29 wt./wt.% kraft lignin decreased WA by about 50.5% compared with the binderless fiberboard and 54.3% if the commercial fiberboard is taken as reference. Therefore, increasing lignin content notably decreased the water absorption and, thus, improved the water resistance and dimensional stability of the fiberboards. Rowell *et al.* (1976) reported that lignocellulosic materials absorb water by forming hydrogen bonds between water molecules and hydroxyl groups in cell wall components. However, the addition of kraft lignin during the preparation of fiberboards reduced their water absorption. This result can be explained by the presence of non-polar hydro-carbon chains and aromatic rings in the lignin molecule (Rozman *et al.* 2000).

Thickness swelling occurs in fiberboards when the cell wall is bulked by water. As shown in Fig. 3(b), the addition of kraft lignin reduced thickness swelling in all fiberboards made of corn. The addition of 29 wt./wt.% kraft lignin decreased TS by about 33.6% compared with the binderless fiberboard and 63% if the commercial fiberboard was taken as reference. These results clearly showed that the addition of kraft lignin reduced swelling in fiberboards. The same behavior was reported by Mancera *et al.* (2012) when studying the effects of adding alkali lignin to *Vitis vinifera* fiberboards.

Effects on Modulus of Rupture and Modulus of Elasticity

The modulus of rupture (MOR) and the modulus of elasticity (MOE) are mechanical properties related to the bending strength of fiberboards. These values were analyzed together in the same bending assay (Figs. 4a and b, respectively).

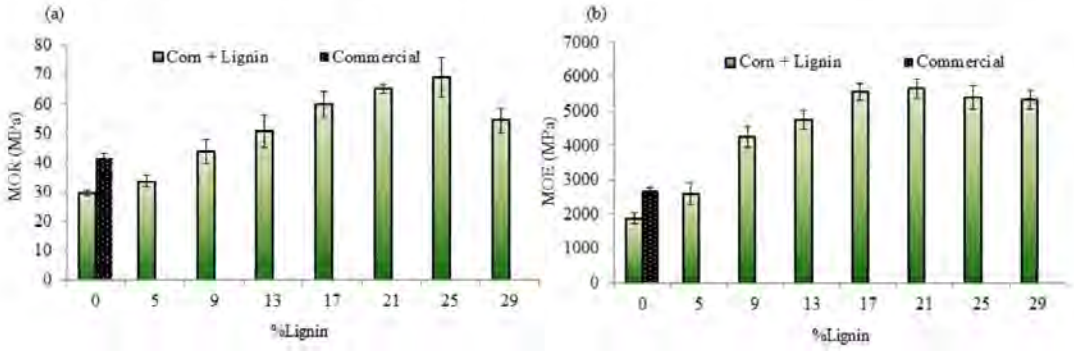


Fig. 4. (a) Mean modulus of rupture (MOR) and (b) modulus of elasticity (MOE) of fiberboards

Fiberboard MOR was enhanced by increasing amounts of added kraft lignin (Fig. 4a). Thus, kraft lignin was effective as a green adhesive. It is particularly interesting to note that the formulation made with just 9 wt./wt.% of kraft lignin showed MOR values higher than those of the standard specifications. More interesting are the results obtained for both formulations made with 17 and 25 wt./wt.%-added kraft lignin, in which the strength of the fiberboards was more than two times higher than that obtained for binderless fiberboards. This result indicated that the addition of kraft lignin improves the MOR of fiberboards made from corn stalk fibers. This improvement can be explained by the good adhesion between fibers produced by the addition of kraft lignin, which is able to overcome discontinuity in the fiber matrix. Recently, Theng *et al.* (2015) added cellulose nanofibres (CNF) to corn biomass to produce HDF, and their results showed that 2 wt.% CNF increased the MOR from 30 to 53 MPa, which is less than that obtained with 25% lignin and equivalent to those obtained with 13% lignin (Fig. 4a). Unlike lignin, an addition of more than 2% CNF did not increase the MOR of the board, suggesting that the surface of the TMP fibers was saturated by CNF nanofibers. Nasir *et al.* (2013) obtained a maximum MOR with a 10% addition of lignin, which was somewhat below the performance level of the commercial board. Figure 4b shows that the MOE of the fiberboards was notably increased as the lignin loading increased to 21%, with a value over 5500 MPa, which is slightly higher than that obtained by adding CNF to corn fibers (Theng *et al.* 2015) and notably higher than that of the commercial board. Thus, kraft lignin enhanced the stiffness of fiberboards, possibly through fiber compatibility. In this regard, other authors have shown that the addition of lignin increased the MOR and MOE more so than phenol-formaldehyde additions (Oluwasina *et al.* 2015).

Effects on the Impact Strength

The impact strength describes the ability of a material to absorb shock and impact energy without breaking. The impact strength of fiberboards increased to 6.4 KJ/m^2 as the lignin content was increased from 0 to 29% (Table 3), which was mainly due to the high-interface bonding strength. It is interesting to note that the impact strength of fiberboards made with 29 wt./wt.% kraft lignin was doubled compared with that of binderless fiberboard. Thus, the results confirmed that lignin improves the impact strength of fiberboards made from corn stalk fibers. This effect was due to the good melting of the kraft lignin at the selected operation conditions, which was able to flow over the fiber surface and form strong inter-fiber bonds (Back 1987). Nevertheless, this value was still lower than the impact strength of commercial fiberboards because formaldehyde-based resins have higher interface bonding strength than lignin. These results were in agreement with previous reports (Castro *et al.* 2012; Silva *et al.* 2012; Theng *et al.* 2015). The lower impact resistance compared with commercial board is probably due to the higher interface bonding strength of formaldehyde-based resins.

Specific Properties of Fiberboards

The physical and specific mechanical properties of the fiberboards are shown in Table 3. These properties were studied against the percentage of added kraft lignin, from 5 wt./wt.% to 29 wt./wt.%.

Table 3. Results of Mechanical Properties of Fiberboards

Trials	ρ (kg/m^3)	f_m/ρ (MPa.m^3/kg)	E_m/ρ (MPa.m^3/kg)	IB/ρ (MPa.m^3/kg)	IS (kJ/m^2)
Commercial	883 ± 19	0.047	3.02	$5.32.10^{-4}$	10.81±0.20
Corn TMP	917 ± 48	0.032	2.04	$2.12.10^{-4}$	2.92±0.11
Corn + 5% Lignin	1063 ± 47	0.032	2.45	$3.24.10^{-4}$	3.45±0.36
Corn + 9% Lignin	1107 ± 38	0.040	3.84	$2.95.10^{-4}$	4.62±0.39
Corn + 13% Lignin	1108 ± 54	0.046	4.29	$4.29.10^{-4}$	5.37±0.35
Corn + 17% Lignin	1168 ± 54	0.051	4.76	$4.12.10^{-4}$	6.35±0.28
Corn + 21% Lignin	1135 ± 45	0.057	4.99	$4.32.10^{-4}$	6.33±0.34
Corn + 25% Lignin	1098 ± 28	0.063	4.92	$4.53.10^{-4}$	4.95±0.32
Corn + 29% Lignin	1128 ± 14	0.048	4.72	$3.11.10^{-4}$	5.47±0.55

Two results for no added kraft lignin were included, which corresponded to binderless corn stalk and commercial fiberboards. All fiberboards (both control samples and kraft lignin-containing fiberboards) had densities from 900 to 1100 kg m^{-3} and were classified as high density fiberboard (HDF) based on European standard EN316 (1999). These results were similar to those in a previous work using nanofibrillated cellulose (NFC) as a reinforcement agent (Theng *et al.* 2015). The results of the trial work included density and specific mechanical properties (Table 3). The specimens of fiberboards with added lignin obtained higher specific strength and specific elasticity than commercial fiberboards, but they were lower in specific internal bonding strength and impact strength. Moreover, as the amount of lignin was increased, specific properties were enhanced as well. This indicates that, in the case of absolute properties, the properties improvement not only comes from the increase on the density, but also in the formation of stronger bonds (*i.e.* covalent) at high temperature.

Discussion on the Green Properties of the Proposed Material

According to circular economy postulates, reintroducing wastes such as corn stalk and lignin into the economy reduces the need for net resources (Iqbal *et al.* 2013; Asim *et al.* 2015), as less synthetic adhesives and wood pulp are extracted from the environment to deliver a product with equal or better physical properties. In addition, substituting natural materials in place of potential carcinogenic agents such as formaldehyde compounds represents an improvement in another area of protection: human health. Finally, avoiding the practice of burning corn stalk decreases CO_2 emissions and, therefore, enhances the protection of the natural environment (Jegatheesan *et al.* 2009).

In the life-cycle thinking (LCT) approach, however, the optimal percentage of lignin needs to be determined in order to know if the proposed alternative is beneficial. In order to balance the ideal with practicality (Baitz *et al.* 2013; Bidstrup *et al.* 2015), a quantitative life cycle assessment (LCA) was not applied at this point, but may come in at a later stage. LCT and LCA are the scientific approaches behind modern environmental policies and business support related to Sustainable Consumption and Production (EC 2010). A complete LCA is not always needed to guide environmental innovation, but a LCT approach is essential. According to various authors (Lazarevic *et al.* 2012; Wolf *et al.* 2012), LCT is essential to the Thematic Strategy on the Sustainable Use of Natural Resources and the Thematic Strategy on the Prevention and Recycling of Waste (EC 2005) and is very important for the Waste Framework Directive. These strategic documents are relevant to the present study, as the main goal of a sustainable use of natural resources is based on waste prevention and

recycling. A condition *sine qua non* identified by the Directorate for General Research and Innovation of the European Commission for the call on Sustainability Assessment of Technologies was that both the framework technology and its derived methods and tools had to be based on LCT approaches, *i.e.*, adequately considering the three pillars of sustainability (economic, environmental, social). Other documents state that sometimes a fully-fledged LCA is not needed (see Bala *et al.* (2010) for a list of examples). Sometimes, the intermediate alternative of a simplified LCA may be used (Delgado-Aguilar *et al.* 2015), which is between a complete LCA and a qualitative life-cycle approach.

Corn stalk is a residue, but dumping it *in situ* gives the soil structural properties and organic matter that enhance the productivity of the soil. The decrease in productivity resulting from the removal of the stalk should be compensated for by the addition of other (synthetic) products, which have their own life cycle of resource needs and emissions. In contrast, if a burning scenario is in place, the emitted CO_2 would equal the absorbed CO_2 used by the corn plant to grow (Garcia and Freire 2014). In addition, processes to collect, pack, and transport the stalk are needed, with, again, evaluations with regard to life cycle impacts. If stalk became a commercial product, an end-of-waste situation might occur, and an allocation of the environmental impacts of corn growth may be needed between corn-related products (food or fuel) and stalk-related products (boards). Therefore, the proposed alternative could be better, for instance, in terms of human toxicity or climate change but worse in terms of eutrophication or acidification.

From a circular economy point of view, using lignin as an adhesive instead of burning the lignin liquor for energy recovery keeps the substance longer in the system; this clearly entails a down-cycling process, as further recovery from the board is not possible. Other less destructive recycling processes could maintain lignin longer in the system, but as long as lignin waste is available in sufficient quantities, this discussion may be postponed.

Parameters such as the lignin extraction efficiency, the needs of energy and water within the thermomechanical processes, the importance of the added chemicals within the lignin production processes, the differential quantity of energy and chemicals needed for fiberboard production, the life expectancy of the boards, the amount of board material required to fulfill the needed function, and the recyclability of the final product have important effects on the total environmental impact of the stated alternatives.

To go beyond life-cycle thinking, a life-cycle management perspective (Fullana i Palmer *et al.* 2011) indicates that to put this system in place, a new value chain is needed, requiring the different actors to agree on the new market conditions and the development of new logistics. Social barriers such as historical practices by corn farmers would have to be overcome.

The proper percentage of lignin may vary from one application to another, and depending on function, the board may require different degrees of strength (structural uses), water resistance (humid environments), or other physical properties. Therefore, the compared environmental impact may vary as well among the foreseen applications.

In sum, with the information gathered from investigating the life-cycle consequences, it is believed that using waste corn stalk in fiberboards is environmentally beneficial and that waste lignin may be called a green adhesive when substituting it for formaldehyde-based adhesives.

CONCLUSIONS

1. The chemical composition of corn stalk revealed high cellulose and moderate lignin content, which supported its suitability as an alternative source for wood fibers used in fiberboards manufacturing.
2. Corn stalk fiberboards made without green adhesive had weaker mechanical properties than commercial ones. However, fiberboards containing more than 20% purified kraft lignin added in fiberboards produced by the wet process had good mechanical and water resistance properties that fully satisfied the relevant standard specifications.
3. Lignin provided fiberboards with benefits such as increased MOR, MOE, and impact strength. However, fiberboards made from corn stalk thermo-mechanical pulp showed lower performance in terms of this last property than commercial fiberboards.
4. Life-cycle thinking has been essential to finding the environmental pros and cons of proposed technologies. Although sometimes a simplified approach is adequate, this work recommends a thorough but practical life cycle assessment study for specific board applications to quantify the environmental impacts of competing alternatives.

ACKNOWLEDGMENTS

The authors thank the Erasmus Mundus project Techno II ref. 372228-1-2012-1-FR-ERA MUNDUS-EMA21 for financial support. Special thanks are given to the Spanish Ministry for the financing through the project CTM2011-28506-C02-02.

REFERENCES CITED

Anglès, M., Ferrando, F., Farriol, X., and Salvadó, J. (2001). "Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition," *Biomass and Bioenergy* 21(3), 211-224. DOI: 10.1016/S0961-9534(01)00031-9

Asim, N., Emdadi, Z., Mohammad, M., Yarmo, M. A., and Sopian, K. (2015). "Agricultural solid wastes for green desiccant applications: An overview of research achievements, opportunities and perspectives," *Journal of Cleaner Production* 91, 26-35. DOI: 10.1016/j.jclepro.2014.12.01

ASTM D1102-84 (2001). "Standard test method for ash in wood," ATSM International, West Conshohocken, PA, USA.

Back, E. L. (1987). "The bonding mechanism in hardboard manufacture review report," *Holzforschung* 41(4), 247-258. DOI: 10.1515/hfsg.1987.41.4.247

Baitz, M., Albrecht, S., Brauner, E., Broadbent, C., Castellan, G., Conrath, P., Fava, J., Finkbeiner, M., Fischer, M., and Palmer, P. F. (2013). "LCA's theory and practice: Like ebony and ivory living in perfect harmony?," *The International Journal of Life Cycle Assessment* 18(1), 5-13. DOI: 10.1007/s11367-012-0476-x

Bala, A., Raugei, M., Benveniste, G., Gazulla, C., and Fullana-i-Palmer, P. (2010). "Simplified tools for global warming potential evaluation: When 'good enough'is best," *The International Journal of Life Cycle Assessment* 15(5), 489-498. DOI: 10.1007/s11367-010-0153-x

Bidstrup, M., Pizzol, M., and Schmidt, J. H. (2015). "Life cycle assessment in spatial planning–A procedure for addressing systemic impacts," *Journal of Cleaner Production* 91, 136-144. DOI: 10.1016/j.jclepro.2014.12.027

BS-EN323 (1993). "Wood-based panels. Determination of density," British Standards Institution, London, UK.

Cao, Q., Xie, K.-C., Lv, Y.-K., and Bao, W.-R. (2006). "Process effects on activated carbon with large specific surface area from corn cob," *Bioresource Technology* 97(1), 110-115.

Castro, D. O., Ruvolo-Filho, A., and Frollini, E. (2012). "Materials prepared from biopolyethylene and curaua fibers: Composites from biomass," *Polymer Testing* 31(7), 880-888. DOI: 10.1016/j.polymertesting.2012.05.011

Chen, G., Zheng, Z., Yang, S., Fang, C., Zou, X., and Luo, Y. (2010). "Experimental co-digestion of corn stalk and vermicompost to improve biogas production," *Waste Management* 30(10), 1834-1840.

Delgado-Aguilar, M., Tarrés, Q., Pèlach, M. A. N., Mutjé, P., and Fullana-i-Palmer, P. (2015). "Are cellulose nanofibers a solution for a more circular economy of paper products?," *Environmental Science & Technology* 49(20), 12206-12213. DOI: 10.1021/acs.est.5b02676

Donghai, S., Junshe, S., Ping, L., and Yanping, L. (2006). "Effects of different pretreatment modes on the enzymatic digestibility of corn leaf and corn stalk," *Chinese Journal of Chemical Engineering* 14(6), 796-801.

Duffy, R., and Marchand, L. (2013). "Development of a business case for a cornstalks to bioprocessing venture," Ontario Federation of Agriculture.

El Mansouri, N. E., Yuan, Q., and Huang, F. (2011). "Characterization of alkaline lignins for use in phenol-formaldehyde and epoxy resins," *BioResources* 6(3), 2647-2662. DOI: 10.15376/biores.6.3.2647-2662

El-Saied, H., and Nada, A.-A. M. (1993). "The thermal behaviour of lignins from wasted black pulping liquors," *Polymer Degradation and Stability* 40(3), 417-421.

EN310 (1993). "Wood based panels – Determination of modulus of elasticity in bending and of bending strength," European Committee for Standardisation, Brussels, Belgium.

EN316 (1999). "Wood fiberboard: Definition, classification and symbols," European Commission for Standardization, Brussels, Belgium,

EN317 (1993). "Particleboards and fiberboards–Determination of swelling of thickness after immersion in water," European Committee for Standardisation, Brussels, Belgium.

EN325 (1993). "Wood based panels – Determination of dimensions of test pieces," European Committee for Standardisation, Brussels, Belgium.

EN382-1 (1993). "Fiberboards – Determination of surface absorption," European Committee for Standardisation, Brussels, Belgium.

Escalante-Ten Hoopen, M., and Maïga, A. (2012). Maize production and processing. ISF Cameroon. Retrieved from https://cgspace.cgiar.org/handle/10568/76782

European Commission (EC) Regulation 75/442/1975 (1975). "Council directive (EU) N° 75/442/1975 of 27 July 1975 laying down that member states shall take appropriate steps to encourage the prevention, recycling and processing of waste and any process to re-use waste listed in Articles 1 to 14 of the aforementioned regulation," European Union, Brussels, Belgium.

European Commission (EC) Regulation 97/C 76/01 (1997). "Council Resolution N° 97/C 76/01 of 24 February 1997 on a community strategy for waste management," European Union, Brussels, Belgium.

European Commission (EC) Communication 670/final/2005 (2005). "Communication from the Commission to the Council, the European Parliament, the European Economic and

Social Committee and The Committee of the Regions N°670/final/2005 of 21 December 2005 - Taking sustainable use of resources forward - A thematic strategy on the prevention and recycling of waste," European Union, Brussels, Belgium.

European Commission (EC), Joint Research Centre, and the Institute for Environment and Sustainability (2010). *Handbook - General Guide for Life Cycle Assessment - Detailed Guidance*, Publications Office of the European Union, Luxembourg. DOI: 10.2788/38479

Food and Agriculture Organization of the United the Nations, Statistics Divison (FAOSTAT) (2016) "FAOSTAT statistical database,"(http://faostat.fao.org/), Accessed 15 November 2016.

Finnveden, G., Johansson, J., Lind, P., and Moberg, Å. (2005). "Life cycle assessment of energy from solid waste—Part 1: General methodology and results," *Journal of Cleaner Production* 13(3), 213-229. DOI: 10.1016/j.jclepro.2004.02.023

Flandez, J., Pèlach, M. À., Vilaseca, F., Tijero, J., Monte, C., Pérez, I., and Mutje, P. (2010). "Lignocellulosic fibers from corn stalks as alternative for the production of brown grade papers," Paper presented at the XXI TECNICELPA Conference and Exhibition / VI CIADICYP 2010, Lisbon, Portugal.

Fullana i Palmer, P., Puig, R., Bala, A., Baquero, G., Riba, J., and Raugei, M. (2011). "From life cycle assessment to life cycle management," *Journal of Industrial Ecology* 15(3), 458-475. DOI: 10.1111/j.1530-9290.2011.00338.x

Garcia, R., and Freire, F. (2014). "Carbon footprint of particleboard: A comparison between ISO/TS 14067, GHG protocol, PAS 2050 and climate declaration," *Journal of Cleaner Production* 66, 199-209. DOI: 10.1016/j.jclepro.2013.11.073

Hauschild, M., and Barlaz, M. A. (2009). "LCA in waste management: Introduction to principle and method," in: *Solid Waste Technology & Management*, T. H. Christensen (ed.), John Wiley & Sons, Ltd, Chichester, UK, pp. 111-136.

Hong, J., Zhou, J., and Hong, J. (2015). "Comparative study of life cycle environmental and economic impact of corn- and corn stalk-based-ethanol production," *Journal of Renewable and Sustainable Energy* 7(2), 023106. DOI: 10.1063/1.4914008

Hurter, R. W. (2015). "Nonwood fibers and moulded products," HurterConsult Inc. (http://www.hurterconsult.com/HTMLobj-1371/Nonwood_Fibres_Moulded_Products_June_2015.pdf), Accessed 19 January 2016.

Iqbal, H. M. N., Kyazze, G., and Keshavarz, T. (2013). "Advances in the valorization of lignocellulosic materials by biotechnology: An overview," *BioResources* 8(2), 3157-3176. DOI: 10.15376/biores.8.2.3157-3176

Jegatheesan, V., Liow, J., Shu, L., Kim, S., and Visvanathan, C. (2009). "The need for global coordination in sustainable development," *Journal of Cleaner Production* 17(7), 637-643. DOI: 10.1016/j.jclepro.2008.11.016

Khitrin, K.S., Fuks, S.L., Khitrin, S.V., Kazienkov, S.A., and Meteleva, D.S. (2012). "Lignin utilization options and methods," *Russian Journal of General Chemistry*, 82 (5), 977-984. DOI: 10.1134/S1070363212050313

Kim, S., and Dale, B. E. (2004). "Global potential bioethanol production from wasted crops and crop residues," *Biomass and Bioenergy* 26(4), 361-375. DOI: 10.1016/j.biombioe.2003.08.002

Klüppel, H.-J. (2005). "The revision of ISO Standards 14040-3-ISO 14040: Environmental management life cycle assessment principles and framework-ISO 14044: Environmental management life cycle assessment requirements and guidelines," *The International Journal of Life Cycle Assessment* 10(3), 165-165. DOI: 10.1065/lca2005.03.001

Lazarevic, D., Buclet, N., and Brandt, N. (2012). "The application of life cycle thinking in the context of European waste policy," *Journal of Cleaner Production* 29, 199-207. DOI: 10.1016/j.jclepro.2012.01.030

Leal, M. R. L., Galdos, M. V., Scarpare, F. V., Seabra, J. E., Walter, A., and Oliveira, C. O. (2013). "Sugarcane straw availability, quality, recovery and energy use: A literature review," *Biomass and Bioenergy* 53, 11-19. DOI: 10.1016/j.biombioe.2013.03.007

Lin, S. (1992). "Commercial spent pulping liquors," in: *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence (eds.), Springer, New York, NY, USA, pp. 75-80.

Li, B., Zhou, D., Cang, L., Zhang, H., Fan, X., and Qin, S. (2007). "Soil micronutrient availability to crops as affected by long-term inorganic and organic fertilizer applications," *Soil and Tillage Research* 96(1), 166-173.

Mancera, C., El Mansouri, N.-E., Pelach, M. A., Francesc, F., and Salvadó, J. (2012). "Feasibility of incorporating treated lignins in fiberboards made from agricultural waste," *Waste Management* 32(10), 1962-1967. DOI: 10.1016/j.wasman.2012.05.019

Mejía, E. H., Quintana, G. C., and Ogunsile, B. O. (2014). "Development of binderless fiberboards from steam-exploded and oxidized oil palm wastes," *BioResources* 9(2), 2922-2936. DOI: 10.15376/biores.9.2.2922-2936

Moberg, Å., Finnveden, G., Johansson, J., and Lind, P. (2005). "Life cycle assessment of energy from solid waste—Part 2: Landfilling compared to other treatment methods," *Journal of Cleaner Production* 13(3), 231-240. DOI: 10.1016/j.jclepro.2004.02.025

Nasir, M., Gupta, A., Beg, M. D. H., Chua, G. K., and Kumar, A. (2013). "Fabrication of medium density fibreboard from enzyme treated rubber wood (*Hevea brasiliensis*) fibre and modified organosolv lignin," *International Journal of Adhesion and Adhesives* 44, 99-104. DOI: 10.1016/j.ijadhadh.2013.02.013

Oluwasina, O. O., Lajide, L., and Owolabi, B. J. (2015). "Performance of bonded boards using lignin-based resins," *Wood Material Science and Engineering* 10(2), 168-177. DOI: 10.1080/17480272.2014.923044

Page, D. (1969). "A theory for tensile strength of paper," *TAPPI* 52(4), 674.

Pang, C., Xie, T., Lin, L., Zhuang, J., Liu, Y., Shi, J., and Yang, Q. (2012). "Changes of the surface structure of corn stalk in the cooking process with active oxygen and MgO-based solid alkali as a pretreatment of its biomass conversion," *Bioresource Technology* 103(1), 432-439.

Pinto, J., Cruz, D., Paiva, A., Pereira, S., Tavares, P., Fernandes, L., and Varum, H. (2012). "Characterization of corn cob as a possible raw building material," *Construction and Building Materials* 34, 28-33.

Rowell, R. M., Gutzmer, D. I., Sachs, I. B., and Kinney, R. E. (1976). "Effects of alkylene oxide treatments on dimensional stability of wood," *Wood Science* 9(1), 51-54.

Rozman, H., Tan, K., Kumar, R., Abubakar, A., Ishak, Z. M., and Ismail, H. (2000). "The effect of lignin as a compatibilizer on the physical properties of coconut fiber–polypropylene composites," *European Polymer Journal* 36(7), 1483-1494. DOI: 10.1016/S0014-3057(99)00200-1

Shinners, K. J., and Binversie, B. N. (2007). "Fractional yield and moisture of corn stover biomass produced in the Northern US Corn Belt," *Biomass and Bioenergy* 31(8), 576-584.

Silva, C. G., Benaducci, D., and Frollini, E. (2012). "Lyocell and cotton fibers as reinforcements for a thermoset polymer," *BioResources* 7(1), 78-98. DOI: 10.15376/biores.7.1. 78-98

Smil, V. (1999). "Crop residues: Agriculture's largest harvest crop residues incorporate more than half of the world's agricultural phytomass," *Bioscience* 49(4), 299-308. DOI: 10.2307/1313613

Sokhansanj, S., Turhollow, A., Cushman, J., and Cundiff, J. (2002). "Engineering aspects of collecting corn stover for bioenergy," *Biomass and Bioenergy* 23(5), 347-355.

Sun, R., Tomkinson, J., and Jones, G. L. (2000). "Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre," *Polymer Degradation and Stability* 68(1), 111-119.

TAPPI T 222 om-98 (1985). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T 223 cm-01 (2001). "Pentosans in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI UM 250 (1991). "Acid-soluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

Tejado, A., Pena, C., Labidi, J., Echeverria, J., and Mondragon, I. (2007). "Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis," *Bioresource Technology* 98(8), 1655-1663.

Theng, D., Arbat, G., Delgado-Aguilar, M., Vilaseca, F., Ngo, B., and Mutjé, P. (2015). "All-lignocellulosic fiberboard from corn biomass and cellulose nanofibers," *Industrial Crops and Products* 76(0), 166-173. DOI: 10.1016/j.indcrop.2015.06.046

Vishtal, A., and Kraslawski, A. (2011). "Challenges in industrial applications of technical lignins," *BioResources* 6(3), 3547-3568. DOI: 10.15376/biores.6.3.3547-3568

Wise, L. E., Murphy, M., and D'Addieco, A. A. (1946). "A chlorite holocellulose, its fractionation and bearing on summative wood analysis and studies on the hemicelluloses," *Paper Trade Journal* 122(2), 35-43.

Wolf, M.-A., Pant, R., Chomkhamsri, K., Sala, S., and Pennington, D. (2012). *The International Reference Life Cycle Data System (ILCD) Handbook: Towards More Sustainable Production and Consumption for a Resource-Efficient Europe*, European Union, Publications Office of the European Union, Luxembourg.

Yaning, Z., Ghaly, A. E., and Bingxi, L. (2012). "Physical properties of corn residues," *American Journal of Biochemistry and Biotechnology* 8(2), 44-53.

Zamagni, A. (2012). "Life cycle sustainability assessment," *The International Journal of Life Cycle Assessment* 17(4), 373-376. DOI: 10.1007/s11367-012-0389-8

Zaman, A. U. (2015). "A comprehensive review of the development of zero waste management: Lessons learned and guidelines," *Journal of Cleaner Production* 91, 12-25. DOI: 10.1016/j.jclepro.2014.12.013

Article submitted: January 4, 2016; Peer review completed: February 27, 2016; Revised version received and accepted: January 31, 2017; Published: February 10, 2017.
DOI: 10.15376/biores.12.2.2379-2393

4.3 Paper III

Title	**Comparison between Two Different Pretreatment Technologies of Rice Straw Fibers Prior to Fiberboard Manufacturing: Twin-screw Extrusion and Digestion plus Defibration**
Authors	Dyna Theng, Gerard Arbat, Marc Delgado-Aguilar, Bunthan Ngo, Laurent Labonne, Philippe Evon, Pere Mutjé
Journal	Industrial Crops and Products
Year	2017
Volume	-
Issue	-
Pages	-
Status	Submitted (Under review)

Your recent submission to INDCRO

Industrial Crops and Products <eesserver@eesmail.elsevier.com>

Mon 1/30, 7:37 PM

Dear Dyna Theng,

You have been listed as a Co-Author of the following submission:

Journal: Industrial Crops and Products
Corresponding Author: Philippe Evon
Co-Authors: Dyna Theng; Gerard Arbat; Marc Delgado-Aguilar; Bunthan Ngo; Laurent Labonne; Pere Mutjé
Title: Comparison between two different pretreatment technologies of rice straw fibers prior to fiberboard manufacturing: Twin-screw extrusion and digestion plus defibration

If you did not co-author this submission, please contact the Corresponding Author of this submission at Philippe.Evon@ensiacet.fr; do not follow the link below.

An Open Researcher and Contributor ID (ORCID) is a unique digital identifier to which you can link your published articles and other professional activities, providing a single record of all your research.

We would like to invite you to link your ORCID ID to this submission. If the submission is accepted, your ORCID ID will be linked to the final published article and transferred to CrossRef. Your ORCID account will also be updated.

To do this, visit our dedicated page in EES. There you can link to an existing ORCID ID or register for one and link the submission to it:

https://ees.elsevier.com/indcro/l.asp?i=216475&l=5E4MSGQ8

More information on ORCID can be found on the ORCID website, http://www.ORCID.org, or on our help page: http://help.elsevier.com/app/answers/detail/a_id/2210/p/7923

Like other Publishers, Elsevier supports ORCID - an open, non-profit, community based effort - and has adapted its submission system to enable authors and co-authors to connect their submissions to their unique ORCID IDs.

Thank you,

Industrial Crops and Products

Comparison between Two Different Pretreatment Technologies of Rice Straw Fibers Prior to Fiberboard Manufacturing: Twin-screw Extrusion and Digestion plus Defibration

Dyna Theng[a,c], Gerard Arbat[b], Marc Delgado-Aguilar[a], Bunthan Ngo[c], Laurent Labonne[d], Philippe Evon[d*], Pere Mutjé[a]

[a] LEPAMAP research group, University of Girona, C/ Maria Aurèlia Capmany, 61, 17003 Girona, Spain

[b] Department of Chemical and Agricultural Engineering and Food Technology, University of Girona, C/ Maria Aurèlia Capmany, 61, 17003 Girona, Spain

[c] Royal University of Agriculture, Dangkor District, 2696, Phnom Penh, Cambodia

[d] Laboratoire de Chimie Agro-industrielle (LCA), Université de Toulouse, INRA, INPT, 4 Allée Emile Monso, BP 44362, 31030 Toulouse Cedex 4, France

*Corresponding author: Philippe.Evon@ensiacet.fr (Ph. Evon)

Abstract

The present work compares two different pretreatment technologies, i.e. twin-screw extrusion, and steaming digestion plus defibration, for producing a thermo-mechanical pulp from rice straw for fiberboard manufacturing. Five liquid/solid ratios from 0.4 to 1.0 were tested for twin-screw extrusion pretreatment, while liquid/solid ratios from 4 to 6 were used for digestion pretreatment. Energy consumption, production cost, and characteristics of the extrudates (twin-screw extrusion) and pulps (digestion) (including fiber morphology, chemical composition, thermal properties, apparent and tapped densities, as well as color) were the analyzed parameters for the resulting lignocellulosic fibers. The results showed that liquid/solid ratio had influence on energy consumption and specific production cost for both defibrating methods. For the twin-screw extrusion method, a lower liquid/solid ratio required more energy while for the digestion plus defibration the effect was the opposite. The corresponding specific production cost ranged from 0.056 to 0.077 €/kg dry matter for twin-screw extrusion, and from 0.49 to 0.68 €/kg dry matter for digestion plus defibration. Thus, the digestion plus defibration cost was about nine times more expensive than that of the twin-screw extrusion. In addition, for twin-screw extrusion, the liquid/solid ratio did not have a substantial effect on fiber characteristics with similar chemical compositions and thermal properties. For twin-screw extrusion, the cost was 37% reduced when the

liquid/solid ratio was increased from 0.4 to 1.0. Instead, for digestion plus defibration, the cost increase was 38% when the liquid/solid ratio increased from 4 to 6.

Keywords: Rice straw, twin-screw extrusion, digestion, defibration, energy consumption, specific production cost.

1. Introduction

Rice (*Oriza Sativa L.*) is cultivated to feed more people and animals over a longer period than any other crop. As far back as 2500 B.C., rice has been documented in the history books as a source of food and for tradition as well (Thomas L., 1997). Rice straw is a by-product of rice crop with a straw to grain ratio of 1.4 (Kim & Dale, 2004). In terms of total production, rice is the second most important grain crop in the world after maize. The world annual rice production in 2014 was about 741 million tons (FAOSTAT, 2016). It gives an estimation of about 1,139 million tons of rice straw per year worldwide (FAOSTAT, 2016), and a large part of this is used for cattle feed, for bioethanol production, or incorporated into the soil as an organic amendment. Possible uses for rice straw are limited by its low bulk density, a slow degradation in the soil, the harboring of rice stem diseases (the possible transmission of diseases to the future crop), and a high ash content which can be a problem for subsequent ethanol or energy production (Binod et al., 2010). Currently, field burning is still the major practice for removing rice straw, particularly in less developed countries, causing air pollution, thus affecting public health (Mussatto & Roberto, 2004) and contributing to the global warming (Kanokkanjana & Garivait, 2013; Sarnklong et al., 2010). According to Kanokkanjana and Garivait (2013), about 56% of the total rice straw production was burned in Thailand in 2010. As climate change is extensively recognized as a threat to development, there is a growing interest to find alternative uses for rice straw.

All plants including rice straw have the form of a heterogeneous complex of carbohydrate polymers. Cellulose and hemicelluloses are densely packed by layers of lignin, which protect them against enzymatic hydrolysis. Thus, a pretreatment step is necessary to break lignin seal, until exposing cellulose and hemicelluloses for a subsequent enzymatic action or contributing to the biomass defibration (Vandenbossche et al., 2016, 2015, 2014).

Several researchers have investigated the use of rice straw and other agricultural wastes as fiber source in the composite industry (El-Kassas & Mourad, 2013; Evon et al., 2012; Halvarsson et

al., 2008; Li et al., 2010; Pan et al., 2010; Theng et al., 2015a; Wu et al., 2011; Zhang & Hu, 2014; Zhao et al., 2011), in particular to produce fiberboards by thermopressing, the latter being usable for furniture or in the building industry. Different methods for fiber pretreatment were tested, i.e. chemical, mechanical, and thermo-mechanical pretreatment to obtain resources for their purposes. Recently, Vandenbossche et al. (2016, 2015, 2014) used the twin-screw extrusion technology for conducting the thermo-mechanical and thermo-chemo-mechanical pretreatment of different lignocellulosic biomass sources, in the case not for the subsequent manufacture of composite materials but for the production of second-generation bioethanol using a biocatalytic action. Evon et al. (2015, 2014, 2012, 2010a, 2010b) also produced self-bonded fiberboards from the cake generated during the biorefinery of sunflower whole plant using a twin-screw extruder. In addition, Theng et al. (Theng et al., 2015a) prepared a thermo-mechanical pulp from corn biomass by digestion plus defibration to produce binder-free fiberboards. Migneault et al. (2010) produced medium-density fiberboards using thermo-mechanical pulps from different pulping processes. Lastly, Mancera et al. (2012, 2011) developed fiberboards using thermo-mechanical pulps from different agricultural wastes, all produced using steam-explosion. However, there is no scientific literature dealing with the cost of fiber preparation using different defibrating technologies prior to board manufacturing.

The present paper aimed to explore the appropriate and beneficial technology for fiber preparation as a raw material for fiberboard manufacturing using the same batch of rice straw, comparing two different techniques: twin-screw extrusion and digestion plus defibration, without any chemical agent addition. A Clextral (France) Evolum HT 53 twin-screw extruder model and a digester reactor (designed by LEPAMAP, University of Girona, Spain) with Sprout-Waldron defibrator (model 105-A) were used in this study. The overall production cost and the properties of the pretreated rice straw fibers (i.e. fiber morphology, apparent and tapped densities, chemical composition and thermal stability) from both technologies were compared to provide more options to industrial sectors.

2. Experimental

2.1 Material

Thermo-mechanical fractionation was conducted using a single batch of rice straw (*Oriza Sativa L.*), i.e. the whole plant except the panicle and the grain. The rice straw was of French origin and it was supplied by the JCL AGRI company (Bouge-Chambalud, France). It was harvested in

October when the plant maturity was reached. The rice straw was previously crushed using a hammer mill (Elecra BC P, France) fitted with a 6 mm screen. The moisture content of the rice straw was 7.4 ± 0.2% (French standard NF V 03-903).

2.2 Twin-screw extruder

The thermo-mechanical fractionation of the grinded rice straw was conducted using a pilot-scale Clextral Evolum HT 53 (France) co-penetrating and co-rotating twin-screw extruder (Fig. 1). The twin-screw extruder had eight modular barrels, each 4D in length (with D corresponding to the screw diameter, i.e. 53 mm), except module 1 having an 8D length (Fig. 2), and different twin-screws which had segmental screw elements (Fig. 3). Module 1 was cooled by water circulation. Modules 2 to 8 were heated by electric resistance and cooled by water circulation. The material temperature was measured at the end of modules 2, 5 and 7, and at the beginning of module 8. The material pressure was measured at the end of modules 2, 5 and 7. The screw rotation speed (Ss), the inlet flow rates of grinded rice straw and water (Qs and Q_L, respectively), and the barrel temperature (θc) were monitored from a control panel.

Fig. 1. Photograph of the Clextral (France) Evolum HT 53 co-penetrating and co-rotating twin-screw extruder used for the thermo-mechanical fractionation of rice straw biomass (53 mm for the D screw diameter, 36D for the total barrel length).

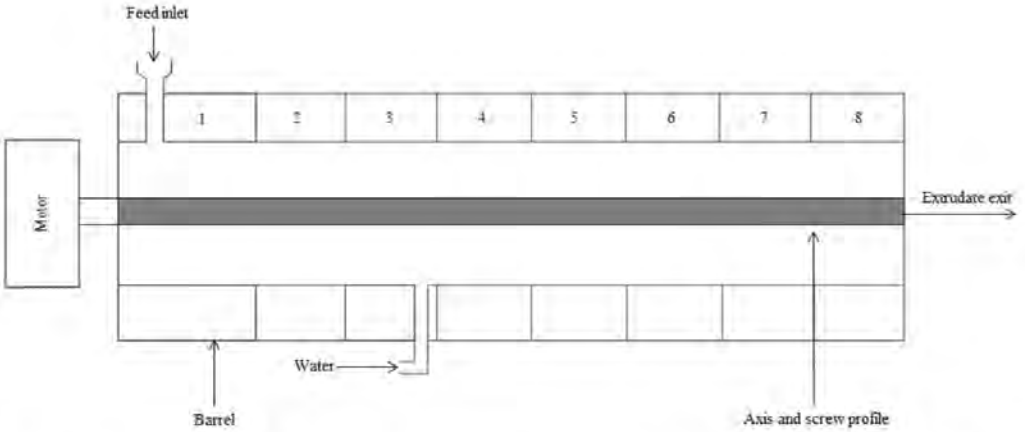


Fig. 2. Schematic modular barrel of the Clextral Evolum HT 53 twin-screw extruder used for the thermo-mechanical fractionation of the grinded rice straw.

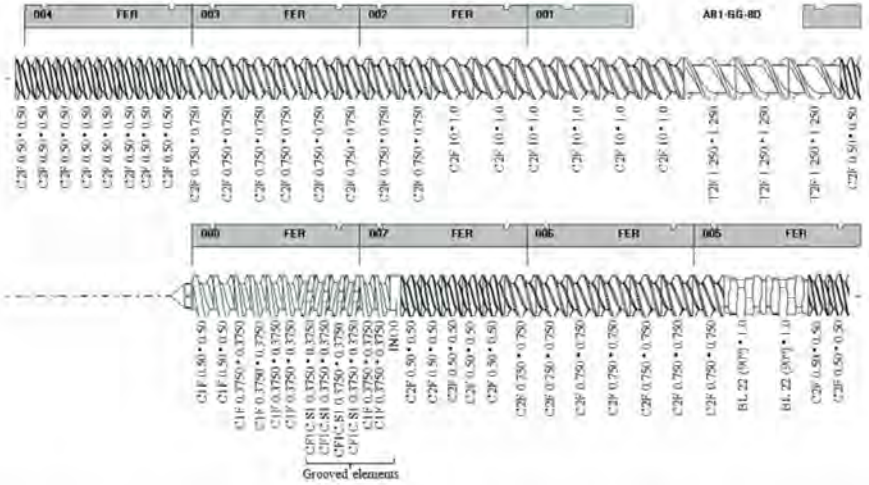


Fig. 3. Screw configuration of the Clextral Evolum HT 53 twin-screw extruder used for the thermo-mechanical fractionation of the grinded rice straw (screw profile drawn using the CompoVis software from Clextral company). C2F, conveying double-thread screws; T2F, trapezoidal double-thread screws; BL22-90°, bilobe paddle-screws with a 90° mounting angle (i.e. positioned in staggered); INO0, linking element between double- and simple-thread screws; C1F, conveying simple-thread screws; and CF1C, reversed simple-thread screws. The two numbers following the type of screw indicate the length and the pitch of C2F, T2F, C1F, and CF1C screws, respectively (numbers in proportion to the screw diameter, i.e. 53 mm). The number following the bilobe paddle-screws indicate the length of the BL22 screws.

Fig. 4. Photographs of the BL22-90° bilobe paddle-screws used for intimate mixing of water and grinded rice straw (module 5) (a), and of the restrictive and filled grooved elements, i.e. CF1C reversed simple-thread screws (beginning of module 8) (b) and C1F conveying simple-thread screws situated immediately upstream (end of module 7) (c), where mechanical shear was applied to the rice straw biomass.

2.3 Thermo-mechanical fractionation of grinded rice straw in the twin-screw extruder

Grinded rice straw was fed into the extruder inlet port using a constant weight feeder (Coperion K-Tron SWB-300-N, Switzerland) in the first module, at a 15 kg/h wet matter inlet flow rate. Water was injected using a piston pump (Clextral DKM Super K Camp 112/12, France) at the end of module 3 (Fig. 2). The screw profile used in this study is given in Fig. 3. After water injection, two series of BL22-90° bilobe paddle-screws (2D in total length) were located in modules 5 to disperse intimately water inside the grinded rice straw (Fig. 4a). The CF1C reversed simple-thread screws with grooves (1.5D in total length) were positioned at the beginning of module 8 to give an intense shearing/mixing action to the liquid/solid mixture (Fig. 4b). The screw speed (S_S) was fixed at 150 rpm and the set values for the barrel temperature were 25, 80, 110, 110, 110, 110, 110 and 100 °C at the level of modules 1 to 8, respectively. The experimental variable of this part of the study was the liquid/solid (L/S) ratio (i.e. Q_L/Q_S), the latter varying in five levels from 1.0 (E_1 extrudate) to 0.4 (E_5 extrudate), as it can be seen in Table 1.

Table 1: Operating conditions used for extrudate production and results of the thermo-mechanical fractionation of rice straw biomass in the Clextral Evolum HT 53 twin-screw extruder.

Trials	**E_1**	**E_2**	**E_3**	**E_4**	**E_5**
Operating conditions					
S_S (rpm)	150.4±1.5	150.4±1.5	150.4±1.5	150.6±1.5	150.6±1.4
Q_S (kg/h)	15.0±0.0	14.9±0.4	15.0±0.0	14.9±0.3	15.0±0.0
H_S (%)	7.4±0.2	7.4±0.2	7.4±0.2	7.4±0.2	7.4±0.2
Q_S (kg/h dry matter)	13.9±0.0	13.8±0.4	13.9±0.0	13.8±0.3	13.9±0.0

Q_L (kg/h)	15.0±0.0	12.7±0.0	10.5±0.0	8.2±0.0	6.0±0.0
Q_L/Q_S (i.e. L/S ratio)	1.0	0.85	0.7	0.55	0.4
W_E (kg/h)	16.0±0.0	13.8±0.0	11.5±0.0	9.3±0.0	7.0±0.0
θ_{C7} (°C)	107	107	107	107	107
	(107.6±0.7)	(109.5±0.7)	(111.3±0.6)	(111.5±0.4)	(111.4±.9)
θ_{C8} (°C)	100	100	100	100	100
	(102.0±0.6)	(100.6±0.4)	(101.2±0.4)	(101.2±0.4)	(101.1±1.7)
Extrudate					
Q_R (kg/h)	26.8±0.0	25.1±0.0	22.9±0.0	21.5±0.0	19.0±0.0
H_R (%)	45.3±0.9	41.7±0.1	37.4±0.4	32.2±2.5	26.0±1.9
Q_R (kg/h dry matter)	14.6±0.0	14.6±0.0	14.3±0.0	14.6±0.0	14.0±0.0
W_R (kg/h)	12.1±0.0	10.5±0.0	8.6±0.0	6.9±0.0	4.9±0.0
E_W (kg/h)	3.9±0.0	3.3±0.0	2.9±0.0	2.3±0.0	2.1±0.0
E_W (%)	24.2±0.0	23.9±0.0	25.6±0.0	25.3±0.0	29.9±0.0
Energy consumed					
I (A)	74.6±4.7	81.7±3.4	81.8±4.1	91.0±4.1	113.4±6.7
SME (W h/kg dry matter)	412.7±26.1	454.9±18.8	452.4±22.8	505.7±22.7	628.3±36.9
m (kg/h)	2370.6±27.7	2432.0±56. 6	2397.3±47.4	2432.4±51.5	2535.6±106.2
$\lvert\Delta T\rvert$ (K)	0.73±0.36	0.77±0.34	0.78±0.35	0.79±0.35	1.01±0.42
SCE (W h/kg dry matter)	144.7±70.4	157.0±69.1	156.9±69.2	161.9±72.0	214.4±89.6
P (kW)	2.04±0.22	1.99±0.25	1.69±0.17	1.66±0.13	1.59±0.24
STE (W h/kg dry matter)	147.0±16.1	144.1±18.3	121.9±12.2	120.2±9.7	114.2±17.0
TSE (W h/kg dry matter)	704.4±112.7	756.0±106.1	731.1±104.3	787.8±104.4	956.9±143.6

S_S is the screw rotation speed (rpm); Q_S is the solid inlet flow rate (kg/h); H_S is the solid moisture content (%); Q_L is the set value for the liquid inlet flow rate (kg/h); L/S ratio is defined as the ratio of the inlet flow rate of liquid (Q_L) to the inlet flow rate of solid (Q_S); W_E is the real liquid inlet flow rate (kg/h); θ_{C7} (°C) is the barrel temperature of module 7 (set value first mentioned, plus temperature measured during sampling in parentheses); θ_{C8} (°C) is the barrel temperature of module 8 (set value first mentioned, plus temperature measured during sampling in parentheses); Q_R is outlet flow rate of the extrudate (kg/h); H_R is the moisture content of the extrudate, measured immediately after sampling; W_R is the calculated water outlet flow rate in the extrudate (kg/h); E_W is the estimated water vapor outlet flow rate (kg/h and % of the inlet flow rate of liquid water); I is the current consumed by the motor of the twin-screw extruder (A); SME is the specific mechanical energy (W h/kg dry matter); m is the cooling water flow rate (kg/h); $\lvert\Delta T\rvert$ is the difference in temperature between the inlet and the outlet of the cooling water circuit (K); SCE is the specific cooling energy (W h/kg dry matter); P is the heating power supplied by the twin-screw extruder;

160 *STE is the specific thermal energy (W h/kg dry matter); TSE is the total specific energy (W h/kg dry*
161 *matter).*

162 Twin-screw extrusion was performed for 10 min before any sampling to ensure the
163 stabilization of the operating conditions. The operating conditions, including in particular the feed
164 rates of grinded rice straw and water, the temperature along the screw profile and the current
165 feeding the motor, were recorded during sampling and then used for the production cost calculation.
166 Upon achieving steady operation, the extrudate was immediately collected over a period of 10 min
167 to avoid any variability of the outlet flow rate. Sample collection time was determined with a
168 stopwatch. For each liquid/solid ratio tested, sample collection was carried out once and the
169 extrudate was then weighed. Its moisture content was also measured immediately after its collection
170 according to the NF V 03-903 French standard.

171 The total production cost of the extrusion process is defined as the sum of three specific
172 terms, i.e. (i) the mechanical cost (MC), (ii) the cooling cost (CC) and (iii) the heating cost (HC).
173 All these three costs are calculated from the recorded data of the operating conditions.

174 The mechanical cost (€/kg dry matter) of the extrusion process was determined according to
175 the following formulas:

176 $$MC = SME / 1000 \times 0.08 \quad (1)$$

177 Where: *SME* is the specific mechanical energy consumed by the motor per unit weight of
178 dried grinded rice straw (W h/kg dry matter). The *SME* was calculated according to the Eq. (2)
179 mentioned below. The electrical energy cost was considered according current costs in Europe,
180 which is of about 0.08 €/kW h assuming cogeneration in Spain and nuclear energy in France.

181 $$SME = (454 \times I \times \cos\varphi \times S_s / S_{max}) / Q_s \quad (2)$$

182 Where: *I* is the current feeding the motor (A), *cos φ* the theoretical yield of the twin-screw
183 extruder motor ($\cos\varphi = 0.95$), S_s the screw rotation speed (rpm), S_{max} the maximal screw rotation
184 speed ($S_{max} = 800$ rpm), and Q_s is the inlet flow rate of dried grinded rice straw (kg dry matter/h).

185 The Eq. (3) mentioned below is used to calculate the cooling cost (€/kg dry matter) of the
186 extrusion process.

187 $$CC = SCE / 1000 \times 0.08 \quad (3)$$

188 Where: *SCE* is the specific cooling energy consumed per unit weight of dried grinded rice
189 straw (W h/kg dry matter). The *SCE* was calculated using the Eq. (4) mentioned below.

$$SCE = m \times C_p \times |\Delta T| / Q_s \times 3600 \quad (4)$$

Where: m is the inlet flow rate of cooling water (kg/h), C_p the calorific capacity of water (C_p = 4180 J/kg K), and $|\Delta T|$ is the difference in temperature between the inlet and the outlet of the cooling water circuit (K).

The heating cost (€/kg dry matter) was calculated using the following formula:

$$HC = STE / 1000 \times 0.08 \quad (5)$$

Where: *STE* is the specific thermal energy consumed per unit weight of dried grinded rice straw (W h/kg dry matter). It was determined using the following formula:

$$STE = P \times 1000 / Q_s \quad (6)$$

Where: P is the heating power. The heating power used in this calculation was the sum of the heating powers of all the heated modular zones along the twin-screw extruder barrel (i.e. modules 2 to 8). The control panel of the extruder was set to record the heating power as a percentage of the maximal value of the heating power available for all the heated modules every 5 seconds. In this study, the twin-screw extruder had seven heated modules, situated from zones 2 to 8, with a maximal value for the heating power of 5.0 kW, except in zone 5 where it was 3.4 kW. The heating power of each module was calculated using the Eq. (7).

$$P_{module} = M \times P_{max} / 100 \quad (7)$$

Where: M is the average percentage of the maximal value of the heating power during sampling (%), and P_{max} is the maximal value of the heating power available for the corresponding heated module (kW).

2.4 Rotary digester reactor and Sprout-Waldron defibrator

The thermo-mechanical pulp of rice straw was conducted using a laboratory scale rotary digester, designed by University of Girona, Spain and a Sprout-Waldron defibrator (model 105-A) (Fig. 5). The digester had two heating resistances with a heating speed of 1 °C/min and a motor making the digester rotating vertically. On the other hand, the Sprout-Waldron defibrator was used to defibrate the grinded and digested rice straw. The Sprout-Waldron defibrator was used with tap water and equipped with a filtrate bath. Both digester and defibrator had an electric monitor to measure the energy consumption for further production cost calculation.

Fig. 5. Photographs of the laboratory scale rotary digester (a), the Sprout-Waldron defibrator (model 105-A) (b), and the screw elements of the defibrator (c and d).

2.5 Thermo-mechanical pulp (TMP) preparation

Grinded rice straw was fed into the digester with distilled water at liquid/solid ratios of 4; 5; and 6 (P_1, P_2 and P_3, respectively), at the maximal biomass plus water mass (8 kg) per batch, previously heated to 80 °C. The temperature (160 °C) and duration (30 min) profile chosen for cooking was previously optimized for the thermo-mechanical pulp (TMP) preparation from rice straw (Theng et al., 2015b). The digested pulp was then washed with tap water, filtered and moisture content of the material was measured according to the French standard NF V 03-903. Operating conditions such as mass of grinded rice straw and water, production yield of TMP and current feeding the motor were recorded. The masses of solid inlet and liquid inlet were calculated using Eq. (8) and Eq. (9), respectively.

$$m_w = m_d / (100 - \%MC_i) \times 100 \quad (8)$$

Where: m_w is the mass of humid inlet (kg); m_d is the mass of dry inlet (kg dry matter); and $\%MC_i$ is the moisture content of the inlet (%).

234 $m_L = L/S \times m_d - (m_w - m_d)$ (9)

235 Where: m_L is the mass of water inlet (kg); and L/S is the liquid/solid ratio, defined as the ratio
236 of the water mass (including both liquid water and moisture inside rice straw) to the dry solid mass.

237 The production yield was calculated following Eq. (10).

238 $\%Yield = (m_p \times (100 - \%MC_p) / 100) / m_d \times 100$ (10)

239 Where: m_P is the mass of digested pulp (kg) and $\%MC_p$ is the moisture content of pulp (%).

240 The production cost for TMP preparation is calculated using the following formula:

241 $PC = P \times 0.08$ (11)

242 Where: PC is the specific production cost (€/kg dry matter); P is the specific energy
243 consumed by the motor (kW h/kg dry matter).

244 The digested pulp was then passed one time through the Sprout-Waldron defibrator with
245 addition of spraying tap water, and filtered again to eliminate the excess of water.

246 *2.6 Chemical composition characterization*

247 Before each analysis, the materials (i.e. rice straw, extrudates (twin-screw extrusion) and
248 TMP (digestion plus defibration)) were milled using a Foss (Denmark) Cyclotec 1093 cutting mill
249 without any sieve. The moisture contents were determined according to the French standard NF V
250 03-903. The mineral contents were determined according to the French standard NF V 03-322. An
251 estimation of the three parietal constituents (cellulose, hemicelluloses, and lignin) was made using
252 the ADF-NDF method of Van Soest and Wine (Van Soest & Wine, 1967; Van Soest PJ, 1968). An
253 assessment of the water-soluble components was made by measuring the mass loss of the test
254 sample after 1 h in boiling water. All analyses were carried out in duplicate.

255 *2.7 Morphological characterization*

256 The morphological analysis was carried out using a MorFi Compact analyzer (TechPap,
257 France), which is, among other parameters, able to calculate average length, average diameter,
258 average aspect ratio and fines percentage. All characterizations were performed in duplicate.

259

260

2.8 Tapped density analysis

Tapped density was measured using a Granuloshop Densitap ETD-20 (France) volumenometer fitted with a 250 mL graduated cylinder. Before compaction, apparent density was also measured. All measurements were conducted in duplicate.

2.9 Color measurement

Color of rice straw, extrudates and TMP was measured using a spectrophotometer (Konica Minota CR-410, Japan). The color measurements were made using the CIE L*a*b* referential, which is widely employed for non-luminous objects. The illuminant was D65, and the observer angle was 2°. In the L*a*b* color space, L* is the lightness and it varies from 0 (black) to 100 (white), and a* and b* are the chromaticity coordinates: +a* is the red direction, -a* is the green direction, +b* is the yellow direction, and -b* is the blue direction. The center is achromatic (Konica Minolta Sensing, 2007). All determinations were carried out six times on each powder of rice straw, extrudate, and TMP. These powders were obtained using a Foss Cyclotec 1093 (Denmark) cutting mill fitted with a 1 mm screen.

The measured L* color values were used to estimate the darkening of the extrudates and TMP compared to the rice straw. In addition, the color difference (ΔE*) between the rice straw and each analyzed extrudate and pulp was calculated using the following formula:

$$\Delta E^* = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2} \quad (12)$$

2.8 TGA measurements

Thermogravimetric analysis (TGA) of rice straw, extrudates and TMP was carried out using a Shimadzu TGA-50 (Japan) analyzer. Dynamic analysis was conducted under air at a heating rate of 5 °C/min, from 25 to 800 °C. The materials were previously crushed using a Foss Cyclotec 1093 (Denmark) cutting mill fitted with a 1 mm screen. For all measurements, the mass of the test sample was around 8 mg. The weights of samples were measured as a function of temperature and stored. These data were later used to plot the percentage of undegraded sample (1 - D) (%) as a function of temperature, where

$$D = (W_0 - W) / W_0 \quad (13)$$

and W_0 and W are the weights at the starting point and during scanning (mg). All measurements were carried out in duplicate.

3. Results and Discussion

3.1 Extrudate production by twin-screw extrusion

The extrudate production using the twin-screw extrusion technology was conducted continuously. When the liquid/solid ratio in the twin-screw extruder reduced from 1.0 to 0.4, the extrudate flow rate (Q_R) decreased progressively from 26.8 to 19.0 kg/h. A decrease in its moisture content (H_R) from 45.3 to 26.0% was logically observed at the same time. Thus, the extrudate flow rate and its moisture content dropped about 29% and 43%, respectively. As the L/S ratio decreased, the mixture became more and more viscous, and its transportation through the CF1C reversed screws was more and more difficult, leading to a progressive increase in both filling of CF1C screws and material residence time in these restrictive elements. Thus, the shearing action given to the rice straw became much higher as the L/S ratio decreased. This was illustrated by the increased material pressure in module 7, from 10.1 to 19.5 bars (Fig. 6b), simultaneously with the increase in the current feeding the extruder motor, from 75 to 113 A (Table 1). In particular, the increase in the material pressure in module 7 was much significant (about one half of all trials) between E_4 (0.55 L/S ratio) and E_5 (0.4 L/S ratio) extrudates, i.e. from 14.9 to 19.5 bars. The same tendency was also observed for the current, the latter increasing from 91 to 113 A in the same L/S ratio range.

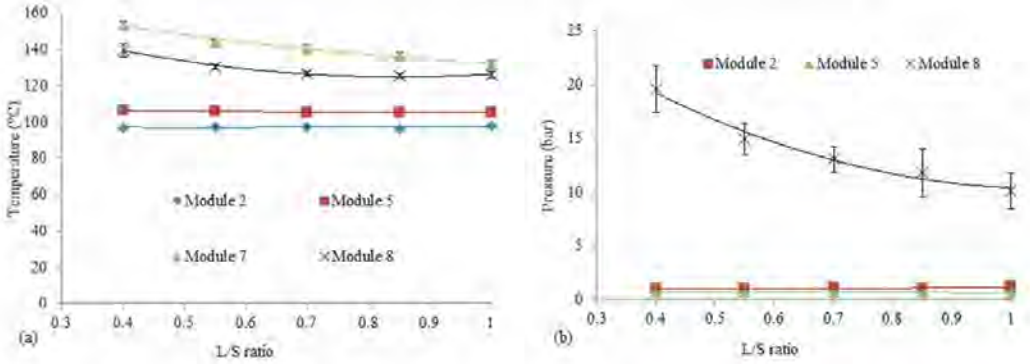


Fig. 6. Temperature (a) and pressure (b) of the material in different places along the Clextral Evolum HT 53 twin-screw extruder barrel.

In addition, the increase in the viscosity of the liquid/solid mixture resulted in higher proportions of water evaporation at the outlet of the twin-screw extruder (until 30% of the injected water for the lowest L/S ratio, i.e. 0.4). The estimated outlet flow rate of water vapor varied from 3.9 to 2.1 kg/h as the L/S ratio decreased from 1.0 to 0.4. In proportion to the amount of liquid water injected at the end of module 3, the evaporated water increased just a little (from 24 to 26%)

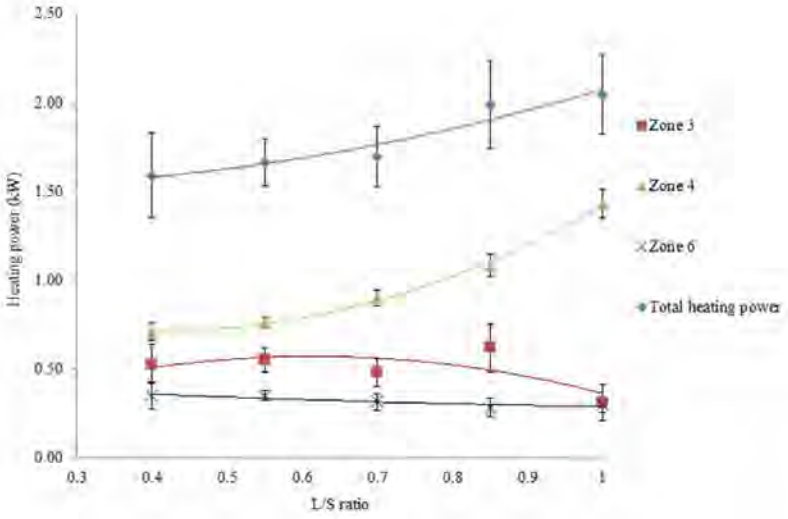
315 for L/S ratios between 1.0 and 0.55. On the contrary, it became much higher (i.e. 30%) for the E_5
316 extrudate. This illustrated that the 0.4 L/S ratio was probably too low, possibly causing a
317 degradation of the rice straw fibers. Thus, no lower L/S ratio was tested in this study for the twin-
318 screw extrusion process.

319 As the current feeding the motor of the twin screw extruder increased when the inlet flow rate
320 of injected water was reduced, the specific mechanical energy (SME) increased at the same time:
321 from 412 to 628 W h/kg dry matter (Table 1). The SME increase was limited until a 0.7 L/S ratio
322 (+10%). Then, it was +23% at 0.55 L/S ratio and it reached +52% for the minimal L/S ratio. Table 1
323 also revealed an increase in the specific cooling energy (SCE), from 145 to 214 W h/kg dry matter,
324 as the L/S ratio decreased. However, this increase was much linear. The latter might be the result of
325 a higher tendency of the mixture to self-heating, in particular at the level of the reversed screws
326 where the machine is completely filled, with lower liquid/solid ratios, the mixing of the mixture
327 plus its transportation along the screw profile thus being more difficult (Gautam & Choudhury,
328 1999a, 1999b; Kartika et al., 2010, 2006, 2005).

329 In contrast, an opposite phenomenon occurred for the specific thermal energy (STE). Indeed,
330 the machine required less heating power when the L/S ratio decreased, the STE value varying from
331 147 to 114 W h/kg dry matter. Firstly, the amount of liquid water, which was injected at ambient
332 temperature, was then reduced and this contributed to a reduction of the heating power required for
333 having the mixture temperature increasing until the set value in modules 4 to 6. In addition, because
334 the mixture was more viscous with lower L/S ratios, the filling of both reversed screws (Fig. 4b)
335 and conveying screws positioned immediately upstream (Fig. 4c) became more and more important,
336 thus leading to a progressive self-heating of the material in this zone of the screw profile (Fig. 6a):
337 from 132 to 153 °C at the end of module 7, and from 126 to 140 °C at the beginning of module 8.
338 And, because the material always suffered self-heating at this location, the machine did not need to
339 provide any heating power at the end of the screw profile. On the contrary, the material temperature
340 remained quite constant in modules 2 and 5, where the filling of the bilobe paddle-screws and
341 especially of the conveying screws was much lower (i.e. no material self-heating in these two zones
342 of the screw profile).

343 Seven modules along the twin-screw extruder barrel were heated by electric resistance, i.e.
344 modules 2 to 8. But, the heating power occurred only in three modules, i.e. modules 3, 4 and 6, all
345 situated at the level or after the injection point of water and consisting only in conveying screws, i.e.
346 non filled elements. The heating power supplied in zones 3 and 6 remained quite independent on the
347 L/S ratio used (Fig. 7). On the contrary, it increased progressively (from 0.7 to 1.4 kW) in zone 4 as

348 the L/S ratio increased. As a reminder, module 4 was situated immediately after the injection point
349 of water. And, because water was at room temperature when injected, the more the inlet flow rate of
350 water, the more the tendency of the mixture temperature to decrease and the more the heating power
351 required. As a consequence, the total heating power supplied by the twin-screw extruder tended to
352 drop linearly when the liquid/solid ratio was reduced.



353

354 **Fig. 7.** Heating power along the barrel of the Clextral Evolum HT 53 twin-screw extruder.

355 *3.2 Production cost of extrudates obtained using the twin-screw extruder*

356 The calculation of the production cost of extrudates using the five different L/S ratios tested
357 was based on the mean price of electricity in France in 2016, i.e. 0.08 €/kW h. Fig. 8 shows the
358 production cost for the different operating conditions used. In accordance with the results of energy
359 consumptions expressed above, the different production costs, i.e. specific mechanical cost, specific
360 cooling cost, specific heating cost and total specific cost, had the same evolutions. Referring to Fig.
361 8a, as the L/S ratio increased, there was a decrease trend on mechanic, cooling and total costs. On
362 the contrary, the heating cost increased a little. The mechanic, cooling and total costs decreased
363 approximately 34%, 33%, and 26%, respectively, when the L/S ratio increased from 0.4 to 1.0. In
364 parallel, the heating cost was increased (+29%). However, the contribution of this specific term was
365 limited compared to the two others, especially the mechanical one (Fig. 8b). As a result, the total
366 production cost decreased from 0.077 to 0.056 €/kg dry matter when the L/S ratio increased, but it
367 seemed to be level off between 0.7 and 1.0 L/S ratios.

In accordance with the above remarks and comparing the three specific costs, mechanical cost had systematically the most important contribution. As an example, with the highest L/S ratio (i.e. 1.0), the mechanical part contributed about 59% of the total cost, followed by the heating and cooling costs (both 21%) (Fig. 8b). In the case of the lowest liquid/solid ratio (i.e. 0.4), the mechanical cost still remained the majority proportion (66%). However, the cooling cost was then much more significant than the heating one (i.e. 22% and 12%, respectively).

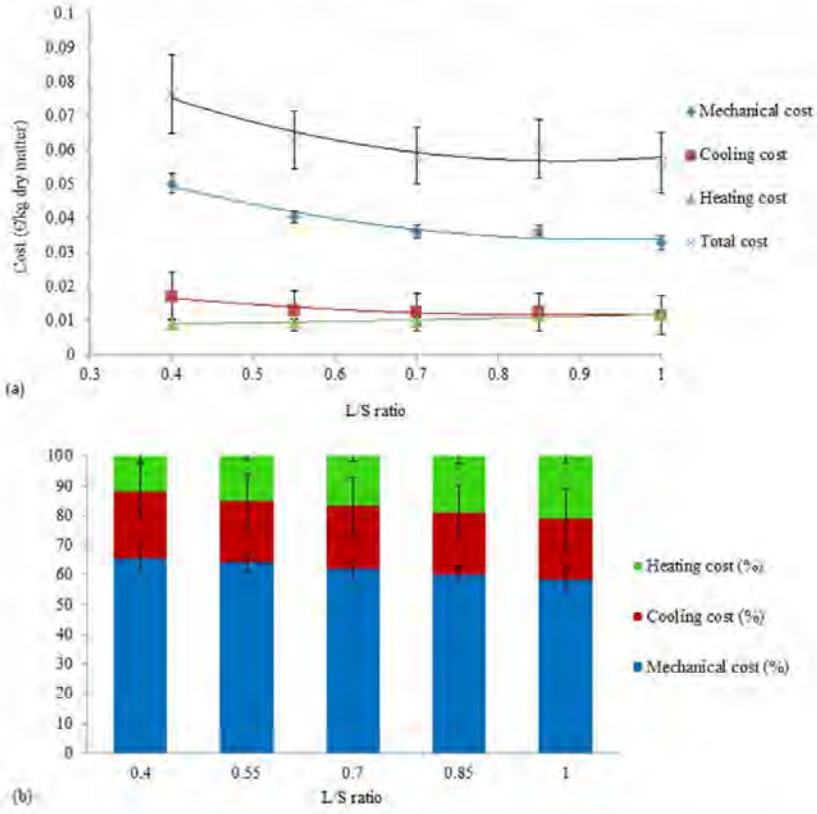


Fig. 8. Production cost of extrudates in the Clextral Evolum HT 53 twin-screw extruder as a function of L/S ratio: price (€/kg dry matter) for mechanical cost, cooling cost, heating cost and total production cost (a), and contribution of these three specific costs on the energy consumption (%) (b).

3.3 Chemical composition of rice straw and extrudates

Rice straw consists predominantly of cell walls (cellulose, hemicelluloses, and lignin), i.e. the same organic compounds as those of wood sources. The chemical composition of rice straw varies between varieties and growing seasons (Shen et al., 1998). In this study, the chemical compositions

383 of rice straw from three different locations in France and Spain, all harvested in October, were
384 determined (Table 2). They showed little differences in the chemical composition of these three rice
385 straw batches However, they were in the range of other chemical compositions mentioned in the
386 literature (Garay et al., 2009; Garrote et al., 2002; Maiorella, 1983; Rahnama et al., 2013; Shen et
387 al., 1998). It is also conceivable to think that the chemical composition of these three batches could
388 differ due to their respective storage conditions. The rice straw used in this work for thermo-
389 mechanical fractionation was purchased from JCL AGRI (Bouge-Chambalud, France), a forage
390 merchant. It was stored almost one year after harvesting, while the rice straws from Spain were
391 provided directly by farmers. Rice straw from Girona (Spain) was collected when the rice was
392 harvested, i.e. at maturity, and then stored during approximately two years in clean and dry
393 conditions at LEPAMAP research group, University of Girona. The third batch originated from
394 Valencia (Spain). It was provided by a farmer from Valencia province, after almost one year storage
395 in its yard after harvesting.

396 **Table 2:** Chemical composition of rice straw from three different origins (% of dry matter).

Origin	Minerals	Cellulose	Hemicelluloses	Lignin	Water-soluble components
Bouge-Chambalud, France	14.7±0.1	37.7±0.3	27.9±0.4	7.2±0.1	16.0±0.1
Girona, Spain	15.5±0.1	34.8±0.1	27.9±0.0	6.5±0.4	18.9±0.1
Valencia, Spain	19.5±0.1	33.8±0.1	25.0±0.5	8.1±0.2	16.6±0.2

397

398 The results in Table 2 reveal that rice straw from France had less minerals and less water
399 soluble components (14.7% and 16.0% of dry matter, respectively), compared to the two batches
400 from Spain (15-20% and 17-19%, respectively). Rice straw from Valencia had the highest mineral
401 content (i.e. 19.5%), and this might be due to its storage conditions. Indeed, because this batch was
402 wet in some parts, it is reasonable to assume that part of the organic compounds were degraded over
403 time due to the proliferation of fungi or leached, in particular the water-soluble ones, thus leading to
404 a concurrent increase in the mineral content.

405 For the three main organic compounds (i.e. cellulose, hemicelluloses and lignin), rice straw
406 from France contained more lignocellulosic fibers than those from Spain, cellulose and
407 hemicelluloses representing 37.7% and 28.0% of its dry matter, respectively (Table 2). On the
408 contrary, the lignin content was medium for the French batch. This is the rice straw batch
409 originating from France which was chosen for this study, not because of its higher fiber proportion

but because it was available in much greater quantity, thus allowing a sufficient feeding of the pilot-scale twin-screw extruder used in this study (much higher inlet flow rate required compared to the digester reactor plus the Sprout-Waldron defibrator). In addition, because minerals, especially silica, can generate phenomena of premature wear on the screw elements and also on the extruder barrels, it also appeared that the most reasonable choice for twin-screw fractionation was the rice straw batch with the least mineral content (i.e. the one from France), in order to reduce wear.

Table 3: Chemical composition of rice straw (French origin), extrudates (E), and pulps (P).

Materials	Moisture (%)	Minerals (% of DM)	Cellulose (% of DM)	Hemicelluloses (% of DM)	Lignin (% of DM)	Water-soluble components (% of DM)
Rice straw	7.4±0.1	14.7±0.1	37.7±0.3	27.9±0.4	7.2±0.1	16.0±0.1
E_1 (L/S ratio 1.0)	7.5±0.1	14.3±0.2	36.2±0.5	33.0±0.6	5.5±0.5	15.9±0.1
E_3 (L/S ratio 0.7)	7.1±0.0	14.4±0.1	37.0±0.9	28.4±0.2	6.8±0.3	17.3±0.3
P_1 (L/S ratio 4.0)	4.8±0.2	10.7±0.0	47.6±0.1	28.6±0.1	8.7±0.1	5.1±0.1
P_2 (L/S ratio 5.0)	4.8±0.3	11.0±0.1	47.5±0.0	29.5±0.9	8.1±0.1	4.8±0.6
P_3 (L/S ratio 6.0)	4.6±0.3	10.5±0.1	48.2±0.3	28.3±0.3	9.7±0.2	5.1±0.0

Moisture contents were measured after conditioning in climatic chamber (25 °C and 60% relative humidity), and DM is dry matter.

Table 3 shows the chemical composition of rice straw before and after twin-screw extrusion. The extrusion thermo-mechanical treatment did not change it a lot, whether the L/S ratio was high (1.0, i.e. E_1 extrudate) or median (0.7, i.e. E_3 extrudate). These results were confirmed by the thermogravimetric analysis of rice straw and extrudates E_1 to E_5 (Fig. 9).

Indeed, thermogravimetric analysis of rice straw and extrudates showed that all TGA degradation curves (Fig. 9a) under air had quite the same appearance, meaning once again that chemical compositions were all comparable and that the different operating conditions used in the twin-screw extruder had no significant influence on the thermal degradation of organic compounds inside the different extrudates. A first mass loss was observed at 100 °C, corresponding to the water evaporation. Moisture content of the starting material was 7.4% (Table 1), and the mass loss observed in the corresponding TGA curve was associated approximately with the same percentage. Then, the thermal degradation of organic compounds took place essentially in one stage (between 220 and 340 °C), leading to a mass loss of approximately 50% of the sample dry mass. Finally, another degradation phenomenon was also observed at higher temperature, i.e. between 400 and

476 °C. However, the latter was associated with a much lower mass loss (about 20% of the sample dry mass).

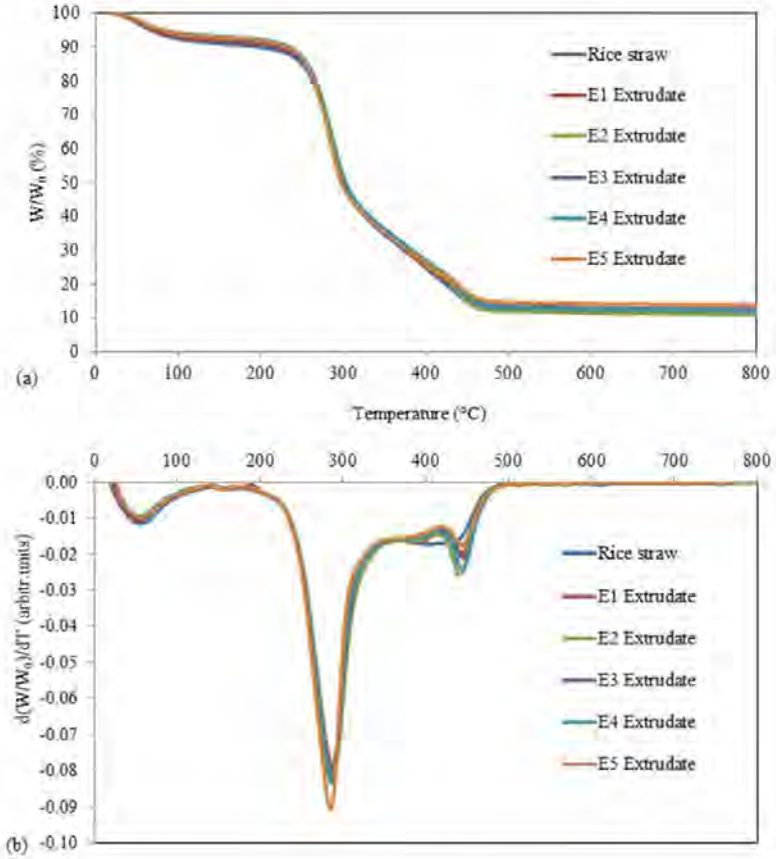


Fig. 9. TGA (a) and dTGA (b) curves of rice straw and extrudates.

Using data dealing with the thermal degradation of fibers, cited by some researchers in previous studies (Beaumont, 1981; Evon et al., 2015; Hatakeyama & Hatakeyama, 2006; Schaffer, 1973), it is reasonable to assume that the main thermal degradation stage (220-340 °C) could be associated with the simultaneous breakdown of water-soluble compounds, hemicelluloses, and cellulose. The subsequent stage, beginning at about 400 °C, would in this case correspond essentially to the thermal degradation of lignin. However, because TGA analysis of all materials was conducted under air atmosphere, part of this second thermal degradation stage could also correspond to the oxidation of the degradation products from the previous stage (Uitterhaegen et al., 2016). At the end of all measurements, the undegraded samples accounted for less than 15% of the test sample mass, corresponding to the minerals contained in rice straw and extrudates (Table 3).

447 *3.4 Physical properties of extrudates*

448 Table 4 shows the main morphological characteristics of fibers inside the extrudates (E_1 to
449 E_5) produced using different operating conditions. Such characteristics were determined using a
450 MorFi Compact analyzer, and they include length, diameter, and aspect ratio (defined as the ratio of
451 the length to the diameter) of fibers, and fine percentage inside the extrudates. From the mean
452 length (L_W) and diameter (D) of the extruded fibers, the corresponding L_W/D aspect ratios were
453 between 20.9 and 22.6. In addition, a slight decrease in the aspect ratio was observed with a
454 decreasing liquid/solid ratio in the twin-screw extruder, especially for its two lowest values (i.e.
455 0.55 and 0.4), and such phenomenon was previously observed for thermo-mechanical pulps
456 produced using steam plus a mechanical defibration treatment (Alila et al., 2013; Flandez et al.,
457 2012; Theng et al., 2015a).. Such aspect ratio decrease resulted mainly in the decrease of the mean
458 length of fibers, from 571 to 494 µm (i.e. -14%), as the L/S ratio decreased from 1.0 to 0.4. And,
459 this illustrated the fact that higher mechanical shear and higher self-heating of the material at the
460 level of the reversed screws caused by low L/S ratios contributed in more cutting of the fibers.

461 **Table 4:** Morphological analysis of fibers in the extrudates (E) and pulps (P) made from rice straw.

Materials	L_W (µm)	D (µm)	L_W/D (aspect ratio)	Fines (%)
E_1 (L/S ratio 1.0)	571.5 ± 7.8	25.5 ± 0.0	22.4 ± 0.3	63.8 ±0.4
E_2 (L/S ratio 0.85)	544.0 ± 4.2	24.5 ± 0.0	22.2 ± 0.2	62.8 ±1.5
E_3 (L/S ratio 0.7)	571.0 ± 7.1	25.3 ± 0.0	22.6 ± 0.3	54.2 ± 4.9
E_4 (L/S ratio 0.55)	505.0 ± 5.7	23.8 ± 0.1	21.2 ± 0.2	74.7 ± 3.4
E_5 (L/S ratio 0.4)	494.0 ± 1.4	23.6 ± 0.1	20.9 ± 0.1	61.8 ± 0.5
P_1 (L/S ratio 4.0)	371.7 ± 9.0	22.8 ± 0.0	16.3 ± 0.4	69.6 ± 2.3
P_2 (L/S ratio 5.0)	377.0 ± 5.7	22.0 ± 0.1	17.0 ± 0.2	68.2 ± 1.5
P_3 (L/S ratio 6.0)	386.0 ± 2.8	21.9 ± 0.1	17.9 ± 0.4	65.3 ± 3.6

462

463 The particle size distribution inside the extrudates (Table 4) revealed also the presence of
464 small particles (approximately 25 µm × 500 µm). This population contained not only the smallest
465 fibers but also spherical particles, i.e. fines, originating from the thermo-mechanical breakdown
466 process of rice straw, and corresponding to a 63% mean content. Lastly, apparent and tapped
467 densities of the extrudates were quite low with maximal values of 162 and 216 kg/m^3, respectively
468 (Fig. 10).

Looking at the influence of the operating conditions tested on the apparent and tapped densities of extrudates, both densities are decreasing when the L/S ratio increased: from 162 to 56 kg/m^3, and from 216 to 81 kg/m^3, respectively. Referring to the results of densities, a lower L/S ratio during twin-screw extrusion made not only shorter fibers (Table 4) but also a denser and heavier extrudate. On the contrary, because fibers originating from the highest L/S ratios were longer, their entanglement between them was favored, leading to a bulkier and therefore to a less dense extrudate.

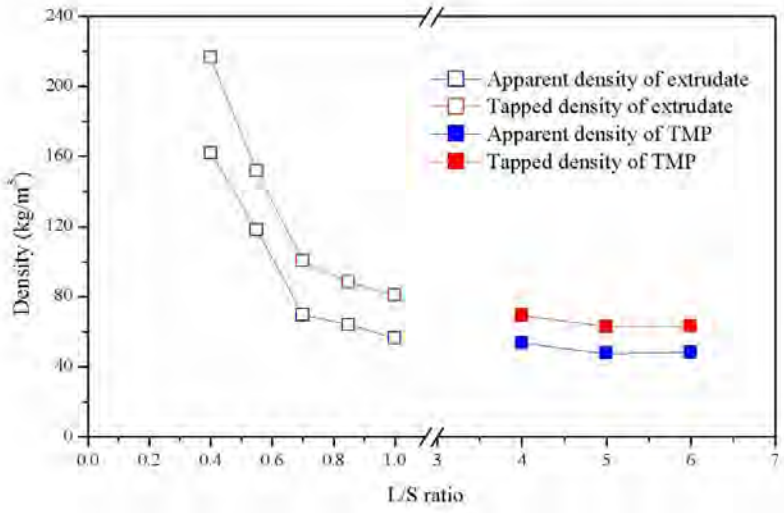


Fig. 10. Apparent and tapped densities of extrudates and pulps.

The effect of the liquid/solid ratio during twin-screw extrusion on the extrudate color, in comparison to the one of rice straw, is provided in Table 5. A decrease in the L/S ratio contributed in the decreases in both L* and b* values, simultaneously with a slight increase in the a* one. The significant L* decrease observed as the decreasing L/S ratio, revealed a progressive darkening of the extrudates in comparison to the initial rice straw color, with a color difference (ΔE*) varying from 6.2 to 8.2. According to Ilo and Berghofer (1999), color is an important quality assurance parameter of feed and biological products, which can also be indirectly related to the nutritional value of the products. In this case (i.e. the thermo-mechanical defibration of rice straw using the twin-screw extrusion), the alteration degree of the structure of rice straw fibers inside the twin-screw extruder barrel is a key factor in the quality of the extrudates. It is largely dependent on the L/S ratio used, the latter largely influencing the mechanical shear transmitted to the material and its self-heating. Therefore, the increase in the darkening of the extrudate observed with the decrease in the L/S ratio could be directly correlated to the progressive self-heating undergone by the material

491 in the restrictive part of the screw profile, i.e. where mechanical shear is applied (from 132 to 153
492 °C for the material temperature at the end of module 7, and from 126 to 140 °C at the beginning of
493 module 8), contributing to the partial degradation of the organic compounds inside rice straw,
494 especially the smaller and the most thermal sensitive molecules.

495 **Table 5:** Influence of the operating conditions on color in the CIE L*a*b* referential of the
496 extrudate (E) and pulp (P) powders, and comparison with color of the starting material (i.e. rice
497 straw powder).

Materials	L*	a*	b*	ΔE*
Rice straw	82.6 ± 0.3	3.7 ± 0.1	16.5 ± 0.2	-
E_1 (L/S ratio 1.0)	77.4 ± 0.3	4.1 ± 0.1	13.2 ± 0.5	6.2
E_2 (L/S ratio 0.85)	77.1 ± 0.4	4.3 ± 0.1	13.3 ± 0.2	6.4
E_3 (L/S ratio 0.7)	75.9 ± 0.1	4.2 ± 0.1	12.9 ± 0.2	7.6
E_4 (L/S ratio 0.55)	76.3 ± 0.3	4.1 ± 0.1	12.9 ± 0.3	7.2
E_5 (L/S ratio 0.4)	74.9 ± 0.7	4.2 ± 0.2	13.9 ± 0.5	8.2
P_1 (L/S ratio 4.0)	75.7 ± 0.4	4.2 ± 0.1	12.7 ± 0.5	7.8
P_2 (L/S ratio 5.0)	75.9 ± 0.3	4.1 ± 0.1	13.5 ± 0.3	7.3
P_3 (L/S ratio 6.0)	75.8 ± 0.3	4.1 ± 0.1	13.2 ± 0.3	7.5

498

499 *3.5 TMP production by digester reactor plus Sprout-Waldron defibrator*

500 Thermo-mechanical pulp from rice straw was produced by digestion plus defibration using a
501 cooking condition in terms of temperature and duration previously optimized, i.e. 160 °C and 30
502 min, respectively (Theng et al., 2015b). Operating conditions for the TMP preparation and its
503 results for energy consumption and production cost are detailed in Table 6.

504 **Table 6**: Operating conditions and results of the thermo-mechanical fractionation of rice straw by
505 steaming in the digester reactor plus defibration using the Sprout-Waldron 105-A defibrator.

Trials	P_1	P_2	P_3
Operating conditions			
Solid mass (kg dry matter)	1.61	1.33	1.15
Water mass (kg)	6.39	6.67	6.85
Solid plus water mass (kg)	8.00	8.00	8.00
L/S ratio	4	5	6
Temperature (°C)	160	160	160

Duration (min)	30	30	30
Digested pulp			
Pulp mass (kg dry matter)	1.38	1.17	1.01
Production yield (%)	85.7	88.0	87.8
Energy consumption (kW h)			
Pre-heating digester (16-80 °C)	*2.79*	*2.73*	*2.81*
Heating digester (80-160 °C)	*5.09*	*5.13*	*5.14*
Digestion (160 °C, 30 min)	*0.61*	*0.61*	*0.62*
Defibration in Sprout-Waldron defibrator	*0.033*	*0.032*	*0.035*
Total energy consumption	8.523	8.502	8.605
Specific energy consumption (kW h/kg dry matter of pulp)			
Pre-heating digester (16-80 °C)	2.022	2.333	2.782
Heating digester (80-160 °C)	3.688	4.385	5.089
Digestion (160 °C, 30 min)	0.442	0.521	0.614
Defibration in Sprout-Waldron defibrillator	0.024	0.027	0.035
Total specific energy consumption	6.176	7.266	8.520
Specific production cost (€/kg dry matter of pulp)			
Pre-heating digester (16-80 °C)	0.162	0.187	0.223
Heating digester (80-160 °C)	0.295	0.351	0.407
Digestion (160 °C, 30 min)	0.035	0.042	0.049
Defibration in Sprout-Waldron defibrillator	0.002	0.002	0.003
Total production cost (€/kg dry matter of pulp)	0.494	0.581	0.682

506 *L/S ratio is defined as the ratio of the water mass (including both liquid water and moisture inside*
507 *rice straw) to the dry solid mass.*

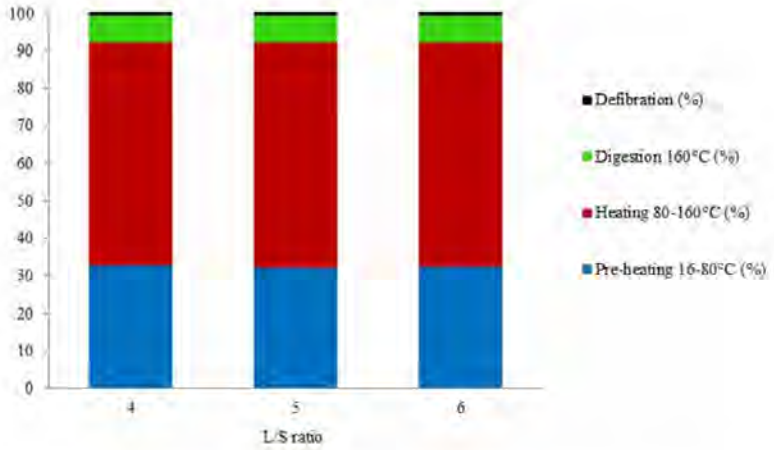
508 Water was added at the maximum mass in terms of the digester reactor capacity, i.e. 8 kg for
509 biomass plus distilled water mass. In parallel, the mass of the starting solid was 1.61, 1.33, and 1.15
510 kg dry matter for P_1, P_2, and P_3 pulps, respectively, corresponding to liquid/solid ratios of 4, 5 and
511 6, respectively. All trials were digested using the same conditions and then cooled to 105 °C before
512 opening and washing using tap water. Depending on the initial liquid/solid ratio used (i.e. 4, 5, and

513 6), the mass of the recovered digested pulp was 1.38, 1.17, and 1.01 kg dry matter, respectively.
514 During digestion, some organic compounds, especially the water-soluble ones, were removed from
515 the biomass. This was illustrated by the results of production yield obtained: 85.7%, 88.0%, and
516 87.8% following the different liquid/solid ratios used (i.e. 4, 5, and 6, respectively), corresponding
517 to a dry mass loss of 14.3%, 12.0%, and 12.2%, respectively. This was also confirmed by the
518 decrease in the contents of water-soluble compounds inside digested pulps compared to the rice
519 straw (Table 3). The TMP production yield (87.8%) for rice straw originating from France was a
520 little higher compared to rice straw grew in Girona (Spain) when cooked using the same operating
521 conditions and inside the same digester reactor, i.e. 84.7% (Theng et al., 2015b) and 82.0% (So,
522 2016), corresponding to a reduction in the dry mass removing during digestion: 12.2% instead of
523 15.3% and 18.0%. This finding is likely to be related with the fact that the chemical composition of
524 French rice straw revealed less water-solubles than the one collected in Girona: only 16.0% instead
525 of 18.9% (Table 2).

526 The energy consumption for the whole process of TMP preparation, i.e. pre-heating, heating,
527 and digestion in the digester reactor plus defibration in the Sprout-Waldron defibrator, was 8.5-8.6
528 kW h for P_1, P_2, and P_3 pulps (Table 6), indicating that it was quite independent on the liquid/solid
529 ratio used. From these values, it can be seen that the digester reactor consumed almost all the
530 energy while the defibration step contribution using the Sprout-Waldron defibrator was only 0.4%.
531 To be more precise, there were three successive steps during the discontinuous digestion process,
532 including (i) the pre-heating of the digester reactor from 16 °C (storage temperature of the machine)
533 to 80 °C (temperature at which the raw material was added), (ii) the heating of the digester reactor
534 plus the liquid/solid mixture from 80 °C to 160 °C (target cooking temperature), and (iii) the
535 digestion itself at the target temperature and during a certain duration (i.e. 30 min). Among these,
536 the heating stage was the one consuming the most energy (approximately 60%), followed by the
537 pre-heating step (around 33%), for all operating conditions tested (Fig. 11). This revealed that the
538 majority of energy consumption was spent on warming the digester reactor and then on heating the
539 raw material after being placed in the digester since the digestion operation was a discontinuous
540 process, meaning that the reactor temperature decreased between two successive digestion batches
541 when it was opened and then cleaned using tap water. Conversely, the electric resistance of the
542 digester reactor transmitted just a little more energy in order to maintain the 160 °C temperature set
543 value during the entire cooking duration.

544 During the digestion plus defibration process, the specific energy consumption increased
545 when increasing the liquid/solid ratio. As revealed in Table 6, the energy consumptions per unit
546 weight of dry matter for pre-heating, heating, digestion and defibration were 2.0-2.8, 3.7-5.1, 0.4-

547 0.6, and 0.024-0.035 kW h/kg dry matter, respectively, as the L/S ratio increased from 4 to 6,
548 corresponding to a total specific energy consumption increasing from 6.2 to 8.5 kW h/kg dry matter
549 of pulp. Thus, the total production cost of pulp logically increased as the liquid/solid ratio used
550 increased: from 0.49 €/kg dry matter at 4 liquid/solid ratio to 0.68 €/kg dry matter at 6 liquid/solid
551 ratio (Table 6).



552

553 **Fig. 11.** Contribution of the different steps for TMP preparation using a rotary digester plus a
554 Sprout-Waldron 105-A defibrator on the energy consumption (%).

555 *3.6 Chemical composition of rice straw TMP*

556 The chemical compositions of the three rice straw TMP produced using digester reactor plus
557 Sprout-Waldron defibrator are indicated in Table 3. The thermo-mechanical treatment using
558 digestion plus defibration contributed in changes in the biomass chemical composition, with an
559 increase in contents of both cellulose and lignin (from 38% to 48%, and from 7% to 10%,
560 respectively), simultaneously with a large decrease in the content of water-soluble compounds
561 (from 16% for initial rice straw to 5% for TMP). Because large amounts of water were used during
562 the digestion step, some of the water-soluble organic compounds, especially free sugars, were
563 removed from rice straw during digestion, thus leading to a 86-88% production yield. These results
564 were confirmed by the thermogravimetric analysis of rice straw and pulps P_1 to P_3 (Fig. 12).

565 Indeed, the TGA degradation curves (Fig. 12a) under air had quite difference appearance
566 between pulps and rice straw, meaning once again that chemical compositions were changed. As a
567 result, because water-soluble compounds were highly thermal sensitive, the beginning of the
568 thermal degradation inside pulps occurred at higher temperature: around 230 °C instead of around
569 205 °C for rice straw. A first mass loss was observed at 100 °C, corresponding to the water

evaporation. Moisture content was 7.4% and 4.6-4.8% for rice straw and pulps, respectively (Table 3), and the mass loss observed in the corresponding TGA curves was associated approximately with the same percentage. Then, the thermal degradation of organic compounds inside pulps took place mainly in one stage (in the range 230-350 °C), leading to a mass loss of approximately 55% of the sample dry mass. In agreement to some researchers in previous studies (Beaumont, 1981; Evon et al., 2015; Hatakeyama & Hatakeyama, 2006; Schaffer, 1973), the main thermal degradation stage is associated with the simultaneous breakdown of organic compounds (i.e. residual water-soluble compounds, hemicelluloses, and cellulose). Finally, another degradation phenomenon was also observed between 365 and 470 °C, however this was associated with a lower mass loss (about 20% of the sample dry mass), corresponding to the degradation of lignin and also to the oxidation of the degradation products from the previous stage, as the TGA analysis was conducted under air atmosphere (Uitterhaegen et al., 2016). At the end of all measurements, the undegraded samples represented around 9% of the test sample mass, corresponding to the minerals contained in pulps (Table 3).

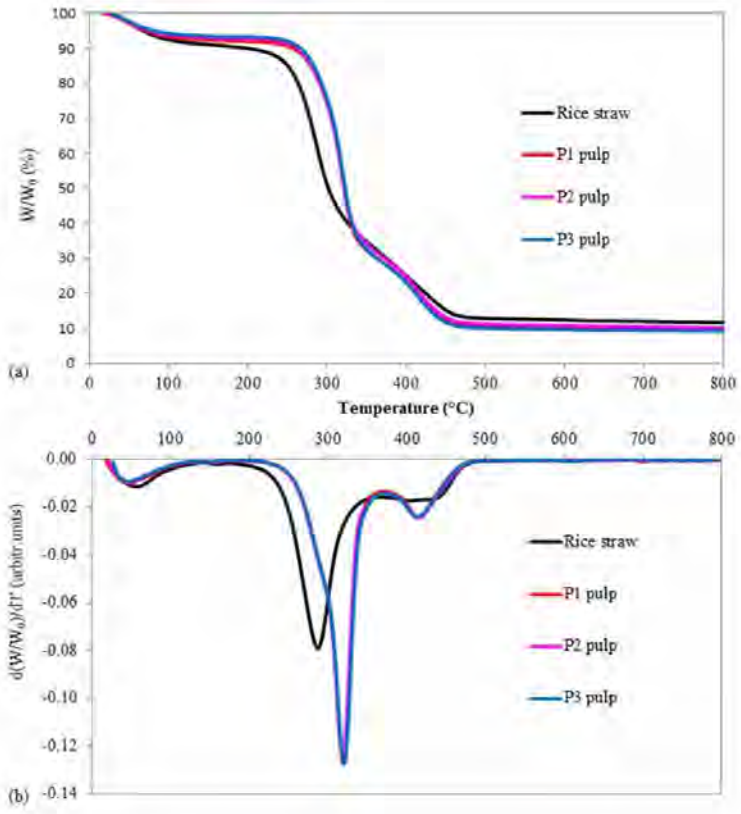


Fig. 12. TGA (a) and dTGA (b) curves of rice straw and TMP.

586 *3.7 Physical properties of TMP*

587 The main morphological characteristics of TMP fibers (P_1 to P_3) produced using different
588 liquid/solid ratios are shown in Table 4. From the mean length (L_W) and diameter (D) of the thermo-
589 mechanical fibers, the corresponding L_W/D aspect ratios were between 16.3 and 17.9. In addition, a
590 slight increase in the aspect ratio was observed with an increasing liquid/solid ratio (i.e. from 4 to 6)
591 in the digester reactor and Waldron-Sprout defibrator, and such phenomenon was previously
592 observed for twin-screw extrusion (Table 4) but also in the case of a steaming plus a mechanical
593 defibration treatment (Alila et al., 2013; Flandez et al., 2012; Theng et al., 2015a). Such aspect ratio
594 increase resulted mainly in the slight increase of the mean length of fibers, from 371 µm to 386 µm
595 (i.e. +4%) as the liquid/solid ratio increased from 4 to 6. This illustrated the fact that lower L/S ratio
596 at high temperature contributed in more degradation and cutting of the fibers.

597 The particle size distribution inside pulps (Table 4) revealed also the presence of small
598 particles (approximately 25 µm × 500 µm). This population contained not only the shortest fibers
599 but also a large amount of fines, originating from the thermo-mechanical breakdown of rice straw
600 and corresponding to a 65-70% range content. Lastly, apparent and tapped densities of the TMP
601 were low with maximal values of 53 and 69 kg/m^3, respectively (Fig. 10).

602 Looking at the influence of the liquid/solid ratio used on the apparent and tapped densities of
603 pulps, both densities are slightly decreasing when the L/S ratio increased: from 53 to 48 kg/m^3 and
604 from 69 to 63 kg/m^3, respectively. And, such tendency was already observed in the case of
605 extrudates (Fig. 10). According to the density results, a lower L/S ratio during steaming digestion
606 and mechanical defibration made not only shorter fibers (Table 4) but also a denser and heavier
607 TMP. On the contrary, because fibers originating from the highest L/S ratios were longer, their
608 entanglement between them was favored, leading to a bulkier and therefore to a less dense pulp.
609 Lastly, due to the high liquid/solid ratios used during digestion, it should also be noted that TMP
610 revealed much lower densities than the extrudates.

611 The effect of the liquid/solid ratio during digestion plus defibration on the color of pulps, in
612 comparison to the one of rice straw, is provided in Table 5. An increase in the L/S ratio from 4 to 6
613 had no influence on the change in color. However, the significant decrease in L* and b* values,
614 simultaneously with the slight increase in the a* one, revealed a darkening of the three pulps
615 produced in comparison to the initial rice straw color, with a color difference (ΔE*) varying from
616 7.3 to 7.8. Such darkening was also observed in the case of extrudates (Table 5), and this was the
617 consequence of the alteration of the structure of rice straw fibers inside TMP. Indeed, from the
618 operating conditions used during digestion plus defibration, i.e. high temperature (160 °C) during

619 30 min, a partial degradation of the organic compounds inside rice straw occurred, especially the
620 smaller and the most thermal sensitive molecules, thus contributing to the darkening of pulps.

621 *3.8 Extrudate (twin-screw extrusion) versus pulp (digestion plus defibration), a comparison*

622 Comparing twin-screw extrusion and digestion plus defibration, the influence of the
623 liquid/solid ratio used on the specific cost of rice straw fiber pretreatment was opposed, i.e. a
624 decrease in the specific cost for extrusion (Fig. 8b) as opposed to its increase for digestion plus
625 defibration (Table 6) with increasing liquid/solid ratio. In addition, the fiber pretreatment using
626 twin-screw extrusion had some advantages compared to the digestion plus defibration method,
627 listed as following:

628 – higher inlet flow rate and, as a continuous process, better productivity;
629 – lower amounts of water and lower temperature;
630 – lower production cost, approximately nine times less important: the twin-screw extrusion
631 technology appeared as a much more economical pretreatment for rice straw fibers;
632 – higher aspect ratio, which should lead to an improvement of the entanglement of fibers
633 inside fiberboards, thus possibly contributing to better mechanical reinforcement;
634 – higher amount of water-soluble components, in particular free sugars: because such
635 components can contribute to the self-bonding of fiberboards using hot pressing (Hashim e
636 al., 2012, 2011a, 2011b; Tajuddin et a., 2016), this could be an advantage for their cohesion
637 and mechanical strength.

638 On the other hand, two disadvantages can be listed for the extrusion method compared with
639 the digestion plus defibration one. Firstly, taking into account the TGA results for both treated
640 materials, extrudates were more thermal-sensitive, and it will be probably necessary to use lower
641 values for molding temperature during thermopressing (i.e. no more than 200 °C) in such a way as
642 to avoid any degradation of organic compounds. In addition, establishing a parallel with
643 papermaking, it is reasonable to assume that the ultimate strength of fiberboards made from TMP
644 should be higher than that of fiberboards made from extrudates. Indeed, in the paper industry, a
645 higher specific surface and a decrease in the mineral content (cases of TMP compared to extrudates)
646 should promote the compatibility of lignocellulosic fibers, leading to an increasing amount of bonds
647 between fibers (i.e. higher relative bonded area) and thus to a higher fiberboard compaction (Page,
648 1969; Vilaseca et al., 2008).

649 The next step will consist in using both pretreated rice straw materials, i.e. extrudates and
650 pulps, to compare their respective performances for fiberboard making, with or without addition of

651 a natural binder. By doing so, in terms of board mechanical strength, a comparison between the
652 contributions of (i) water-solubles inside extrudates to self-bonding and (ii) the higher relative
653 bonded area for TMP will become possible (Theng et al., In preparation).

654 **4. Conclusions**

655 The thermo-mechanical pretreatment of rice straw fibers was investigated in this study using
656 two different technologies, i.e. twin-screw extrusion, and digestion plus defibration. For both
657 technologies, the specific production cost depended on the liquid/solid ratio used. For the twin-
658 screw extrusion process, it ranged from 0.08 to 0.06 €/kg dry matter as the liquid/solid ratio
659 increased from 0.4 to 1.0, meaning that a bigger expense occurred at lower liquid/solid ratio. On the
660 contrary, for the digestion plus defibration method, the more the liquid/solid ratio, the more the
661 energy consumed and the more the specific production cost (until 0.7 €/kg dry matter for a 6
662 liquid/solid ratio). Comparing both technologies, twin-screw extrusion was about nine times
663 cheaper than the digestion plus defibration process. The pretreated rice straw fibers obtained using
664 these two thermo-mechanical processes will then be usable for the manufacture of fiberboards using
665 hot pressing (Marechal, 2001; Theng et al., In preparation; Theng et al., 2015b).

666 For twin-screw extrusion, the total production cost was a combination of three specific costs,
667 including a mechanical cost, a cooling cost, and a heating cost. Among these three specific costs,
668 the mechanical one was the most important contribution. It was between 59 and 66% of the total
669 cost, depending on the liquid/solid ratio used. For digestion plus defibration, the total production
670 cost was the combination of a digestion cost through steaming in a rotary digester (for thermo-
671 mechanical fractionation) and a defibration cost using a Sprout-Waldron defibrator (for refining the
672 particle size). The digestion step represented almost 100% of the total production cost, while
673 defibration contributed to less than 0.4%.

674 The different liquid/solid ratios used for extrusion had no effect on the main characteristics of
675 treated lignocellulosic fibers, including their chemical compositions and their thermal properties.
676 However, for the morphology of these treated fibers, a slight decrease in their mean length, their
677 mean diameter and their mean aspect ratio was observed when the quantity of water was reduced.
678 The same effect was observed for fibers treated using digestion plus defibration. In addition, the
679 shortest treated fibers revealed higher apparent and tapped densities, in particular inside the
680 extrudates produced using the two lowest liquid/solid ratios.

681 Furthermore, in comparison to the initial rice straw biomass, the chemical compositions and
682 thermal properties of the extrudates remained the same, although the extrudates were a little

683 browner than the starting material. On the contrary, the chemical compositions and thermal
684 properties of the TMP were changed, compared to the rice straw raw material. The most important
685 change was their contents in water-soluble components, which were partly removed during the
686 digestion step, conducted using high amounts of water, at a high temperature (160 °C), and for a
687 long duration (30 min). And, pulps were also a little browner than the initial rice straw biomass.

688

689 **Acknowledgements**

690 The authors wish to thank the Erasmus+ KA107 project for financial support. Special sincere
691 gratitude is given to Laboratoire de Chimie Agro-Industrielle (LCA), INP-ENSIACET, Toulouse,
692 France and LEPAMAP research group, University of Girona, Spain for both raw materials and
693 experimental support.

694

695 **References**

696 Alila, S., Besbes, I., Vilar, M.R., Mutjé, P., Boufi, S. 2013. Non-woody plants as raw materials for
697 production of microfibrillated cellulose (MFC): a comparative study. *Ind. Crops Prod.*, **41**,
698 250-259.
699 Beaumont, O. 1981. Pyrolyse extractive du bois. Ph.D Thesis, Ecole Nationale Supérieure des
700 Mines de Paris, France.
701 Binod, P., Sindhu, R., Singhania, R.R., Vikram, S., Devi, L., Nagalakshmi, S., Kurien, N.,
702 Sukumaran, R.K., Pandey, A. 2010. Bioethanol production from rice straw: an overview.
703 *Bioresour. Technol.*, **101**, 4767-4774.
704 El-Kassas, A., Mourad, A.I. 2013. Novel fibers preparation technique for manufacturing of rice
705 straw based fiberboards and their characterization. *Mater. & Des.*, **50**, 757-765.
706 Evon, P., Vandenbossche, V., Pontalier, P.-Y., Rigal, L. 2014. New thermal insulation fiberboards
707 from cake generated during biorefinery of sunflower whole plant in a twin-screw extruder.
708 *Ind. Crops Prod.*, **52**, 354-362.
709 Evon, P., Vandenbossche, V., Pontalier, P.-Y., Rigal, L. 2010a. Thermo-mechanical behaviour of
710 the raffinate resulting from the aqueous extraction of sunflower whole plant in twin-screw
711 extruder: manufacturing of biodegradable agromaterials by thermo-pressing. *J. Adv. Mater.*
712 *Res.*, **112**, 63-72.
713 Evon, P., Vandenbossche, V., Pontalier, P.-Y., Rigal, L. 2010b. The twin-screw extrusion
714 technology, an original and powerful solution for the biorefinery of sunflower whole plant.

715 *18th European Biomass Conference and Exhibition*, Lyon, France. Open Archieve Toulouse
716 Archieve Ouverte (OATAO). pp. 1481-1489.
717 Evon, P., Vandenbossche, V., Rigal, L. 2012. Manufacturing of renewable and biodegradable
718 fiberboards from cake generated during biorefinery of sunflower whole plant in twin-screw
719 extruder: Influence of thermo-pressing conditions. *J. Polym. Degrad. Stab.*, **97**, 1940-1947.
720 Evon, P., Vinet, J., Labonne, L., Rigal, L. 2015. Influence of thermo-pressing conditions on the
721 mechanical properties of biodegradable fiberboards made from a deoiled sunflower cake.
722 *Ind. Crops Prod.*, **65**, 117-126.
723 FAOSTAT, F.A.O. 2016. FAOSTAT statistical database, Vol. 2016.
724 http://www.fao.org/faostat/en/#data/QC (accessed 18.12.16).
725 Flandez, J., González, I., Resplandis, J.B., El Mansouri, N.E., Vilaseca, F., Mutjé, P. 2012.
726 Management of corn stalk waste as reinforcement for polypropylene injection moulded
727 composites. *BioResour.*, **7**, 1836-1849.
728 Garay, M., Marie, R., Rallo de la B, M., Carmona, C., Araya, C. 2009. Characterization of
729 anatomical, chemical, and biodegradable properties of fibers from corn, wheat, and rice
730 residues. *Chil. J. Agric. Res.*, **69**, 406-415.
731 Garrote, G., Domí, H., Parajó, J.C. 2002. Autohydrolysis of corncob: study of non-isothermal
732 operation for xylooligosaccharide production. *J. Food Eng.*, **52**, 211-218.
733 Gautam, A., Choudhury, G.S. 1999a. Screw configuration effects on residence time distribution and
734 mixing in twin-screw extruders during extrusion of rice flour. *J. Food Process Eng.*, **22**,
735 263-285.
736 Gautam, A., Choudhury, G.S. 1999b. Screw configuration effects on starch breakdown during twin-
737 screw extrusion of rice flour. *J. Food Process. Preserv.*, **23**, 355-375.
738 Halvarsson, S., Edlund, H., Norgren, M. 2008. Properties of medium-density fibreboard (MDF)
739 based on wheat straw and melamine modified urea formaldehyde (UMF) resin. *Ind. Crops*
740 *Prod.*, **28**, 37-46.
741 Hashim, R., Nadhari, W.N.A.W., Sulaiman, O., Kawamura, F., Hiziroglu, S., Sato, M., Sugimoto,
742 T., Seng, T.G., Tanaka, R. 2011a. Characterization of raw materials and manufactured
743 binderless particleboard from oil palm biomass. *Mater. & Des.*, **32**, 246-254.
744 Hashim, R., Nadhari, W.N.A.W., Sulaiman, O., Sato, M., Hiziroglu, S., Kawamura, F., Sugimoto,
745 T., Seng, T.G., Tanaka, R. 2012. Properties of binderless particleboard panels manufactured
746 from oil palm biomass. *BioResour.*, **7**, 1352-1365.
747 Hashim, R., Said, N., Lamaming, J., Baskaran, M., Sulaiman, O., Sato, M., Hiziroglu, S., Sugimoto,
748 T. 2011b. Influence of press temperature on the properties of binderless particleboard made
749 from oil palm trunk. *Mater. & Des.*, **32**, 2520-2525.

750 Hatakeyama, T., Hatakeyama, H. 2006. *Thermal properties of green polymers and biocomposites*,
751 Springer Science & Business Media.
752 Ilo, S., Berghofer, E. 1999. Kinetics of colour changes during extrusion cooking of maize grits. *J.*
753 *Food Eng.*, **39**, 73-80.
754 Kanokkanjana, K., Garivait, S. 2013. Alternative rice straw management practices to reduce field
755 open burning in Thailand. *Int. J. Environ. Sci. Dev.*, **4**, 119.
756 Kartika, I.A., Pontalier, P., Rigal, L. 2006. Extraction of sunflower oil by twin screw extruder:
757 Screw configuration and operating condition effects. *Bioresour. Technol.*, **97**, 2302-2310.
758 Kartika, I.A., Pontalier, P., Rigal, L. 2005. Oil extraction of oleic sunflower seeds by twin screw
759 extruder: influence of screw configuration and operating conditions. *Ind. Crops Prod.*, **22**,
760 207-222.
761 Kartika, I.A., Pontalier, P., Rigal, L. 2010. Twin-screw extruder for oil processing of sunflower
762 seeds: Thermo-mechanical pressing and solvent extraction in a single step. *Ind. Crops Prod.*,
763 **32**, 297-304.
764 Kim, S., Dale, B.E. 2004. Global potential bioethanol production from wasted crops and crop
765 residues. *Biomass and Bioenerg.*, **26**, 361-375.
766 Konica Minolta Sensing, I. 2007. *Precise color communication*, Japan.
767 Li, X., Cai, Z., Winandy, J.E., Basta, A.H. 2010. Selected properties of particleboard panels
768 manufactured from rice straws of different geometries. *Bioresour. Technol.*, **101**, 4662-
769 4666.
770 Maiorella, B. 1983. Ethanol industrial chemicals. *Biochem. Fuels*, **86**.
771 Mancera, C., El Mansouri, N.-E., Pelach, M.A., Francesc, F., Salvadó, J. 2012. Feasibility of
772 incorporating treated lignins in fiberboards made from agricultural waste. *Waste Manag.*,
773 **32**, 1962-1967.
774 Mancera, C., El Mansouri, N.-E., Vilaseca, F., Ferrando, F., Salvado, J. 2011. The effect of lignin as
775 a natural adhesive on the physico-mechanical properties of Vitis vinifera fiberboards.
776 *BioResour.*, **6**, 2851-2860.
777 Marechal, P. 2001. Analyse des principaux facteurs impliques dans le fractionnement combine de
778 pailles et de sons de ble en extrudeur bi-vis : obtention d'agro-materiaux, Ph.D., INP.
779 Toulouse, France.
780 Migneault, S., Koubaa, A., Nadji, H., Riedl, B., Zhang, S., Deng, J. 2010. Medium-density
781 fiberboard produced using pulp and paper sludge from different pulping processes. *Wood*
782 *and Fiber Sci.*, **42**, 292-303.
783 Mussatto, S.I., Roberto, I.C. 2004. Optimal experimental condition for hemicellulosic hydrolyzate
784 treatment with activated charcoal for xylitol production. *Biotechnol. Prog.*, **20**, 134-139.

785 Page, D. 1969. A theory for tensile strength of paper. *Tappi J.*, **52**, 674-&.
786 Pan, M., Zhou, D., Ding, T., Zhou, X. 2010. Water resistance and some mechanical properties of
787 rice straw fiberboards affected by thermal modification. *BioResour.*, **5**, 758-769.
788 Rahnama, N., Mamat, S., Shah, U.K.M., Ling, F.H., Rahman, N.A.A., Ariff, A.B. 2013. Effect of
789 alkali pretreatment of rice straw on cellulase and xylanase production by local Trichoderma
790 harzianum SNRS3 under solid state fermentation. *BioResour.*, **8**, 2881-2896.
791 Sarnklong, C., Cone, J., Pellikaan, W., Hendriks, W. 2010. Utilization of rice straw and different
792 treatments to improve its feed value for ruminants: a review. *Asian-Australas. J. Anim. Sci.*,
793 **23**, 680.
794 Schaffer, E. 1973. Effect of pyrolytic temperatures on the longitudinal strength of dry Douglas-fir.
795 *J. Test. Eval.*, **1**, 319-329.
796 Shen, H.S., Ni, D., Sundstøl, F. 1998. Studies on untreated and urea-treated rice straw from three
797 cultivation seasons: 1. Physical and chemical measurements in straw and straw fractions.
798 *Anim. Feed Sci. Technol.*, **73**, 243-261.
799 So, S. 2016. Fiberboard made with agro-forestry residues and natural adhesives, Vol.
800 Undergraduate. BSc., Department of Agricultural Engineering and Agri-Food Technology,
801 High Polytechnical School, University of Girona.
802 Tajuddin, M., Ahmad, Z., Ismail, H. 2016. A Review of Natural Fibers and Processing Operations
803 for the Production of Binderless Boards. *BioResour.*, **11**, 5600-5617.
804 Theng, D., Arbat, G., Delgado-Aguilar, M., Ngo, B., Labonne, L., Evon, P., Mutjé, P. In
805 preparation. Production of fiberboards from rice straw thermo-mechanical extrudates using
806 thermopressing: influence of molding parameters. *Ind. Crops Prod.*
807 Theng, D., Arbat, G., Delgado-Aguilar, M., Vilaseca, F., Ngo, B., Mutjé, P. 2015a. All-
808 lignocellulosic fiberboard from corn biomass and cellulose nanofibers. *Ind. Crops Prod.*, **76**,
809 166-173.
810 Theng, D., Arbat, G., Delgado-Aguilar, M., Vilaseca, F., Ngo, B., Mutjé, P. 2015b. Feasibility of
811 incorporating treated cellulose nanofiber in all-lignocellulosic fiberboards made from rice
812 straw biomass. *3rd International Symposium on Green Chemistry*, 3-7 May 2015, La
813 Rochelle, France. ISGC.
814 Thomas L., R., Section of Plant Biology, Division of Biological Sciences, University of California
815 Davis. 1997. Rice anatomy, Vol. 2016. http://www-
816 plb.ucdavis.edu/labs/rost/rice/Introduction/intro.html (accessed 11.12.16).
817 Uitterhaegen, E., Nguyen, Q.H., Merah, O., Stevens, C.V., Talou, T., Rigal, L., Evon, P. 2016. New
818 Renewable and Biodegradable Fiberboards from a Coriander Press Cake. *J. Renew. Mater.*,
819 **4**, 225-238.

820 Van Soest, P.J., Wine, R.H. 1967. Use of detergents in the analysis of fibrious feeds. IV.
821 Determination of plant cell wall constituents. *J. AOAC Int.*, **50**, 50-55.
822 Van Soest PJ, W.R. 1968. Determination of lignin and cellulose in acid detergent fiber with
823 permanganate. *J.AOAC Int.*, **51**, 780-784.
824 Vandenbossche, V., Brault, J., Hernandez-Melendez, O., Evon, P., Barzana, E., Vilarem, G., Rigal,
825 L. 2016. Suitability assessment of a continuous process combining thermo-mechano-
826 chemical and bio-catalytic action in a single pilot-scale twin-screw extruder for six different
827 biomass sources. *Bioresour. Technol.*, **211**, 146-153.
828 Vandenbossche, V., Brault, J., Vilarem, G., Rigal, L. 2015. Bio-catalytic action of twin-screw
829 extruder enzymatic hydrolysis on the deconstruction of annual plant material: case of sweet
830 corn co-products. *Ind. Crops Prod.*, **67**, 239-248.
831 Vandenbossche, V., Doumeng, C., Rigal, L. 2014. Thermomechanical and Thermo-mechano-
832 chemical Pretreatment of Wheat Straw using a Twin-screw Extruder. *BioResour.*, **9**, 1519-
833 1538.
834 Vilaseca, F., Mendez, J., Lopez, J., Vallejos, M., Barbera, L., Pelach, M., Turon, X., Mutje, P. 2008.
835 Recovered and recycled kraft fibers as reinforcement of PP composites. *Chem. Eng. J.*, **138**,
836 586-595.
837 Wu, J., Zhang, X., Wan, J., Ma, F., Tang, Y., Zhang, X. 2011. Production of fiberboard using corn
838 stalk pretreated with white-rot fungus Trametes hirsute by hot pressing without adhesive.
839 *Bioresour. Technol.*, **102**, 11258-11261.
840 Zhang, L., Hu, Y. 2014. Novel lignocellulosic hybrid particleboard composites made from rice
841 straws and coir fibers. *Mater. & Des.*, **55**, 19-26.
842 Zhao, Y., Qiu, J., Feng, H., Zhang, M., Lei, L., Wu, X. 2011. Improvement of tensile and thermal
843 properties of poly (lactic acid) composites with admicellar-treated rice straw fiber. *Chem.*
844 *Eng. J.*, **173**, 659-666.
845

RESULTS AND DISCUSSION

Raw materials characterization

Pulps and extrudates characterization

Characterization of CNF

Characterization of lignin

Fiberboards

5 RESULTS AND DISCUSSION

This section summarizes the main results from the articles that constitute this Thesis, shown in the previous section. Generally, the relationship between the articles is illustrated in Figure 24. As explained in the Materials and Methods section, corn and rice biomasses were used as raw material for the production of binderless fiberboards, together with cellulose nanofibers (CNF) and lignin with the purpose of substituting synthetic resins.

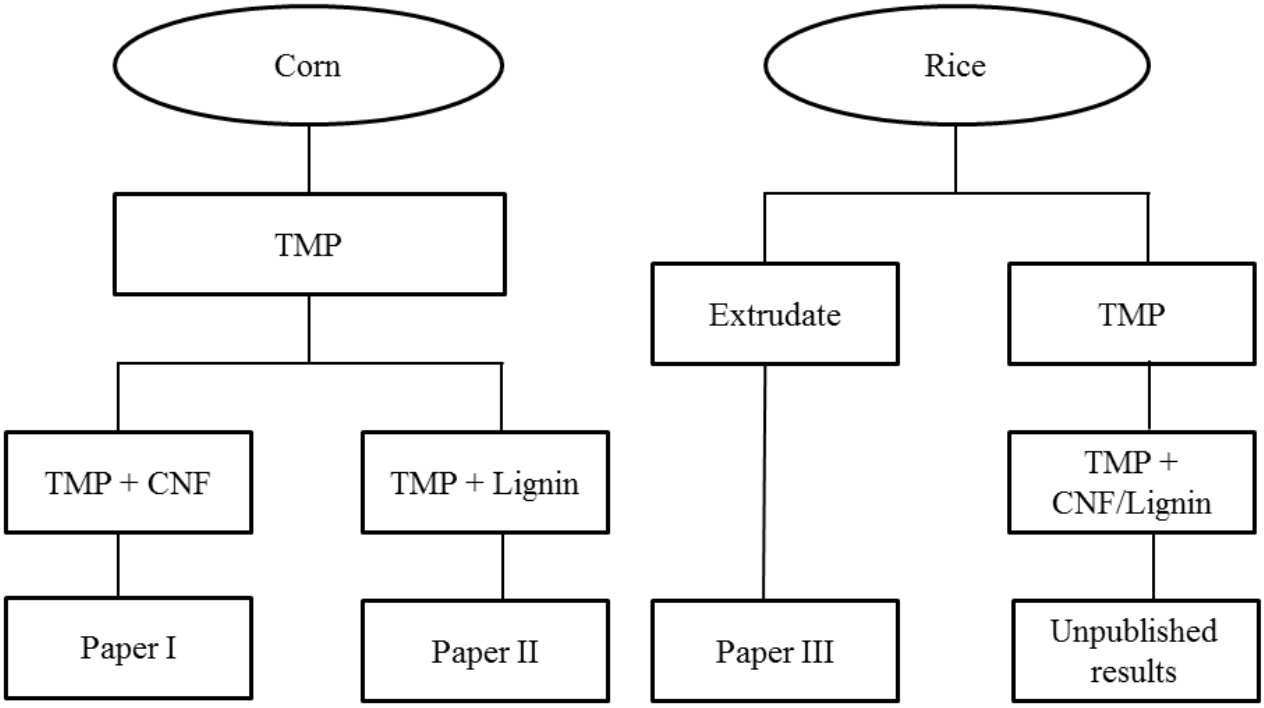


Figure 24. *Flowchart of the experimental study on fully biodegradable fiberboards manufactured from corn and rice residues*

5.1 Raw materials characterization

The chemical composition of the original corn and rice biomass is shown in Table 4. Corn had lower ash and extractives content (3.2% and 3.1%, respectively) compared to those in rice straw (14.7% and 16.0%, respectively). For the three main organic compounds (i.e. cellulose, hemicellulose and lignin) corn stalk contained more cellulose and lignin, accounting for 50.6 % and 16.0 %, than rice, that presented 37.7 % of cellulose and 7.2 % of lignin. These results are in agreement to those found in the existing literatures (Flandez et al., 2012; Hurter, 2006; Rahnama et al., 2013).

Table 4. *Chemical composition contains in the raw materials (% on dry matter).*

Raw materials	Corn stalk (Paper I & II)	Rice straw (Paper III)
Ash (%)	3.2	14.7
Cellulose (%)	50.6	37.7
Hemicellulose (%)	27.0	27.9
Lignin (%)	16.0	7.2
Extractives or water-soluble component (%)	3.1	16.0

In comparison to other agricultural wastes and wood fibers, they showed similar cellulose content (37.7-50.6%) such as sunflower stalk (López et al., 2005), triticale (Tarrés et al., 2017), wheat (Halvarsson et al., 2008), as well as to softwood (Mousavi et al., 2013). Hemicellulose accounted for 27 % similar to other lignocellulosic fiber source including sunflower, wheat, barley, rye, and oat straw (Tarrés et al., 2017). At first sight, due to the high cellulose content and moderate lignin content, corn biomass could be a good candidate to be used as raw material for papermaking, as well as for the low mineral content. This is not the case for rice, which although having low lignin content, presented excessive ash.

5.2 Pulps and extrudate characterization

5.2.1 Corn and rice straw TMP optimization

Thermo-mechanical pulp (TMP) was firstly selected to pretreat corn and rice biomass in order to obtain fibers for binderless fiberboard manufacturing. An optimum operating condition of steam-water digestion treatment using the laboratory scale rotary digester, i.e. cooking temperature and duration was determined at 140 – 180 °C and duration between 15 and 30 minutes with L/S 6:1. The optimum operating conditions were determined following both production yield of and bending strength of fiberboards. As shown in Table 5, the production yield decreased when temperature and treatment time were increased, from about 90 % to 60 % and 85 % to 72 % for corn and rice biomass, respectively. The maximum production yield was 89.6 % and 84.8 %, corresponding to cooking condition 1 (140 °C, 30 min) and 2 (160 °C, 15 min) for corn stalk and rice straw, respectively. The maximum bending strength were 30 MPa of MOR and 1874 MPa MOE, obtained on fiberboards made from CS-TMP$_2$, and 46 MPa of MOR and 3420 MPa of MOE of the fiberboards made of RS-TMP$_4$. However, the optimum operating condition at digestion stage for corn and rice biomass were selected at 160 °C for 15 min (CS-TMP$_2$) and 160 °C for 30 min (RS-TMP$_3$) as the results of quite high on yield and bending properties. Similar conditions were found by Flandez et al. (2012) for corn biomass.

Table 5. *Digestion parameters, production yield of TMP pulps and bending strength of binderless fiberboards (unpublished results)*

Materials		Temperature (°C)	Time (min)	Yield (%)	MOR (MPa)	MOE (MPa)
Corn stalk	CS-TMP$_1$	140	30	89.6 ± 0.3	24.3 ± 1.7	1520 ± 163
	CS-TMP$_2$	160	15	87.2 ± 1.0	29.6 ± 0.9	1874 ± 164
	CS-TMP$_3$	160	30	84.8 ± 0.4	25.1 ± 1.3	1693 ± 266
	CS-TMP$_4$	180	15	60.6 ± 1.4	16.2 ± 1.8	1422 ± 376
Rice straw	RS-TMP$_1$	140	30	82.1 ± 0.2	32.5 ± 1.1	2558 ± 152
	RS-TMP$_2$	160	15	84.7 ± 0.6	29.0 ± 2.1	2277 ± 199
	RS-TMP$_3$	160	30	82.8 ± 0.3	40.4 ± 3.4	3421 ± 399
	RS-TMP$_4$	180	15	72.2 ± 1.5	46.2 ± 1.8	3420 ± 179

CS: Corn Stalk; RS: Rice Straw; TMP: thermomechanical pulp; MOR: modulus of rupture; MOE: modulus of elasticity

These pulps were used for the development of the Thesis, leading to the experimentation from the articles shown in the previous section.

5.2.2 TMP and extrudate characterization

The chemical composition of corn stalk and rice straw after pulping and/or extrusion is shown in Table 6. As expected, the chemical composition of the TMP fibers changed when compared with the initial corn and rice biomass (Table 4). The ash content decreased considerably from 3.2 to 0.8 % and from 14.7 to 10.5 % for corn and rice, respectively (Table 4 and Table 6), as a result of the steam and defibrillation processes. On the contrary, there was a slight increase in contents of both cellulose and lignin (from 51 to 55 % and from 16 to 17 %, respectively for corn) and (from 38 to 48 % and from 7 to 10 %, respectively for rice). The increase of cellulose and lignin contents was because of the decrease of other organic and inorganic compounds such as extractives and ash. A large decrease in the content of extractives or water-soluble compounds was occurred (from 3 to 1 % and from 16 to 5 % for corn and rice, respectively). Since large amounts of water were used during the digestion step, some of the water-soluble organic compounds, especially free sugars, were removed from the initial biomass during digestion, thus leading to a production yield approximately 87 % and 83% in the cases of optimum digestion conditions (CS-TMP$_2$ and RS-TMP$_3$, respectively) (Table 5).

On the other hand, the extrusion thermo-mechanical treatment did not cause significant changes, whether the L/S ratio was high (1.0, i.e. E$_1$ extrudate) or low (0.4, i.e. E$_5$ extrudate). These results were confirmed by thermogravimetric analysis of the raw material, the TMP and the extrudate fibers (Figure 25).

Table 6. *Chemical compositions corn stalk TMP, rice straw TMP, and rice straw extrudate.*

Materials	Ash (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Corn stalk TMP (Paper I & II)	0.8	55.2	25.8	17.2	1.1
Rice straw extrudate (Paper III)					
E_1 (L/S ratio 1.0)	14.3 ± 0.2	36.2 ± 0.5	33.0 ± 0.6	5.5 ± 0.5	15.9 ± 0.1
E_3 (L/S ratio 0.7)	14.4 ± 0.1	37.0 ± 0.9	28.4 ± 0.2	6.8 ± 0.3	17.3 ± 0.3
E_5 (L/S ratio 0.4)	15.8 ± 0.0	33.8 ± 0.1	29.3 ± 0.2	6.3 ± 0.2	16.2 ± 0.2
Rice straw TMP (Paper III)					
P_1 (L/S ratio 4.0)	10.7±0.0	47.6±0.1	28.6±0.1	8.7±0.1	5.1±0.1
P_2 (L/S ratio 5.0)	11.0±0.1	47.5±0.0	29.5±0.9	8.1±0.1	4.8±0.6
P_3 (L/S ratio 6.0)	10.5±0.1	48.2±0.3	28.3±0.3	9.7±0.2	5.1±0.0

Thermal degradation curves of both rice straw and extrudates showed similar behavior (Figure 25a) under air atmosphere, while TMP not. This illustrated once again that chemical compositions were all comparable and that the different operating conditions used in the twin-screw extruder had no significant influence on the thermal degradation of organic compounds of the different extrudates. On the contrary, pulping had significant influence on the thermal degradation of organic compounds inside the different TMPs. As a result, because water-soluble compounds were highly thermal sensitive, the beginning of the thermal degradation of pulps occurred at higher temperature: around 230 °C instead of around 205 °C for rice straw (Figure 25). A first mass loss was observed at 100 °C, corresponding to water evaporation. Then, the thermal degradation of organic compounds took place (between 205 and 340 °C for rice straw and extrudate and between 230 and 350 °C for TMP), leading to a mass loss of approximately 50 and 55% of the sample dry mass, respectively. In agreement to some researchers in previous studies (Beaumont, 1981; Evon et al., 2015; Hatakeyama et al., 2006; Schaffer, 1973), the main thermal degradation stage is associated with the simultaneous breakdown of organic compounds (i.e. residual water-soluble compounds, hemicelluloses, and cellulose). Finally, another degradation phenomenon was also observed between 365 and 470 °C. However, this was associated with a lower mass loss (about 20% of the sample dry mass), corresponding to the degradation of lignin and also to the oxidation of the degradation products from the previous stage, as the TGA analysis was conducted under air atmosphere (Uitterhaegen et al., 2016). At the end of all measurements, the non-degraded samples represented around 9 – 15 % of the test sample mass, corresponding to the minerals contained in rice straw, extrudates and pulps (Table 4 and Table 6).

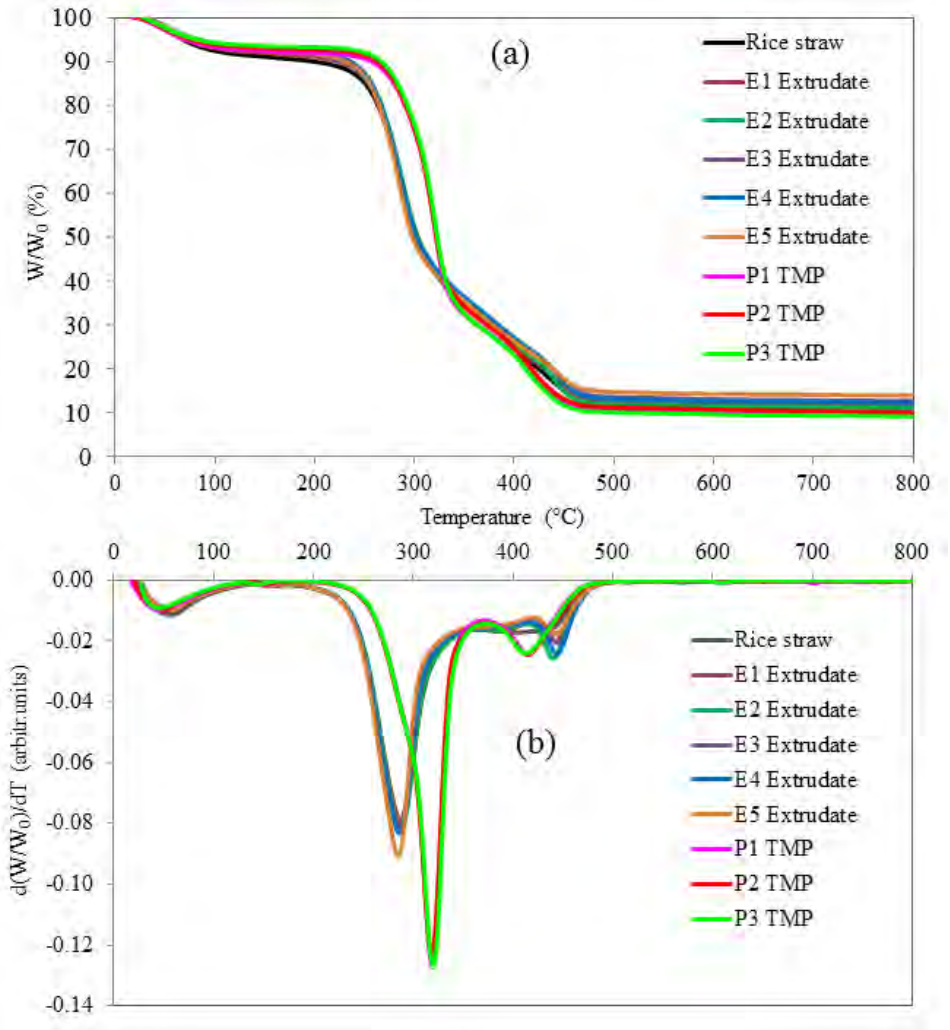


Figure 25. *TGA (a) and dTGA (b) of the raw materials (rice straw, rice straw extrudate and rice straw TMP)*

Table 7. *Morphological properties of corn stalk TMP, rice straw TMP, and rice straw extudate.*

Materials	Length (µm)	Diameter (µm)	L_W/D aspect ratio	Fines (%)	°SR
Corn stalk TMP (Paper I & II)	652.8	24.4	26.7	59.7	44.0
Rice straw extrudate (Paper III)					
E_1 (L/S ratio 1.0)	571.5 ± 7.8	25.5 ± 0.0	22.4 ± 0.3	63.8 ±0.4	-
E_2 (L/S ratio 0.85)	544.0 ± 4.2	24.5 ± 0.0	22.2 ± 0.2	62.8 ±1.5	-
E_3 (L/S ratio 0.7)	571.0 ± 7.1	25.3 ± 0.0	22.6 ± 0.3	54.2 ± 4.9	-
E_4 (L/S ratio 0.55)	505.0 ± 5.7	23.8 ± 0.1	21.2 ± 0.2	74.7 ± 3.4	-
E_5 (L/S ratio 0.4)	494.0 ± 1.4	23.6 ± 0.1	20.9 ± 0.1	61.8 ± 0.5	-
Rice straw TMP (Paper III)					
P_1 (L/S ratio 4.0)	371.7 ± 9.0	22.8 ± 0.0	16.3 ± 0.4	69.6 ± 2.3	-
P_2 (L/S ratio 5.0)	377.0 ± 5.7	22.0 ± 0.1	17.0 ± 0.2	68.2 ± 1.5	-
P_3 (L/S ratio 6.0)	386.0 ± 2.8	21.9 ± 0.1	17.9 ± 0.4	65.3 ± 3.6	54.5

Table 7 shows the morphological characteristics of fibers inside the extrudates (E_1 to E_5) and TMP (P_1 to P_3), produced using different operating conditions. From the mean length (L_W) and diameter (D) of the extruded fibers, the corresponding L_W/D aspect ratios were between 20.9 and 22.6 for extrudates and between 16.3 and 17.9 for TMPs (Table 7). In addition, a slight decrease in the aspect ratio was observed with a decreasing liquid/solid ratio in the twin-screw extruder, especially for its two lowest values (i.e. 0.55 and 0.4). Whereas, a slight increase in the aspect ratio was found with an increasing liquid/solid ratio (i.e. from 4 to 6) in the digester and defibrator. Such phenomenon was previously noticed for thermo-mechanical pulps produced using steam plus a mechanical defibration treatment (Alila et al., 2013; Flandez et al., 2012; Theng et al., 2015). The decrease or increase aspect ratio resulted mainly in the mean length of fibers decreasing or increasing, from 571 to 494 µm (i.e. -14 %) as the L/S ratio decreased from 1.0 to 0.4 for extrusion and from 371 µm to 386 µm (i.e. +4 %) as the L/S ratio increased from 4 to 6 for pulping (Table 7). This illustrated the fact that higher mechanical shear and higher self-heating of the material at the level of the reversed screws inside the twin-screw extruder caused by low L/S ratios contributed in more cutting of the fibers. On the other hand, at high temperature (low liquid mass) inside digester contributed in more degradation and cutting of the fibers.

The particle size distribution inside the extrudates and TMPs (Table 7) revealed also the presence of small particles. This population contained not only the smallest fibers but also spherical particles, i.e. fines, originating from the thermo-mechanical breakdown process of rice straw, and corresponding to a range 54-75 % and 65-70 % for extrudates and pulps, respectively.

However, the value of Schopper-Riegler degree (44.0 and 54.5 °SR for corn and rice TMP, respectively) were relatively high, but consistent with the fines content (60 % and 70 %), which were also significantly high (González et al., 2013).

The apparent and tapped densities of the rice straw extrudates were sensibly low (with maximal values of 162 and 216 kg/m^3, respectively), and lower for TMP (with maximal values of 53 and 69 kg/m^3, respectively) (Figure 26). Looking at the influence of the operating conditions tested on the apparent and tapped densities of extrudates, both densities were decreased as the L/S ratio increased: from 162 to 56 kg/m^3, and from 216 to 81 kg/m^3, respectively. Referring to the densities, a lower L/S ratio during twin-screw extrusion made not only shorter fibers but also a denser and heavier extrudate. On the contrary, since fibers originating from the highest L/S ratios were longer, their entanglement between them was favored, leading to a bulkier and therefore to a less dense extrudate. The same phenomenon was also observed on pulps.

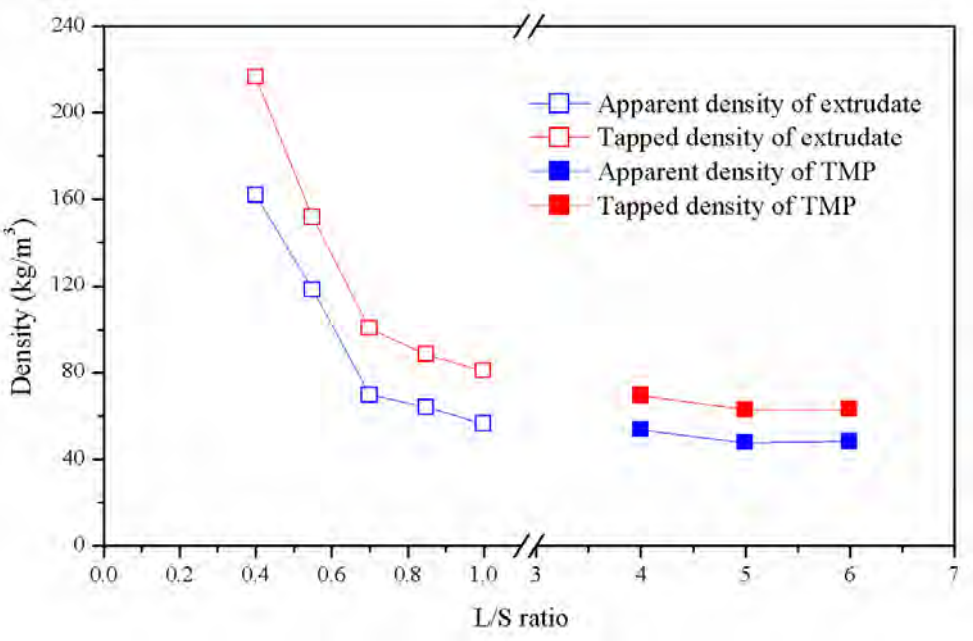


Figure 26. *Apparent and tapped densities of rice straw extrudate and rice straw TMP.*

The effect of the L/S ratio on the extrudate and pulp color (using the CIE L*a*b* referential, which L* is the lightness, a* is the chromaticity coordinate color from red to green, and b* from yellow to blue direction) in comparison to the one of rice straw is shown in Table 8. A decrease in the L/S ratio contributed decreasing both L* and b* values, simultaneously with a slight increase in the a* one. The significant L* decrease was observed in the extrudate and pulp in comparison to the initial rice straw color, revealing a darkening after treatment. Additionally, the decreasing L/S ratio at extrusion resulted the lower L* values, revealed a progressive darkening of the extrudates with a color difference (ΔE*) varying from 6.2 to 8.2, but not significant different for TMP with different L/S ratios. According to Ilo and Berghofer (1999), color is an important quality assurance parameter of feed and biological products, which can also be indirectly related to the nutritional value of the products. In board, it shows the strengthen capacity since the darkening color probably as a cause of nutrition or organic compounds degradation. The organic compound such as free sugar was observed providing good self-bonding in composites (Hashim et al., 2012, 2011a, 2011b; Tajuddin et al., 2016). In this case (i.e. the thermo-mechanical defibration of rice straw using the twin-screw extrusion), the alteration degree of the structure of rice straw fibers inside the twin-screw extruder barrel is a key factor in the quality of the extrudates. It is largely dependent on the L/S ratio used, the latter largely influencing the mechanical shear transmitted to the material and its self-heating. Therefore, the increase in the darkening of the extrudate observed with the decrease in the L/S ratio could be directly correlated to the progressive self-heating undergone by the material in the restrictive part of the screw profile, i.e. where mechanical shear is applied (from 132 to 153 °C for the material temperature at the end of module

7, and from 126 to 140 °C at the beginning of module 8), contributing to the partial degradation of the organic compounds inside rice straw, especially the smaller and the most thermal sensitive molecules. It was also observed the same phenomenon on TMP.

Table 8. *Influence of the operating conditions on color in the CIE L*a*b* referential of the extrudate (E) and pulp (P) powders, and comparison with color of the starting material (i.e. rice straw powder).*

Materials	L*	a*	b*	ΔE*
Rice straw	82.6 ± 0.3	3.7 ± 0.1	16.5 ± 0.2	-
E_1 (L/S ratio 1.0)	77.4 ± 0.3	4.1 ± 0.1	13.2 ± 0.5	6.2
E_2 (L/S ratio 0.85)	77.1 ± 0.4	4.3 ± 0.1	13.3 ± 0.2	6.4
E_3 (L/S ratio 0.7)	75.9 ± 0.1	4.2 ± 0.1	12.9 ± 0.2	7.6
E_4 (L/S ratio 0.55)	76.3 ± 0.3	4.1 ± 0.1	12.9 ± 0.3	7.2
E_5 (L/S ratio 0.4)	74.9 ± 0.7	4.2 ± 0.2	13.9 ± 0.5	8.2
P_1 (L/S ratio 4.0)	75.7 ± 0.4	4.2 ± 0.1	12.7 ± 0.5	7.8
P_2 (L/S ratio 5.0)	75.9 ± 0.3	4.1 ± 0.1	13.5 ± 0.3	7.3
P_3 (L/S ratio 6.0)	75.8 ± 0.3	4.1 ± 0.1	13.2 ± 0.3	7.5

5.2.3 Comparison on production cost (Paper III)

The calculation of the production cost of extrudates using the five different L/S ratios , and of the TMP using the three different L/S ratios tested was based on the mean price of electricity in Spain in 2016, i.e. 0.08 €/kW h (Endesa, 2016). Figure 27 shows the production cost for the different tested operating conditions. In accordance with the results of energy consumptions expressed in Paper III in the publication section, the different production costs, i.e. specific mechanical cost, specific cooling cost, specific heating cost and total specific cost followed the same trends. Referring to Figure 27 and Figure 28, as the L/S ratio increased, there was a decrease trend on mechanic, cooling and total costs. On the contrary, the heating cost increased a little. The mechanic, cooling and total costs decreased approximately 34%, 33%, and 26%, respectively, when the L/S ratio increased from 0.4 to 1.0 (Figure 28). In parallel, the heating cost was increased (+29%). However, the contribution of this specific term was limited compared to the two others, especially the mechanical one. As a result, the total production cost decreased from 0.077 to 0.056 €/kg dry matter when the L/S ratio increased, but it seemed to be level off between 0.7 and 1.0 L/S ratios (Figure 27).

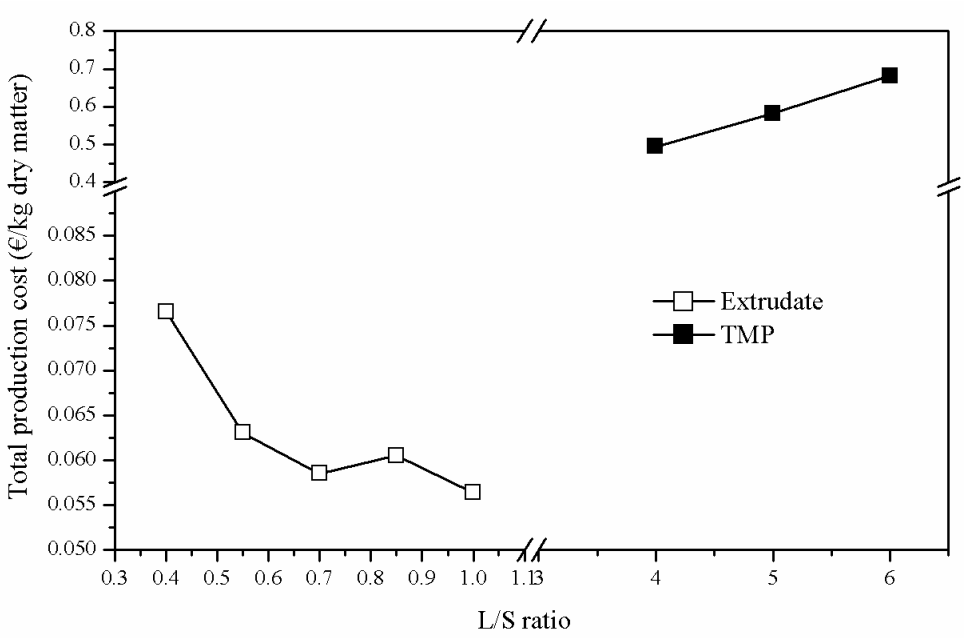


Figure 27. *Comparison on total production cost between extrusion and thermo-mechanical pulp.*

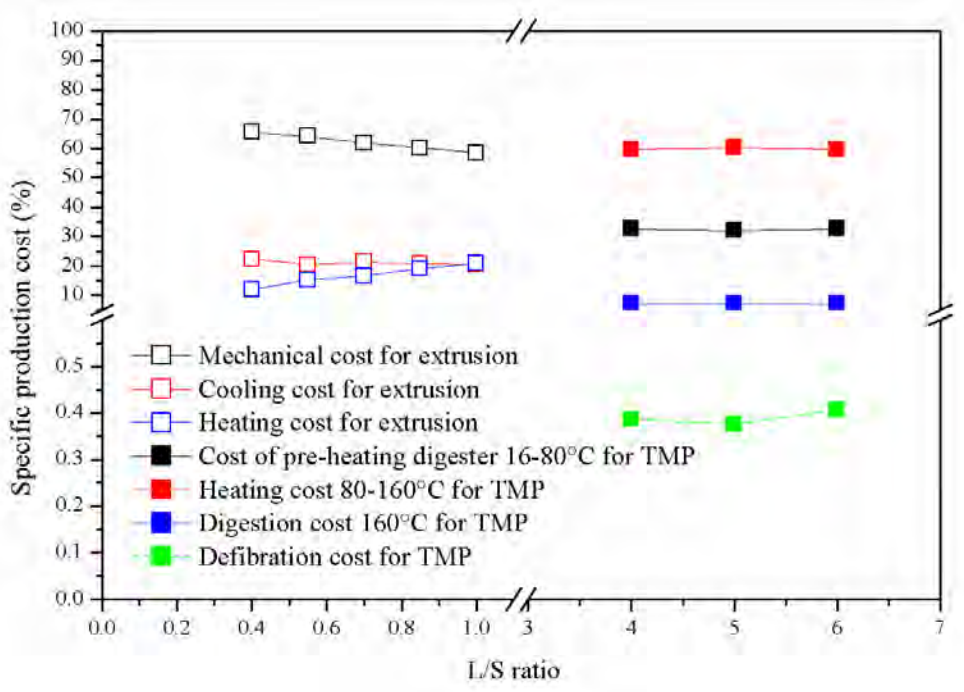


Figure 28. *Specific production cost of extrusion and pulping.*

Comparing twin-screw extrusion and digestion plus defibration, the influence of the liquid/solid ratio used on the specific cost of rice straw fiber pretreatment was opposed, i.e. a decrease in the total production cost for extrusion as opposed to its increase for digestion plus defibration with increasing liquid/solid ratio (Figure 27). The total production cost of pulp logically increased as the liquid/solid ratio used increased: from 0.49 €/kg dry matter at 4

liquid/solid ratio to 0.68 €/kg dry matter at 6 liquid/solid ratio. Thus, the price is about nine times more expensive than the twin-screw extrusion.

5.2.4 Pros and cons of twin-screw extrusion and pulping (Paper III)

Although, the twin-screw extrusion is cheaper on total production cost than pulping, the fiber pretreatment using these technologies have advantages and disadvantages as following. The advantages of extrusion including:

- Higher inlet flow rate and better productivity as a continuous process,;
- Lower amounts of water and lower temperature;
- Lower production cost, approximately nine times less important: the twin-screw extrusion technology appeared as a much more economical pretreatment for rice straw fibers;
- Higher aspect ratio, which should lead to an improvement of the entanglement of fibers inside fiberboards, thus possibly contributing to better mechanical reinforcement;
- Higher amount of water-soluble components, in particular free sugars: because such components can contribute to the self-bonding of fiberboards using hot pressing (Hashim et al., 2012, 2011a, 2011b; Tajuddin et al., 2016), this could be an advantage for their cohesion and mechanical strength.

On the other hand, taking into account the TGA results for both treated materials, extrudates were more thermal-sensitive than TMP. It will be probably necessary to use lower values for molding temperature during thermopressing (i.e. no more than 200 °C) in such a way as to avoid any degradation of organic compounds. In addition, establishing a parallel with papermaking, it is reasonable to assume that the ultimate strength of fiberboards made from TMP should be higher than that of fiberboards made from extrudates. Indeed, in the paper industry, a higher specific surface and a decrease in the mineral content (cases of TMP compared to extrudates) should promote the compatibility of lignocellulosic fibers, leading to an increasing amount of bonds between fibers (i.e. higher relative bonded area) and thus to a higher fiberboard compaction (Page, 1969; Vilaseca et al., 2008).

5.3 Characterization of CNF (Paper I)

In the present research, cellulose nanofibers (CNF) were prepared by means of TEMPO-mediated oxidation from commercial bleach eucalyptus pulp. The oxidized cellulose fibers consisted of 1006 μeq/g, 1460 μeq/g, 8.3 g/g, 95%, and 352 for carboxylic content, cationic demand, water retention value, production yield, and degree of polymerization, respectively (Table 9).

Table 9. *Properties of TEMPO-mediated oxidation CNF*

Sample	-COOH content (μeq/g)	Yield (%)	Cationic demand (μeq/g)	WRV (g/g)	DP
CNF	1006	>95	1460	8.3	352

The introduction of carboxylic groups in the cellulose chains produces swelling of the fibers in aqueous suspension (Da Silva Perez et al., 2003), due to the increase in its hydrophilic character (Saito et al., 2007). In addition, carboxylic groups also affect the degree of defibrillation; therefore pulps with higher carboxylic content require less passes through the homogenizer to achieve a good degree of microfibrillation (Alila et al., 2013; Benhamou et al., 2014; Besbes et al., 2011; Shinoda et al., 2012). CNF with high COOH content have a lower degree of polymerization (DP) than untreated fibers. The yield of fibrillation was also very high, meaning that almost all the solid material was effectively nanosized. CNF with low COOH content results in a lower yield of fibrillation (Besbes et al., 2011).

The cationic demand (CD) is a methodology to determine the outer surface charge of fibers, usually applied to pulp suspensions (Klemm et al., 2011; Rouger & Mutjé, 1984). It represents the anionic nature of the fibers and has been traditionally used to determine the extent of fiber delamination of beaten papermaking pulps. High cationic demand is expected for CNF due to large fibrillation and the anionic nature of cellulosic materials suspended in water (Carrasco et al., 1996; Mutjé et al., 2006).

The water retention value (WRV) is a papermaking parameter that is commonly used as a measure of fibers' internal fibrillation. WRV actually measures the water chemically bound to cellulose. A higher fibrillation allows larger amounts of moisture to bind to CNF through hydrogen bonds (Alcalá et al., 2013; González et al., 2014). The value found in this study was 8.3 g/g (Table 2) is in the range of that for other TEMPO-mediated oxidized fibers.

5.4 Characterization of lignin (Paper II)

The lignin used in this study was extracted from black liquor (a waste of pulp and paper factory using kraft pulping process). It was characterized the thermal sensitivity through thermogravimetric analysis (TGA). The TG and dTG curves of the lignin sample displayed the mass loss of polymeric materials *vs*. the temperature of thermal degradation (Figure 29).

A first mass loss was observed at 100 ºC, concurring with water vaporization. Then, the thermal degradation of all lignin compounds took place at a stage between 200 ºC and 500 ºC (approximately 72% of mass loss). At this stage, all carbohydrate volatile components in the lignin

sample were degraded. At higher temperature, there was no more weight loss, since the remaining mass corresponded to ash (about 19% of the total mass) by the end of the measurement. These results are in accordance with a previous study of (El Mansouri, Yuan, & Huang, 2011).

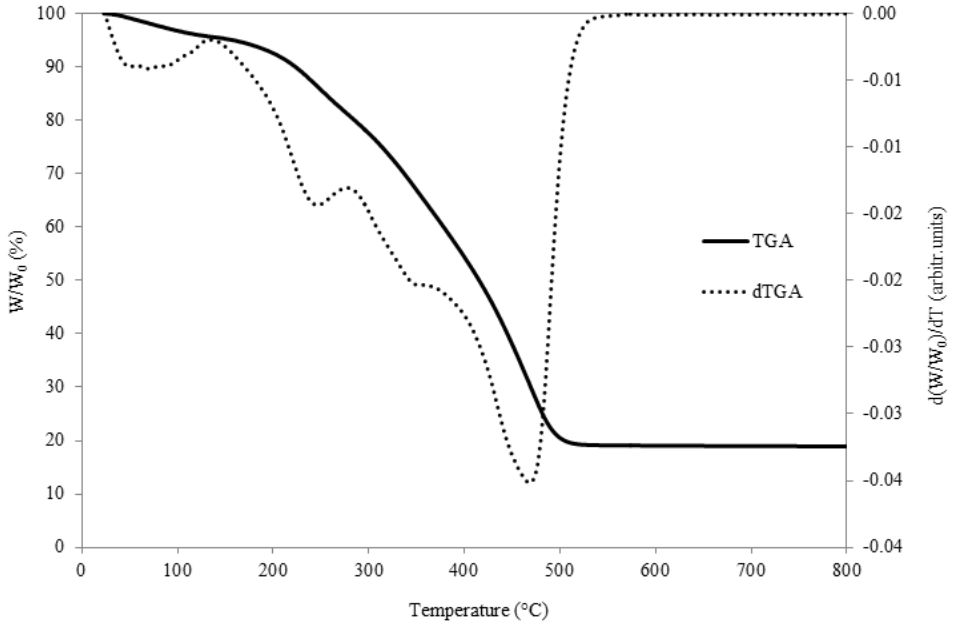


Figure 29. *Thermogravimetric analysis of kraft lignin.*

The peak of dTGA (derivative thermogravimetry) curve can be expressed as a single thermal decay temperature and used to compare its polymeric materials in term of thermal characteristics. This analysis illustrated that when the lignin sample was heated at about 450 ºC, pyrolytic deprivation took place and the inter-unit linkage of the lignin structure became fragmented, with the release of monomeric phenols into vapor phase. The range of obtained maximum derivative thermogravimetric was in agreement with other previous findings (El Mansouri et al., 2011; Tejado et al., 2007). The high temperature of lignin degradation allows applicable of blending it with other lignocellulosic materials and compress at quite high temperature to produce fiberboards without decomposed lignin.

5.5 Fiberboards

5.5.1 Binderless fiberboards made from corn TMP (Paper I & II) and rice straw TMP

The mechanical performance of fiberboard was characterized by the modulus of rupture (MOR) and the modulus of elasticity (MOE) (Teixeira & Moslemi, 2001). As shown in Table 10, the MOR and MOE of non-reinforced fiberboard were approximately 30 and 1874 MPa for corn stalk TMP, and 40 and 3421 MPa for rice straw TMP, respectively. The MOR were lower than that of commercial fibreboard (about 42 MPa), but the MOE of rice straw TMP was higher (2670

MPa for MOE of commercial fiberboard). However, as the binderless fibreboards made from corn stalk TMP and rice straw was denser than the commercial, leading the specific value of the MOR and MOE obtained lower than the commercial between 0.032 and 0.047 MPa.m^3/kg and 2.043 and 3.023 MPa.m^3/kg, respectively. In addition, all binderless fiberboards are classified as hardboard, following the European standard EN 316 (EN316, 1999) with density ≥ 900 kg/m^3 and ≥ 800 kg/m^3, wet process and dry process, respectively.

Binderless fiberboards made from RS-TMP showed greater values of MOR and MOE than that made with CS-TMP of about 37% and 83%, respectively (Table 10). Moreover, the RS-TMP fiberboard also obtained much higher on internal bonding strength and impact resistance than the CS-TMP fiberboard. The results confirmed that higher amount of water-soluble components, in particular free sugars can contribute to the self-bonding of fiberboards using hot pressing (Hashim et al., 2012, 2011a, 2011b; Tajuddin et al., 2016) . Additionally, the shorter fibers provided the denser fibers (Figure 26) and fiberboard (Table 10).

Table 10. *Results of mechanical properties and dimensional stability of binderless fiberboard.*

Properties	Commercial	CS-TMP	RS-TMP
Mechanical properties			
ρ (kg/m^3)	883 ± 19	917 ± 48	1106 ± 14
MOR (MPa)	41.7 ± 1.6	29.6 ± 0.9	40.4 ± 3.4
MOE (MPa)	2670 ± 110	1874 ± 164	3421 ± 399
MOR/ρ (MPa.m^3/kg)	0.047	0.032	0.037
MOE/ρ (MPa.m^3/kg)	3.023	2.043	2.850
IB (MPa)	0.47 ± 0.11	0.19 ± 0.07	0.35 ± 0.03
K (kJ/m^2)	10.8 ± 0.2	3.2 ± 0.5	4.3 ± 0.4
Dimensional stability			
TS (%)	65.7 ± 2.7	37.6 ± 0.7	33.9 ± 2.2
WA (%)	81.3 ± 0.5	76.8 ± 6.6	49.8 ± 1.3

The internal bonding strength (IB) refers to the strength of the internal bond between fibers (Mancera et al., 2012), while the resilience of impact strength (K) refers to the fragile rigidity of fiberboard (Evon et al., 2015). The same phenomenon was observed as the IB and K of the binderless fiberboards made from RS-TMP were stronger than those from CS-TMP, although all are still lower than the commercial fiberboard made from eucalyptus and pine wood fibers with urea-formaldehyde binder. The IB values were 0.19, 0.35, and 0.47 MPa for CS-TMP, RS-TMP and commercial fiberboard, respectively. The *Izod* impact strength, the resilience (K) values were 3.2, 4.3, and 10.8 kJ/m^2.

Thickness swelling (TS) and water absorption (WA) are two important parameters when determining the dimensional stability of fiberboards. The results in Table 10 indicated that the binderless made from CS-TMP and RS-TMP improved the TS over the commercial fiberboard, by decreasing about 43% and 48%, respectively.

Not only this, but also that the binderless fiberboard made from crop residues such as corn and rice meet the requirements for hardboards type used in dry conditions, i.e. board with thickness ≤ 3.5 mm (recommended 30 MPa, 0.5 MPa, and 37% for MOR, IB, and TS, respectively) (EN622-2, 2004).

5.5.2 Fiberboards with CNF incorporation (Paper I and Results and discussion)

The mechanical bending properties of fiberboards made from corn stalk and rice straw TMP fibers, the MOR and MOE was greater with increasing the CNF content. The maximum values were about 53 and 5160 MPa, respectively at 8 wt% of CNF for CS-TMP fiberboard, and about 55.8 and 3975 MPa, respectively at 2 wt% of CNF for RS-TMP fiberboard. The addition of CNF content was stopped at 10 % and 3% on CS-TMP and RS-TMP, respectively because of the decreasing on mechanical properties on these amount and higher (Table 11). The improvement mechanical properties of the fiberboard is due to several factors such as the high intrinsic mechanical properties of CNF, their high specific surface that enlarges the number of feasible hydrogen bonds, the reduction of void spaces between fibers due to tension forces and CNF shrinkage, and the homogeneous distribution of the fibers (Alcalá et al., 2013; Delgado-Aguilar et al., 2015). These factors are also contributed in the denser of the fibreboard panels. A scheme showing the interaction between fibers and CNF can be seen in Figure 30, where CNF are linked between them and to the macro fibers by creating a network (Alcalá et al., 2013).

It was also noticed that the modulus of rupture did not improve from the formulation from 2 to 8% of CNF on CS-TMP (Theng et al., 2015) and dropped when higher than 2% of CNF added on RS-TMP (Table 11). This might be due to the saturation of CNF nanofibers on the micro size fibers of corn TMP surface, or a poor dispersion condition during the biocomposites preparation, as indicating that more energy is needed in order to obtain a better dispersion and interaction between CNF and the larger fibers (Alcalá et al., 2013). Moreover, it is worth to consider that if the pulp has a high content of fines elements or the external fibrillation of fibers, this saturation may appear at lower levels of CNF (Delgado-Aguilar et al., 2015). In this case, the fines element of TMP was higher than 60%. Hypothetically if these fines were removed, the enhancement of mechanical properties provided by CNF would be higher and, consequently, the saturation level for CNF would be also higher (Kojima et al., 2016). Nonetheless, these results are in agreement with the results obtained by Cui et al. (2014) on particleboard made of *Pine (Pinus pinaster* L.),

for which it was found that the board with CNF 2% was the strongest. In addition, compared to the tested commercial fiberboard, they were also stronger on bending resistance. However, the density (above 1000 kg/m^3) was denser, too. Because of the high density of fiberboard with CNF reinforcement, it is noticed a similar specific strength with the commercial fiberboard.

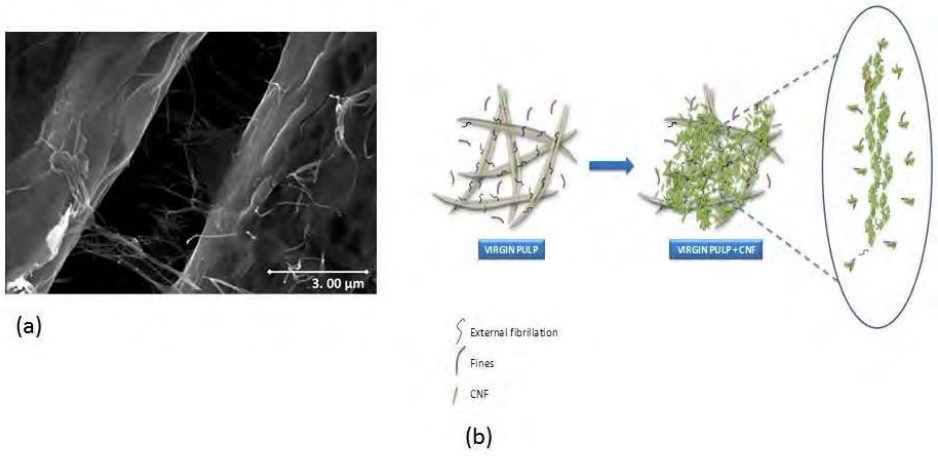


Figure 30. *SEM imaging of pulp slurry with CNF in bulk (a) and Mechanism of strengthening of fiberboards with CNF (b)*

Regarding the IB strength, a similar trend was observed compared to the other mechanical parameters mentioned above and the same to the report of González et al. (2013). The IB of the fiberboards was improved with the CNF addition. It is that the high specific area of CNF helped to strengthen the bonding capacity of fibers. The fiberboard with just 1% of CNF had an IB strength meet the required specification standard (EN622-2, 2004). The maximum strength was 1.53 MPa and 0.54 MPa obtained with 4% and 5% of CNF added on CS-TMP and RS-TMP fibers, respectively. The IB strength of CS-TMP with 4% CNF incorporation was about 8 times stronger than that of the neat fiberboard, while the RS-TMP plus 3% CNF was about double, compared to the neat. Additionally, all the CNF added on TMP improved the IB over the commercial fiberboard (Table 10 and Table 11).

Table 11. *Results of mechanical properties and dimensional stability of fiberboards made from corn stalk and rice straw TMP with CNF incorporation.*

Fiberboards' properties	**CS-TMP + CNF**							**RS-TMP + CNF**		
	0.5%	1%	2%	4%	6%	8%	10%	1%	2%	3%
Mechanical properties										
ρ (kg/m^3)	1106 ± 14	1110 ± 33	1143 ± 31	1100 ± 38	1115 ± 26	1129 ± 33	1069 ± 40	1069 ± 41	1103 ± 49	1063 ± 44
MOR (MPa)	42.7 ± 2.6	47.6 ± 1.6	52.0 ± 5.4	52.0 ± 1.1	52.8 ± 2.5	52.9 ± 4.2	47.3 ± 3.4	42.9 ± 2.5	55.8 ± 3.7	42.1 ± *3.6*
MOE (MPa)	4196 ± 201	4470 ± 303	4542 ± 224	4787 ± 194	5045 ± 376	5160 ± 506	4421 ± 284	3560 ± 282	3975 ± 290	3393 ± 339
MOR/ρ (MPa.m^3/kg)	0.039	0.043	0.046	0.047	0.047	0.047	0.044	0.040	0.051	0.040
MOE/ρ (MPa.m^3/kg)	3.79	4.03	3.97	4.35	4.52	4.57	4.14	3.120	3.605	3.192
IB (MPa)	0.46 ± 0.22	0.81 ± 0.20	1.26 ± 0.19	1.53 ± 0.12	0.98 ± 0.18	0.64 ± 0.14	0.54 ± 0.17	0.40 ± 0.02	0.40 ± 0.01	0.54 ± 0.04
K (kJ/m^2)	4.3 ± 0.6	4.4 ± 0.2	4.7 ± 0.6	5.6 ± 0.8	5.0 ± 0.5	4.8 ± 1.3	3.6 ± 0.5	4.7 ± 0.8	4.7 ± 0.9	4.2 ± 0.7
Dimensional stability										
TS (%)	35.8 ± 0.4	34.2 ± 0.5	33.3 ± 5.2	35.4 ± 1.8	34.1 ± 2.4	36.5 ± 2.4	37.1 ± 0.9	35.1 ± 1.6	31.3 ± 4.8	31.3 ± 1.9
WA (%)	51.0 ± 1.1	49.8 ± 3.8	47.3 ± 2.5	48.6 ± 2.0	47.9 ± 1.7	46.8 ± 2.1	55.9 ± 0.8	51.6 ± 2.1	43.8 ± 2.6	55.3 ± 3.4

Concerning on the results of Izod impact strength, the energy required to break fiberboard made with CNF addition was around 5 kJ/m^2 (Table 11), higher than that of non-reinforced fiberboards, but still very low with respect to the market products (10.8 kJ/m^2) (Table 10). The availability reason is that the formaldehyde-based resin present higher interface bonding strength (Castro et al., 2012) than the CNF.

The presence of CNF diminished the dimensional stability (Table 11). One explanation can be that CNF bring to a more compact final structure that prevents the penetration of water into the fiberboard. Even if they are hydrophilic, CNF are quite compatible with the rest of the components. Therefore, in a well distributed system, the interface between CNF and microfibers of pulps is favourable and the final result may be a more compacted material that absorbs less water than the non-reinforced one, and particularly compared to the commercial fiberboard.

Dynamic Mechanical Analysis (DMA) is a sensitive technique that characterizes the mechanical response of materials by monitoring property change with respect to the temperature and frequency of applied sinusoidal stress. This technique separates the dynamic response of materials into two distinct parts: an elastic part (E′) and a viscous component (E″). The complex modulus E* (E* = E′+iE″) is defined as the instantaneous ratio of the in-phase or elastic response E′ (which is proportional to the recoverable or, stored energy) and viscous response E″ (which is proportional to the irrecoverable or, dissipated energy). DMA has been also used to analyze the structural and thermo-mechanical properties of thermosetting adhesives (Kumar, Gupta, & Sharma, 2015). The DMA for commercial and CS-TMP fiberboards was also performed. The complex modulus is depicted in Figure 31. All fiberboards made from corn stalk TMP fibers gave better results than the commercial product. Moreover, the CNF incorporation produced a higher complex modulus that increased with increasing the CNF content (Alcalá et al., 2013; Besbes et al., 2011). In all cases, the stiffness decreased with increasing temperature (Kumar et al., 2015), as expected. However, while commercial and non-reinforced fiberboards show a constant decrease of rigidity with temperature, fiberboards reinforced with CNF exhibited some different tendency. Thus, the stiffness of the fiberboards show a diminish after 60-70°C due to an increase of mobility and start softening of the lignin and low molecular weights compounds. Afterwards, between 100-120ºC the complex modulus seems to stabilize and the slope decrease is very low. This preservation of the complex modulus, or even small stiffening in some formulation, may be caused by the release of water from the material that prevents the loss of rigidity of fiberboards (between 120 and 170 ºC approximately) (Barbosa et al., 2011). Thereafter, above 190°C, the complex modulus clearly diminished and the material began degradation (Alcalá et al., 2013) that is evident after 240°C.

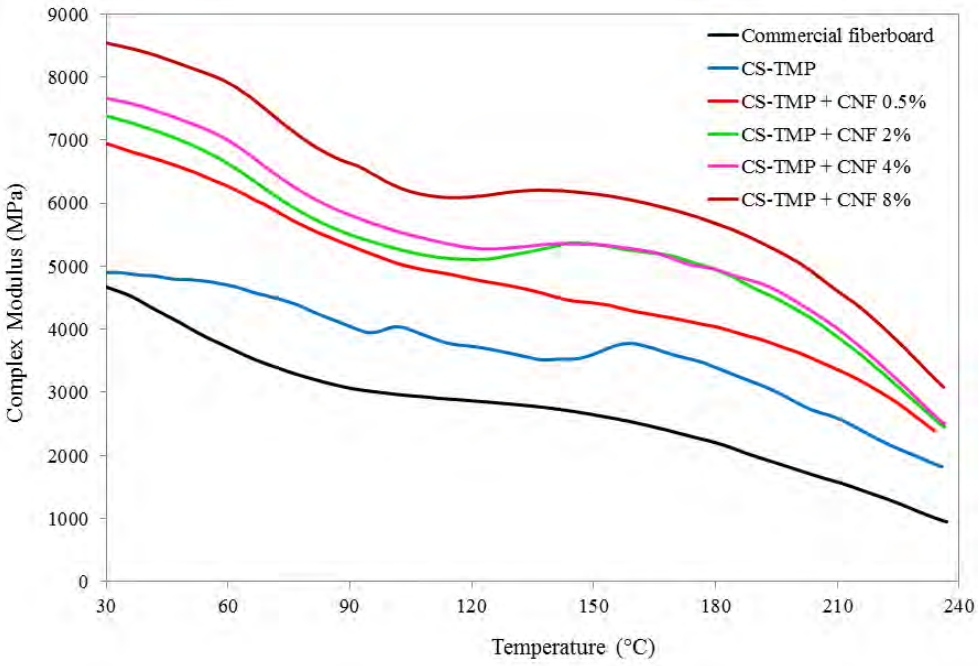


Figure 31. *Dynamic mechanical analysis (DMA) of corn stalk TMP fiberboard with CNF incorporation.*

5.5.3 Fiberboards with lignin incorporation (Paper II and Results and discussion)

The mechanical properties of bending for fiberboard made from CS-TMP and RS-TMP were enhanced by increasing amounts of added kraft lignin (Table 12). This improvement can be explained by the good adhesion between fibers produced by the addition of kraft lignin, which is able to overcome discontinuity in the fiber matrix. The maximal values of MOR for fiberboard made from CS-TMP and RS-TMP incorporated with kraft lignin addition were about 69 MPa (25% lignin) and 53 MPa (13% lignin), respectively. While the MOE was obtained at a little lower added lignin proportion, i.e. 21% and 9%, accounted for 5664 and 3955 MPa, for CS-TMP and RS-TMP fiberboard, respectively. To compare with the fiberboard made with CNF incorporation, the maximum MOR and MOE obtained with 2% added CNF was equilibrium to the one made with about 13% lignin addition with both raw materials (Table 11 and Table 12). The MOE of the fiberboards was notably increased as the lignin loading increased to 21% on CS-TMP, with a value over 5500 MPa, which is slightly higher than that obtained by adding CNF. However, it is not significant for RS-TMP between CNF and lignin addition. However, all are greater that of the commercial fiberboard.

The same tendency on density of the fiberboard was observed between kraft lignin and CNF addition on the TMP fibers of corn and rice. They are denser than 900 kg/m^3, regarded as hardboard (EN316, 1999). The specimens of fiberboards made from corn stalk TMP with lignin obtained higher specific strength, specific elasticity and internal bonding strength than the tested

commercial fiberboard, but they were lower in impact strength. Moreover, as the amount of lignin was increased, specific properties were enhanced as well. This indicates that, in the case that the addition of lignin and the high temperature at the thermopressing produced stronger bonds (*i.e.* covalent) increasing the density of the resulting panels as well as their mechanical properties. However, these properties were observed not significant difference for RS-TMP with lignin addition, compared to the market product.

The Table 12 also reveals the dimensional properties of fiberboard. The results showed that the values of TS and WA were decreased when increasing the amount of kraft lignin content on CS-TMP fiberboard. However, they were not significant different on RS-TMP fiberboard. Specifically, the addition of 29% kraft lignin decreased the TS and WA by about 50.5% and 33.6% compared with the binderless fiberboard and 54.3% and 63% with the commercial fiberboard, respectively. Therefore, increasing lignin content notably decreased the water absorption and, thus, improved the water resistance and dimensional stability of the fiberboards. Rowell *et al.* (1976) reported that lignocellulosic materials absorb water by forming hydrogen bonds between water molecules and hydroxyl groups in cell wall components. However, the addition of kraft lignin during the preparation of fiberboards reduced their water absorption. This result can be explained by the presence of non-polar hydro-carbon chains and aromatic rings in the lignin molecule (Rozman et al., 2000).

Table 12. *Results of mechanical properties and dimensional stability of fiberboards made from corn stalk and rice straw TMP with lignin incorporation.*

Fiberboards' properties	**CS-TMP + Lignin**							**RS-TMP + Lignin**		
	5%	9%	13%	17%	21%	25%	29%	9%	13%	17%
Mechanical properties										
ρ (kg/m^3)	1063 ± 47	1107 ± 38	1108 ± 54	1168 ± 54	1135 ± 45	1098 ± 28	1128 ± 14	1099 ± 41	1099 ± 53	1115 ± 44
MOR (MPa)	33.6 ± 1.8	43.9 ± 4.1	50.6 ± 5.6	60.0 ± 4.4	65.1 ± 1.4	69.1 ± 6.8	54.5 ± 4.3	41.2 ± 2.6	53.5 ± 4.4	43.9 ± 3.0
MOE (MPa)	2602 ± 319	4252 ± 322	4749 ± 271	5557 ± 252	5664 ± 283	5399 ± 351	5327 ± 283	3955 ± 394	3612 ± 137	3637 ± 346
MOR/ρ (MPa.m^3/kg)	0.032	0.040	0.046	0.051	0.057	0.063	0.048	0.38	0.49	0.39
MOE/ρ (MPa.m^3/kg)	2.45	3.84	4.29	4.76	4.99	4.92	4.72	3.60	3.29	3.26
IB (MPa)	0.34 ± 0.09	0.43 ± 0.15	0.48 ± 0.03	0.48 ± 0.06	0.51 ± 0.05	0.50 ± 0.2	0.35 ± 0.16	0.60 ± 0.05	0.47 ± 0.14	0.51 ± 0.04
K (kJ/m^2)	3.45±0.36	4.62±0.39	5.37±0.35	6.35±0.28	6.33±1.62	4.95±0.94	5.47±0.55	4.7 ± 0.5	5.2 ± 0.7	4.4 ± 0.3
Dimensional stability										
TS (%)	36.7 ± 3.6	32.6 ± 1.4	30.9 ± 2.2	29.1 ± 3.0	28.6 ± 0.1	26.7 ± 1.2	25.0 ± 2.8	30.4 ± 0.7	31.9 ± 3.3	29.7 ± 3.9
WA (%)	55.4 ± 1.7	50.5 ± 1.5	49.0 ± 3.1	37.6 ± 6.2	35.9 ± 3.7	37.4 ± 1.6	35.8 ± 2.1	47.1 ± 3.8	48.0 ± 4.0	44.0 ± 3.1

5.5.4 General comparison between commercial and green fiberboards

With the purpose of summarizing the obtained results, the main studied properties were used for comparison between the commercial fiberboards and those from both rice and corn (either binderless or containing CNF/lignin). The selected properties were Specific MOR, Specific MOE, WA and TS.

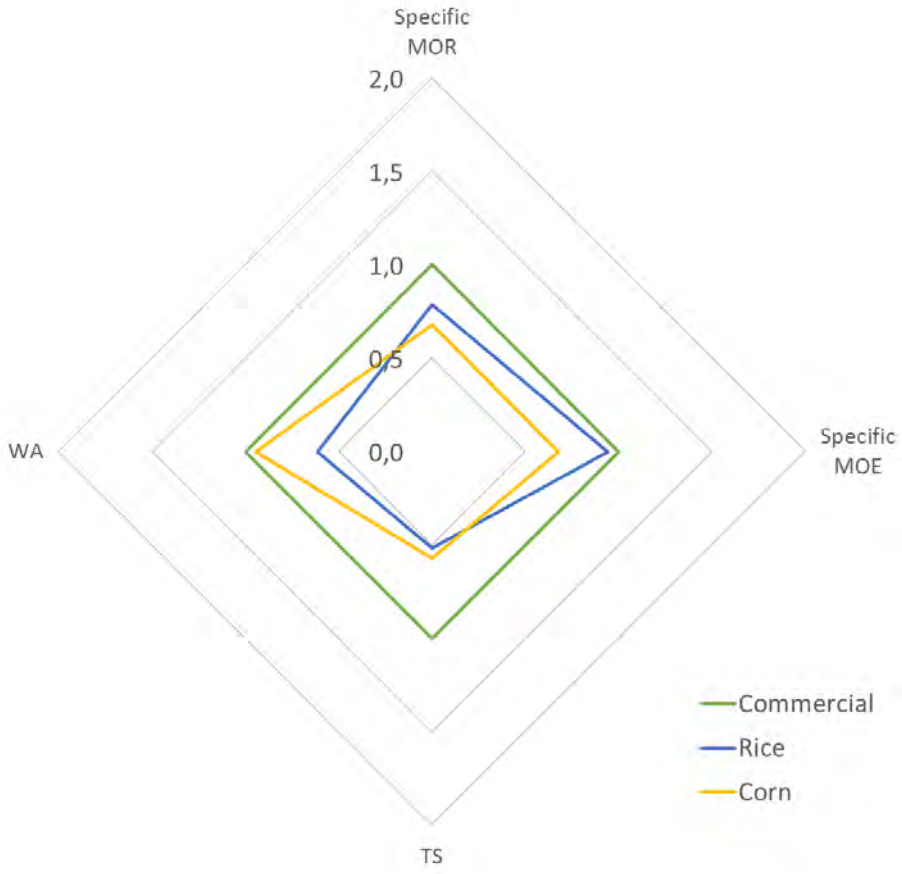


Figure 32. *Properties comparison between commercial and binderless fiberboards*

Figure 32, Figure 33 and Figure 34 show this comparison for binderless fiberboards, fiberboards containing CNF and fiberboards containing lignin, respectively. The original values of the obtained properties were relativized to the ones obtained for the commercial fiberboards, which a value of 1 was assigned. From this value, the rest of the properties were recalculated, showing the relative improvement with regard to the commercial fiberboard. In this sense, Figure 32 shows that binderless fiberboards (both from rice and corn) presented lower Specific MOR and MOE than the commercial fiberboard. Nonetheless, water absorption and thickness swelling were significantly lower. Exemplarily, TS was almost the half in both cases than commercial fiberboard, fact that brings to the light that the dimensional stability of the binderless fiberboards was significantly better and, thus, the feasibility of these fiberboards to be used outdoor becomes apparent. Something interesting is that binderless rice fiberboards presented improved physico-

mechanical properties than those made of corn, probably due to the higher presence of silica, wax and other extractables that made them less sensitive to water.

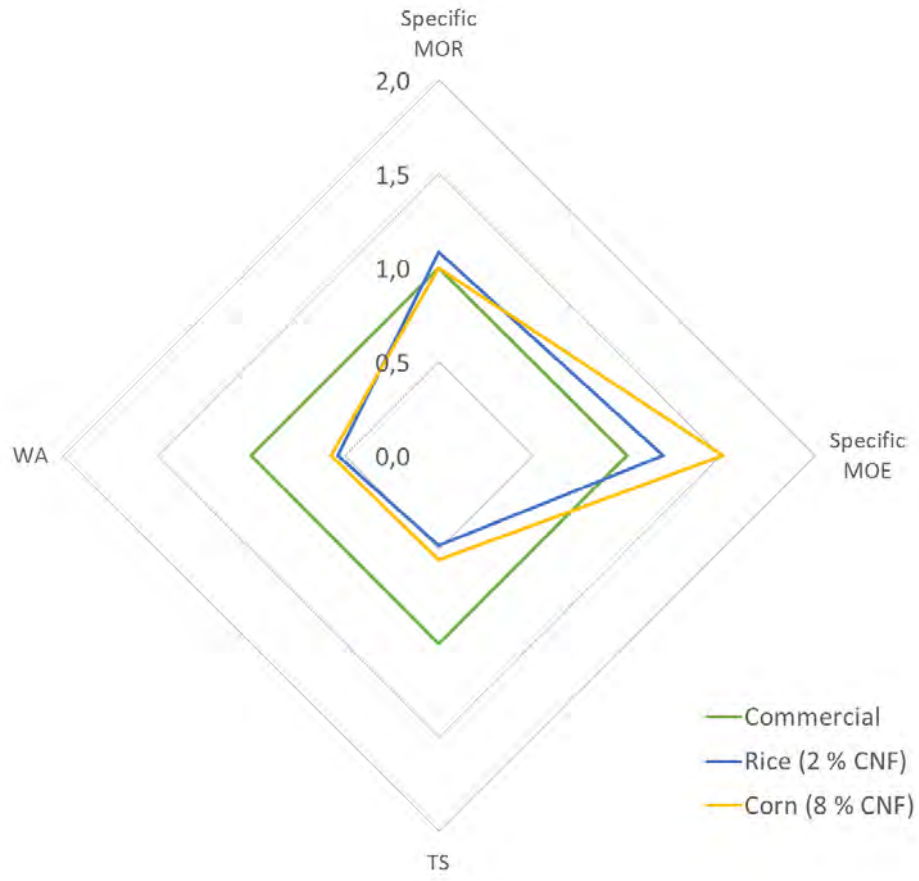


Figure 33. *Properties comparison between commercial and CNF-reinforced fiberboards*

Figure 33 shows the relative properties of the fiberboards containing CNF compared to the commercial one. As it is possible to see, 2 % CNF/rice and 8 % CNF/corn fiberboards have been selected for comparison, since these were those that presented better properties in each case. Corn fiberboard presented a MOR of the same magnitude than the commercial one, while that made of rice presented a slightly higher value. Contrarily, corn fiberboard presented higher MOE than both rice and commercial fiberboards, being about 50 % higher than the commercial one. No significant changes were observed in TS and WA of rice fiberboards, while corn fiberboards experienced a significant improvement, especially in the case of WA. At this point, green fiberboards absorbed the 50 % of the water that commercial fiberboards did.

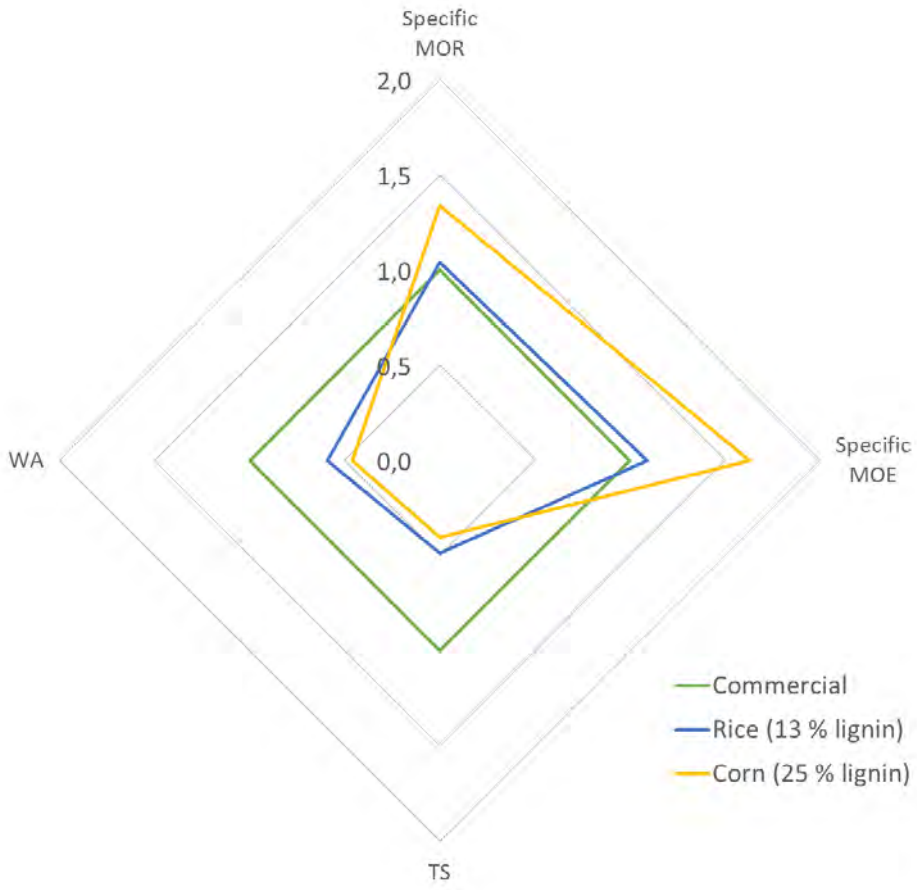


Figure 34. *Properties comparison between commercial and fiberboards containing lignin*

Finally, Figure 34 shows the relative properties of those fiberboards containing 13 and 25 % of lignin made of rice and corn fibers, respectively. Once again, these percentages were selected according to the above-mentioned criteria. As reflected, the mechanical properties of corn fiberboards were notably better than those from rice (13 % of lignin) and commercial fiberboards. In addition, physical properties (TS and WA) were significantly better as well. In the case of rice, mechanical properties were not significantly different from commercial fiberboards, while physical properties were considerably better.

Overall, the utilization of these alternative raw materials in combination with natural binders leaded to stronger and stiffer fiberboards than those made of wood with urea-formaldehyde resins. In addition, dimensional stability under wet environment was significantly better as well.

GENERAL CONCLUSIONS

6 GENERAL CONCLUSIONS

The conclusions of the thesis are the ones extracted in the two published papers as well as the other paper in review and some additional results from the experimental work that will be used to write new papers.

The chemical composition of corn and rice biomass revealed high cellulose and moderate lignin content, comparable to those of softwood, hardwood and other cellulosic sources. The cellulose and lignin were about 50 % and 16 % in corn biomass, 38 % and 7% in rice straw, 40-45 % and 26-34 % in softwood, and 38-49 % and 23-30 % in hardwood, respectively. Therefore, corn and rice biomass could be good candidates to be used as raw material for board making, substituting wood fibers.

Four different digestion conditions namely temperature and time of digestion were tested to identify the optimum condition based on high production yield with high mechanical properties of fiberboards. The temperatures were in range from 140 °C to 180 °C with time between 15 min and 30 min. The optimum condition for TMP preparation was selected at 160 °C, 15 min and 160 °C, 30 min for corn and rice biomass due to the yield (obtained about 87 % and 83 %) and the MOR and MOE (about 30 MPa and 1874 MPa for corn TMP, and 40 MPa and 3421 MPa, respectively).

A pilot scale twin-screw extruder was selected to study as a novel method to pretreat thermo-mechanical fractionation fibers for fiberboard manufacturing. The pilot scale twin-screw extrusion was conducted continuously at 15 kg/h wet matter of inlet flow rate. The fibers pulp produced by pulping and extrusion had similar characteristics, but a slightly different on morphological and thermal properties. The extrusion had no effect on chemical compositions change of the thermo-mechanical treatment, compared to the initial biomass. On contrary, some components were degraded at digestion step of pulping (particularly organic compounds of extractives), leading to a mass loss between 10 to 40 % depending on the different operating conditions such as temperature, time and L/S ratio. Nevertheless, as the result of degradation of some weak organic compounds in TMP, the pulps were higher thermal sensitive, compared to extrudates (the beginning of the thermal degradation on pulps occurred at around 230 °C instead of 205 °C on extrudates). The morphology of both TMP and extrudate were a slight decrease in mean length, mean diameter and mean aspect ratio when the quantity of water was reduced (from 22.4 to 20.9 of E_1 extrudate (L/S ratio 1.0) to E_5 (L/S ratio 0.4), and from 17.9 to 16.3 of P_3 TMP (L/S ratio 6.0) to P_1 (L/S ratio 4.0), respectively). In term of production costs, both thermo-mechanical treatment technologies expended more or less dependent on the L/S ratio. The total

production cost increased from 0.056 to 0.077 €/kg dry matter when the L/S ratio decreased from 1.0 to 0.4 at extrusion, and from 0.49 to 0.68 €/kg dry matter when the L/S ratio increased from 4 to 6 at digestion. In comparison the maximum total production costs of the two technologies, the twin-screw extrusion was about nine times cheaper than the pulping.

Fiberboards could be made from corn and rice TMP fibers through wet process methodology without any synthetic adhesives. The binderless fiberboards were somewhat good in term of mechanical and physical properties. For the fiberboards produced from the optimum TMP preparation condition, the MOR, MOE, TS, and WA obtained approximately 30 MPa, 1874 MPa, 38 %, and 77%, respectively for corn TMP fiberboard, and 40 MPa, 3421 MPa, 34 % and 50 %, respectively for rice straw TMP fiberboard. Cellulose nanofibers (CNF) were regarded as a high performance material with good mechanical and physical improvement in papermaking and other composites. However, it has a limited study on using it to improve the fiberboards' properties, replacing synthetic resin. Therefore, the CNF obtained by TEMPO-mediated oxidation was tried to incorporate with corn and rice TMP fibers to produce a strong and good fiberboard. At the same time, lignin obtained from industrial black liquor was also pretreated and integrated into the TMP fibers to produce green with good performance fiberboard products. As the influence of the natural binders (CNF and lignin), the MOR of fiberboards made from corn TMP and rice TMP were increased from 30 to 52 MPa and from 40 to 56 MPa with 2% CNF reinforcement, respectively. Additionally, the MOE were increased from 1874 MPa to 4542 MPa and from 3421 MPa to 3974 MPa, respectively (the optimum values). Meanwhile, the maximum MOR and MOE obtained around 69 MPa and 5399 MPa at 25 % lignin added on CS-TMP fibers, and about 53 MPa and 3612 MPa at 13 % lignin addition on RS-TMP, respectively. (The proportion of CNF and lignin added were stopped at10 % and 3 %, and 29 % and 17 % for corn and rice, respectively because of the MOR of fiberboards were declined). However, the density, TS and WA of all fiberboards made from different quantity of CNF and lignin added on CS-TMP and RS-TMP were not significantly different.

In comparison with the tested commercial fiberboard made from pine and eucalyptus wood and urea-formaldehyde as synthetic resin, the properties of fiberboards made from TMP fibers of corn stalk and rice straw with addition of CNF and lignin were improved. The optimum MOR obtained about 52 MPa and 56 MPa with 2 % of CNF added on CS-TMP and RS-TMP, respectively, while it was approximately 42 MPa for the commercial fiberboard. Furthermore, with 25 % of added lignin on CS-TMP (about 69 MPa MOR), and 13 % added on RS-TMP (around 53 MPa MOR). However, the density and impact resistance still need to be improved.

REFERENCES

7 REFERENCES

Abe, K., Iwamoto, S., & Yano, H. (2007). Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules, 8*(10), 3276-3278.

Alcalá, M., González, I., Boufi, S., Vilaseca, F., & Mutjé, P. (2013). All-cellulose composites from unbleached hardwood kraft pulp reinforced with nanofibrillated cellulose. *Cellulose, 20*(6), 2909-2921.

Alila, S., Besbes, I., Vilar, M. R., Mutjé, P., & Boufi, S. (2013). Non-woody plants as raw materials for production of microfibrillated cellulose (MFC): a comparative study. *Industrial Crops and Products, 41*, 250-259.

Anglès, M., Ferrando, F., Farriol, X., & Salvadó, J. (2001). Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition. *Biomass and Bioenergy, 21*, 211-224.

ASTM-D256-10e1. (2010). Standard test methods for determining the Izod pendulum impact resistance of plastics. ASTM International, West Conshohocken, PA.

Ayyachamy, M., Cliffe, F. E., Coyne, J. M., Collier, J., & Tuohy, M. G. (2013). Lignin: untapped biopolymers in biomass conversion technologies. *Biomass Conversion and Biorefinery, 3*(3), 255-269.

Barbosa, V., Ramires, E. C., Razera, I. A. T., & Frollini, E. (2010). Biobased composites from tannin–phenolic polymers reinforced with coir fibers. *Industrial Crops and Products, 32*(3), 305-312.

Barla, P. (2007). ISO 14001 certification and environmental performance in Quebec's pulp and paper industry. *Journal of Environmental Economics and Management, 53*(3), 291-306.

Beaumont, O. (1981). *Pyrolyse extractive du bois* (Unpublished doctoral dissertation). Ecole Nationale Supérieure des Mines de Paris, France.

Besbes, I., Vilar, M. R., & Boufi, S. (2011). Nanofibrillated cellulose from alfa, eucalyptus and pine fibres: preparation, characteristics and reinforcing potential. *Carbohydrate Polymers, 86*(3), 1198-1206.

Binod, P., Sindhu, R., Singhania, R. R., Vikram, S., Devi, L., Nagalakshmi, S., . . . Pandey, A. (2010). Bioethanol production from rice straw: an overview. *Bioresource Technology, 101*, 4767-4774.

Brady, B., & Dahlgren, T. (1998). *Chemical pulp mills*. Washington state air toxic sources and emission estimation methods. Department of Ecology. Washington State, USA.

Cotana, F., Cavalaglio, G., Gelosia, M., Coccia, V., Petrozzi, A., Ingles, D., & Pompili, E. (2015). A comparison between SHF and SSSF processes from cardoon for ethanol production. *Industrial Crops and Products, 69*, 424-432.

Cui, J., Lu, X., Zhou, X., Chrusciel, L., Deng, Y., Zhou, H., . . . Brosse, N. (2014). Enhancement of mechanical strength of particleboard using environmentally friendly pine (Pinus pinaster L.) tannin adhesives with cellulose nanofibers. *Annals of Forest Science, 72*(1), 27-32.

Chen, G., Zheng, Z., Yang, S., Fang, C., Zou, X., & Luo, Y. (2010). Experimental co-digestion of corn stalk and vermicompost to improve biogas production. *Waste Management, 30*, 1834-1840.

Chen, H. (2014). Chemical composition and structure of natural lignocellulose. In Chen H., *Biotechnology of Lignocellulose* (pp. 25-71). Chemical Industry Press, Beijing and Springer Science + Business Media Dordrecht. Springer Netherlands.

De Vrije, T., De Haas, G., Tan, G., Keijsers, E., & Claassen, P. (2002). Pretreatment of Miscanthus for hydrogen production by Thermotoga elfii. *International Journal of Hydrogen Energy, 27*(11), 1381-1390.

Delgado-Aguilar, M., González, I., Pèlach, M., De La Fuente, E., Negro, C., & Mutjé, P. (2015). Improvement of deinked old newspaper/old magazine pulp suspensions by means of nanofibrillated cellulose addition. *Cellulose, 22*(1), 789-802.

El Mansouri, N. E., Yuan, Q., & Huang, F. (2011). Characterization of alkaline lignins for use in phenol-formaldehyde and epoxy resins. *BioResources, 6*(3), 2647-2662.

EN310. (1993). Wood-based panels - Determination of modulus of elasticity in bending and of bending strength. European Committee for Standardization, Brussels, Belgium.

EN316. (1999). Wood fiberboard: Definition, classification and symbols. European Committee for Standardization, Brussels, Belgium.

EN317. (1993). Particleboards and fiberboards - Determination of swelling in thickness after immersion in water. European Committee for Standardization, Brussels, Belgium.

EN319. (1993). Particleboards and fiberboards - Determination of tensile strength perpendicular to the plane of the board. European Committee for Standardization, Brussels, Belgium.

EN323. (1993). Wood-based panels - Determination of density. European Committee for Standardization, Brussels, Belgium.

EN622-2. (2004). Fiberboard - Specifications Part 2: Requirements for hardboard. DIN Deutsches Institut für Normung e.V., Berlin. Beuth Verlag GmbH, 10772 Berlin, Germany,.

Endesa. (2016). Latest electricity and gas rates. Recovered March 1, 2017 https://www.endesaclientes.com/articles/latest-gas-light-regulated-rates.html

Espinosa, E., Tarrés, Q., Delgado-Aguilar, M., González, I., Mutjé, P., & Rodríguez, A. (2016). Suitability of wheat straw semichemical pulp for the fabrication of lignocellulosic nanofibres and their application to papermaking slurries. *Cellulose, 23*(1), 837-852.

Evon, P., Vinet, J., Labonne, L., & Rigal, L. (2015). Influence of thermo-pressing conditions on the mechanical properties of biodegradable fiberboards made from a deoiled sunflower cake. *Industrial Crops and Products, 65*, 117-126.

FAOSTAT. (2017). Production - Crops. Recovered January 20, 2017 http://www.fao.org/faostat/en/#compare

Flandez, J., González, I., Resplandis, J. B., El Mansouri, N. E., Vilaseca, F., & Mutjé, P. (2012). Management of corn stalk waste as reinforcement for polypropylene injection moulded composites. *BioResources, 7*, 1836-1849.

Garrote, G., Dominguez, H., & Parajo, J. (1999). Hydrothermal processing of lignocellulosic materials. *European Journal of Wood and Wood Products, 57*(3), 191-202.

Gosselink, R. J., van Dam, J. E., de Jong, E., Gellerstedt, G., Scott, E. L., & Sanders, J. P. (2011). Effect of periodate on lignin for wood adhesive application. *Holzforschung, 65*, 155-162.

Halvarsson, S., Edlund, H., & Norgren, M. (2008). Properties of medium-density fibreboard (MDF) based on wheat straw and melamine modified urea formaldehyde (UMF) resin. *Industrial Crops and Products, 28*, 37-46.

Hashim, R., Nadhari, W. N. A. W., Sulaiman, O., Kawamura, F., Hiziroglu, S., Sato, M., . . . Tanaka, R. (2011). Characterization of raw materials and manufactured binderless particleboard from oil palm biomass. *Material & Design, 32*, 246-254.

Hashim, R., Nadhari, W. N. A. W., Sulaiman, O., Sato, M., Hiziroglu, S., Kawamura, F., . . . Tanaka, R. (2012). Properties of binderless particleboard panels manufactured from oil palm biomass. *BioResources, 7*, 1352-1365.

Hashim, R., Said, N., Lamaming, J., Baskaran, M., Sulaiman, O., Sato, M., . . . Sugimoto, T. (2011). Influence of press temperature on the properties of binderless particleboard made from oil palm trunk. *Material & Design, 32*, 2520-2525.

Hatakeyama, T., & Hatakeyama, H. (2006). *Thermal properties of green polymers and biocomposites*. Springer Netherlands. doi: 10.1007/1-4020-2354-5.

Henriksson, M., Henriksson, G., Berglund, L., & Lindström, T. (2007). An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal, 43*(8), 3434-3441.

Hong, J., Zhou, J., & Hong, J. (2015). Comparative study of life cycle environmental and economic impact of corn-and corn stalk-based-ethanol production. *Journal of Renewable and Sustainable Energy, 7*(2), 023106.

Hoopen, E.-T., & Maïga, A. (2012). *Maize production and processing*. Recovered February 21, 2017 https://publications.cta.int/en/publications/publication/1724/

Hubbe, M. A. (2014). Puzzling aspects of the hydrophobic sizing of paper and its inter-fiber bonding ability. *BioResources, 9*(4), 5782-5783.

Hurter, R. (2006). Nonwood plant fiber characteristics. Recovered February 21, 2017 http://www.hurterconsult.com/HTMLobj-1361/plant%20fiber%20characteristics.pdf

IETD (Inudstrial Efficiency Technology Database). (2010). Mechanical pulping. Recovered February 21, 2017 http://ietd.iipnetwork.org/content/mechanical-pulping

Ilo, S., & Berghofer, E. (1999). Kinetics of colour changes during extrusion cooking of maize grits. *Journal of Food Engineering, 39*, 73-80.

Kabel, M. A., Bos, G., Zeevalking, J., Voragen, A. G., & Schols, H. A. (2007). Effect of pretreatment severity on xylan solubility and enzymatic breakdown of the remaining cellulose from wheat straw. *Bioresource Technology, 98*(10), 2034-2042.

Kanokkanjana, K., & Garivait, S. (2013). Alternative rice straw management practices to reduce field open burning in Thailand. *International Journal of Environtal Science and Development, 4*, 119-123.

Kartika, I. A., Pontalier, P., & Rigal, L. (2010). Twin-screw extruder for oil processing of sunflower seeds: Thermo-mechanical pressing and solvent extraction in a single step. *Industrial Crops and Products, 32*(3), 297-304.

Kim, S., & Dale, B. E. (2004). Global potential bioethanol production from wasted crops and crop residues. *Biomass and Bioenergy, 26*, 361-375.

Kojima, Y., Kawabata, A., Kobori, H., Suzuki, S., Ito, H., Makise, R., & Okamoto, M. (2016). Reinforcement of fiberboard containing lingo-cellulose nanofiber made from wood fibers. *Journal of Wood Science, 62*(6), 518-525.

Konica Minolta Sensing, I. (2007). *Precise color communication*. Recovered February 21, 2017 https://www.konicaminolta.com/instruments/knowledge/color/pdf/color_communication.pdf

Kramer, K. J., Masanet, E., Xu, T., & Worrell, E. (2009). Energy efficiency improvement and cost saving opportunities for the pulp and paper industry. An Energy Star Guide for Energy and

Plant Managers. Berkeley, US: Energy Analysis Department, University of California, USA.

Kumar, A., Gupta, A., & Sharma, K. V. (2015). Thermal and mechanical properties of urea-formaldehyde (UF) resin combined with multiwalled carbon nanotubes (MWCNT) as nanofiller and fiberboards prepared by UF-MWCNT. *Holzforschung, 69*(2), 199-205.

Lay, M., Méndez, J. A., Delgado-Aguilar, M., Bun, K. N., & Vilaseca, F. (2016). Strong and electrically conductive nanopaper from cellulose nanofibers and polypyrrole. *Carbohydrate Polymers, 152*, 361-369.

Lee, C. M., & Hunt, J. F. (2013). Binderless panel made from wood particles and cellulosic fibers. *US Patent No. 20130199743.* Washington, DC: US Patent and Trademark Office.

Lin, S. (1992). Commercial spent pulping liquors. In Stephen Y. L. & Carlton W. D. (eds.) *Methods in lgnin chemistry* (Part of the series in Springer series in wood science, pp. 75-80). Berlin: Springer.

Lin, Z., Liu, L., Li, R., & Shi, J. (2013). Screw extrusion pretreatments to enhance the hydrolysis of lignocellulosic biomass. *Journal of Microbial Biochemistry and Technology,* S12:002. doi: 10.4172/1948-5948.S12-002

López, F., Eugenio, M., Díaz, M., Nacimiento, J., García, M., & Jiménez, L. (2005). Soda pulping of sunflower stalks. Influence of process variables on the resulting pulp. *Journal of Industrial and Engineering Chemistry, 11*(3), 387-394.

Lora, J. H., & Glasser, W. G. (2002). Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials. *Journal of Polymers and the Environment, 10*(1-2), 39-48.

Luo, H., Yue, L., Wang, N., Zhang, H., & Lu, X. (2014). Manufacture of binderless fiberboard made from bamboo processing residues by steam explosion pretreatment. *Wood Res, 59*(5), 861-870.

Mancera, C., El Mansouri, N.-E., Pelach, M. A., Francesc, F., & Salvadó, J. (2012). Feasibility of incorporating treated lignins in fiberboards made from agricultural waste. *Waste Management, 32*, 1962-1967.

Mason, W. (1926). Process and apparatus for disintegration of wood and the like. *US Patent No. US1578609 A*. Washington, DC: US Patent and Trademark Office.

Mousavi, S. M. M., Hosseini, S. Z., Resalati, H., Mahdavi, S., & Garmaroody, E. R. (2013). Papermaking potential of rapeseed straw, a new agricultural-based fiber source. *Journal of Cleaner Production, 52*, 420-424.

Norgren, M., & Edlund, H. (2014). Lignin: Recent advances and emerging applications. *Current Opinion in Colloid & Interface Science, 19*(5), 409-416.

Oksman, K., Mathew, A. P., Bismarck, A., Rojas, O., & Sain, M. (2014). Handbook of green materials, bionanomaterials: *separation processes, characterization and properties Vol.5.* World Scientific.

Page, D. (1969). A theory for tensile strength of paper. *Tappi Journal, 52*(4), 674-681.

Pang, C., Xie, T., Lin, L., Zhuang, J., Liu, Y., Shi, J., & Yang, Q. (2012). Changes of the surface structure of corn stalk in the cooking process with active oxygen and MgO-based solid alkali as a pretreatment of its biomass conversion. *Bioresource Technology, 103*(1), 432-439.

Pelaez-Samaniego, M. R., Yadama, V., Lowell, E., & Espinoza-Herrera, R. (2013). A review of wood thermal pretreatments to improve wood composite properties. *Wood Science and Technology, 47*(6), 1285-1319.

Pinto, J., Cruz, D., Paiva, A., Pereira, S., Tavares, P., Fernandes, L., & Varum, H. (2012). Characterization of corn cob as a possible raw building material. *Construction and Building Materials, 34*, 28-33.

Rahnama, N., Mamat, S., Shah, U. K. M., Ling, F. H., Rahman, N. A. A., & Ariff, A. B. (2013). Effect of alkali pretreatment of rice straw on cellulase and xylanase production by local Trichoderma harzianum SNRS3 under solid state fermentation. *BioResources, 8*, 2881-2896.

Randy, D., & Lynn, M. (2013). Development of a business case for a cornstalks to bioprocessing venture. University of Guelph, Ridgetown Campus.

Rigal, L. (1996). Twin-screw extrusion technology and fractionation of vegetable matter. ENSC, Toulouse, France.

Rizvi, S. S., & Mulvaney, S. (1992). Extrusion processing with supercritical fluids. In Yano, T., Matsuno, R., & Nakamura, K. (eds.) *Development in Food Engineering* (pp. 814-816). New York: Springer.

Rowell, R. M., Gutzmer, D. I., Sachs, I. B., & Kinney, R. E. (1976). Effects of alkylene oxide treatments on dimensional stability of wood. *Wood Science, 9*(1), 51-54.

Rozman, H., Tan, K., Kumar, R., Abubakar, A., Ishak, Z. M., & Ismail, H. (2000). The effect of lignin as a compatibilizer on the physical properties of coconut fiber–polypropylene composites. *European Polymer Journal, 36*(7), 1483-1494.

Salthammer, T., Mentese, S., & Marutzky, R. (2010). Formaldehyde in the indoor environment. *Chemical Reviews, 110*(4), 2536-2572.

Sanjay, M., Arpitha, G., Naik, L. L., Gopalakrisha, K., & Yogesha, B. (2016). Applications of natural fibers and its composites: an overview. *Natural Resources, 7*(03), 108.

Schaffer, E. (1973). Effect of pyrolytic temperatures on the longitudinal strength of dry Douglas-fir. *Journal of Testing and Evaluation, 1*, 319-329.

Searle, S., & Malins, C. (2013). Availability of cellulosic residues and wastes in the EU. Recovered http://www.theicct.org/sites/default/files/publications/ICCT_EUcellulosic-waste-residues_20131022.pdf

Shao, S., Wen, G., & Jin, Z. (2008). Changes in chemical characteristics of bamboo (Phyllostachys pubescens) components during steam explosion. *Wood Science and Technology, 42*(6), 439.

Siró, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose, 17*(3), 459-494.

Sokhansanj, S., Turhollow, A., Cushman, J., & Cundiff, J. (2002). Engineering aspects of collecting corn stover for bioenergy. *Biomass and Bioenergy, 23*(5), 347-355.

Sridach, W. (2010). The environmentally benign pulping process of non-wood fibers. *Suranaree Journal of Science and Technology, 17*(2), 105-123.

Stelte, W. (2013). Steam explosion for biomass pre-treatment. Report. Energy & Climate Centre for Renewable and Transport, Section for Biomass, Danish Technological Institute.

Suchsland, O., & Woodson, G. E. (1987). Fiberboard manufacturing practices in the United States. Agriculture handbook/United States. Department of Agriculture, USA.

Sun, X., Wu, Q., Lee, S., Qing, Y., & Wu, Y. (2016). Cellulose Nanofibers as a Modifier for Rheology, Curing and Mechanical Performance of Oil Well Cement. *Scientific Reports*, 6:31654.
doi: 10.1038/srep31654.

T211. (1993). Ash in wood, pulp, paper and paperboard: combustion at 525 °C. *TAPPI Technical Services Department*. Georgia, USA.

T222. (1998). Acid-insoluble lignin in wood and pulp. *TAPPI Technical Services Department*. Georgia, USA.

T223. (2001). Pentosans in wood and pulp. *TAPPI Technical Services Department*. Georgia, USA.

Tajuddin, M., Ahmad, Z., & Ismail, H. (2016). A review of natural fibers and processing operations for the production of binderless boards. *BioResources, 11*, 5600-5617.

Tarrés, Q., Ehman, N. V., Vallejos, M. E., Area, M. C., Delgado-Aguilar, M., & Mutjé, P. (2017). Lignocellulosic nanofibers from triticale straw: The influence of hemicelluloses and lignin in their production and properties. *Carbohydrate Polymers*. Manuscript submitted for publication.

Teixeira, D. E., & Moslemi, A. (2001). Assessing modulus of elasticity of wood-fiber cement (WFC) sheets using nondestructive evaluation (NDE). *Bioresource Technology, 79*(2), 193-198.

Tejado, A., Pena, C., Labidi, J., Echeverria, J., & Mondragon, I. (2007). Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis. *Bioresource Technology, 98*(8), 1655-1663.

Thakur, V. K., & Thakur, M. K. (2015). Eco-friendly polymer nanocomposites. *Chemistry and Applications. Springer, 51*.

Theng, D., Arbat, G., Delgado-Aguilar, M., Vilaseca, F., Ngo, B., & Mutjé, P. (2015). All-lignocellulosic fiberboard from corn biomass and cellulose nanofibers. *Industrial Crops and Products, 76*, 166-173.

Thomas L., R. (1997). Rice anatomy. Section of Plant Biology, Division of Biological Sciences, University of California Davis. Recovered December 11, 2016
http://www-plb.ucdavis.edu/labs/rost/rice/Introduction/intro.html

Uitterhaegen, E., Nguyen, Q. H., Merah, O., Stevens, C. V., Talou, T., Rigal, L., & Evon, P. (2016). New Renewable and Biodegradable Fiberboards from a Coriander Press Cake. *Journal of Renewable Materials, 4*, 225-238.

Van Soest, P. J., & Wine, R. H. (1967). Use of detergents in the analysis of fibrious feeds. IV. Determination of plant cell wall constituents. *Journal of the Association of Official Analytical Chemists, 50*, 50-55.

Van Soest PJ, W. R. (1968). Determination of lignin and cellulose in acid detergent fiber with permanganate. *Journal of the Association of Official Analytical Chemists, 51*, 780-784.

Vandenbossche, V., Brault, J., Hernandez-Melendez, O., Evon, P., Barzana, E., Vilarem, G., & Rigal, L. (2016). Suitability assessment of a continuous process combining thermo-mechano-chemical and bio-catalytic action in a single pilot-scale twin-screw extruder for six different biomass sources. *Bioresource Technology, 211*, 146-153.

Vandenbossche, V., Brault, J., Vilarem, G., & Rigal, L. (2015). Bio-catalytic action of twin-screw extruder enzymatic hydrolysis on the deconstruction of annual plant material: case of sweet corn co-products. *Industrial Crops and Products, 67*, 239-248.

Vandenbossche, V., Doumeng, C., & Rigal, L. (2014). Thermomechanical and thermo-mechano-chemical pretreatment of wheat straw using a twin-screw extruder. *BioResources, 9*, 1519-1538.

Vignon, M., Dupeyre, D., & Garcia-Jaldon, C. (1996). Morphological characterization of steam-exploded hemp fibers and their utilization in polypropylene-based composites. *Bioresource Technology, 58*(2), 203-215.

Vilaseca, F., Mendez, J., Lopez, J., Vallejos, M., Barbera, L., Pelach, M., . . . Mutje, P. (2008). Recovered and recycled kraft fibers as reinforcement of PP composites. *Chemical Engineering Journal, 138*, 586-595.

Wegener, G. (1992). Pulping innovations in Germany. *Industrial Crops and Products, 1*(2-4), 113-117.

Wei, H., Rodriguez, K., Renneckar, S., & Vikesland, P. J. (2014). Environmental science and engineering applications of nanocellulose-based nanocomposites. *Environmental Science: Nano, 1*(4), 302-316.

Wilson, R. (2007). Early 20th-century building materials: Fiberboard and Plywood. Recovered February, 2017 https://www.fs.fed.us/t-d/pubs/pdfpubs/pdf07732308/pdf07732308dpi72.pdf

Wise, L. E., Murphy, M., & D Adieco, A. (1946). A chlorite holocellulose, its fractionation and bearing on summative wood analysis and studies on the hemicelluloses. *Paper Trade Journal, 122*(2), 35-43.

WPIF, TRADA, B., & TTF. (2014). Panel guide version 4. Wood Panel Industries Federation, and National Panel Products Division, and Timber Trades Federation. Recovered February 17, 2017 http://wpif.org.uk/uploads/PanelGuide/PanelGuide_2014_Annex2F.pdf

Yaning, Z., Ghaly, A. E., & BingXi, L. (2012). Physical properties of corn residues. *American Journal of Biochemistry and Biotechnology, 8*(2), 44-53.

Yu, Z., Zhang, B., Yu, F., Xu, G., & Song, A. (2012). A real explosion: The requirement of steam explosion pretreatment. *Bioresource Technology, 121*, 335-341.

Zhang, D., Zhang, A., & Xue, L. (2015). A review of preparation of binderless fiberboards and its self-bonding mechanism. *Wood Science and Technology, 49*(4), 661-679.

Zheng, J., & Rehmann, L. (2014). Extrusion pretreatment of lignocellulosic biomass: a review. *International Journal of Molecular Sciences, 15*(10), 18967-18984.