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BIORREFINERÍA FORESTAL INTEGRADA A PARTIR DEL PROCESO AL SULFITO ÁCIDO. SIMULACIÓN Y VÍAS DE VALORIZACIÓN

Integrated Forest Biorefinery from acid sulfite pulping process. Simulation and valorization opportunities

Memoria de Tesis Doctoral presentada para optar al título de Doctor por la Universidad de Cantabria

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RESUMEN GENERAL

Los conceptos de biorrefinería e ingeniería verde están teniendo una mayor importancia en el sector industrial. Existe un creciente interés en obtener productos tradicionalmente derivados del petróleo a partir de materias primas y procesos biológicos para alcanzar una economía sostenible. La disminución de la disponibilidad de materiales petrolíferos crea la necesidad de incrementar la eficiencia de los procesos existentes a través de la utilización de corrientes residuales o de subproductos, dando la oportunidad de avanzar en investigación y desarrollo de diferentes tipos de materia prima, productos y procesos. La industria de la pasta y el papel tiene el potencial de proporcionar dicha materia prima a través de la valorización de sus materiales residuales para producir biocombustibles, productos químicos y biomateriales.

La biorefinería es el procesado sostenible de biomasa en un espectro de productos comercializables (comida, pienso, materiales, químicos) y energía (combustibles, energía, calor) vía procesos bioquímicos, termoquímicos, químicos o mecánicos. Una biorrefinería puede desarrollarse a partir de varias plataformas, que son intermediarios que conectan diferentes sistemas y sus procesos. Son ejemplos las plataformas de azúcares, gas de síntesis y lignina. Las plataformas de azúcares y gas de síntesis están respectivamente basadas en la fermentación de los azúcares extraídos de la biomasa y en la gasificación de los residuos y subproductos de biomasa.

Una biorrefinería puede existir de forma independiente o puede ser implementada en una instalación existente, como una fábrica de pasta y papel, y compartir materia prima, energía y recursos materiales. Las fábricas con procesos Kraft y sulfito son adecuadas para implementar una biorrefinería. Varios estudios en bibliografía se han dedicado a la conversión de fábricas de pasta Kraft en biorefinerías pero muy pocos se han centrado en aquellas con proceso al sulfito. El caso de estudio de esta tesis doctoral está basado en una fábrica de pasta celulósica española que utiliza el proceso al sulfito y madera de *Eucalyptus globulus* y base cálcico-magnésica como materias primas.

Durante la etapa de cocción en el proceso al sulfito alrededor del 89% de la celulosa contenida en los chips de madera es transferida a la pasta mientras que el resto de fibras, parte de las hemicelulosas y la lignina van a parar al licor gastado, el cual es concentrado utilizando evaporadores de múltiple efecto antes de ser utilizado para la producción de lignosulfonatos, normalmente destruyendo los azúcares contenidos en el licor. Otra alternativa es utilizar el licor como fuente de partida para producir químicos de valor añadido y convertir la fábrica en una biorrefinería forestal integrada.

El objetivo principal de esta tesis es determinar la viabilidad técnica y económica de la integración de una biorrefinería en la fábrica existente. Con este propósito ha sido

necesaria la caracterización del subproducto del proceso, el licor gastado, con el fin de determinar sus componentes principales. El análisis químico determinó que los mayores componentes son los lignosulfonatos (50,6%) y los azúcares en forma monomérica (25.9%). Como la plataforma de lignina ya está explotada para la fabricación de lignosulfonatos, se ha propuesto la integración de la biorrefinería a partir de la plataforma de azúcares. Con esta premisa se ha realizado una búsqueda bibliográfica para determinar los potenciales productos que pueden fabricarse en la biorrefinería. De acuerdo a las referencias estudiadas, xilitol, etanol, polihidroxibutirato, polibutileno-succinato, furfural e hidrógeno aparecen como las opciones con más posibilidades, y además otros productos en menor proporción como ácido acético, metanol o vainilla. Debido al mercado, precio y disponibilidad del substrato de azúcares apropiado en el licor gastado, se han propuesto furfural, xilitol y etanol para ser estudiadas en mayor profundidad.

Teniendo en cuenta la caracterización y los resultados obtenidos en bibliografía, se realizó el diseño y la simulación de procesos de biorrefinería para transformar el licor gastado en productos de valor añadido. Primero, se realizó un análisis técnico mediante el estudio de la etapa detoxificación o fraccionamiento, esencial para recuperar una corriente rica en azúcares, la materia prima para las unidades de biorrefineria. A continuación se procedió con el desarrollo de los tres procesos previamente seleccionados (furfural, xilitol y etanol). El diseño de todos los equipos se llevó a cabo mediante simulación usando el software Aspen Plus. Este estudio dio como resultado tres procesos con capacidades de 19,9; 15,8 y 14,6 t/día respectivamente a partir de 1970 t/día de licor gastado.

Partiendo de los resultados obtenidos anteriormente, se realizó la evaluación económica de los tres procesos. Primero se realizó el dimensionado de los equipos así como los costes asociados a cada uno de ellos. A continuación se calculó el capital fijo de inversión y los costes de operación para cada escenario. Finalmente se computaron dos indicadores de rentabilidad, el Periodo de Retorno (PR) y el Valor Actual Neto (VAN). Teniendo en cuenta criterios como los costes estimados, el precio de venta, el potencial de mercado y las barreras técnicas de cada opción, se ha determinado que la opción más ventajosa es la implementación de una biorrerinería de xilitol en la fábrica existente.

Por otro lado y con la vista exclusivamente en el proceso actual, se ha llevado a cabo la modificación de diversas variables que afectan al proceso al sulfito, seleccionando primero el control del proceso de cocción mediante la modificación de la temperatura, obteniendo el modelado cinético de la etapa de digestión respecto al contenido de azúcares presentes en el licor gastado y no en la pasta. Estos resultados permiten adquirir el conocimiento necesario para predecir la evolución de los polisacáridos, monosacáridos y los productos de degradación a diferentes temperaturas (130-150ºC) desde un punto de vista de una futura biorrefinería. La novedad de este estudio se basa en el análisis del comportamiento del ácido acético, monosacáridos y productos de descomposición durante la hidrólisis de la madera de *Eucalyptus globulus* en contraste con otros estudios encontrados en bibliografía centrados en macrocomponentes de la madera como celulosa, hemicelulosa y lignina. Además la hidrólisis de la madera fue previamente estudiada por otros autores utilizando ácidos fuertes como el ácido sulfúrico. Sin embargo en este trabajo se ha utilizado el licor de cocción (formado por dolomita, agua y dióxido de azufre) como agente hidrolizante. Otro hecho importante es que los parámetros cinéticos fueron estimados usando el software Aspen Custom Modeler y no mediante análisis de regresión de los datos obtenidos a escala laboratorio, obteniéndose órdenes cinéticos superiores a uno en algunos casos. Los resultados mostraron que la transformación de los polisacáridos en monosacáridos se describe mejor mediante una reacción de orden cercano a tres, mientras que la transformación de monosacáridos en productos de descomposición puede ser descrita mediante una cinética de orden uno. Para la conversión de los grupos acetilo en ácido acético se consideró una reacción paralela dando como resultado una cinética de orden uno. El modelo muestra que temperaturas más altas promueven una obtención más rápida de azúcares; sin embargo, esto da como resultado valores más bajos de conversión máxima y también más productos de descomposición, dañinos en procesos posteriores. Teniendo en cuenta la conversión máxima de azúcares, 130ºC resulta la mejor alternativa, dando una conversión máxima de azúcares de 33,91mol% y de 13,81mol% para los productos de descomposición.

Finalmente se han estudiado dos grupos más de variables que afectan al proceso al sulfito: 1) chips de madera, mediante la comparación de dos especies (*Eucalyptus globulus* y *Eucalyptus nitens*) y 2) ácido de cocción, mediante la elección de la base (cálcica o magnésica) o el incremento de pH (de 1,5 a 2).

El eucalipto es uno de los géneros más utilizados para producir pasta de papel en Europa y específicamente en el norte de España, sin embargo en años recientes algunas enfermedades como la *Mycosphaerella* y pestes como *Gonipterus scutellatus* han afectado la cantidad disponible de esta madera. En este sentido, el *Eucalyptus nitens* puede ser utilizado como materia prima en el proceso de pasteado debido a su densidad, crecimiento, resistencia a enfermedades y su habilidad de producir vástagos.

En esta tesis se ha estudiado hasta qué punto la utilización de *E. nitens* afecta a los parámetros del proceso existente así como a las propiedades de la pasta obtenida y las oportunidades de valorización del licor gastado. En términos de plantación, el *E. nitens* se ve menos afectado por pestes y enfermedades y además es menos sensible a las heladas; además, tiene mayor tasa de crecimiento. Otra característica importante es la densidad, que en el caso estudiado es menor para el *E. nitens*. Sin embargo esta especie puede marcar la diferencia con crecimientos mayores y ocupando áreas donde el *E. globulus* no resiste, lo que significa que puede ser plantado satisfactoriamente en dichas áreas. Respecto a la composición química de ambas especies, el *E. nitens* presentó un mayor contenido de lignina que el *E. globulus* y un contenido similar de alfacelulosa, lo que teóricamente significaría que el *E. nitens* es un buen candidato para producir pasta *dissolving* y que además se conseguirían más subproductos, válidos para propósitos de biorrefinería. Para verificar estas premisas, se llevaron a cabo algunos experimentos a escala laboratorio, mostrando que en la primera parte del proceso, la etapa de impregnación, el *E. nitens* necesita un poco más de tiempo para alcanzar la impregnación deseada de la madera. Sin embargo, en la segunda etapa del proceso, la etapa de cocción, el *E. nitens* da una mayor concentración de lignina en el licor gastado con solo un ligero decremento en el contenido de azúcares además de peores resultados en los parámetros de calidad de la pasta. Por ello se recomienda reducir la temperatura de la etapa de digestión para mejorar las propiedades de la pasta y disminuir la formación de productos de descomposición a partir de la fracción hemicelulósica del licor gastado, consiguiendo así mayor productividad en el proceso.

Con respecto a las modificaciones realizadas sobre el licor de cocción, se ha corroborado como un incremento del pH consigue menores velocidades en el proceso al sulfito y además una reducción de los lignosulfonatos y el contenido total de azúcares en el licor gastado. También se estudió otro factor, la base del licor de cocción, que fue modificada sustituyendo el calcio por magnesio. El resultado de estos experimentos mostró que no se consigue la producción de una mayor cantidad de azúcares en el licor.

ABSTRACT

The biorefinery and green engineering concepts are becoming increasingly important in the industrial sector. There is an increasing industrial interest in obtaining traditional petrochemical based products from bio-based feedstocks and processes in order to attain a sustainable economy. The reduction of the available petrochemical feedstocks creates the necessity to increase the efficiency of existing processes through the utilization of existing waste and by-product streams, giving the opportunity to advance the research and development of different types of feedstock, products and processes. The pulp and paper industry has the potential to provide the feedstock through the valorization of its waste materials to produce biofuels, chemicals and biomaterials.

Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat) via biochemical, thermo-chemical, chemical or mechanical processes. A biorefinery can be built around several platforms which are intermediates that connect different biorefinery systems and their processes. Examples are sugar, syngas and lignin. Sugar and syngas platforms are respectively based on the fermentation of sugars extracted from biomass feedstock and on the gasification of biomass residues and by-products. Another platform of importance is the lignin platform. Lignin can be burnt for electricity and heat generation but can also be used as feedstock for the production of chemicals, novel materials and syngas.

A biorefinery can be a standalone facility or can be implemented within an existing facility such as a Pulp and Paper (P&P) mill to share feedstock, energy and material resources. Kraft and sulfite mills are suitable to be used as receptors for biorefinery implementation. Several studies in literature have been dedicated to the conversion of Kraft pulp mills into Integrated Forest Biorefineries but very few have focused on the sulfite pulping process. The case study presented in this thesis is based on a Spanish acid sulfite mill using *Eucalyptus globulus* wood and calcium-magnesium base as raw materials.

During the cooking step of the sulfite pulping process, about 89% of the cellulose contained in the wood chips is transferred to the pulp while the rest of the fibers, part of the hemicelluloses and lignin end up in the spent liquor, which is concentrated using multiple effect evaporators before being used for lignosulfonate production, normally destroying the sugar substrate of the liquor. Another alternative is to use the spent liquor as a resource for the production of value added chemicals and convert the sulfite pulp mill into an Integrated Forest Biorefinery.

The main objective of the thesis is to determine the feasibility of integrating a forest biorefinery into the existing sulfite pulp mill, technically and economically. For this purpose it has been necessary to characterize the resulting by-product of the process,

the spent liquor, in order to determine its main components. The chemical analysis determined that lignosulfonates (50.6%) and sugars in monomeric form (25.9%) are the major components. As the lignin platform is already exploited by the manufacturing of lignosulfonates, the proposal of the integration of the forest biorefinery through the sugar platform has been the selected option. Thus, a literature search has been done in order to determine the potential end-products of the biorefinery. According to the studied references, xylitol, ethanol, polyhydroxybutyrate, polybutylene-succinate, furfural and hydrogen seem to be the most feasible options. Other minor alternatives can be acetic acid, methanol and vanillin. Due to the market, price and the availability of the appropriate sugar substrate in the spent liquor; furfural, xylitol and ethanol were proposed to be further studied.

Taking into account the characterization and literature results obtained up to now, the design and simulation of biorefinery processes to transform the spent liquor into value-added products has been done. A technical study was carried out firstly by the study of the detoxification/fractionation step, essential to recover a stream rich in sugars, the raw material for the biorefinery units. Afterwards, the development of the three previously selected processes (furfural, xylitol and ethanol) has been carried out. The design of all the equipment has been performed by simulation using the software Aspen Plus. This assessment resulted in processes with respective capacities of 19.9, 15.8 and 14.6 Ton/d from 1970 Ton/d of spent liquor.

From these results an economic evaluation was performed. Firstly the sizing and costing of all the equipment has been done. Then the fixed capital invested (FCI) and the manufacturing costs (COM) of each option were carried out. And finally two profitability indicators as Return Period (RP) and Net Present Value (NPV) were developed. Taking into account criteria such as estimated costs, selling price, market potential, and technical barriers, it was determined that the implementation of a xylitol biorefinery into the selected sulfite pulp mill would be the most advantageous option.

On the other hand and with a view to the existing process, the modification of some variables affecting sulfite pulping has been carried out, selecting firstly the cooking control by means of the temperature variation, obtaining the kinetic modeling of the digestion stage regarding the sugar content present in the spent liquor and not in the obtained pulp. These results allow the acquisition of the knowledge for the prediction of the evolution of polysaccharides, monosaccharides and degradation products at different temperatures (130^{o}C-150^{o}C) from a future biorefinery point of view. The novelty relies on the study of the behaviour of acetic acid, monosaccharides and decomposition products during the hydrolysis of *Eucalyptus globulus* wood in contrast to other studies which were focused on macrocomponents such as cellulose, hemicellulose and lignin. Furthermore the hydrolysis was previously reported mainly using strong acids such as sulfuric acid. However in this work, the cooking liquor of the sulfite process, formed by dolomite, water and sulfur dioxide, was used as an hydrolysis agent. Another important issue is that the kinetic parameters were estimated using Aspen Custom Modeler Software and not by regression analysis of data produced at laboratory scale, giving kinetic orders of more than one in some cases. The results obtained show that the transformation of polysaccharides into monosaccharides is better described by a reaction order close to 3 while the transformation of monosaccharides into decomposition products can be described with a kinetics of 1. The conversion of acetyl groups into acetic acid has been considered as a parallel reaction giving first order kinetics results. The model shows that higher temperatures accelerate the production of sugars; however this induces a lower sugar conversion and also more decomposition products which are harmful to further processing. Taking into account the maximum sugar conversion, 130^{o}C is the best alternative, giving a maximum sugar conversion of 33.9 mol% and 13.8 mol% for decomposition products production.

Also, two additional groups of variables that affect the sulfite cooking have been studied. Wood chips by means of the comparison of two species (*Eucalyptus globulus* and *Eucalyptus nitens*); and cooking acid by means of the choice of base (Calcium or Magnesium) and the increase of pH (from 1.5 to 2).

Eucalyptus is one of the genus most commonly used in Europe and specifically in the north of Spain to produce pulp. However, in recent years some diseases, such as *Mycosphaerella,* and pests, such as *Gonipterus scutellatus,* have affected the quantity available of this wood. In this way, *Eucalyptus nitens* can be used as raw material in the pulping process due to its wood density, growth, disease resistance and coppice ability.

In this thesis, how far *E. nitens* affects the parameters of the existing process as well as the properties of the obtained pulp and the valorization opportunities of the spent liquor is studied. In terms of forestry characteristics, *E. nitens* is less affected by pests and diseases and is also less sensitive to frosts. Furthermore it has higher growing data. Another important characteristic is the wood density which in the studied case is lower for *E. nitens*. However, *E. nitens* can make a difference with higher growth and occupying areas where *E. globulus* does not survive; which means that it could be planted successfully in these areas. Regarding the chemical composition of both species, *E. nitens* presented a higher content of lignin and similar content of alpha-cellulose than *E. globulus* in the studied case, which theoretically would mean that *E. nitens* is a good candidate for producing dissolving pulp and furthermore it would produce more byproducts, utilizable for biorefinery purposes. To verify this, some laboratory tests were carried out, showing that in the first part of the process, the impregnation step, *E. nitens* needs a bit more time to reach the desired impregnation of the wood. However, in the second step of the process, the cooking stage, *E. nitens* gives a higher concentration of lignin in the spent liquor with only a little decrease in the sugar content and worse results of the quality parameters in the dissolving pulp. A decrease of the temperature of the digestion is recommended in this case in order to improve the properties of pulp and decrease other decomposition products in the hemicellulose fraction of the spent liquor, giving more productivity in the process.

It has been corroborated that the increase of the pH induces slow rates in sulfite pulping and a reduction of lignosulfonates and total sugar content in the spent liquor. Also, the base of the cooking acid was modified substituting Calcium with Magnesium, and also the results corroborated that the reaction rates were faster using Magnesium, however this fact did not benefit the production of sugars in the spent liquor.

LIST OF ABBREVIATIONS

AC	Acetyl Groups
ATR	Attenuated Total Reflectance
BR	Biorefinery
COM	Manufacturing Costs
DcP	Decomposition Products
DM	Dry matter
DP	Degree of polymerization
FCI	Fixed Capital Invested
FP	Final Products
FTIR	Fourier Transform Infrared
GBR	Green Biorefinery
GHG	Green House Gases
HMF	Hydroxymetylfurfural
HPLC	High Performance Liquid Chromatography
IFBR	Integrated Forest Biorefinery
LCF-BR	Lignocellulosic Feedstock Biorefinery
LS	Lignosulfonates
MF	Total Mass Flow
MS	Monosaccharides
NPV	Net Present Value
PBS	PolyButylene-Succinate
PHA	PolyHydroxyAlkanoates
PHB	Polyhydroxybutyrate
PHK	Prehydrolisis Kraft
POL	Polymers

PS	Polysaccharides
P&P	Pulp and Paper
RP	Return Period
SEW	SO_2, ethanol, water
SL	Spent liquor
SPORL	Sulfite pretreatment to overcome recalcitrance of lignocellulose
SSL	Strong Spent Liquor
TGA	ThermoGravimetric Analysis
TOC	Total Organic Carbon
TSS	Total Suspended Solids
WC-BR	Whole Crop Biorefinery
WSL	Weak Spent Liquor

GENERAL INTRODUCTION

1. BIOREFINERIES

Biorefinery has been defined by the International Energy Agency as the "sustainable processing of biomass into a spectrum of marketable products and energy" (IEA, 2008). The products can be intermediates or final products such as food, feed, materials or chemicals whereas energy includes fuels, power and heat. Different feedstocks and technologies can be used to obtain these products and from different platforms (Diep et al., 2012).

The concept was born a long time ago. In the preindustrial era until the 19th century, renewable raw materials were the major source of energy and material use (Schlosser and Blahušiak, 2011). With the Industrial Revolution, the use of other products increased. Coal was used to produce energy and chemicals.

Nowadays the environmental concern, mainly due to green house gases (GHG) emission and the reduction of the availability of fossil fuels, have meant that other sources to get energy and chemicals are being explored, such as biomass (Pandey et al., 2015).

Biomass is a renewable source of carbon, composed of a mixture of organic molecules containing hydrogen, usually including oxygen, often nitrogen and also small quantities of other components, including alkali, alkaline earth and heavy metals. Biomass takes CO_2 from the atmosphere while it is growing and returns it as it is burned, thus its use can reduce the carbon emissions compared to fossil fuels. The replacement of fossil-based carbon by renewable carbon from biomass leads to the development of biorefinery facilities (IEA, 2008).

1.1. Classification

Biorefineries can be classified into standard types based on different criteria: feedstock used, the platform-type, products made, type of technology used or the source of auxiliary energy (IEA, 2008). The basic idea of this classification approach is that each individual biorefinery system can be classified using the following main features (listed in order of importance): Platforms, products, feedstocks and processes. Each feature consists of several subgroups which are described below.

Platforms

Platforms are intermediates which link feedstock and final products and constitute the main "pillars" of this biorefinery classification, since they might be reached via different conversion processes applied to various raw materials (Cherubini et al., 2009). Conversion of these platforms to marketable products can be carried out using the different processes described later.

The most important platforms which can be recognized in energy-driven biorefineries are the following (Cherubini et al., 2009):

- Six carbon sugars, from hydrolysis of sucrose, starch, cellulose and hemicellulose.
- Five carbon sugars, from hydrolysis of hemicellulose and food and feed side streams. They are more difficult to be fermented to biofuels and bioproducts.
- Oils, from oilseed crops, algae and oil based residues.
- Biogas, from anaerobic digestion.
- Syngas, from gasification.
- Hydrogen, from water-gas shift reaction, steam reforming and fermentation.
- Organic juice, which is the liquid phase extracted after pressing wet biomass.
- Pyrolytic liquid, a multicomponent mixture, from pyrolysis.
- Lignin, from the processing of lignocellulosic biomass.
- Electricity and heat, which can be internally used to meet the energy needs of the biorefinery or sold to the grid.

Products

Another classification can be made focusing on the products from the biorefinery which can be energetic and non-energetic and can be grouped into two main classes (Cherubini et al., 2009):

1. Energy-driven biorefinery systems where the biomass is primarily used for the production of secondary energy carriers (transportation biofuels, power and/or heat); feed products are sold (current situation), or can be upgraded to added-value biobased products, to optimize economic and ecological performances of the full biomass supply chain.

2. Material-driven biorefinery systems which primarily generate biobased products (biomaterials, lubricants, chemicals, food, feed, etc.) and process residues that can be further processed or used to produce energy (for internal use or sale).

Feedstock

Kamm et al. (2006) established four different systems which use different feedstock: dedicated crops (which include crops from oil, sugar or starch, lignocellulosic crops, grasses and marine biomass), or residues such as lignocellulosic residues, organic or oil-based residues.

1. The Lignocellulosic Feedstock Biorefinery (LCF-BR) extracts different compounds (cellulose, lignin and hemicellulose) from cereals, reed, forest biomass or paper and cellulosic municipal solid waste using biotechnological or chemical methods (Van Ree and Annevelink, 2007). The conversion products which can be obtained such as furfural or hydroxymethylfurfural (HMF) have a good position within both the traditional petrochemical and the future biobased products.

2. Another kind of biorefinery is the Whole Crop Biorefinery (WC-BR), in which the major use of the feedstock and a wider range of products can be achieved. As its own name suggests, different parts of the raw material can be taken into account, the grain, the meal and the straw (Langeveld et al., 2012). As the LCF-BR this BR can use biotechnological, chemical and physical pathways to obtain isolated sugars or lignin which are the precursors to obtain different products.

3. Green Biorefinery (GBR) starts from green biomass and can obtain on one hand the press juice, which is a source of proteins and soluble sugars, and on the other hand the press cake, a source of lignocellulose and cellulose by means of different pathways (biochemical, physical, hydrothermal, enzymatic...) with the purpose to obtain feed, fuels, chemicals and materials (Van Dyne et al., 1999).

4. The Two-Platform Concept includes the sugar platform and the syngas platform. The “sugar platform” is based on biochemical conversion processes and focuses on fermentation of sugars extracted from biomass feedstocks. The “syngas platform” is based on thermochemical conversion processes and focuses on the gasification of biomass feedstocks and by-products from conversion processes (Kamm et al., 2006). Lignin is thermochemically treated (Langeveld et al., 2012).

Figure 1 shows schematically the different systems described above.

Processes

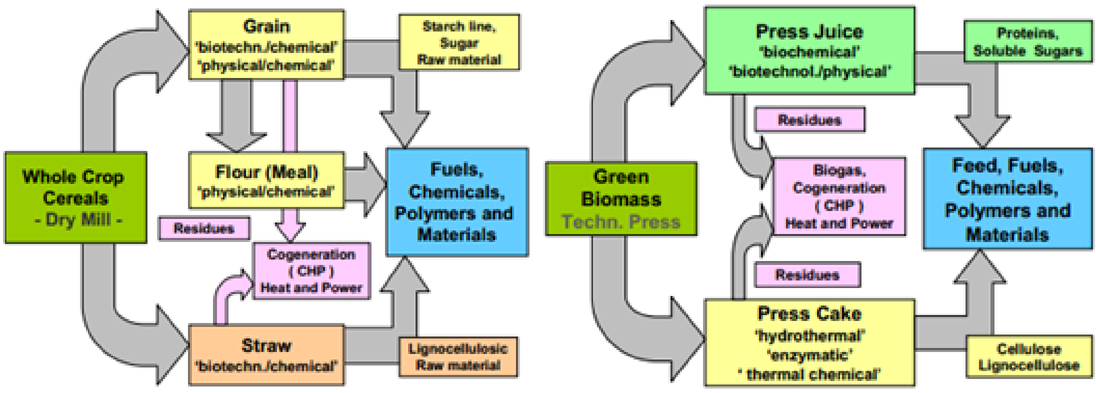
In biorefinery systems, several technological processes can be applied to convert biomass feedstock into marketable products. This classification approach identifies four main subgroups of processes:

1. Mechanical/physical (e.g., pressing, pre-treatment, milling, separation, distillation), which do not change the chemical structure of the biomass components, but they only perform a size reduction or a separation of feedstock components (FitzPatrick et al., 2010; Menon and Rao, 2012).

2. Biochemical (e.g., anaerobic digestion, aerobic and anaerobic fermentation, enzymatic conversion), which occur at mild conditions (lower temperature and pressure) using microorganisms or enzymes (Demirbas, 2009a; Octave and Thomas, 2009).

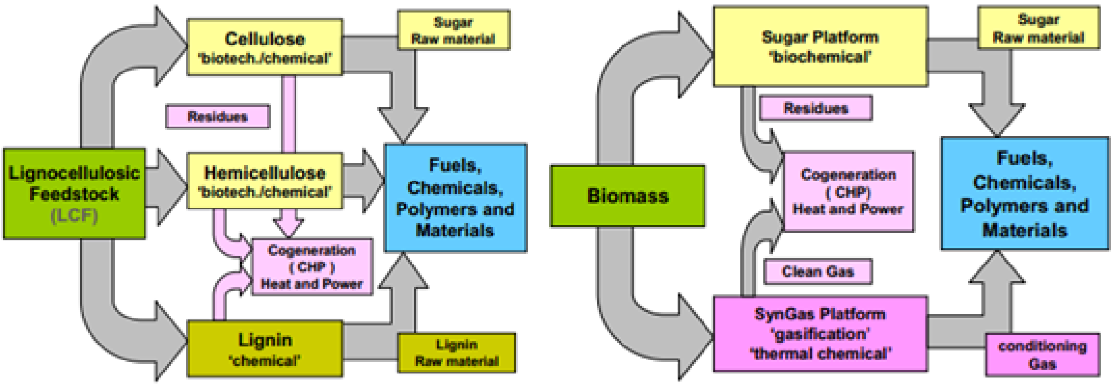
3. Chemical processes (e.g., hydrolysis, transesterification, hydrogenation, oxidation, pulping), where a chemical change in the substrate occurs (Naik et al., 2010; Cheng et al., 2011).

4. Thermochemical (e.g., pyrolysis, gasification, hydrothermal upgrading, combustion), where feedstock undergoes extreme conditions (high temperature and/or pressure, with or without a catalytic mean) (Demirbas 2009b; Menon and Rao, 2012).



Whole Crop Biorefinery

Green Biorefinery



Lignocellulosic Feedstock Biorefinery

Two-platform Concept

Figure 1. Biorefinery systems proposed by Kamm et al. (2006)

One of the first introducers of biorefinery units is the pulp and paper (P&P) industry because they have the knowledge about wood and the technology to transform it.

2. PULP INDUSTRY

A biorefinery can be a standalone facility or can be implemented within an existing facility such as a pulp and paper (P&P) mill to share feedstock, energy and material resources. The P&P industry consists of manufacturing enterprises that convert predominantly woody plant material into a wide variety of pulps, papers and paperboards. It is a driving force in many areas and it is at the heart of the forest products industry, as can be seen in figure 2.

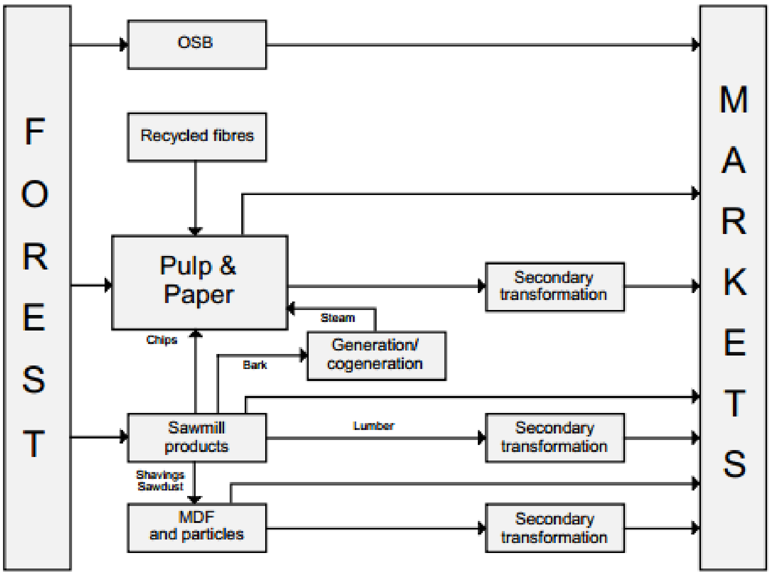


Figure 2. Interconnection of the P&P industry with other areas (Ministère des Ressources Naturelles du Québec, 2000)

The pulp industry is globally competitive and attractive from the standpoint of sustainability and environmental compatibility. In many ways, this industry is an ideal example of a desirable, self-sustaining industry which contributes favorably to many areas of our daily lives. Moreover, there is no doubt that it will continue to play an important role in the future (Sixta, 2006).

From the raw material, the wood, a wide variety of products can be manufactured depending on the process used. In this epigraph a detailed description of both raw material and transformation processes has been done.

2.1. Raw material: wood

Wood has remained an important substance throughout history because of its unique and useful properties. Wood is recyclable, renewable and biodegradable. Nowadays wood is used in tools, buildings, furniture, packaging, and thousands of other products.

The forest is an abundant source of renewable biomass. If managed and exploited responsibly, the forest biomass has a net zero carbon footprint. In addition, forests are not in competition with food crops for arable land and they can grow on marginal land.

According to data extracted from EUROSTAT (Statistical Office of the European Communities), in 2010 Spain had a total area of 27.74Mha of forest and other wooded land (18.17Mha and 9.57Mha respectively), which turned it into the second country of Europe in forest resources, behind Sweden. The upward trend of the forest surface can lead Spain to increase the productivity of forest products, decreasing the dependence of imports as well as increasing the opportunities for the forest industry of this country.

Wood is mainly formed by four components: cellulose, hemicellulose and lignin in more grade, followed by the extractives content in a minor proportion. Each of these components contributes to fiber properties, which ultimately impact on the product properties. Below these components are described.

Cellulose

Cellulose is the main component of wood as well as the most abundant organic compound in nature. Structurally, it can be defined as a lineal homopolymer constituted by β-D-glucopiranose units, linked by glucosidic bonds β (1→4), by those two molecules of glucose are joined by two hydroxyls of 1 and 4 carbons, removing a water molecule (Fengel and Wegener 1984; Sjöström 1993). The numerous hydroxyl groups facilitate the formation of intra and inter-molecular hydrogen bonds. These hydrogen bonds are established with other chains that are on the same plane or with chains of higher or lower planes. In this way the cellulose chains are joined forming microfibers, and the union among them, the cellulose fiber, those aggregates constitute the cell wall (Lennholm and Henriksson, 2007).

Regarding its macromolecular structure, the cellulose is organized by crystalline and amorphous zones. The inter-molecular hydrogen bonds are what give the uniform structure, that is, they give it a high degree of crystallinity. This structure is less uniform giving amorphous zones, more reactive regions since the accessibility to the hydroxyl groups is higher (Annergren, 1996). The usual degree of polymerization (DP) is around 10000. The structure of cellulose can be seen in figure 3.

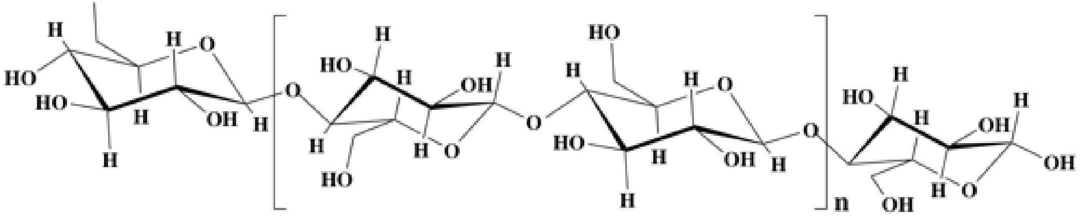


Figure 3. Cellulose structure

Hemicellulose

The hemicelluloses are a wide group of polysaccharides located in the plant cell wall and they constitute the second more abundant polysaccharide in nature. Their function is to serve as a bridge between cellulose and lignin. Hemicelluloses have more hydrolysis rate in acid medium and alkali solubility and lower DP than cellulose (200-300). Hemicelluloses have a heterogeneous composition of various sugar units, being classified as xylans (β-1,4-linked D-xylose units), mannans (β-1,4-linked D-mannose units), arabinans (α-1,5-linked L-arabinose units) and galactans (β-1,3-linked D-galactose units) (Spiridon and Popa, 2008).

There are different types and amount of hemicelluloses in hardwoods (angiosperms) and softwoods (gimnosperms). Hardwoods contained primarily glucuronoxylans, while softwoods contain mainly galactoglucomannans (Spiridon and Popa, 2008). Both hardwood and softwood oligomers are composed essentially by monomers of different types, such as xylose, glucose, mannose, galactose, arabinose, glucuronic acid and acetic acid. These quantities of monomers make the hemicelluloses a material with a great interest for research, for the sake of obtaining different products from the valorization of those sugars. The structure of the main monomers of the hemicelluloses can be seen in figure 4.

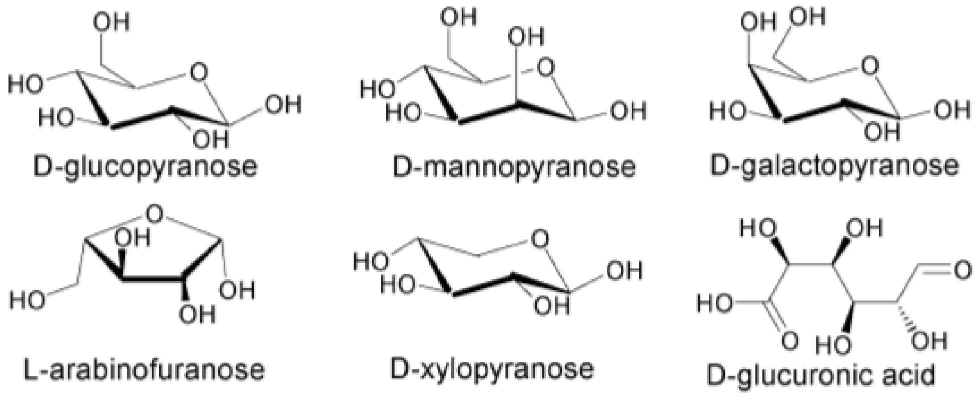


Figure 4. Main monomers of the hemicelluloses

Lignin

Lignin is a natural macromolecule of phenolic character which is found in the plant cell wall. It is formed by three main units of phenylpropanoids (monolignos) whose precursors are the guaiacyl alcohol (G), syringyl alcohol (S) and p-hydroxyphenil (H) (Santos et al., 2013).

The structure of lignin is especially complex and consists of a three-dimensional network randomly connected to the hemicelluloses which are associated to the lignin through xylose, arabinose and galactose units and glucosidic, bencilic eter and ester bonds, creating lignin-polysaccharides complex (Watanabe, 2003). The main function of the lignin in the plant is to act as a biologic barrier as well as union material which links the hemicelluloses with the cellulose, forming the cell wall.

Due to the difficulty of isolating the lignin from the wood without causing its partial degradation, it is not possible to know precisely its molecular weight, although it is estimated that it can oscillate between 1000 and 20000 Da (Adler, 1977). The structure of lignin proposed by Adler (1977) is shown in figure 5.

Extractives

Extractives, also called accessory compounds, are molecules of diverse nature with low to moderately high molecular weights, which by definition are soluble (extracted) in organic solvents (terpenes, fats, waxes and phenols) or hot water (tannins and inorganic salts) (Sixta, 2006). They impart color, odor, taste, and, occasionally, decay resistance to wood. There are hundreds of compounds in the extractives of a single sample of wood. The composition of extractives varies widely from species to species, from heartwood to sapwood and with the age of the tree (Biermann, 1996). Also there are variations depending on the geographical site and seasons (Sixta, 2006).

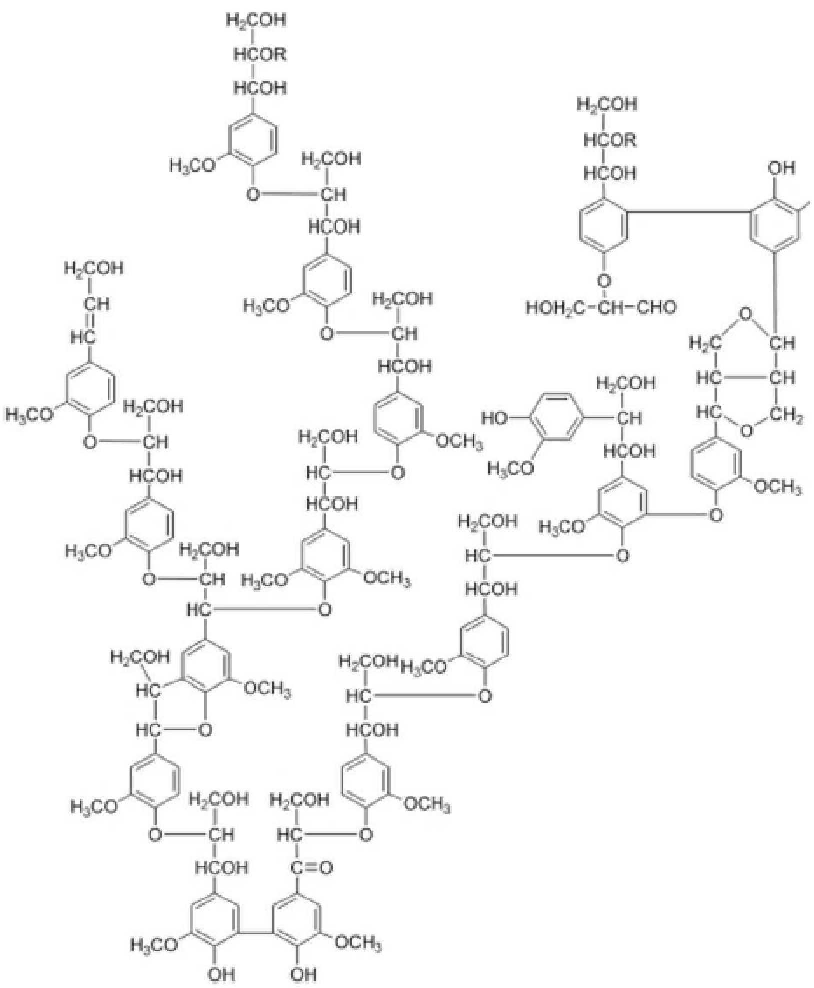


Figure 5. Structural model of the molecule of lignin proposed by Adler in 1977 (Adler, 1977)

2.2. Pulping processes and dissolving pulp

The isolation of lignin from the carbohydrates of wood is necessary for the production of cellulosic pulps. The quality of the pulp derives from the technology used in its production, which procures the release of the cellulosic fibers by combining the chemical or mechanical action in different proportions, including the thermal action (Smook, 2002).

The pulping processes can be divided into three main groups taking into account the character of separation (mechanical, semi-chemical and chemical).

Figure 6 presents a diagram with the characteristics of the pulps related to the actions used in their manufacturing. The chemical pulps, on the left, are obtained by means of a cooking or digestion process with chemicals. At the other extreme are the mechanical pulps, which are obtained by means of physical defibration and refining of the wood and which require a significant electrical energy consumption. Between both extremes of quality, it is important to point out the differences among processes, given by the final yield with respect to the initial quantity of wood, the level of organic components content (mainly lignin) and the energy consumption (Casey, 1990; Smook, 2002).

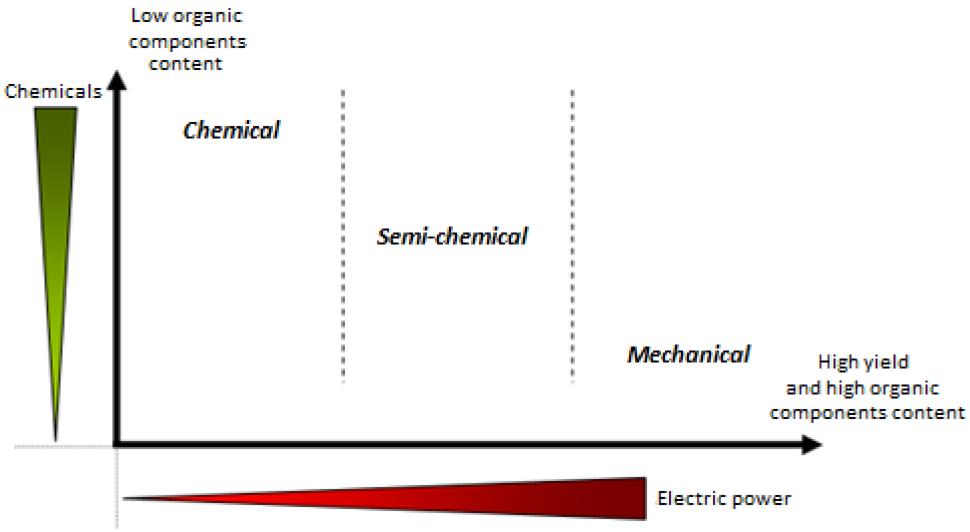


Figure 6. Comparison of pulp production processes

The production of mechanical pulp requires a pretreatment of the wood with steam (even in some cases with a sulfite solution) prior to the separation of the fibrous material by means of abrasive refining (Smook, 2002).

Semi-chemical pulping processes consist of a combination of chemical and mechanical processes. Fundamentally, they are based on a chemical treatment preceded by a mechanical refining step. These processes are normally included in the classification of chemical processes.

In chemical processes, the delignification or separation of the fibrous constituent of the wood (the cellulose) from the binding agent (the lignin), is carried out by means of the action of several chemicals (acid, alkali or organic) in digesters that operate at high temperature and pressure. At these conditions, the major part of the lignin is dissolved and withdrawn in the spent liquors of the cooking process (Fardim, 2011).

In this work, the pursued product of the pulping process is the dissolving pulp, a type of pulp that is primarily intended for the preparation of chemical derivatives of cellulose also referred to as high alpha-cellulose pulp. The main characteristics of dissolving pulps contrary to paper pulps are a higher purity in cellulose with low content of hemicelluloses, lignin, extractives and ash. In addition, dissolving pulps represent pulps with a uniform molecular weight distribution, a pre-determined viscosity, high brightness and a high reactivity towards specific chemicals (Strunk, 2012). This kind of pulp is used for the manufacturing of a wide variety of products included in three big groups: i) regenerated fibers or films (e.g. viscose, Lyocell or

Cuprammonium processes; used mostly in apparel, furnishing, tires, packaging, feminine products or diapers); ii) cellulose ethers (carboxymethyl-, ethyl-, methyl-, propyl-; used mostly in detergents, cosmetics, food, pharmaceuticals, textiles, paper, paints, oil drilling muds, coatings and inks); and iii) cellulose esters (acetates, propionates, butyrates, nitrates; used mostly in apparel, cigarette filters, furnishing, plastics; lacquers, films and explosives (nitrates)) (Paleologou, 2012). The hemicelluloses content is a critical quality parameter for the dissolving pulp grade, as the presence of hemicelluloses, such as mannan and xylan, has a strong negative effect on the post processing operations of dissolving pulp (Liu et al., 2011).

The two main processes for the production of dissolving pulp are the caustic pre-hydrolysis sulfate process (also called PHK) and the acid sulfite process (Hiett, 1985). Both present variations, fundamentally in pulping and bleaching (Sixta, 2006). Below a brief description of each one is given.

PHK process

The PHK process is an adaptation of the traditional Kraft process in which the quantity of hemicelluloses extracted from the wood during the cooking stage is lower in comparison to the acid sulfite process. Thus, a pre-hydrolysis stage is needed and a pulp with better brightness conditions is obtained (Bajpai, 2012).

The pre-hydrolysis stage is carried out at elevated temperatures (150-180^{o}C) with water or diluted inorganic acid (sulfuric or aqueous sulfur dioxide) requiring times up to two hours. Hemicelluloses removal results in an improvement of the delignification rate, which reduces the cooking time and/or the chemical charge required for getting an equal target of delignification degree, and enhances the subsequent bleaching process (Martín-Sampedro et al., 2014).

The hemicelluloses-depleted wood chips are then subjected to a simple Kraft process to remove lignin. The second stage is an alkaline delignification using sodium hydroxide (NaOH) and sodium sulfide (NaS), giving a cooking liquor with high pH. The cooking process is carried out at 160-180^{o}C for 2-4 hours (Smook, 2002). After this time, the unbleached pulp is obtained and it is submitted to several purification stages: washing, where the black liquor is recovered; bleaching and drying.

Sulfite process

Sulfite pulping can be carried out over a wide range of pH. A mixture of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-) is used to attack and solubilize the lignin. "Acid sulfite" denotes pulping with an excess of free sulfurous acid (pH 1-2), while "bisulfite" process is carried out under less acidic conditions (pH 3-5) (Smook, 2002).

The chemical base for the cooking liquor can be calcium, magnesium, sodium or ammonium. Table 1 shows the main differences in the behavior of the bases in the sulfite process. Each of the bases present slightly different optimal conditions. Monovalent bases (Na^+, NH_4^+) have the advantage of being soluble in all of the pH scale, which simplifies the equipment of SO_2 absorption. The solubility of sodium and ammonium decreases the inlays at the preparation of liquor and in the digester. Magnesium base does not cause problems of inlays at the pH levels of bisulfite in the digester; however, it is much more susceptible to producing them in the absorption stage, where the pH has to be maintained as high as possible in order to maximize the efficacy of the absorption process (Casey, 1990).

Table 1. Comparison of the behavior of the different bases in sulfite pulping (Casey, 1990)

	Calcium	Magnesium	Sodium	Ammonium
SO_2 absorption system	Complex	Relatively simple	Simple	Simple
pH range for the digestion	Below 2	Below 5	From 0 to 14	From 0 to 14
Pulp production rate	Intermediate	Intermediate	Slowest	Fastest
Sifted level	Moderate	Moderate	Low	Low
Inlays production tendency	High	Moderate	Low	Low
Incineration of the liquor ease	Difficult, without base and SO_2 recovery	Simple, the base and SO_2 are recovered	Complex, base and SO_2 recovered	Simple, but the base is not recovered

The pulping rate varies slightly depending on the base used in the sulfite process , but in a more noticeable way in bisulfite pulping in order: NH_4^+>Mg^{+2}>Na^+>Ca^{+2}. Monovalent bases give less rejections in the pulp sifting stage than the Magnesium or Calcium. It is not possible to recover reagents when calcium is used, even when the spent liquor is burnt to recover at least some energy (Casey, 1990; Smook, 2002).

Comparison between sulfite and PHK processes

There are major differences between the two most used processes to obtain dissolving pulp.

The PHK process produces pulp with an alpha-cellulose content of about 94-96%. However with special alkaline purification treatments can yield even 98%. This process can be carried out both in continuous or batch digesters. The main advantage compared to other processes is that it requires relatively low cooking times because the sulfur accelerates the delignification, reducing the degradation of the wood and obtaining high quality pulps. On the other hand the sulfite process produces pulp with a cellulose content of 90-92% and, as well as in PHK with alkaline purification, it can yield up to 96%. This process is stronger than alkaline processes and produces a better separation with regard to the cellulose quality. However it is limited in terms of raw material because wood from conifers cannot be used because at low pH phenols and resin acids are condensed with lignin forming colored compounds which stain the pulp (Sixta, 2006).

During both types of processes, a by-product is obtained, the spent liquor, called brown liquor or spent sulfite liquor in the case of the sulfite process and black liquor in the case of the PHK process. Higher levels of lignin (lignosulfonates, LS) than in the PHK process (Kraft lignin) can be reached with the sulfite process. This spent liquor can be used as a feedstock in further biorefinery processes such as the integrated forest biorefinery.

Although world production of dissolving pulp has been decreased since the mid-1970s, the developments of the past two years have signaled a slight change in this trend. The world demand for dissolving pulp is expected to grow from about 4.5 million adt/year in 2013 to 6.3 million adt/year by 2025 (Sixta, 2013). With an annual global production averaging 5.59 million tons in 2013 according to Food and Agriculture Organization of the United Nations (FAO), dissolving pulp accounted for only 3.22% of the total wood pulp production. However, the high demands for cellulose purity and reactivity, as well as its manifold routes of utilization, are the main reasons for the advanced state of technology within the pulp industry (Sixta, 2006). Thus, in recent years two new processes have been developed, SPORL and SEW processes.

Other novel processes

SPORL Process

The sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) consists of reacting wood chips with a solution of calcium or magnesium sulfite at elevated temperatures for a short time, and then size reducing the resulting material using a disk refiner to generate fibrous substrate for subsequent pulping, saccharification and/or fermentation. The process corresponds to the patent US20090298149 (Wang et al., 2009). By making full use of existing infrastructure, capital, processes, resource, and knowledge base of the pulp and paper industry, the SPORL has low technological and environmental barriers for commercialization (Zhu et al., 2009).

SEW process

This process was developed as an alternative to PHK and acid sulfite processes, in order to eliminate the drawbacks that these two processes present, such as very high capital costs due to a complicated recovery cycle in the case of PHK process; or inefficient chemical recovery due to presence of an alkali, long cooking durations due to the need of an impregnation stage and high sensitivity to raw material, in the case of acid sulfite process (Iakovlev, 2014). The fractionation of wood is carried out by means of a SO_2, ethanol and water (SEW) mixture. The suitability of SEW process for production of dissolving pulps is confirmed by good to very good filterability of viscose prepared from them. SEW process has a high potential to fulfill the requirements of future biorefineries (Iakovlev, 2014).

3. INTEGRATED FOREST BIOREFINERY

A new concept has been formulated to transform P&P mills towards a biorefinery, the Integrated Forest Biorefinery (IFBR). IFBR is a biorefinery that can process forest-based biomass such as wood and forestry residues to bioenergy and bioproducts (Christopher, 2013). The IFBR has four production platforms that can be used in an integrated manner for production of biofuels and high value-added products depending on the four major components of the wood: cellulose, hemicellulose, lignin and extractives. A schematic representation of the IFBR proposed by Christopher (2013) is shown in figure 7.

The core of the future IFBR are P&P mills, in particular chemical pulp mills, mainly because the pulp and paper industry has the world's largest non-food biomass collection system that provides a primary source of cellulosic feedstocks (Christopher, 2013).

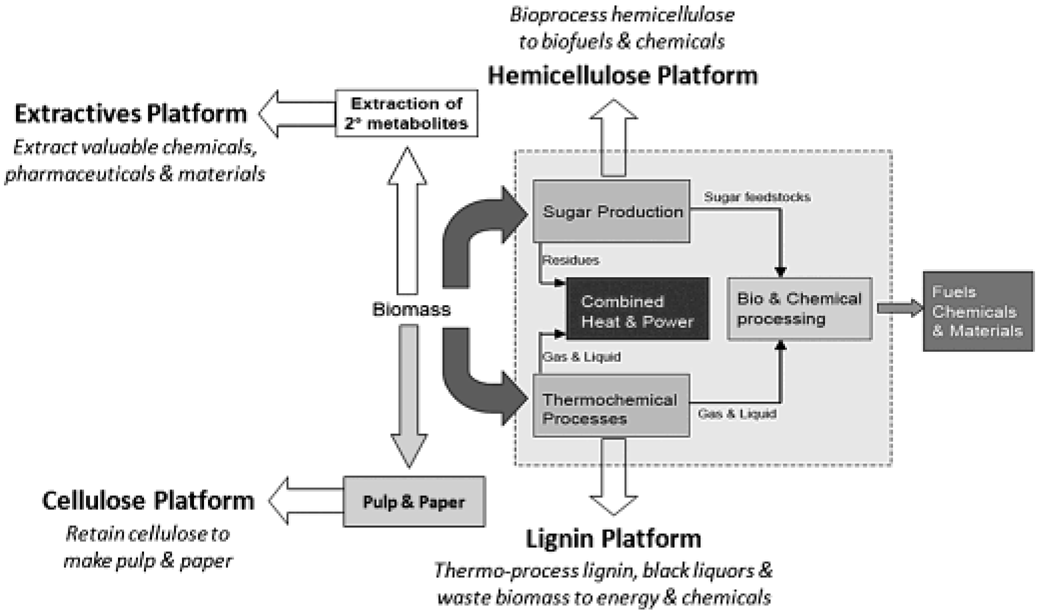


Figure 7. The IFBR concept (Christopher, 2013)

By integrating forest biorefinery activities into an existing plant, pulp and paper mills have the opportunity to produce significant amounts of bioenergy and bioproducts and to drastically increase their revenues while continuing to produce wood, pulp, and paper products. Manufacturing new value-added byproducts (e.g. biofuels, bulk and specialty chemicals, biopolymers and pharmaceuticals) from biomass represents an unprecedented opportunity for revenue diversification for some forestry companies (Bajpai, 2013).

The current pulp and paper mills use logs and fiber, chemicals and energy to produce commodity pulp and paper products. Future mills, which we can consider Integrated Forest Biorefineries, will import regional biomass instead of purchased energy. They will expand the industry's mission from simply manufacturing low-margin paper products to creating new revenue streams by producing "green" power and creating new, high-value products such as biofuels and biochemicals, all while improving the efficiency and profitability of their core paper-making operations (Bajpai, 2013).

How to implement an IFBR into an existing mill

Let us take as examples the main processes to manufacture dissolving pulp, PHK and sulfite since they are established at industrial scale but with high degree commercialized. How can we implement an IFBR into an existing mill? A schematic diagram of the configuration of the mill where biorefinery units have been implemented can be seen in figures 8 and 9. The pulp line is represented in yellow, auxiliary stages in green, with white or spent liquors. Finally, in white and red, where the biorefinery units can be implemented.

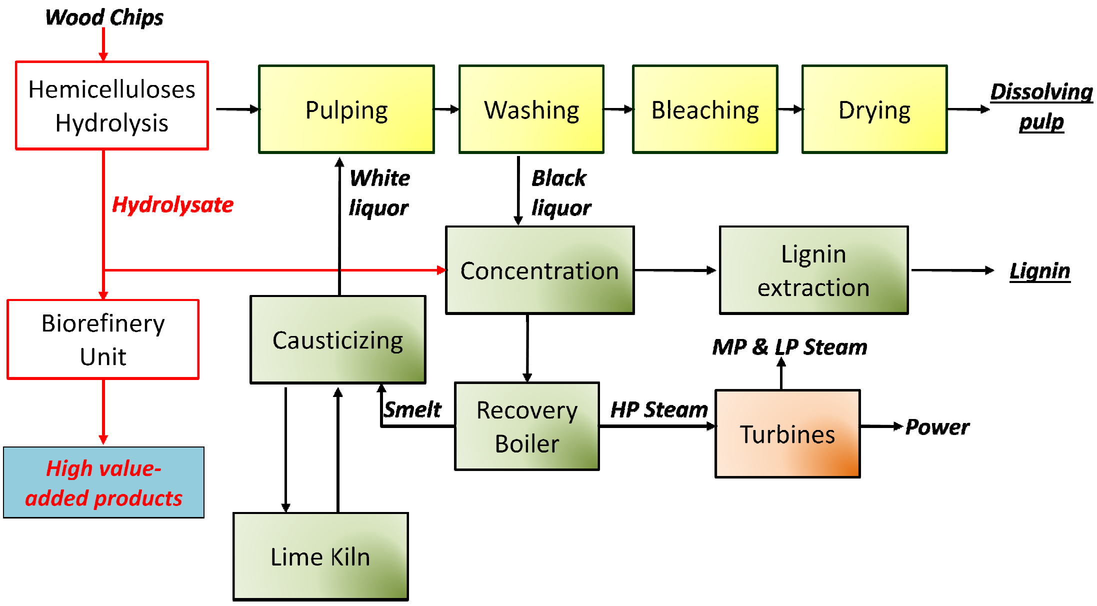


Figure 8. IFBR from PHK process of dissolving pulp manufacturing

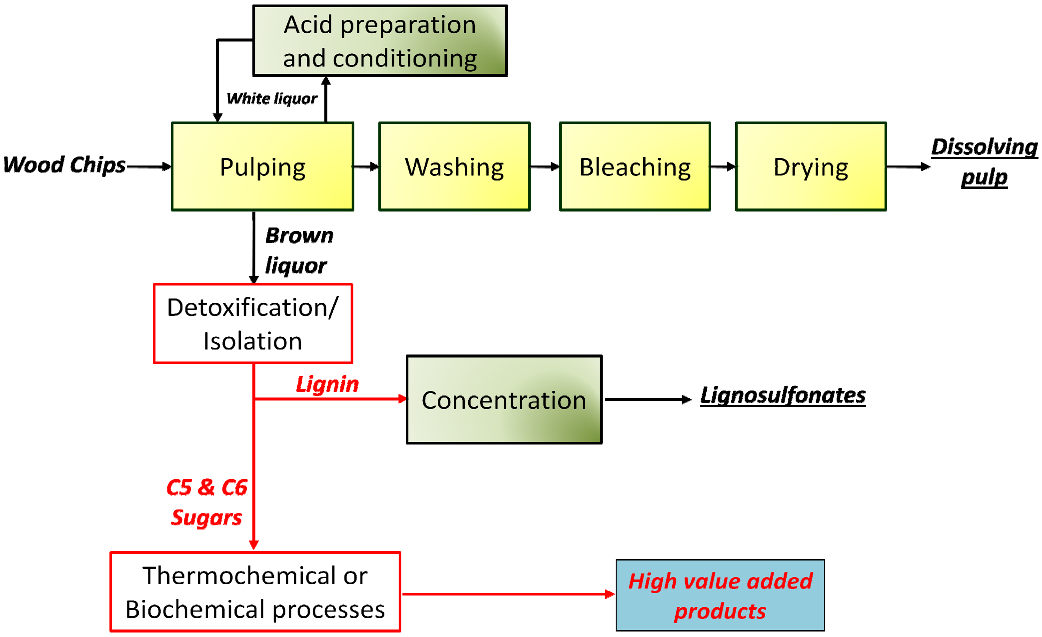


Figure 9. IFBR from sulfite process of dissolving pulp production

In the case of PHK, the fractionation of the hemicelluloses into sugars takes place with the prehydrolysis. The resulting hydrolyzate will go to further purification, detoxification or fractionation stages of the biorefinery. In the case of sulfite pulping, the spent liquor is obtained after the cooking stage and is here when some separation/detoxification stages are needed to isolate the lignin from the hemicelluloses. With these purposes, ultrafiltration, adsorption, ion exchange, precipitation or extraction technologies can be used (Llano et al., 2015). Later, thermochemical or biochemical processes can be used to upgrade the hemicellulose into high value-added products.

4. OBJECTIVES AND THESIS STRUCTURE

The case study of this work is an existing facility in the north of Spain (Sniace S.A. group, Torrelavega) that uses the acid sulfite pulping process. The current products of the industrial cluster are dissolving pulp (from cellulose) and lignosulfonates (from lignin). The sugar content of the hemicellulose is considered a waste in the factory. However, the hypothesis of this work is that the hemicellulose can be separated from the lignosulfonates in order to exploit all of the main components of the wood. This platform constitutes the main objective of this work.

The main goal of the thesis was carried out in compliance to the requirements of the mill and it focused on the assessment of the acid sulfite process in the factory with a biorefinery addition in order to find feasible and profitable pathways for the comprehensive exploitation of the wood. In this sense, the aim was divided into two different studies:

- the physico-chemical characterization of the current spent liquor and the proposal of its potential valorization options,
- the techno-economic assessment of the main valorization options proposed in the previous stage, by means of the simulation of different biorefinery scenarios.

In addition to this goal, this thesis incorporates the study of the previous pulping stage of the factory in order to improve the biorefinery options. This second goal was also divided into two different studies:

- the kinetic behavior of the carbohydrates degradation within the cooking stage,
- the determination of the effect of the raw materials (fresh liquor and different species of wood) together with some cooking control parameters.

According to the goals stated above, the present work has been divided into four chapters. In each chapter the reader will find the specific objectives, the experimental methodology used as well as the results obtained and the main conclusions.

In **Chapter I** the physico-chemical characterization of the industrial spent liquor is shown and from the results obtained, the main valorization options were established.

In **Chapter II**, different techniques of fractionation/detoxification of the spent liquor were tested and one was selected to continue with the study. A technical evaluation of three of the valorization options found in Chapter I was subsequently carried out, followed by an economic evaluation in order to select the most feasible option.

In **Chapter III**, the kinetic modeling of the sulfite process from a biorefinery point of view was investigated since monosaccharides present in the spent liquor can be used as a raw material in further biorefinery processes to produce other value-added products.

Finally, in **Chapter IV**, the effects that some factors have over the sulfite cooking and the spent liquor were examined. The wood specie, the characteristics of the fresh liquor and some digestion variables were studied in order to increase the possibilities to transform the current mill within the biorefinery concept.

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CHAPTER I

SPENT SULFITE LIQUOR: CHARACTERIZATION AND VALORIZATION OPTIONS

The first objective of this dissertation concerns an exhaustive physico-chemical characterization of an industrial spent liquor in a P&P factory in the north of Spain, (Sniace S.A. group, Torrelavega) in order to study the possible valorization options of this by-product within the biorefinery concept. This chapter presents a description of the industrial process in the mill, followed by the results of the physico-chemical characterization of the spent liquor and a review of the possible biorefinery options to be integrated in the mill. Finally it concludes by the presentation of the best options that will be studied in the next chapter.

The results presented in this chapter were published as "**Biorefinery options to valorize the spent liquor from sulfite pulping",** in Journal of Chemical Technology and Biotechnology 90(12), 2218-2226 (2015).

1. THE ACID SULFITE PROCESS. OBTAINING THE SPENT LIQUOR

A schematic diagram of the acid sulfite process of the mill used in this work is shown in figure 10. Wood and fresh liquor (formed by dolomite, water and SO_2) are introduced in the digesters operating at high temperature and pressure conditions. At the end of the cooking process, a liquid purge is implemented in order to facilitate the following displacement of the spent liquor and subsequent separation of it from the pulp. The next step is the discharge of the digester, by transferring the pulp into a blowtank and the SL into storage tanks. The pulp undergoes following subsequent operations of screening, washing, bleaching (ozone, Z; alkaline extraction, EOP; and peroxide oxidation, PO) and drying. The SL goes to the evaporator plant where it is concentrated from 10% to 55% solids. The strong SL is sent to a chemical company where it is treated to extract the lignosulfonates. The sugars remaining in the strong SL are destroyed. The reference mill considered in this work produces 110 ton/d of dissolving grade pulp and 1972 ton/d of spent liquor with 10% solids, by the process shown in figure 10.

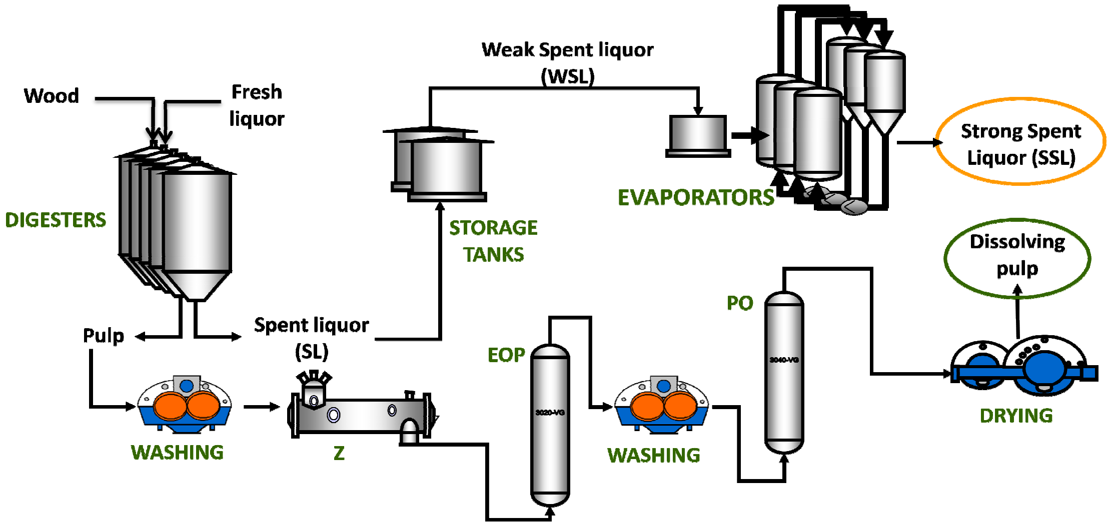

Figure 10. Representation of the sulfite pulp mill used in this work

2. PHYSICO-CHEMICAL CHARACTERIZATION OF THE INDUSTRIAL SPENT LIQUOR

2.1. Materials and Methods

Materials

Several industrial SLs from calcium-magnesium base acidic sulfite pulping of *Eucalyptus globulus* supplied by Sniace SA (Torrelavega, Spain) were analyzed in order to determine the homogeneity of the industrial liquor: 34 samples in total, 17 samples of pre-evaporation (weak SL, WSL) and 17 of post-evaporation (strong SL, SSL) over a period of 5 months.

Methods

The pH was measured by a pH meter Crison Kit 2012T with electrode 5012T. For the measurements of Total Suspended Solids (TSS), 10 mL of the samples were filtered through a membrane filter Millipore with diameter 47 mm and pore size 0.45 µm and then dried at 103-105^{o}C. Both parameters (pH and TSS) were determined according to the standard methods 423 and 209C described in Clesceri et al. (1998). Density and viscosity were determined at 20^{o}C, using a glass picnometer and a viscometer Fungilab Alpha L series. Dry matter was measured by drying at 103-105^{o}C using a Selecta muffle. Ash was determined according to the Tappi T211 (Tappi, 1993) and T413 (Tappi, 1993) using a Selecta furnace. All of these Tappi methodologies are specific for wood, pulp, paper and paperboard.

The thermal degradation of the samples was carried out using thermogravimetric analysis (TGA) on a TGA 4000 Perkin Elmer. Air flow rate was 20 mL/min and the oven was heated from 30 to 525^{o}C for TGA at 5^{o}C/min heating rate. Infrared spectra were recorded on a Shimadzu Fourier Transform Infrared (FTIR) Spectrophotometer FTIR-8400S equipped with Attenuated Total Reflectance (ATR) made by Pike Technologies. The spectra resolution was 4 cm^{-1} and 32 scans were averaged.

Free, total and combined SO_2 were determined according to a titration method with iodine based on the Tappi UM 667 (Tappi, 1991). Total content of carbon, hydrogen, nitrogen and sulfur was determined by an external laboratory with an elemental analyzer. Ca, Mg, Na, K and Fe were measured by an atomic absorption spectrometer Shimadzu AA7000 and other heavy metal components by Agilent ICP-MS 7500 ce. Anionic compounds were analyzed with a Dionex DX-120 chromatograph and the total organic carbon (TOC) was analyzed by an external laboratory, using the TOC-V of Shimadzu equipment.

An UV–visible spectrophotometer Perkin Elmer Lambda 25 was used to measure the lignosulfonates (LS) fraction. The analysis of LS was carried out by measuring the solution absorbance at 232.5 nm. Five types of sugars (D-xylose, D-glucose, L-arabinose, D-mannose and D-galactose), furfural, hidroxymethylfurfural (HMF) and acetic acid were measured by a Shimadzu HPLC using Transgenomic CARBOSep CHO-782 and SHODEX SH-1011 columns and refraction index detector (Llano et al., 2013).

2.2. Results and discussion

Table 2 shows the main characteristics of the SL obtained by the sulfite process. The concentration of solids increased from 10% (106 g/L, WSL) up to 58% (761 g/L, SSL) in the evaporators. The obtained results are similar to those found in literature, 145 g/L and 743 g/L in the work of Chipeta et al. (2005) and 148 g/L in Xavier et al. (2010) for WSL.

The pH values increase with the concentration of SL in the evaporators, from 1.8 to 2.35. These pH values are more acidic than the values found in literature (previously reported pH~3.4) (Chipeta et al., 2005; Restolho et al., 2009; Xavier et al., 2010). The differences are probably due to the use of different bases for the cooking liquor production. In this case study, dolomite with 57% of CaO and 37% MgO was the base used. In other works magnesium or ammonia bases were used.

Table 2. Properties of 34 industrial SL samples

	Weak SL (17 samples)	Strong SL (17 samples)
Dry matter (%)	10.72± 1.32	58.5 ± 5.01
pH	1.8 ± 0.084	2.35 ± 0.51
Density (g/L)	1054.91 ± 12	1300 ± 35
Viscosity (cP)	1.827 ± 0.14	385 ± 426
TSS (g/L)	2.68 ± 0.96	60.01 ± 35.73
Ash[a] (%)	12.10 ± 0.94	12.45 ± 4.03
Ash[b] (%)	9.99 ± 2.61	8.66 ± 1.33
TOC (g/L)	52.3 ± 8.92	260.23 ± 102.57
Free SO_2 (g/L)	0.45 ± 0.12	0.87 ± 0.30
Combined SO_2 (g/L)	2.17 ± 0.63	1.37 ± 0.32
C (%)	5.26 ± 0.05	29.07 ± 0.01
H (%)	10.25 ± 0.07	7.15 ± 0.07
N (%)	0.07 ± 0.01	0.09 ± 0.01
S (%)	0.56 ± 0.00	4.36 ± 0.14
Ca (g/L)	4.07 ± 0.06	18 ± 3.50
Mg (g/L)	0.840 ± 0.01	5.33 ± 0.91
Na (g/L)	0.313 ± 0.23	2.06 ± 1.7
K (g/L)	0.146 ± 0.04	1.05 ± 0.2
Fe (g/L)	0.056 ± 0.01	0.346 ± 0.06
Ba (mg/L)	1.09 ± 0.50	5.59 ± 0.23
Cr (mg/L)	0.15 ± 0.24	0.63 ± 0.21
Ni (mg/L)	0.08 ± 0.05	2.75 ± 1.05
Cu (mg/L)	0.35 ± 0.44	1.92 ± 0.84
Zn (mg/L)	2.07 ± 1.45	44.22 ± 21.58
Se (mg/L)	0.76 ± 0.11	8.29 ± 4.81
Pb (mg/L)	0.51 ± 0.34	4.67 ± 2.31
F^- (g/L)	0.76 ± 0.25	3.96 ± 0.15
Cl^- (g/L)	0.42 ± 0.06	3.57 ± 3.28
SO_4^{-2} (g/L)	5.76 ± 0.12	18.90 ± 4.26

[a] 525°C [b] 900°C

No direct relation between density and viscosity was found in the experiments carried out. The density value for strong liquor is moderately higher than for the weak liquor. However, the values of viscosity are much higher for the strong liquor. Also, the viscosity data are variable and the deviation exceeds the mean value. This strong variability is probably due to the increase of different organic compounds, especially lignosulfonates, present in the sample after passing through the evaporation stage.

A high increase of the total suspended solids in the strong SL has been observed. The WSL parameters have been compared with a previous work that only shows values for

WSL (Restolho et al., 2009). TSS according to Restolho et al. (2009) vary from 1.8 to 3.0 g/L and the average value of TSS presented in this work is 2.68 g/L, with a 0.96 standard deviation. Therefore, both studies give very similar results probably due to the use of the same type of wood in the cooking process, *Eucalyptus globulus*. Regarding the SSL, the standard deviation value of TSS is quite high, showing a large variability in the industrial liquor. The corresponding TOC value increased as organic compounds did the same during the evaporation stage (from 52.3 to 260.23 g/L). This means that if the spent liquor was discharged and not treated, it would be an important source of pollution, decreasing the available oxygen in the medium, which emphasizes the benefit of converting it into other products.

Similar results have been obtained for the ash content using two different temperatures of ignition (Tappi T211 and T413). The second method is used in conjunction with the first one in order to investigate the influence of non-cellulosic materials present in the samples. To complete this data and to determine the loss of weight, a thermogravimetric test was performed. The TGA curves for WSL and SSL are shown in figure 11.

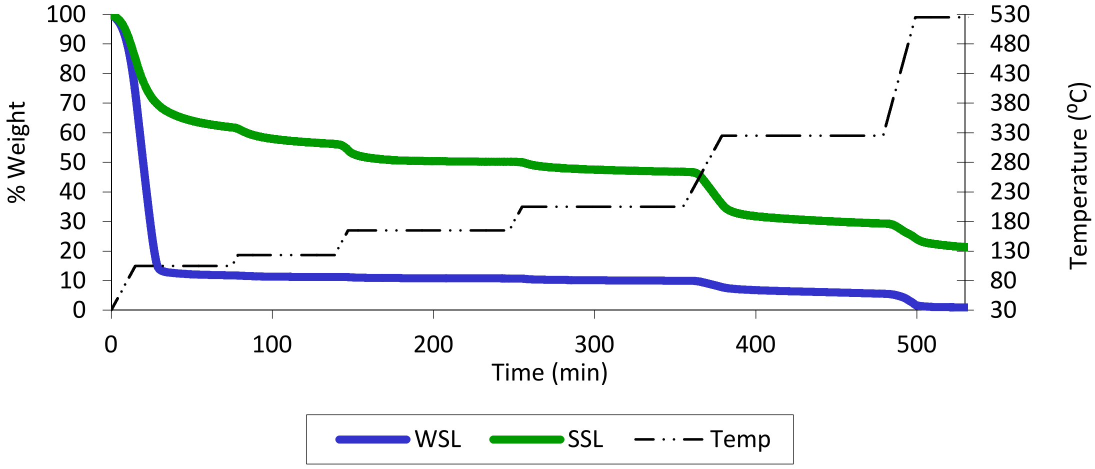

Figure 11. TGA curves of WSL and SSL samples

As can be seen in the thermogram, there is a big loss of weight in the WSL at about 105°C, largely due to the evaporation of water and the most volatile compounds. A loss of weight can also be observed in the SSL, although in this case in a minor proportion since this SSL has higher dry residue. Furthermore an important loss of weight in the SSL at 325°C is observed due to the degradation and volatilization of organic compounds. From the elemental analysis of carbon, hydrogen, nitrogen and sulfur (Table 2), it can be concluded that the percent of both, sulfur and carbon, increases significantly in the evaporators. However, the amount of total SO_2 decreases from 2.62 to 2.24 g/L when SL is concentrated. The total SO_2 parameter gives an idea of how good the gas-liquid separation is in the evaporators and how this compound can negatively affect the subsequent SL treatment.

The concentration of five major metals was measured: calcium, magnesium, sodium, potassium and iron. The study of calcium and magnesium progression is interesting since the fresh liquor is formed by dolomite, composed of calcium magnesium carbonate. Furthermore the presence of some specific metals in the structure of the lignosulfonates will influence their valorization options and applications (Alonso et al., 2001), i.e., iron gives them good properties as fertilizers (Carrasco et al., 2012). Other metals can have an effect on the fermentation process, such as sodium in the hydrogen production (Kim et al., 2009), which can decrease the microbial catabolism as higher concentrations are used.

All the physical properties shown in Table 2 have a good reproducibility, except the viscosity, density and total suspended solids of the strong liquor. In addition, the value of combined SO_2 has a big variability in both types of liquor.

During the evaporation stage dry matter, TSS, density and viscosity followed the same tendencies; all interrelated due to the fact that some of the volatile compounds have been removed, such as SO_2 or acetic acid. All the metals and anions except Zinc, despite the big concentration variability, increased by four times with a R^2 of 0.90.

Figure 12 shows the obtained FTIR spectra for the weak and strong liquors. It is represented by the percent of transmittance versus the wave number. The transmittance is the fraction of incidence light, at a specified wave length, which passes through a sample. The wave number is a frequency magnitude which indicates the number of times that a wave vibrates in a distance unit; it is the inverse of wavelength (Conley, 1972; Rana et al., 2010).

According to the FTIR results the composition of both liquors is similar although the concentration of the different components changes. The following functional groups were found in the spent liquor (Rana et al., 2010). Between 3550-3100 cm^{-1} O-H stretching, at 2942 and 2849 cm^{-1} C-H stretching vibration in methyl and methylene groups. Changes between 1600-900 cm^{-1} can be indicative of some structural changes of lignosulfonates during the evaporation process. Furthermore at 1636 cm^{-1} C=O a stretching of conjugated or aromatic ketones has been localized. At 1517 cm^{-1} C=C stretching vibration in aromatic structure of lignin, at 1464 cm^{-1} C-H deformations and also vibration of $-CH_3$ and $-CH_2-$ groups from lignin. Finally at 1429 cm^{-1} $-CH_2$ bending vibrations; aromatic skeletal vibrations.

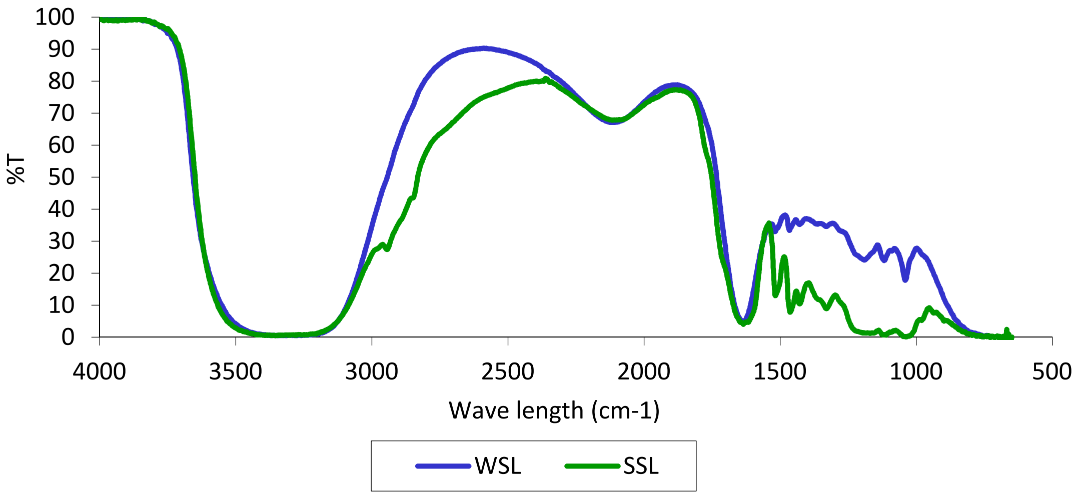

Figure 12. FTIR spectra of weak and strong SL

Table 3 shows the organic composition of the spent liquors in g/L and on a dry weight basis. The chemical composition of the SL mainly depends on the wood species and the base of fresh liquor used for pulp production; this information is essential for the evaluation of the SL application for different purposes.

Obtained values of lignosulfonates content show a high increase, from 47.32 g/L to 427.05 g/L after the evaporation stage. The standard deviation in both liquors is around 9%, denoting not much variety in the behavior of these compounds at industrial scale.

Table 3. Industrial SL properties (organic compounds)

	Weak SL		**Strong SL**	
	g/L	**%w/w**	**g/L**	**%w/w**
Glucose	2.35 ± 0.72	2.08	19.21 ± 3.74	2.53
Xylose	25.01 ± 6.23	22.12	138.24 ± 18.3	18.18
Galactose	2.44 ± 0.64	2.16	17.60 ± 2.48	2.31
Mannose	1.73 ± 0.22	1.53	7.41 ± 1.3	0.97
Arabinose	1.67 ± 0.39	1.48	14.44 ± 2.99	1.90
Furfural	0.17 ± 0.057	0.15	0.12 ± 0.09	0.02
HMF	0.03 ±0.005	0.03	0.04 ± 0.01	0.01
Acetic Acid	6.92 ± 1.87	6.12	5.03 ± 0.9	0.66
Lignosulfonates	47.32 ± 4.51	41.84	427.05 ± 38.6	56.15
Not identified organics	-	10.40	-	4.82

The five carbon sugars (xylose and arabinose) concentration in SL is higher than that of six carbon sugars (glucose, galactose and mannose). The main sugar present in the liquor is xylose with a concentration of 25.01 g/L in WSL and 138.24 g/L in SSL. Values of standard deviation vary from 12.7% to 30.6% for WSL and from 13.2 to 20.7% for SSL.

By analyzing the organic compounds, 77.5% in WSL of the total dry matter are identified and 82.73% in SSL. Ash involved 12.1% and 12.45% respectively. Thus, almost 90% (WSL) and 95% (SSL) of the material have been identified and quantified, decreasing the quantity of non-identified substances on the SSL. The sugar content remained constant throughout the evaporation process, giving a total LMW Sugars of 25.9%; however, the decomposition products such as furfural, HMF, and the acetic acid decreased their contribution over the process, with 0.66% of acetic acid and 0.03% of furans. The concentration of lignosulfonates has the highest contribution in the strong liquor, with a 56.2%.

Sugar concentrations obtained by other studies can be seen in Table 4. As shown in this table, there is some variability in the obtained results probably due to the different wood used in every study.

Table 4. Sugars and inhibitors of SL found in literature

	Xavier et al., 2010	**Nigam, 2001**		**Chipeta et al., 2005**		**Marques et al., 2009**		**Fatehi and Ni, 2011**	
	WSL	WSL	SSL	WSL	SSL	WSL	SSL	WSL1	WSL2
Wood	*E. globulus*	Red oak		Hardwood		*E. globulus*		Hardwood	
Base	Magnesium	-		-		Magnesium		Ammonia	
pH	3.4	1.7	6.5	2.7	3.3	2.9	3.7	-	-
Solids (g/L)	148	220	-	145	753	151	841	-	-
Glucose (g/L)	2.3	3.0	5.4	2.2	10.9	3.54	10.36	1.8	3
Xylose (g/L)	24.6	26.7	40.2	23.6	119.0	24.78	81.4	20.8	24
Galactose (g/L)	4.5	-	-	2.4	11.1	5.9	31.08	-	-
Mannose (g/L)	8.5	6.5	9.0	-	-	1.18	4.44	7.1	6.5
Arabinose (g/L)	7.8	1.5	21.0	0.9	4.2	1.18	4.44	-	-
Acetic Acid (g/L)	8.2	9.3	4.2	10.3	12.6	9.44	4.44	9.3	7.6
Furfural (g/L)	<0.1	0.2	0.06	-	-	2.36	traces	-	-

The percentage of each of the five studied sugars present in each SL has been represented in figure 13 (WSL) and figure 14 (SSL).

As expected, in all studies, the main sugar is xylose, because the major group of hemicelluloses found in hardwoods is glucuronoxylans, which contain xylosidic bonds between xylose units and are easily hydrolyzed by acids. Similar results have been found for glucose in all references. However, the content of arabinose, galactose and mannose differ largely.

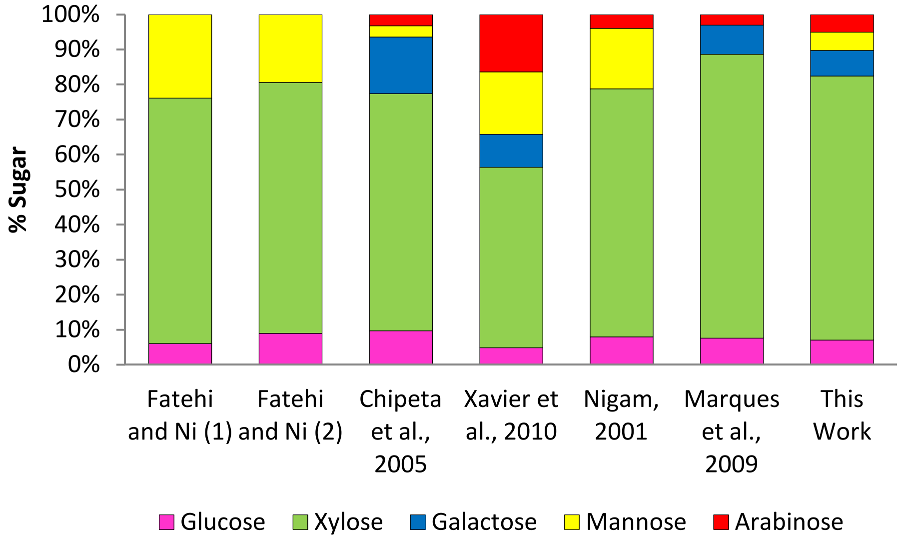

Figure 13. Sugar content in WSL

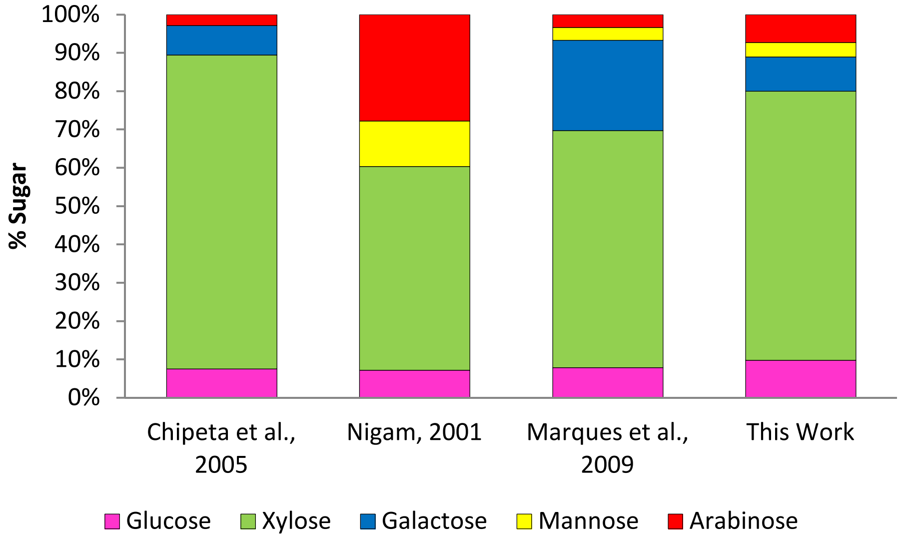

Figure 14. Sugar content in SSL

Purification of spent liquor is needed when chemical methods are used to valorize this stream since some undesirable products can be formed. On the other hand, a detoxification step is necessary to obtain good yields in further fermentation processes, removing possible inhibitors from the initial stream. The main inhibitors in fermentation steps from lignocellulosic biomass can be divided into the following groups: sugar degradation products such as furfural, HMF and weak acids from cellulose and hemicellulose; lignosulfonates and other lignin derived products, inorganic compounds as SO_2, anionic compounds and heavy metals (Chandel et al., 2013; Mussatto and Roberto, 2004; Palmqvist and Hahn-Hägerdal, 2000).

The effect of these components depends on the kind of toxic compounds and their concentration. Furfural and HMF can inhibit cells and affect the specific growth rate and cell-mass yield per ATP (Mussatto and Roberto, 2004). Several studies reported by Mussatto and Roberto (2004) stated that concentrations of these products around 0.5 and 0.25 g/L respectively, decreased the growth and the yield. In this work the concentration of both components is under these values but should not be ignored. The inhibitory effect of the acetic acid takes place when the pH of the medium is low (the SSL has low pH values) because it diffuses across the plasma membrane and once inside the cells due to an increase in proton concentration, it inhibits cell activity even causing death (Chandel et al., 2013; Mussatto and Roberto, 2004). The effect of heavy metals has also been reported in literature (Chandel et al., 2013; Mussatto and Roberto, 2004), showing that much higher concentrations than those of this work inhibit the enzymes in the microorganism's metabolic pathways. Finally, regarding the concentration of anionic compounds, in spite of the fact that they can have detrimental effects over some microorganisms in sugar fermentation (Maiorella et al., 1984), they have not been shown previously by other authors. In this work, they are in significant proportions in the SSL, around 4 and 19 g/L, showing similar values to those of several sugars.

The methods to develop purification/detoxification can be classified into various groups and they have different effects on the raw material which is going to be treated, but the main objectives are either to transform inhibitors into inactive compounds or reduce their concentration (Mussatto and Roberto, 2004). They can be divided into physical methods, such as evaporation or ultrafiltration; chemical methods, like overliming, adsorption with activated charcoal, ion-exchange resins or extraction; and biological methods, which need the use of microorganisms or specific enzymes (Chandel et al., 2010; Evtuguin et al., 2010; Larsson et al., 1999). The study of the feasibility of some of these methods and the selection of the best one or a combination is currently being done by the research group.

3. VALORIZATION OPTIONS OF THE SPENT LIQUOR

A literature review was carried out to identify the potential valorization options for the SL of the mill studied. Extraction and conversion steps must be done on site; however, SL components can also be employed as raw materials for further transformation.

A technically feasible environmental alternative already practiced by the company is the recovery of **lignosulfonates**. They are used as plasticizers in concrete and cement applications. In addition, they help to control the viscosity of particle suspensions in brick production. Also due to their ability to couple smooth dispersion with tackiness, they are used as soil stabilizers on soft shoulders or unfinished roads. They also find applications in metallurgy, animal feeds and agriculture. They are widely used as dispersants and can be included in some additives. The world production is about 1.5 Mt/yr (Duval et al., 2013). By 2016, Central and Eastern Europe is expected to increase its share of world lignosulfonate consumption and China is expected to become the second-largest consumer of lignosulfonates. Overall, world consumption of these compounds is expected to grow modestly up to 2016 (IHS, 2014). Several methods have been used to recover these components from the SL: ionic-resin method, ultrafiltration, long-chain aliphatic amine extraction and liquid membrane and solvent extraction (Chakrabarty et al., 2009; Restolho et al., 2009; Ringena et al., 2005). This alternative is widely implemented worldwide by several companies. The major producers are Borregard LignoTech with more than 500,000 tons of lignin (dry basis), Tembec which has three sulfite plants in Europe and North America and produces 570,000 tons of lignosulfonates. La Rochette Venizel in France, Nippon Paper Chemicals in Japan, Cartiere Burgo in Italy and Domsjö Fabriker AB in Sweden are also important producers (Lora, 2008).

One of the potential chemical to be developed from the sugar platform is **xylitol.** Xylitol is often used in the food industry, more particularly as a substitute for sucrose, fructose and glucose due to its health benefits. Xylitol is found in low concentrations in many natural sources such as fruits and vegetables. It also has high bactericidal, antibiotic and antifungal properties and can also be used as adhesive. Xylitol demand is expected to grow. The global market for xylitol is estimated at 161.5 thousand tons, valued at US$670 million in 2013 and 242 thousand tons valued at just above US$1 billion by 2020 (Industry Experts, 2014). Xylitol production can be performed using a chemical or biological path with xylose as a raw material (Helle et al., 2004; Nair and Zhao, 2010; Rodrigues et al., 2008). Presently xylitol is produced at industrial scale through catalytic hydrogenation of pure xylose, extracted from hemicellulosic hydrolysates, under low pressure and temperatures (Nair and Zhao, 2010). Another possibility is to obtain xylitol through the xylose fermentation. In this case, a pretreatment prior to fermentation is necessary to remove substances, such as acetic acid and furfural, that adversely affect the fermentation process because of their toxic properties and high concentration. Some of the detoxification/purification methods mentioned above can be applied to remove inhibitors in the case of fermentation however, new and more efficient methods are currently under research such as genetic engineering, mixed cultures and enzymatic biocatalysis (Christopher, 2013). The microbial production of xylitol has been reviewed by Saha (2003). In this study some of the natural xylose-fermenting yeasts known to produce xylitol are collected:

Candida bodini, *Candida guillermondii*, *Candida tropicalis*, *Candida parapsilosis* and *Debaryomuces hansenii*. The latest studies are assessing the use of some microorganisms to produce xylitol in a mixture of sugars containing glucose or arabinose (Bridgwater et al., 2010; Nair and Zhao, 2010) or even using SL as feedstock (Lai and Bura, 2012).

Another alternative for the valorization of the sugars in SL is the production of **ethanol** (Martín et al., 2002; Sanchez and Cardona, 2008; Xavier et al., 2010). Most of the ethanol, approximately 70% of global production, is derived from the fermentation of sugar crops, including sugarcane, sugar beets or molasses (IHS, 2014). The global production of ethanol is 46 million tons per year (Bridgwater et al., 2010). The United States and Brazil are the major producers. Bioethanol has mostly been used as fuel for transport, especially in Brazil. However it can be used for the production of chemicals with a wide range of uses in the pharmaceutical, cosmetic, beverage and medical sectors. In recent years there has been an increasing interest in producing ethanol from raw materials that are not in competition with food, from lignocellulosic biomass, agricultural residues or waste, that is, the second generation bioethanol. The spent liquor, a byproduct of the pulp and paper industry, can be used as feedstock for its production. A pretreatment is necessary to release the sugars from the woody biomass, and then alcohol is obtained by means of fermentation. For the bioprocessing of SL microorganisms capable of selectively converting pentoses into ethanol by fermentation must be used. The presence of other components like acetic acid, furfural or methanol, can inhibit the fermentation. Strains of the yeast *Pichia stipitis* have been used (Jeppsson et al., 2006; Xavier et al., 2010) to metabolize pentoses and hexoses. Since xylose is the predominant sugar in the SSL from the mill, this organism could achieve high rates of conversion into ethanol if a method of detoxification or purification suited to the substrate is applied. This can generate a number of options that range from chemical (neutralization and pH adjustment with different alkali) and enzymatic (with *phenoloxidase laccase*) detoxification, to the total elimination of the substrate of organic acids and phenolic compounds by ion-exchange resins. In fact, it was found that the detoxification of SL by this method is very effective to remove all types of fermentation inhibitors with *Pichia stipitis* (Panagiotopoulos et al., 2009; Xavier et al., 2010). In addition, Keating et al. (2006) have studied the tolerance of two kinds of strains with respect to some inhibitors such as furfural, HMF and acetic acid. The results of this work also show that it is possible to produce ethanol under certain conditions. M-Real, Hallein AG (Austria) has already developed this option, producing bioethanol, electricity and heat from SL. Borregaard from 1000 kg softwood produces 50 kg of ethanol and Tembec (Canada) produces ethanol from aspen and maple wood (Klitkou, 2014; Tembec, 2014).

Furfural production from the SL represents another opportunity since this compound is an important chemical feedstock used to manufacture products such as furfuryl alcohol, furan of other furan-based chemicals (Zeitsch, 2000). China is the dominant player in the world furfural market. With 80% of global capacity and 72% of world consumption, China will continue to drive the overall market (IHS, 2014). The production of furfural according to Bridwater et al. (2010) is around 54 million tons/year. Its demand is projected to grow at a substantial rate due to the demand of green and bio-based products and 1Mton/y may be achieved by 2020 (Marcotullio, 2013). Furfural is produced during the cooking stage of pulping when the hemicellulose is hydrolyzed to release its composing monosaccharides (mainly xylose). Under some conditions of temperature (200-250^{o}C) or in the presence of mineral acids, xylose and other five carbon sugars undergo dehydration, losing three water molecules to become furfural (Mamman et al., 2008). In this case inhibitors do not interfere since no fermentation process is involved since furfural is produced using a thermochemical pathway. The goal is to obtain a purified stream without lignin (lignosulfonates in this case) and with the highest quantity of sugars using, for instance, ultrafiltration as in Restolho et al´s work (2009). Some existing processes to obtain furfural are the "Biofine" process, in which furfural is obtained as an intermediate in the production of levulinic acid and the "Lignol" process, with an organosolv step as a pretreatment.

Other valorization options could be the production of polyhydoxybutyrate or **PHB**, a homopolymer of the family of polyhydroxyalkanoates (PHA) (Bertrand et al., 1990) or succinic acid, a building block for the production of many specialty and commodity chemicals such as polybutylene-succinate or **PBS** (Bozell and Petersen, 2010). These components are considered to be very useful in the world of thermoplastic and elastomeric materials because they are derived from renewable and biodegradable materials. PHAs can replace conventional plastics in many applications and their mechanical properties are quite satisfactory (Mumtaz et al., 2010). This makes them good feedstock to contribute to sustainable development. Currently, the production of PHB is around 50 ton/year and of the succinic acid 45,000 ton/year (Bridgwater, 2010). However, an increase in the production of those polymers is expected. The raw material for this process is mainly xylose, but the problem is that it is necessary to find a microorganism capable of converting xylose by fermentation into PHB (Lopes et al., 2009). It was found that certain bacteria both gram-positive (*Bacillus* sp.) and gram-negative (*Escherichia coli* and *Burkholderia sacchari*) have higher yields and volumetric productivity in the intracellular synthesis of PHB from a medium containing a pure single sugar (glucose or xylose), as well as mixtures of two or three different types of monosaccharides (glucose, xylose and arabinose). On the other hand, the production of PBS is also possible by means of fermentation of xylose and other sugars contained in spent liquor using *Actinobacillus succinogenes* and *Basfia succiniciproducen* (Vlysidis et al., 2013).

Hydrogen can be produced from glucose or xylose thermophilic fermentation (de Vrije et al., 2009; Kádár et al., 2004). This option offers the possibility of producing an alternative fuel by way of a fermentative pathway. The problem of hydrogen fermentation is that only a small fraction of the organic starting material is converted into hydrogen, even when the starting material is only glucose (Lee et al., 2010; Wang and Wan, 2011). This is because hydrogen production is influenced by factors such as type and concentration of substrate (Okamoto et al., 2000; Panagiotopoulos et al., 2011), pH (Fang and Liu, 2002), temperature (Zhang et al., 2003), hydraulic retention time (HRT) of the reactor (Wu et al., 2008) or gas stripping (Willquist et al., 2009), therefore new strategies for increasing hydrogen production rates and yields are necessary such as the optimization of bioprocess parameters or the elimination of competing reactions, to decrease hydrogen partial pressure (Hallenbeck, 2009). Taking into account the results of Kim et al. (2009), concentration of sodium presented in this work would not inhibit the microbial catabolism in a significant way. Opportunities in hydrogen production look strong in the forecast period (2013-2018), with an estimated consumption of about 868 billion normal cubic meters in 2018. Currently the production of hydrogen is 54 million tons per year (Bridgwater et al., 2010). Overall global demand for this component is expected to increase by around 5-6% during the next five years. Hydrogen is also expected to undergo a surge in consumption for the manufacture of methanol (IHS, 2014).

Methanol is considered a basic petrochemical product, from which several secondary products are obtained such as formaldehyde, and also it is a fuel with a high calorific value (Kamm et al., 2006). Currently, the industrial production of methanol is based exclusively on the catalytic conversion of pressurized synthesis gas (hydrogen, carbon monoxide and carbon dioxide) in the presence of heterogeneous metal catalysts. It is mainly used as feedstock for the production of methyl tertiary butyl ether (MTBE), a gasoline additive (Wu et al., 2008). Worldwide, formaldehyde production is the largest consumer of methanol, accounting for 31% of world methanol demand in 2013. Overall, global methanol demand for formaldehyde production will grow at an average rate of just over 5% per year from 2013 to 2018; it will remain the single-largest end use in 2018. Nevertheless, its share of total world methanol demand will decline to 28% in 2018 as a result of higher growth rates displayed by other end-use segments for methanol (IHS, 2014). Global methanol demand increased 23% from 2010 to 2012 and currently the production is around 40 million tons per year (Bridgwater et al., 2010). However annual demand is expected to rise to an unprecedented level of 137 million tons in 2022, according to a market study released by IHS (2014).

Acetic acid is of interest to organic chemistry as a reagent, to inorganic chemistry as a ligand, and to biochemistry as metabolite (activated as acetyl-coenzyme A). Acetic acid is produced commercially by bacterial fermentation of sugar, molasses or alcohol, or by chemical synthesis from acetaldehyde. In the SSL case, the best option would be to separate this component from the rest and concentrate it using membrane technologies (Afonso, 2012) or anionic exchange resin (Takahashi et al., 2013). The remaining sugar can then be fermented avoiding the inhibitory effect of the acetic acid. The production of acetic acid is 190,000 ton/year (Bridgwater et al., 2010). Future growth of the acetic acid market will continue to be driven by the Chinese market. New capacity is expected to come on stream in the next few years, while strong growth in Chinese consumption of about 7% per year is expected; compared to the global average rate of 4-5% per year (IHS, 2014). Lenzing AG (Austria) can produce food grade acetic acid from the spent liquor of magnesium sulfite cooking.

Vanillin is another product that can be obtained from the SL by different pathways (Bjørsvik and Minisci, 1999). The prevalent process is by oxidation of the SL followed by different processes such as evaporation, acidification, extraction or cationic-exchange to isolate the vanillin (Hocking, 1997). In addition, vanillin can be obtained from the lignosulfonate by catalytic conversion (Pacek et al., 2013). This product is typically used in the food and pharmaceutical industries as an intermediate in the synthesis of various products with applications for hypertension (L-methyldopa), Parkinson's syndrome (L-dopa) or respiratory system infections (trimethaprim) and in the cosmetics industry, which employs vanillin in the preparation of sunscreen for the absorption of ultraviolet radiation (Hocking, 1997). World trade in natural and synthetic vanillin production amounts to 12,000 tons per year (Bridgwater et al., 2010). Borregaard is the first producer of vanillin from spent sulfite liquor; the yield in vanillin is about 3 kg of vanillin from 1000 kg of softwood (Klitkou, 2014).

Table 5 gives a summary of the market and price of each of the components obtained from the spent liquor. Taking into account these parameters, the assessment of the technical feasibility of the development of some of these products will be carried out selecting four options: lignosulfonates, furfural, xylitol and ethanol. The first three because they are chemical platforms and their demand is anticipated to grow, the latter because of the recent regulations in terms of fuels for transportation in which the bioethanol is a major player. The options concerning biopolymers as PHB and PBS should not be ignored.

The main disadvantages to be overcome to the use of this kind of waste in integrated biorefinery are the following: (i) the low pH and high viscosity of the strong liquor, which probably would need a previous neutralization and/or dilution step (ii) the difficulties in the separation of the lignosulfonates from the hemicelluloses hydrolyzate, (iii) the possible inhibition in post-bioconversion processes not only due to furans and acids but also other compounds such as lignosulfonates, inorganic components and SO_2; underscoring the importance of the feasibility assessment of the detoxification step.

Table 5. Market and price of the biobased products

Product	Price (€/ton)	Market (ton/y)	Starting components (%$_{w/w}$ in SL)
Lignosulfonates	400-2000	1,500,000	Lignosulfonates (50.6%)
Vanillin	10,000	12,000	Lignosulfonates (50.6%)
Xylitol	5,830*	242,000**	Xylose (18.18%)
Furfural	500	250,000	Xylose and arabinose (20.08%)
PHB	9,000	50	Sugars (25.89%)
Succinic Acid	5,000	45,000	Sugars (25.89%)
Hydrogen	2,000	54,000,000	Glucose (2.53%) or xylose (18.18%)
Acetic Acid	900	190,000	Sugars (25.89%)
Ethanol	740	46,000,000	Sugars (25.89%)
Methanol	254	40,000,000	Sugars (25.89%)

* Xylitol Canada. Xylitol price list. Available in: http://wwwxylitolcanadacom (2012)
** Estimated market for 2020 (IHS, 2014)

4. CONCLUSIONS

An in-depth analysis of physico-chemical characteristics of weak and strong liquors from calcium-magnesium sulfite pulping of *Eucalyptus globulus* wood has been carried out in this work. The results of the physical properties such as dry matter, pH and total solids revealed that they increase with the evaporation stage. No relation between viscosity and density has been found. Metals and anions, except Zinc, increased in concentration four times by passing through the evaporators. Lignosulfonates (47.32 g/L WSL and 427.05 g/L SSL) and xylose (25.01 g/L WSL and 138.24 g/L SSL) are the main components in spent sulfite liquor used in this work. Furans, weak acids and other inorganic compounds such as chlorides, fluorides, sulfates and heavy metals have been identified as possible fermentation inhibitors to further conversion.

Based on the chemical composition obtained for the spent liquor, a literature search was carried out to establish the possible SL valorization options in order to integrate a biorefinery unit into the existing mill. According to the compiled references and taking into account the current detoxification methods and the processes, the main valorization options for the spent liquor are the production of lignosulfonates, xylitol, ethanol, polyhydroxybutyrate, polybutylene-succinate, furfural and hydrogen as the most alternative options. Other minority alternatives can be acetic acid, methanol and vanillin.

As a general conclusion, the spent liquor fulfills all the requirements to be valorized using biorefinery processes. Due to the market, the price and the availability of the appropriate sugar substrate in the spent liquor; furfural, xylitol and ethanol are proposed to be further studied.

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CHAPTER II

DESIGN, SIMULATION AND ECONOMICAL EVALUATION OF BIOREFINERY PROCESSES

Taking into account the composition of the SL (Chapter I), the lignin and hemicelluloses platforms are favored to manufacture products such as lignosulfonates, ethanol, xylitol, furfural, PHB, hydrogen and acetic acid, vanillin or methanol. As a conclusion, lignosulfonates from lignin and furfural, xylitol and ethanol from hemicelluloses were selected as promising options in this work.

Due to the fact that lignosulfonates are currently valorized in the mill, in the current chapter, the integration of biorefinery units into the existing mill is evaluated techno-economically based on the three selected end-products of the hemicelluloses platform: furfural, xylitol and ethanol.

The results shown in this chapter have been published as a scientific paper called "**Technoeconomic assessment of different biorefinery approaches for a spent sulfite liquor**" at Journal of Chemical Technology and Biotechnology. DOI DOI: 10.1002/jctb.4868, 2016.

1. PROCESS OVERVIEW

The raw materials used in the mill and in this work are *Eucalyptus globulus* wood from Cantabrian forests and fresh liquor composed of dolomite, water and sulfur dioxide.

The pulping process was detailed in epigraph 1 of Chapter I and schematically represented in figure 10. As it was mentioned in Chapter I, the mill studied in this work produces 110 ton/d of dissolving pulp grade and 1970 ton/d of SL at 10% solids content from 346 ton/d of dry wood and 165 m^3 of fresh liquor. The characterization of the SL given in Chapter I gave a composition of 50.6% lignosulfonates and 25.9% sugars. The SL also contains lesser amounts of acids, decomposition products and SO_2.

In order to exploit the sugar platform in a biorefinery context, fractionation or detoxification units should be added to the SL line before the evaporators. The resulting stream rich in sugars from this unit is diverted to the conversion plant. Therefore, the new designed process will have the appearance shown in figure 15.

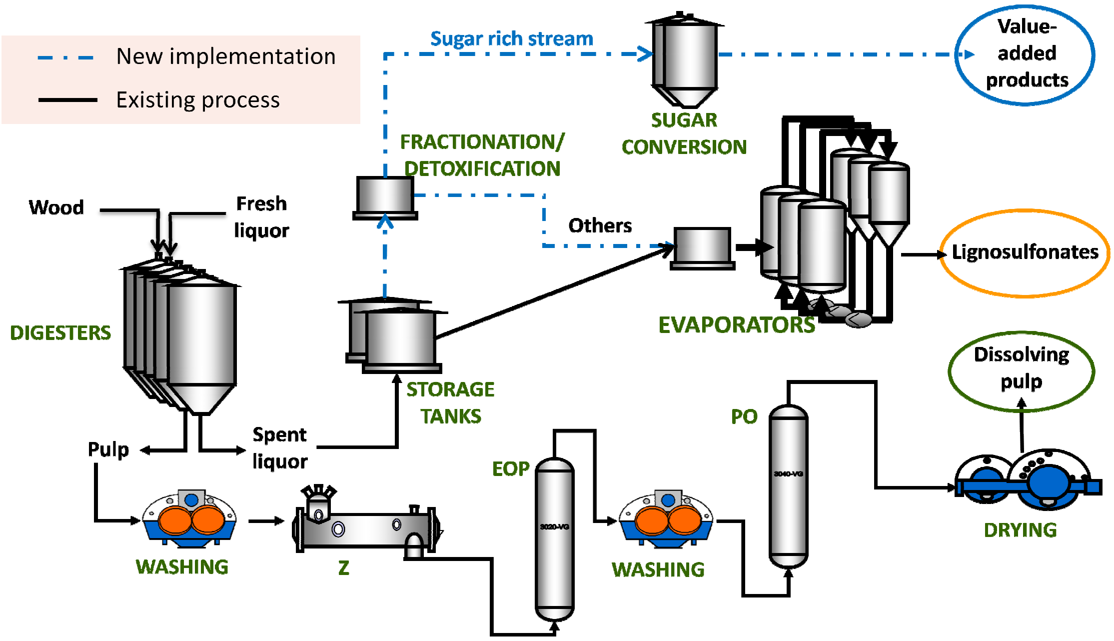

Figure 15. Schematic representation of an IFBR based on a sulfite pulp mill

2. SIMULATION DEVELOPMENT

Aspen Plus® has been used to model and design various sugar transformation processes on the basis of experimental data from previous studies and literature. Aspen Plus® is the market-leading chemical process optimization software used by the bulk, fine, specialty and biochemical industries, as well as the polymers industry for the design, operation, and optimization of safe profitable manufacturing facilities. It is a sequential simulator and in each simulation unit (block) are implemented several equations of mass and energy balances. It uses simple blocks, easy to calculate, and complex units as distillation, gas adsorption, etc. Table 6 summarizes the modules used in this work. Wood components such as cellulose, lignin or hemicelluloses were defined by their chemical structure and physical properties, obtained from the National Renewable Energy Laboratory (NREL) database (Wooley and Putsche, 1996) whereas other components were defined by their molecular formula from the Aspen Plus® data bank.

The first step in this work was to study the different fractionation/detoxification processes in order to valorize both lignosulfonates and sugars from the spent liquor. A flow diagram of the process was developed and the mass and energy balances were calculated using Aspen Plus. Once the main parameters were obtained, the sugar platform of the mill was studied. According to the previous chapter, three different biorefinery options were considered. The flowchart for each of the three options was developed and the balances were obtained by Aspen Plus. Finally, a technical analysis was carried out. The sizing and costing of the equipment was calculated using Microsoft Excel®.

Table 6. Modules of Aspen Plus used in this work

Aspen module	Real module	Description
Decanter	Decanter	Decanters and other single stage separators without a vapor phase
Dist	Distillation column	Multistage multicomponent columns with a feed stream and two product streams
Flash2	Flash, Evaporator or other single-stage separator	Vapor-liquid or vapor-liquid-liquid equilibrium calculation
Fsplit	*Divider*	*Combines streams of the same type (material, heat, or work streams) and divides the resulting stream into two or more streams of the same type*
Heater	Heater, Cooler, Valves, Pumps	Determines the thermal and phase conditions of a mixture with one or more inlet streams
HeatX	*Shell and tube heat exchanger*	*Performs a full zone analysis with heat transfer coefficient and pressure drop estimation for single- and two-phase streams*
Mixer	Mixer	Combines material streams (or heat streams or work streams) into one stream
Pump	Pump or a Hydraulic Turbine	Changes pressure when the power requirement is needed or known
RadFrac	Distillation column	Rigorous model for simulating all types of multistage vapor-liquid fractionation operations
Rstoic	Reactor	Can model reactions occurring simultaneously or sequentially and can perform product selectivity and heat of reaction calculations
Sep	Valid for several equipment	Combines streams and separates the result into two or more streams according to splits specified for each component
Ssplit	Divider	Combines material streams and divides the resulting stream into two or more streams
Valve	Valves and pressure changers	Relates the pressure drop across a valve to the valve flow coefficient

2.1. SL fractionation/detoxification and lignosulfonate concentration

Several techniques for the fractionation and detoxification of the SL prior to its valorization have been studied by Fernández-Rodríguez et al. (2015) and Llano et al. (2015). The selected methods were overliming, evaporation, ultrafiltration, ion exchange resins and adsorption with activated charcoal and black carbon. The more effective treatment to remove lignosulfonates (65.38%) (Fernández-Rodríguez et al., 2015) that could be integrated in an existing facility is ultrafiltration because of its easy scale-up. However, it may involve high sugar losses (60%) and high investment costs. Ion exchange resins could be an alternative as a first treatment of the SL because it can deliver good lignosulfonates removal (62.10 %) with low sugar losses (15.76 %) (Llano et al, 2015).

The SL is passed through an anionic resin unit in order to remove the highest possible amount of lignosulfonates and decomposition products which will inhibit the subsequent sugars conversion. At the same time, a second anionic resin unit is being regenerated with 4% NaOH. The inhibitors removal yield was estimated on the basis of the experimental results (Llano et al., 2015). Two streams are obtained: i) a stream rich in sugars (DETOX), which is free of potential fermentation inhibitors and that will be the feedstock for further processing; and ii) a stream rich in lignosulfonates (PREEVAP) containing the components retained by the resin. The second stream can be sent to the evaporators after the regeneration of the resin.

The existing process has two evaporation plants used to concentrate the SL. Both were simulated in Aspen Plus and the energy requirements were obtained. For the existing configuration (direct concentration of the spent liquor), plant #1, which consists of five effects, requires 23600 kW and plant #2, with four effects, requires 15600 kW. If the resin unit is placed before the evaporators, only one of the evaporation plants can be used to concentrate the stream exiting from the resin unit. Plant #1 has been retained in the new process design.

The Aspen Plus model of the redesigned concentration process is shown in figure 16. The feed stream (PREEVAP) coming from the resin unit enters the evaporation plant. The order of the evaporators is EF1-EF2-EF3-EF4-EF5. The required concentration at the exit of the evaporation plant is 55% solids (LSC). The condensates (COND) are sent to the wastewater treatment plant. Each effect of the evaporation plant has been simulated with two units in Aspen Plus, flash and heater.

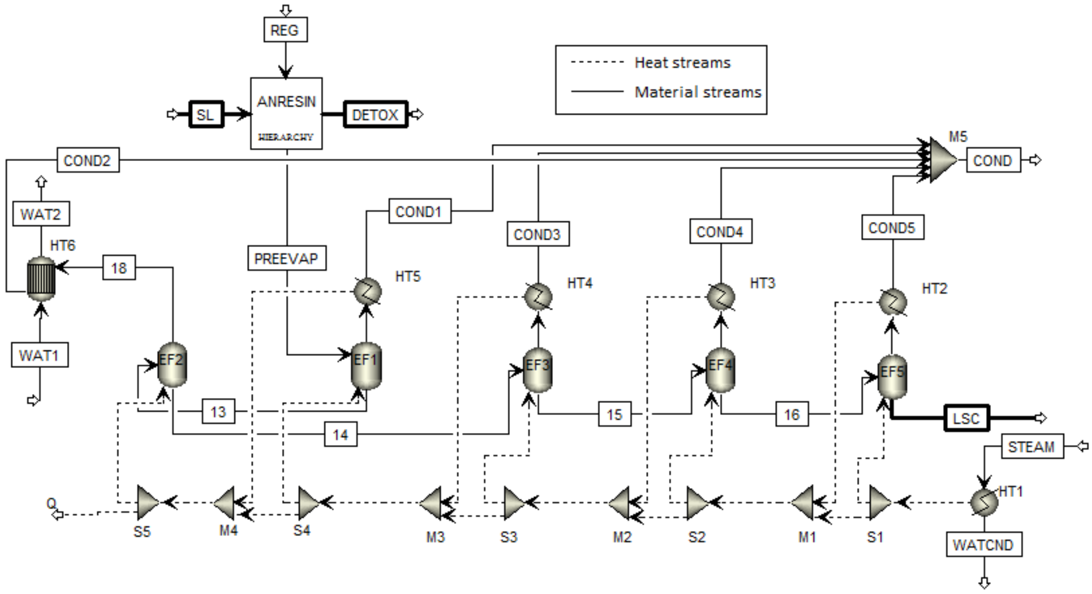

Figure 16. Flowsheet of the purification of the spent liquor and lignin concentration stages

The main streams of the simulated SL purification and lignin concentration process are given in table 7. MF represents the total mass flow of each stream.

Table 7. Mass balance of main streams of the process described in figure 16

Stream ID	MF (ton/h)	Sugars (ton/h)	LS (ton/h)	Water (ton/h)	Dec. Products (ton/h)
SL	82.2	2.77	3.94	74.9	0.59
DETOX	**77.6**	**2.14**	**1.38**	**73.7**	**0.40**
PREEVAP	39.1	0.62	2.57	35.7	0.20
LSC	**5.87**	**0.62**	**2.57**	**2.6**	**0.03**
COND	33.2	-	-	33.1	0.16

The evaporation plant #2 is not required because the flow rate of PREEVAP stream to be concentrated is reduced to 39 ton/h. The new requirement of plant #1 is 23400 kW and is close to the current duty. The energy demand of the concentration process has been reduced by 40.36% and represents a significant energy saving.

The concentrated stream after evaporation (LSC) contains 55% solids in both cases. However, the content of lignosulfonates on a dry basis regarding the rest of components of the stream in the existing process is 0.73 and it will be reduced to 0.26 in the new design. This corresponds to 57.9% and 79.6% of dry matter respectively. This improvement could be a significant advantage for the subsequent treatments of the lignosulfonates.

2.2. Sugar biorefinery options based on the purified/detoxified spent liquor

The stream exiting from the resin unit (DETOX), which is rich in sugars, is the feedstock to further biorefinery processes and could be converted into value-added products. In the previous chapter it was concluded that in the current market context of price and demand, furfural (option 1), xylitol (option 2) and ethanol (option 3) were the best candidates for techno-economic evaluation in view of the integration of biorefinery processes into the existing mill. The results obtained by the respective simulations are presented below.

Furfural production

The process flowsheet (figure 17) is based on the one proposed by Monstrastuc et al. (2011). The detoxified stream (DETOX) is sent to the reactor where it is mixed with H_2SO_4. Then the mixture of C5 & C6 sugars is transformed into furfural and HMF at 170°C and 21 bar. The conversion rate in the reactor of C5 sugars into furfural is 0.75 and that of C6 sugars into HMF is 0.05. Afterwards, the stream rich in furfural (F2) is sent to a distillation column, then is decanted (F10) and finally sent to a second distillation column (F11). The design parameters, including the operation parameters of the distillation columns and the heat exchangers were selected in order to recover as much furfural as possible, keeping a high pre-determined purity level.

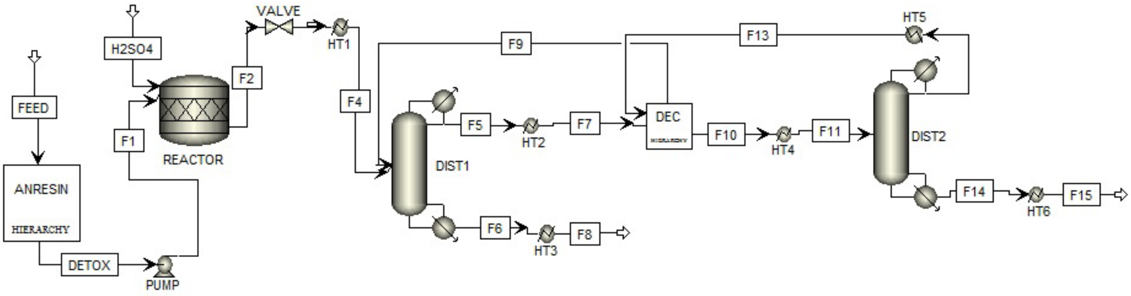

Figure 17. Flowsheet of the furfural production process

The mass balances of the simulated process are shown in table 8. The end product stream (F15) has a furfural flow rate of 19.9 ton/d with a purity of 99.95 %.

Table 8. Mass balance of the furfural process described in Figure 17

Stream ID	MF (ton/h)	Sugars (ton/h)	LS (ton/h)	Water (ton/h)	Furfural (ton/h)
DETOX	77.6	2.14	1.38	73.7	-
F2	77.7	0.83	1.38	74.1	0.83
F15	0.83	-	-	0.0004	0.83

Xylitol production

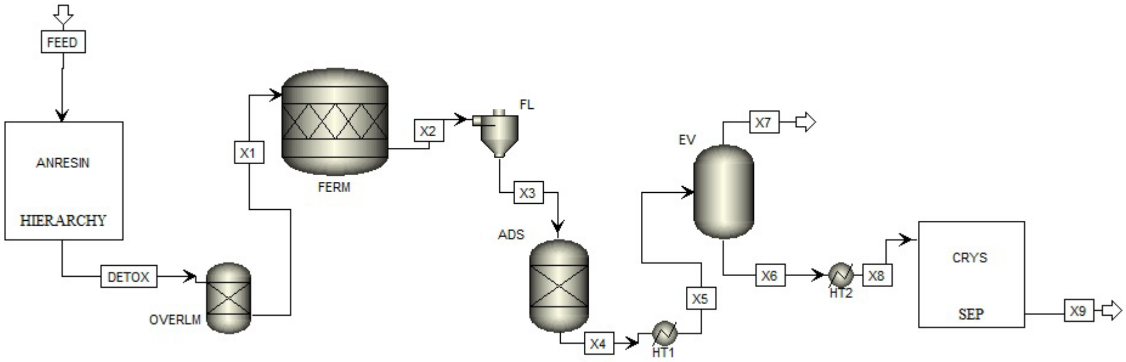

Figure 18. Flowsheet of the xylitol production process

Figure 18 shows the proposed xylitol process as simulated in Aspen Plus. The previously detoxified stream (DETOX) is first further detoxified by overliming before the fermentation step. This method was selected because it has low costs and high selectivity (Llano et al., 2015). The chosen agent was $Ca(OH)_2$, which achieved higher inhibitors removal than NH_4OH as well as lesser sugar losses. Furthermore with this treatment the pH can be adjusted to the value required for fermentation. The purified stream (X1) is fed to the fermentation reactor. The microorganisms *Candida*

Guilliermondii and *Debaromyces hansenii* have been reported to produce xylitol from sugars (Canilha et al., 2004; Fatehi et al., 2014). For this study *Debaromyces hansenii* was selected to carry out the fermentation at the required pH of 5.5. A concentration of xylitol of 9.73 g/L is obtained. The fermentation liquid (X2) is filtered and purified in an adsorption column, using activated charcoal to remove the remaining lignin, discolor and deodorize the xylitol stream as recommended by Rivas et al. (2006). The resulting stream (X4) is then concentrated since the final crystallization requires a stream with 40% solids (Fatehi et al., 2014). The crystallization is simulated by a separator in which the water is removed to obtain a crystalized xylitol (da Silva and Chandel, 2012).

The main data of the process corresponding to the simulation diagram of figure 18 are shown in table 9. The process end product (X9) is 15.8 ton/d of xylitol.

Table 9. Mass balance of the main streams of the xylitol process described in figure 18

Stream ID	MF (ton/h)	Sugars (ton/h)	LS (ton/h)	Water (ton/h)	Xylitol (ton/h)
DETOX	77.6	2.14	1.38	73.7	-
X2	76.9	1.02	0.97	73.6	0.77
X9	0.66	-	-	-	0.66

Ethanol production

The process simulation diagram is shown on figure 19. The detoxified stream (DETOX) is first subjected to overliming as in the case of xylitol, to be suitable for fermentation. The following microorganisms are able to produce ethanol from sugars contained in this type of feedstock, *Pichia stipitis*, *Saccharomyces cerevisiae* and *Thermoanaerobacterium saccharolyticum* (Lee et al., 2011; Millati et al., 2002; Takahashi et al., 2013). The microorganism selected for this study is *Saccharomyces cerevisiae* because it can survive at pH higher than 4.5 and a concentration of undissociated acetic acid less than 5 g/L (Purwadi et al., 2004). The stream resulting from the fermentation (E2) is filtered to separate the microorganisms and the undissolved material from the liquid and passed through an adsorption column to remove the remaining lignin and other impurities. To purify and concentrate the produced ethanol (Aden et al., 2002), the stream (E5) is distilled in a stripping column and the ethanol recovered in the stream (E6) is condensed in a heat exchanger prior to being sent to a rectification column. Finally, the stream (E9) is passed through a molecular sieve to eliminate the remaining water (Al-Asheh et al., 2004).

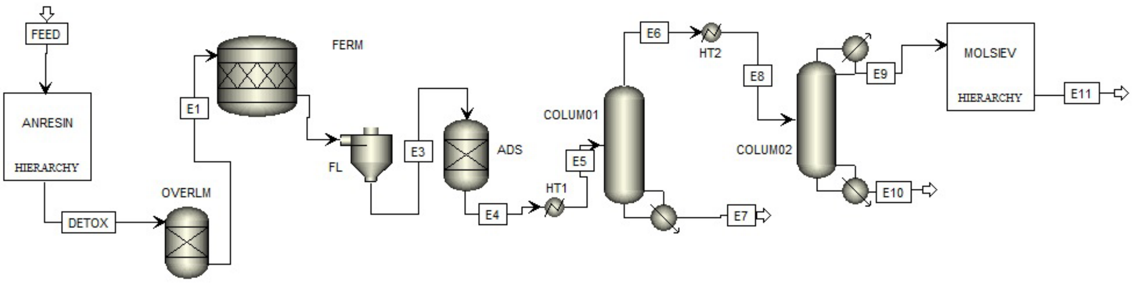

Figure 19. Flowsheet of the ethanol production process

The overall mass balances of the process are displayed in table 10. The final stream (E11) contains 14.6 ton/d of ethanol at 99.6% purity.

Table 10. Mass balance of the ethanol process described in figure 19

Stream ID	MF (ton/h)	Sugars (ton/h)	LS (ton/h)	Water (ton/h)	Ethanol (ton/h)
DETOX	77.6	2.14	1.38	73.7	-
E2	75.9	0.52	0.85	72.9	0.68
E11	0.612	-	-	0.002	0.61

It can be concluded from the mass balances of the three simulations, that the highest product yield is obtained in the furfural process. However, the capital investment for the different processes and the market prices of the three products considered are quite different. An economic assessment to determine the economic feasibility of each case is required.

3. ECONOMIC PERSPECTIVES

The development of a biorefinery integrated in an existing sulfite pulp mill is an attractive possibility to generate additional revenues. In addition to conventional pulp production the biorefinery would generate high value byproducts for sale or for further transformation by the downstream chemical industry.

3.1. Methodology of the economic analysis

The economic analysis was performed following standard methods described by Peters et al. (2011) and Turton et al. (2013). It was assumed that the life of the project is 10 years. The depreciation of the capital investment was calculated using the straight-line depreciation method (by means of which an equal amount of depreciation is charged each year over the depreciation period allowed) and zero salvage value (the fixed capital investment of the plant minus the value of the land, evaluated at the end of the plant life; often assumed to be zero). The feasibility of the project was determined by estimating the discounted cash flow rate of return and the payback period, as described by Turton et al. (2013).

Equipment sizing and costing

All equipment was sized and priced using Guthrie's method (Biegler et al., 1997). It was considered that the units are constructed of stainless steel. Several assumptions were made for the various units. For the reactor vessels, it was assumed that the length to diameter ratio is four. For the distillation columns, it was assumed that the tray efficiency is 80%, the tray spacing is 0.6 m, an extra feed space of 1.5 m is taken, a disengagement space of 3 m and a skirt height of 1.5 m. The column would use sieve trays and would operate at 80% of flooding capacity. Pumps are centrifugal and all heat exchangers are fixed tube sheet. Using these assumptions, complete calculations were made to size all the equipment. The mid-market dollar rate was taken as 0.880 €, on the 22nd of June 2015.

The Fixed Capital Invested (FCI) was estimated using the on-site costs, obtained by Guthrie's method, taking into account the off-site and indirect costs, the working capital and the plant startup cost. The Manufacturing Costs (COM) were estimated taking into account the operating labor cost, the costs of utilities, of waste treatment and of raw materials (Turton et al, 2013). Table 11 shows the main economic parameters in this study.

Table 11. Main economic parameters used in this work

Parameter	Calculation/Value
On-site Cost	BMC
Off-site Cost	0.45·On-site Cost
Indirect Cost	0.25·(On-site+Off.site)
FIXED CAPITAL	On-site+Off-site+Indirect Cost
FCI= (1.3·Fixed Capital)	
Operators Salary	41600*(1.03^(Current year-2003))
Utilities Cost	
Cooling water	0.037€/m^3
Low pressure steam	11€/t
Electricity	0.0659€/kWh
Refrigerant R407C	14000€/t
Raw material Costs	
H_2SO_4	39.6€/t
$COM=0.280FCI+2.73C_{OL}+1.23(C_{UT}+C_{WT}+C_{RM})$	

3.2. Fractionation/detoxification techniques cost comparison

The selection of the suitable fractionation/detoxification technique depending on the targeted product was done in a previous section based on the mass balances. The costs associated to each technique, expressed as FCI and the COM, are shown in table 12.

Table 12. FCI and COM for the proposed fractionation/detoxification techniques

Technique	FCI (M€)	COM (M€/year)
Ultrafiltration	20.6	0.42
Ionic exchange	1.08	5.48
Adsorption in black carbon	2.06	2.35
Adsorption in activated charcoal	1.55	2.24
Overliming	*	0.11

The overliming is not included in the table because its capital investment is low compared to that of other techniques. It requires a mixing tank for the homogenization of the $Ca(OH)_2$ and the SL. In addition, the overliming does not give good separation results according to Llano et al. (2015).

As can be seen in table 12, the FCI of ultrafiltration is much higher than that of the other techniques. This value has been estimated by the method proposed by Jönsson and Wallberg (2009), which is based on experimental laboratory tests that makes the scale-up hazardous. Ion exchange, the selected technique by mass balances criteria, present the lowest FCI. Ultrafiltration have the lowest COM after overliming, while ion exchange has the highest manufacturing costs. From these premises, the assessment of the fractionation and detoxification techniques was carried out using anionic resins.

3.3. Sugar conversion plants cost comparison

The computed FCI and COM values for the considered three options are calculated. The detoxification step is common to the three options. The FCI and COM for each option is developed separately.

The three FCI values are 4.25 M€ for the furfural plant, 5.13 M€ for the xylitol plant and 6.01 M€ for the ethanol plant. The values obtained for the COM are 3.59 M€, 4.83 M€ and 4.20 M€ for furfural, xylitol and ethanol respectively. These values are relatively close.

Main Profitability Indicators

The calculation of two main profitability indicators has been computed to select the best option. The indicators are the Return Period (RP) and the Net Present Value (NPV).

The market prices of the three end products were taken from the previous chapter and are 500 €/ton for furfural, 5830 €/ton for xylitol and 740 €/ton for ethanol. The prices for the targeted products are considered constant throughout the whole plant life.

The obtained results for the RP are given in table 13. A process is considered profitable when the RP is between 3 and 4 years. If it is between 4 and 10 years, an additional assessment is required, while if it is higher than 10 or negative, the project is not profitable.

Table 13. Return Period for the different product options

Detoxification excluded		**Detoxification included**	
Project	**RP (year)**	**Project**	**RP (year)**
Furfural	> 10	Resins + Furfural	NC
Xylitol	0.32	Resins + Xylitol	0.47
Ethanol	> 10	Resins + Ethanol	NC

NC= Not computed

The RP parameter was computed for two cases: i) with detoxification included and ii) with detoxification excluded. The results show that furfural and ethanol processes are not profitable. The complete xylitol process (resins + xylitol) is profitable with detoxification. The biorefinery in this case is an attractive option because of the high product market price.

In order to confirm the profitability predicted by the RP parameter, the NPV parameter has been computed for the options with a positive RP value. The useful life of each project was set to 10 years, and the NPV was estimated for three different interest rates, 3, 7 and 10%. %. 6-7% has been used in other similar references (Lammers et al., 2015; Mussatto et al., 2015). In addition, a wider interval, from 3 to 10% has been considered in this work. The results are given in table 14.

Table 14. Net Present Value for the different product options with positive Return Period

Project	**NPV (M€)**		
	R.I. 3%	R.I. 7%	R.I. 10%
Xylitol	128	105	90.9
Resins + Xylitol	101	81.7	70.7

Both cases are profitable under specified conditions. However, the estimated revenues may be inflated since they are based on the assumption that the long-term market prices will not vary.

In order to determine the impact of several influential parameters on the profitability of the production of xylitol from SL, a sensitivity analysis was performed for market price and fixed costs. The results are shown in figure 20. Utilities and labor costs were studied, however, they did not have a significant effect on profitability.

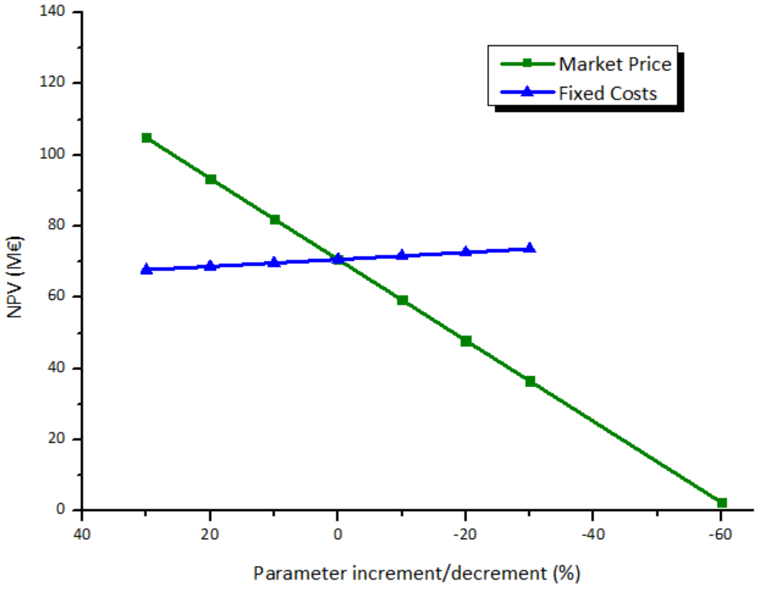

Figure 20. Impact of variation of market price and fixed costs on NPV

The selling price of xylitol has a large effect on the NPV, which increases with the increase of xylitol price. The project would not be profitable for a xylitol market price decrease to about 2300 €/ton. The project will remain profitable even if the fixed costs increase by a factor of 5 or more.

4. CONCLUSIONS

The spent sulfite liquor obtained as a by-product in the manufacturing of dissolving pulp by means of the acid sulfite process, contains a high amount of sugars that can be converted into value-added bioproducts. In the previous chapter, three potential products were identified as the best alternatives, furfural, xylitol and ethanol. In this work, a technoeconomic assessment of the three options has been developed, and different detoxification and fractionation techniques have been considered. Ion exchange adsorption using anionic resins was selected as the most cost effective technique. Furfural, xylitol and ethanol, production processes with respective capacities of 19.9, 15.8 and 14.6 ton/d were proposed and evaluated. These processes would be compatible with the amount of spent liquor available.

The mass balances were determined using Aspen Plus. An economic evaluation was performed, based on the sizing and costing of all the equipment. The fixed capital invested (FCI) and the manufacturing costs (COM) for each option were first carried out. Two profitability indicators, Return Period (RP) and Net Present Value (NPV) were computed.

Taking into account criteria such as estimated costs, selling price, market potential, and technical barriers, it was determined that the implementation of a xylitol biorefinery into the selected sulfite pulp mill would be the most advantageous option to diversify the product mix of the mill and generate additional revenues.

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CHAPTER III

CARBOHYDRATE DEGRADATION DURING THE ACID SULFITE PULPING. KINETIC STUDY

Up to now the design of an integrated biorefinery has been done using the parameters and data from the existing mill. However, it is possible to increase the available quantity of monomers in the spent liquor by modifying basic variables of the conventional sulfite process used by the mill. In this sense, the next two chapters of this thesis study the effect of different variables in the existing pulping process within the integrated forest biorefinery concept.

The current chapter studies the cooking control, responsible for one of the three major "driving forces" of the conventional sulfite pulping, the temperature, developing the kinetic modeling of the process under the premise that the monosaccharides present in the spent liquor (characterized in Chapter I) can be used as raw material in further biorefinery units. Thus, the knowledge of the kinetic parameters with the purpose of obtaining the maximum sugar conversion, will allow the determination of the optimal operation conditions of the process in order to integrate a biorefinery into the existing mill.

The results presented in this chapter were published as "**Monosaccharide production in an acid sulfite process: Kinetic modeling",** at Carbohydrate Polymers 116, 18-25 (2015).

1. MATERIALS AND METHODS

1.1. Raw material

Eucalyptus globulus wood from Cantabrian forests supplied by Sniace SA group (Torrelavega, Spain) has been chipped and classified for the cooking experiments. Chips with 15-30 mm length and 2-4 mm thickness were used.

Cooking liquor with a calcium base has been used. The parameters of the cooking liquor have to be as homogeneous as possible between the following values: total SO_2 (7.5-8.5g/100 mL liquor), combined SO_2 (1.5-1.8g/100 mL liquor), pH (1.1-1.5) and density (1050-1070 g/L).

1.2. Cooking experiments

For this study, one-liter stainless steel vessel reactors were used. The reactors have temperature and pressure control and an external electric heating system.

The cooking experiments have two main steps, impregnation (the cooking liquor penetrates the pores in the wood) and cooking at maximum temperature (when delignification takes place). For this work and in order to simplify the kinetic model, a reduced impregnation stage of 120 minutes was studied and concluded to be enough and thus it has been used in all the experiments. Three sets of experiments were carried out in duplicate at three different temperatures, 130, 140 and 150°C. These values were selected because the process to obtain dissolving pulp by means of an acid sulfite process works with temperatures inside this range (Sixta, 2006).

The process is the following: wood and cooking liquor are loaded into the digesters using a liquid/solid ratio of 20:1 L/kg. Then, the reactors are pressurized using argon gas until 9 bar of pressure and the heating ramp until desired constant temperature is set. The digesters have an automatic system of pressure control which maintains a constant pressure throughout the whole process. After the desired time at maximum temperature, the heating is stopped and the pressure is relieved. Once atmospheric pressure is achieved the digesters are discharged. Finally, the composition of the resulting spent liquor is analyzed.

1.3. Analytical methods

The **spent liquor** was characterized as follows. Free, total and combined SO_2 were determined according to the titration method Tappi T604 (Tappi, 1993) with iodine and sodium hydroxide. Sugar content (glucose, xylose, arabinose, rhamnose and galactose), acids (acetic, levulinic and formic) and other decomposition products (furfural and HMF) were measured by HPLC with SHODEX SH1011 column and Refraction Index detector according to Llano et al. (2013) method using 0.5mL/min of 0.005M H_2SO_4 as a mobile phase, 60°C in the oven and 198psi of column pressure.

The following methods were used for **wood** characterization. Tappi T257 (Tappi, 1993) was used to carry out the sample preparation. Extractives were determined according to the standard UNE EN ISO 14453 (ISO, 1999) for pulp, modified for its use with wood by means of an extraction with acetone as solvent using a soxhlet apparatus. Ash was measured using the standard Tappi T211 (Tappi, 1993) and a furnace at 525°C. Lignin was determined by Tappi T222 (Tappi, 1993) as follow: carbohydrates in wood are hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin is filtered off, dried, and weighed; the acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation at 205nm. Cellulose content was measured using the Seifert method (Klash et al., 2010; Rodríguez, 1978; Wahab et al., 2013). The procedure consists of the addition to the sample of 1,4-dioxane, acetyl acetone and hydrochloric acid and its subsequent boiling. Once the sample is cold, it is filtered and washed with methanol, hot water and acetone; finally dried and weighed. Holocellulose was determined with the Wise method (Wahab et al., 2013; Wise et al., 1946). The sample is treated with water and sodium chlorite in an acid medium achieved by the addition of some drops of acetic acid and it is heated using a water-bath at 75-80°C. This procedure is repeated until the sample is bleached. In this case, three times have been needed. After that, the sample is cooled, filtered and washed with water and acetone. Finally the sample is dried and weighed. Lastly, hemicellulose content was calculated as the difference between hollocelulose and cellulose.

2. KINETIC MODELING

Reactions which take place during the hydrolysis of wood are many and complex, therefore simplified kinetic models which are useful for engineering purposes are proposed. The approach of these models is done in two steps: first a simplified reaction scheme is taken into account and the following kinetic equations for each reaction are considered. The modeling has been done regarding the sugar and inhibitor content present in the liquor phase, spent liquor, in order to be used from a biorefinery point of view.

2.1. Reaction schemes assumption

A summary of the considered reaction schemes in this work is shown in figure 21.

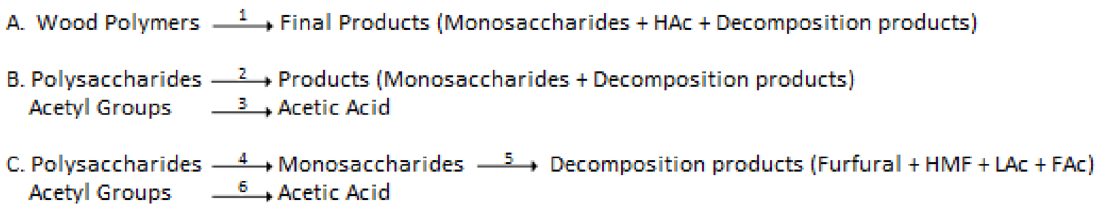

Figure 21. Considered reaction schemes

Scheme A

Scheme A considers that polymers (POL) are transformed into final products (FP). In this scheme, the degradation of the polymers of wood over time is described by equation 1:

$$Polymers\ (POL) \xrightarrow{1} Final\ Products\ (FP)$$

$$(-R_{POL}) = r_1 \tag{1}$$

Scheme B

Several authors (Lu and Mosier, 2008; Rahman et al., 2006) consider that the acetic acid (HAc) produced during the hydrolysis is due to the acetyl groups (AC) and is not a consequence of the degradation of polysaccharides; therefore parallel reactions have been considered in scheme B as is shown by equation 2:

$$Polysaccharides\ (PS) \xrightarrow{2} Products\ (P)$$

$$Acetyl\ Groups\ (AC) \xrightarrow{3} Acetic\ Acid\ (HAc)$$

$$(-R_{PS}) = r_2$$

$$(-R_{AC}) = r_3 \tag{2}$$

Scheme C

On the other hand, monosaccharides can degrade during the process and produce non desired products (Aguilar et al., 2002; Rahman et al., 2006; Zhuang et al., 2009). Scheme C is suggested in which polysaccharides (PS) are transformed into monosaccharides (MS) and these into decomposition products (DcP). Furthermore the reaction of acetyl groups in parallel is maintained.

$$Polysaccharides\ (PS) \xrightarrow{4} Monosaccharides\ (MS) \xrightarrow{5} Decomposition\ Products\ (DcP)$$

$$Acetyl\ Groups\ (AC) \xrightarrow{6} Acetic\ Acid\ (HAc)$$

$$(-R_{PS}) = r_4$$

$$(-R_{AC}) = r_6 \tag{3}$$

$$(-R_{MS}) = r_4 - r_5$$

2.2. Kinetic equations

Hydrolysis reactions during the cooking stage are very complex due to the fact that the substrate is in a solid phase (wood) and the catalyst is in a liquid phase (cooking liquor). These reactions depend on a large number of variables. The models proposed in literature consider irreversible pseudo-homogeneous first-order reactions (Malester et al., 1992; Orozco et al., 2007; Saeman, 1945) in order to simplify the modeling.

In this work the equations of reaction rate will be compared using different reaction orders following the general expression 4:

$$r_i = -k_i \cdot C_j{}^n \tag{4}$$

r_i being the reaction rate of the reaction i, C_j the concentration of the corresponding reactive component j, k_i the rate constant of the reaction i and n the reaction order.

Furthermore in order to know the dependency of the rate constant with temperature, Arrhenius' Law was used by means of equation 5:

$$k_i = k_{0i} \cdot e^{\frac{-Ea_i}{RT}} \qquad (5)$$

k_{0i} being the pre-factor, Ea_j the activation energy and R the Universal gas constant.

3. RESULTS AND DISCUSSION

Eucalyptus globulus wood samples were analyzed to determine their main components, which are shown in table 15.

Table 15. General composition of wood in this study

Composition (%)			
Cellulose	42.25	Extractives	1.50
Hemicellulose	24.92	Lignin	26.98
Holocellulose	67.18	Others	4

Hemicelluloses of *Eucalyptus globulus* as a hardwood are formed by xylans and only a small quantity of glucomannan. In order to facilitate calculation, only xylans as the major compound present in them have been taken into account in this work. Starting from the general composition of *Eucalyptus globulus* wood, a characterization of the oligomers as well as the acetyl groups present in this type of wood has been done and it is shown in table 16.

Table 16. Theoretical homopolymers in *Eucalyptus globulus* wood

Oligomer decomposition (%)			
Glucan	42.25	Galactan	7.36
Xylan	13.27	Mannan	1.04
Arabinan	0.52	Acetyl groups	2.78

With the hydrolysis, the glucosidic bonds of polysaccharides (cellulose and hemicellulose) are broken after the addition of water, generating monomeric sugars or sometimes disaccharides such as cellobiose (Kaar et al., 1991). Furthermore different byproducts are generated such as furfural, HMF or acids. The weight of each constituent, determined quantitatively during acid hydrolysis, has to be multiplied by a factor to calculate its contribution to the original wood component (as a theoretical homopolymer) stoichiometrically (Santana and Okino, 2007). This grouping can be done by means of stoichiometric factors and empiric correlations. Thus the grouping starts with the measuring of the weight of each element determined by HPLC. (Kaar et al., 1991; Santana and Okino, 2007; Alves et al., 2010). The glucose factor is 162/180 as it is expressed as glucan. The numerator indicates the molecular mass of the anhydro unit and the denominator the molecular mass of the glucose. In the same way for the rest of the components: HMF 162/126 and levulinic acid 162/116 both expressed as glucan; xylose 132/150 and furfural 132/96 expressed as xylan; arabinose 132/150, galactose 162/180, mannose 162/180 and acetic acid 43/60 expressed as arabinan, galactan, mannan and acetyl groups respectively (Santana and Okino, 2007).

The obtained values are used as initial points to calculate the initial concentration of polysaccharides and acetyl groups in wood, assuming that glucan is completely converted to glucose, xylan to xylose, galactan to galactose, arabinan 67% to arabinose and 33% to fucose, and finally acetyl groups to acetic acid. Thus, the initial concentration of each polymer, expressed as a monomer (mol/L) can be calculated as follows:

$$P_0 = \frac{X_{P0} \cdot SLR}{100 \cdot SF \cdot MW} \qquad (6)$$

Where X_{P0} is the initial amount of polymers present in the wood on dry basis, SLR is the solid/liquid ratio, SF is the stoichiometric factor and MW the molecular weight of each monomer.

In the work of Rahman et al. (2006) the initial value of xylan expressed as g xylose/L was estimated theoretically using equation 6 however for the glucan the concentration was obtained by means of estimation from the experimental data. In this work, the initial concentration values have been calculated using the obtained SLR for each set of experiments and the values of table 16. The average values of polysaccharide concentration for each temperature are shown in table 17.

Table 17. Maximum available concentrations (mol/L) for each component

	Glucan	Galactan	Xylan	Arabinan	Acetyl
150°C	0.1004	0.0175	0.0387	0.0015	0.0248
140°C	0.1075	0.0187	0.0414	0.0016	0.0265
130°C	0.1188	0.0207	0.0458	0.0018	0.0294

3.1. The effect of temperature on product conversion

To study the influence of temperature on wood depolymerization, experiments were carried out at three different temperatures, 130, 140 and 150°C with a liquid/solid ratio of 20:1 L/kg. Figure 22 shows the graphic representation of the obtained results for the conversion of polysaccharides into monosaccharides and the latter into decomposition products (furfural, HMF, levulinic acid and formic acid) as well as the conversion of acetyl groups into acetic acid. The experimental data is represented by symbols and the predicted curves of the posed model by lines.

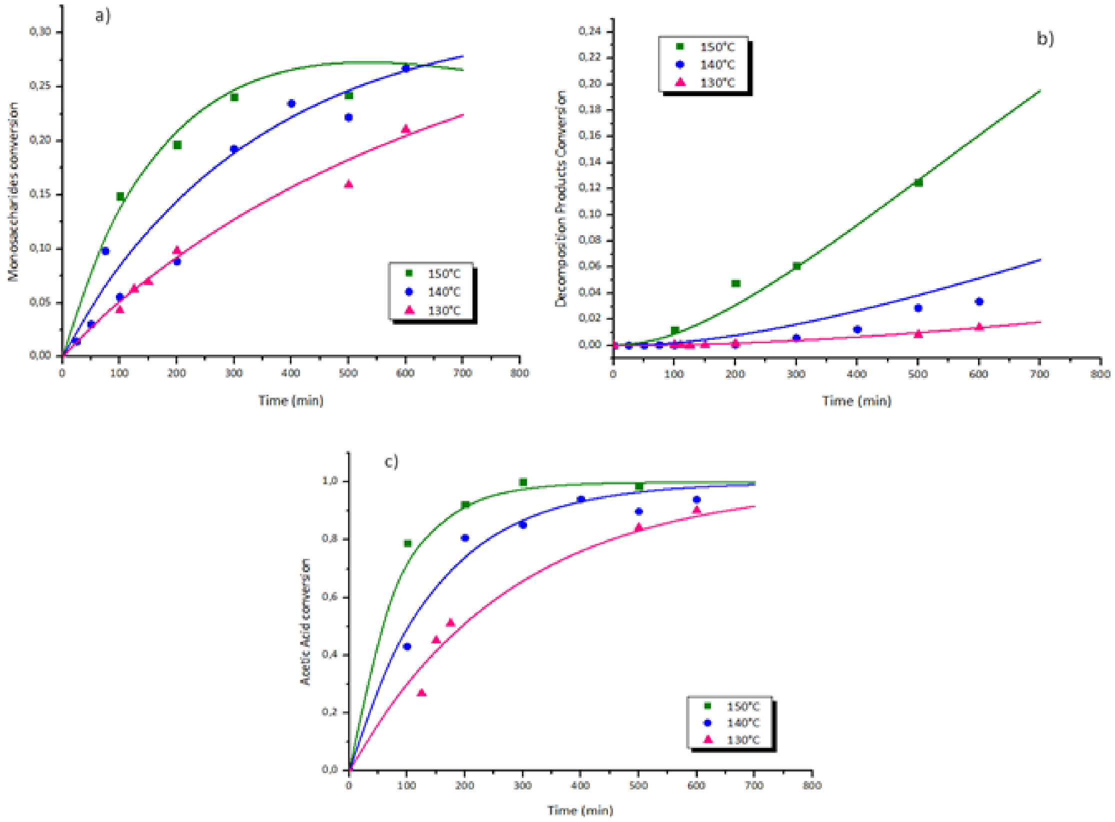

Figure 22. Obtained results at different temperatures for the conversion of: a) Polysaccharides into monosaccharides; b) Monosaccharides into decomposition products; c) Acetyl groups to Acetic Acid

As it was expected, higher conversions were reached faster at higher temperatures for all products. Thus at 150°C and low times, higher conversions of monosaccharides and acetic acid are reached but also the highest amount of decomposition products, which are not desired for further biorefinery processes. This makes a compromise solution necessary between obtaining more sugar content with the minimum decomposition products content as possible and the use of resources such as energy and time.

3.2. Results of the kinetic experiments

The kinetic schemes proposed have been validated taking into account the experimental results described in the previous epigraph and considering that there are no limitations for mass transport. Values of kinetic parameters were estimated using Aspen Custom Modeler of AspenTech®. As estimation criteria, the minimization of the sum of weight squared errors has been followed, $\sum (C_{exp} - C_{sim})^2$, where C_{exp} are the experimental concentrations and C_{sim} the obtained concentrations by simulation from the considered model.

Scheme A allows the study of the conversion of polymers into final products. The mass balance for polymers is:

$$C_{POL} = C_{POL,0} - \int_0^t r_1 \, dt \qquad (7)$$

The obtained kinetic parameters for this model are shown in table 18. The corresponding representation of the experimental and simulated data with the posed model curves are shown in figure 23. As can be seen, the experimental data (dots) fit quite well with the simulated curves (solid and dash lines) and also that the experimental data grow quickly and they reach the maximum conversions at relatively low times. This means that a model with a reaction order superior to n=1 can adjust better to the experimental results. The proposed model with a reaction order of n=2.99 leads to a maximum polymer conversion of approximately 50%, which agrees with the experimental data also shown by the values of the regression coefficient. The R^2 value for n=1 is 92.79% and for n=2.99 is 97.54%. Thus, the kinetic equation to describe the polymer conversion to final products is:

$$r_1 = 9.9010^{13} \, e^{\frac{-14633.4}{T}} \, C_{POL}^{2.99} \qquad (8)$$

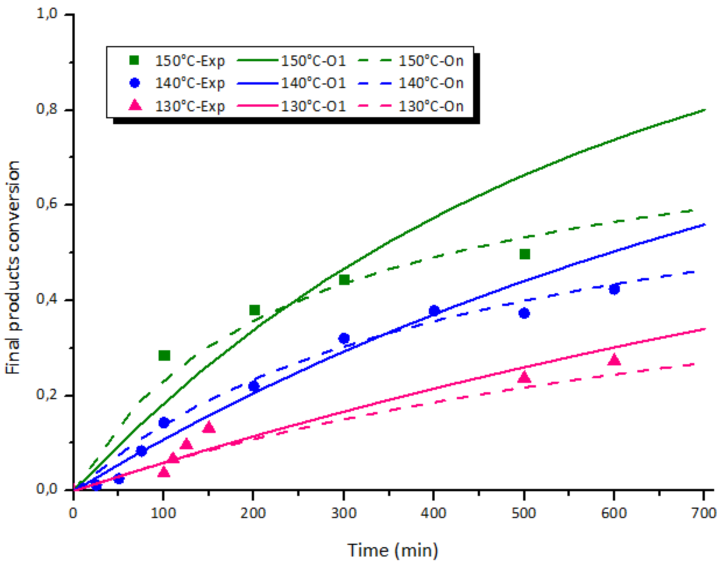

Figure 23. Comparison between simulated curves (n=1 and n=2.99) and experimental values in both models for the conversion of polymers to final products, FP (scheme A).

Table 18. Kinetic parameters obtained for all the schemes and different reaction orders

Scheme	Parameter	Order	
		n=1	**n=2.99**
A	k_{01} (mol^{1-n} L^{n-1} min^{-1})	$1.58\cdot10^{6}$	$9.90\cdot10^{13}$
	Ea_1(J/mol)	$7.24\cdot10^{4}$	$1.22\cdot10^{5}$
	R^2_1 (%)	92.78	97.54
		n=1	**n=3.61**
B	k_{02} (mol^{1-n} L^{n-1} min^{-1})	$3.15\cdot10^{5}$	$8.85\cdot10^{13}$
	Ea_2(J/mol)	$6.84\cdot10^{4}$	$1.18\cdot10^{5}$
	R^2_2 (%)	91.93	95.90
		n=1	
	k_{03} (mol^{1-n} L^{n-1} min^{-1})	$8.39\cdot10^{8}$	
	Ea_3 (J/mol)	$8.77\cdot10^{4}$	
	R^2_3 (%)	90.33	
		n=1	**n=3.2**
C	k_{04} (mol^{1-n} L^{n-1} min^{-1})	$1.81\cdot10^{6}$	$1.46\cdot10^{13}$
	Ea_4 (J/mol)	$7.44\cdot10^{4}$	$1.14\cdot10^{5}$
	R^2_4 (%)	93.12	95.91
		n=1	**n=1.06**
	k_{05} (mol^{1-n} L^{n-1} min^{-1})	$3.61\cdot10^{12}$	$3.04\cdot10^{13}$
	Ea_5 (J/mol)	$1.25\cdot10^{5}$	$1.32\cdot10^{5}$
	R^2_5 (%)	90.38	94.18

In scheme B, two reactions are considered: polysaccharides (PS) are transformed into products such as monosaccharides, some oligosugars and decomposition products; and the acetyl groups are transformed into acetic acid by a parallel reaction.

Mass balances for polysaccharides and acetyl groups are given by the following equations:

$$C_{PS} = C_{PS,0} - \int_0^t r_2 \, dt \qquad (9)$$

$$C_{AC} = C_{AC,0} - \int_0^t r_3 \, dt \qquad (10)$$

To explain the transformation of polysaccharides into products, kinetic equations of first order and n order were considered; however, for the formation of acetic acid only first reaction order kinetic was taken into account. Using higher reaction orders, the adjustment of the experimental data did not improve significantly.

Estimated values of kinetic parameters are shown in table 18 and figures 24 and 22c show the evolution of the conversion for polysaccharides and acetyl groups at the three studied temperatures. In figure 24, as with the conversion of POL to products, a better adjustment for a kinetics of n=3.61 order is observed with R^2 equal to 95.9%. For the second reaction, the formation of acetic acid, shown in figure 22c, conversions around the unit are achieved. This means that practically all of acetyl groups are converted into acetic acid, faster for higher temperatures. Thus, the kinetic equations for polysaccharides and acetyl group conversions are:

$$r_2 = 8.85 10^{13} \, e^{\frac{-14172.0}{T}} \, C_{PS}^{3.61} \qquad (11)$$

$$r_3 = 8.39 10^{8} \, e^{\frac{-10549.2}{T}} \, C_{AC} \qquad (12)$$

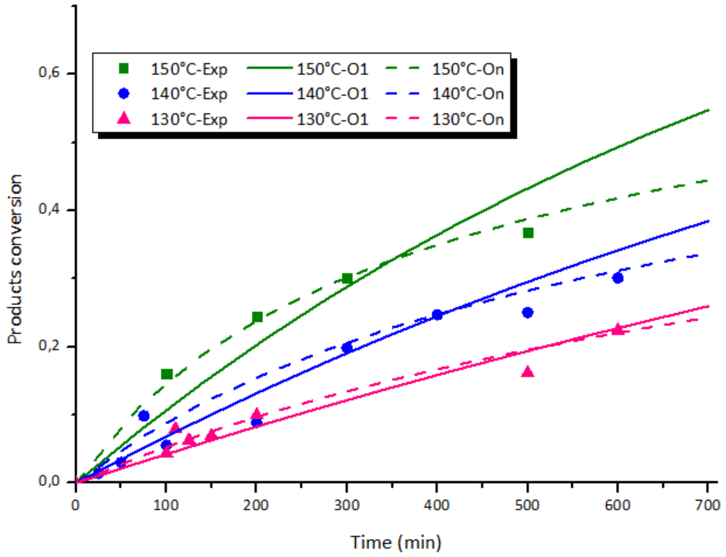

Figure 24. Comparison between simulated curves (n=1 and n= 3.61) and experimental values for the conversion of polysaccharides into products (scheme B).

If figures 23 and 24 are compared, it can be seen that the tendency of the products for all temperatures has been improved by eliminating the acetic acid of the first reaction. This confirms that the acetic acid is not a degradation product from sugar as is going to be corroborated by scheme C.

The last proposed scheme, scheme C, starting from scheme B, also has two parallel reactions. The difference lies in the fact that the other reaction was separated into two reactions in series following equation 3, polysaccharides form monosaccharides and these in turn are decomposed into non-desired products. At the same time, the parallel reaction of acetyl groups is maintained because it does not change with respect to the previous scheme.

Mass balances of polysaccharides, monosaccharides and decomposition products are:

$$C_{PS} = C_{PS,0} - \int_0^t r_4 \, dt \qquad (13)$$

$$C_{MS} = C_{MS,0} + \int_0^t (r_4 - r_5) \, dt \qquad (14)$$

$$C_{DP} = C_{DP,0} + \int_0^t r_5 \, dt \qquad (15)$$

Kinetic parameters obtained for scheme C are shown in table 18 and the evolution over time of monosaccharides and decomposition products in figures 25 and 26 respectively. It is observed that the model with reaction order n=3.2 for the reaction of polysaccharide transformation into monosaccharides predicts the behavior of the experimental data with more accuracy than a reaction order of n=1. However, the estimated reaction order for the monosaccharide degradation is n=1.06, very close to n=1. The kinetic equations will be:

$$r_4 = 1.47 \cdot 10^{13} \, e^{\frac{-13760}{T}} \, C_{PS}^{3.2} \qquad (16)$$

$$r_5 = 3.04 \cdot 10^{13} \, e^{\frac{-15878.1}{T}} \, C_{MS}^{1.06} \qquad (17)$$

The regression coefficients of the model using reaction order n for both reactions, the evolution of monosaccharides and the formation of decomposition products are higher than those obtained using reaction order n=1. As can be seen in figure 26, the adjustment for the decomposition products is acceptable due to the complexity of the reactions which can take place. Simulated curves are well-adjusted to the experimental data. This means that the global mass balance is fulfilled, which validates the reaction scheme considered and the proposed kinetic models. Also, it indicates that the considered species in the analyses carried out are the majority and any other species are present at very low concentrations.

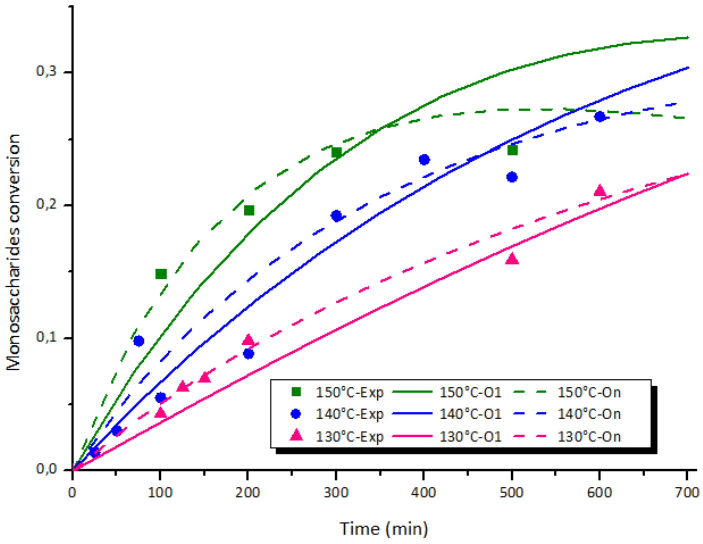

Figure 25. Comparison between experimental values and simulated curves (n=1 and n=3.2) for the conversion of polysaccharides into monosaccharides (scheme C).

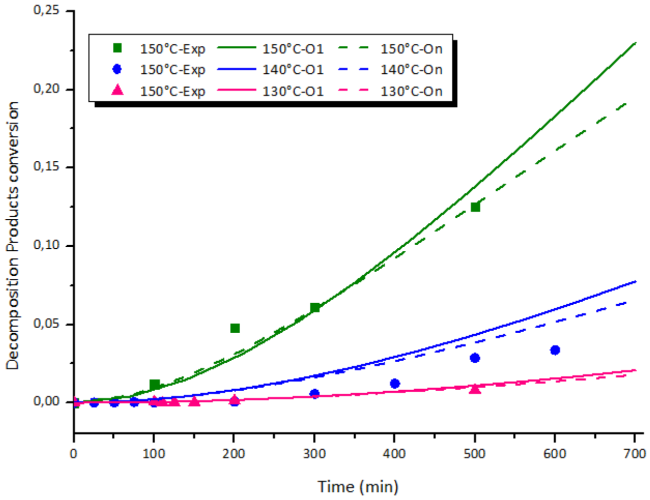

Figure 26. Comparison between experimental values and simulated curves (n=1 and n=1.06) for the conversion of monosaccharides into decomposition products (scheme C).

Using scheme C, it is possible to predict the release of monosaccharides to develop the valorization options of the spent liquor which allows the implementation of the biorefinery concept. Furthermore it describes both the release of monosaccharides as well as the formation of decomposition products. On the other hand, the sugar content is as important as the decomposition products content because for further processes such as detoxification and fermentation those values are necessary in order to obtain value added products.

Figure 27 shows the evolution of the conversion of monosaccharides into degradation products using the model of scheme C. As can be seen, the maximum conversion is reached faster for higher temperatures. Values of maximum conversion of monosaccharides, expressed as sugar content present in the spent liquor with respect to the initial quantity in wood, in mol, for the three different temperatures are shown in table 19 as well as the necessary time to reach them and also the conversion of decomposition products reached at those times.

Maximum monosaccharide conversion is 33.91 mol%, 30.15 mol% and 27.30 mol% for 130°C, 140°C and 150°C respectively. And the conversion for decomposition products is 13.81 mol% for 130°C, 13.83 mol% for 140°C and 13.69 mol% for 150°C. As can be seen in table 19, the maximum conversion is reached at higher times for 130°C but it reaches higher values. At low temperatures a stream with higher concentrations of sugar and similar content of decomposition products at longer operation times is obtained which facilitates the valorization of the stream.

Table 19. Maximum conversion obtained using scheme C and reaction orders n=3.2 (MS) and 1.06 (DP)

T (°C)	**Maximum sugar release (mol%)**	**Inhibitors release at maximum sugar release (mol%)**
	n= 3.2	**n=1.06**
150°C	27.30 (530min)	13.69
140°C	30.15 (1180 min)	13.83
130°C	33.91 (2650min)	13.81

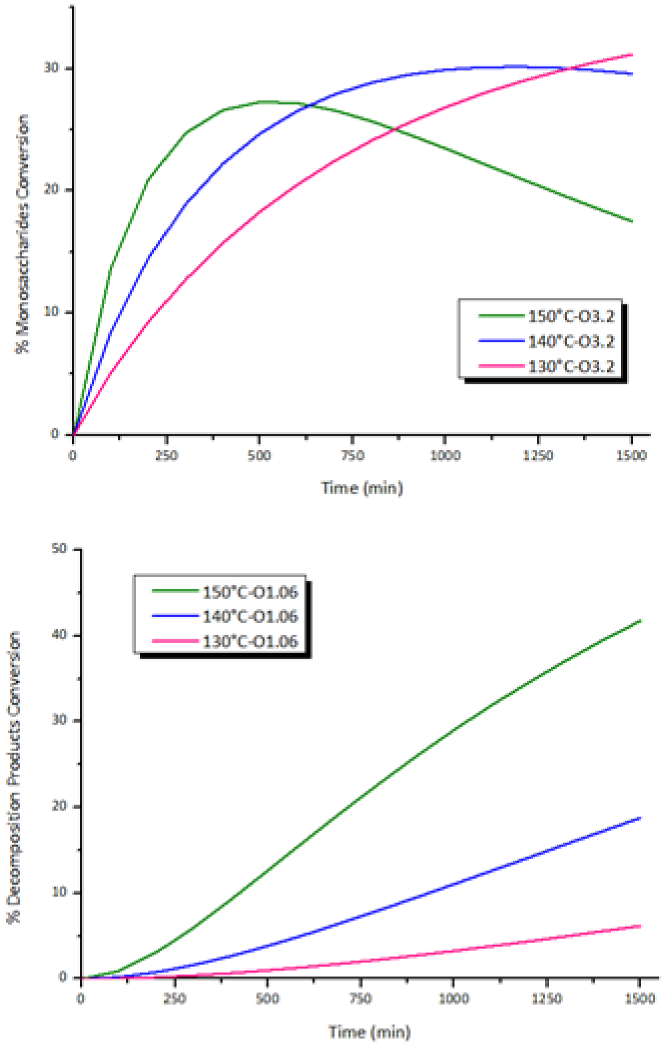

Figure 27. Evolution of conversion using scheme C and reaction orders n=3.2 (MS) and 1.06 (DP)

4. CONCLUSIONS

The kinetic behavior of the carbohydrate degradation on sulfite process has been studied at laboratory scale at three different temperatures: 130°C, 140°C and 150°C, in order to valorize the hemicellulosic hydrolyzate. Kinetic models were posed considering different reaction schemes which allow the description of the conversion of wood polysaccharides into monosaccharides and the formation of decomposition products. In all cases, kinetic equations of first or n order were considered using Aspen Custom Modeler. All schemes fitted well with the experimental results. In addition, the results show that the transformation of polysaccharides into monosaccharides is better described by a reaction order close to 3 while the transformation of monosaccharides into decomposition products can be described with a kinetics of 1. On the other hand, the conversion of acetyl groups into acetic acid has been considered as a parallel reaction giving first order kinetics results. The model shows that higher temperatures promote the obtaining of sugars faster; however these give less maximum sugar conversion and also more decomposition products, harmful for further processing. Taking into account the maximum sugar conversion, 130°C is the best alternative, giving a maximum sugar conversion of 33.91 mol% and 13.81 mol% for decomposition products production.

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CHAPTER IV

INFLUENCE OF INPUT VARIABLES IN SULFITE PULPING OVER THE RESULTING PRODUCTS

Apart from the cooking control (studied in Chapter III), other variables affect the sulfite pulping. In this chapter, the main variables of the pulping process have been studied.

The first issue that is assessed in this chapter is the wood, in the case study, *Eucalyptus globulus,* which in recent years is suffering from some diseases and pests which cause its defoliation, affecting its available quantity. In this sense, how to avoid the loss of pulp yield as well as the optimization of byproducts using biorefinery processes are the main important keys to study for the mill. One of the possible options is to complete the consumption of *E. globulus* with other species such as *Eucalyptus nitens*. For this purpose the behavior of the two species, taking into account the obtained dissolving pulp as well as the characteristics of the resulting products, has been assessed.

The second issue treated in this chapter is the cooking acid, which can affect the process by means of the choice of base and the pH. The results obtained with the currently used base are compared to those are obtained i) increasing the pH and ii) selecting magnesium as base instead of calcium.

Part of the results shown in this chapter were published as a scientific paper called "**Influence of Input Variables over the Wood Digestion in a Sulfite Pulp Mill for Biorefinery Purposes**" at Journal of Biology and Life Sciences, 6(2), 160-171 (2015).

1. MATERIALS AND METHODS

1.1 Raw Materials

The wood used has been *Eucalyptus globulus* and one selected tree of *Eucalyptus nitens* from Cantabrian forests supplied by Sniace SA group (Torrelavega, Spain). Logs have been chipped and classified. The chips used in the cooking experiments have 15-30 mm length and 2-4 mm thickness.

The parameters of the cooking liquor (made by dolomite, water and SO_2) have to be as homogeneous as possible. In this work, the parameters have been the following: total SO_2 (7.5-8.5g/100 mL liquor), combined SO_2 (1.5-1.8g/100 mL liquor).

1.2 Cooking Experiments

The cooking experiments were carried out in one-liter stainless steel reactors with temperature and pressure control and an external electric heating system. For this, wood and fresh liquor were loaded into the digesters and after some operation conditions (pressure, SO_2 content and residence time) unbleached pulp and spent liquor were obtained.

The process for each experiment has been the following: wood and cooking liquor are loaded into the digesters using a fixed liquid/solid ratio. Then, the reactors are pressurized using argon gas until 9 bar of pressure and the heating ramp until desired constant temperature is set. The digesters have an automatic system of pressure control which maintains a constant pressure throughout the whole process. After the desired time at maximum temperature, the heating is stopped and the pressure is relieved. Once atmospheric pressure is achieved, digesters are discharged. Finally, the composition of resulting spent liquor and pulp, if applicable, is analyzed.

1.3 Analytical Methods

The following methods were used for **wood** characterization. Tappi T257 (Tappi, 1993) was used to carry out the sample preparation. Extractives were determined according to the standard UNE EN ISO 14453 (ISO, 1999) for pulp, modified for its use with wood by means of an extraction with acetone as a solvent using a soxhlet apparatus. Ash was measured using the standard Tappi T211 (Tappi, 1993) and a furnace at 525°C. Lignin was determined by Tappi T222 (Tappi, 1993) as follow: carbohydrates in wood are hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin is filtered off, dried, and weighed; the acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation at 205nm. Cellulose in this chapter was determined as alpha-cellulose. Its content was measured using the standard Tappi T203 (Tappi, 1993) by means of which, the obtained material after the holocellulose determination is extracted consecutively with 17.5% and 9.45% sodium hydroxide solutions at 25°C. The soluble fraction, consisting of beta- and gamma-celluloses, is determined volumetrically by oxidation with potassium dichromate, and the alpha-cellulose, as an insoluble fraction, is derived by difference. Holocellulose was determined with the Wise method (Wahab et al., 2013; Wise et al., 1946). The sample is treated with water and sodium chlorite in acid medium achieved by the addition of some drops of acetic acid and it is heated using a water-bath at 75-80°C. This procedure is repeated until the sample is bleached. In this case, it has been repeated three times. After that, the sample is cooled, filtered and washed with water and acetone. Finally the sample is dried and weighed. Lastly, hemicellulose content was calculated as the difference between hollocelulose and cellulose.

The quality grade of cellulose **pulp** was evaluated by means of kappa index according to Tappi T236 standard (Tappi, 1993) and intrinsic viscosity following the guidelines of ISO/FDIS 5351 (ISO, 2010).

The **spent liquor** was characterized as follows. Free, total and combined SO_2 were determined according to the titration method Tappi T604 (Tappi, 1993) with iodine and sodium hydroxide. Sugar content (glucose, xylose, arabinose, rhamnose and galactose), acids (acetic, levulinic and formic) and other decomposition products (furfural and HMF) were measured by HPLC with SHODEX SH1011 column and Refraction Index detector according to Llano et al.'s (2013) method using 0.5mL/min of 0.005M H_2SO_4 as a mobile phase, 60°C in the oven and 198psi of column pressure.

2. INFLUENCE OF THE WOOD CHIPS

Eucalyptus is one of the genus most commonly used in Europe and specifically in the north of Spain to produce pulp because of its fiber size, quality and lighter color as well as its productivity and plasticity (Pérez Cruzado et al., 2011). It is the most profitable in Europe for this type of use, beating birch and other hardwoods.

Pulp manufacturers in northern Spain had traditionally used *Eucalyptus globulus* as raw material in their pulping processes to obtain dissolving pulp. However, in recent years some diseases, such as *Mycosphaerella*, and pests, such as *Gonipterus scutellatus*, have affected the quantity available of this wood (Otero et al., 2006; Sánchez et al., 2011). These pests and diseases cause massive defoliation in young leaves annually, producing important losses of growth and weakness of the masses, with generalized mortality in frost exposed zones (Tejedor, 2004).

In this way, some factories are studying how to palliate this situation. One option is the selection of the most resistant families and the cloning of the best trees of *Eucalyptus globulus* in order to get varieties tolerant to the diseases. Another option is to improve *Eucalyptus nitens* characteristics, such as wood density, growth, diseases resistance and coppice ability.

In this sense, the basic knowledge of the chemical composition and structure of the wood as raw material (Sixta, 2006) is fundamental to understand the pulping process and the possible valorization of the waste materials obtained in this process. Wood is formed mainly by cellulose, hemicellulose, lignin and small percentages of extractives and ash. In an acid sulfite process, the process in which this work is focused, the fraction of cellulose is oriented to obtain dissolving pulp; however, the rest of the components, lignin and hemicellulose, are byproducts that can be valorized into new high value-added products such as ethanol or xylitol from fermentable sugar (from the hemicellulose) and lignosulfonates (from the lignin) (Rueda et al., 2015).

The objective of the first part of the chapter is to study how far *E. nitens* affects the parameters of the existing process as well as the properties of the obtained pulp but also of the spent liquor for its valorization opportunities. Different characteristics of two species (*Eucalyptus globulus* and *Eucalyptus nitens*) have been analyzed in order to study the possibilities of consuming both species in a pulp mill; starting with the forestry characteristics and followed by their density and chemical composition.

Finally, the behavior in the chemical pulping has been assessed to improve the separation of the main components of the wood, giving the best valorization options of the spent liquor.

It is important to mention that the timber arriving to any factory is quite a heterogeneous material because many factors are involved in the wood quality: the genetic of the tree (not just the species, but also the provenance, the family, clones…) the soil of the forest, the age of the trunk, the position inside the trunk, etc. (Tejedor, 2004). So, this *Eucalyptus* species cannot be seen as a unique value applicable for *E. nitens* or *E. globulus* but a wide variety of values that can be found inside each species.

2.1 Plantation

Eucalyptus globulus is very sensitive to frosts, especially during the first two years, putting up with 5 and 30 frosts per year although in coastal areas this phenomenon is less frequent, but in higher altitudes these can occur more than 70 times per year (Brinkmann, 1992). The most favorable temperature for the specie is situated as an annual average between 10 and 15^{o}C, with limits of -4.5^{o}C and 40.5^{o}C for short periods of time (Brinkmann, 1992). This specie must not exceed seven dry months.

However, *Eucalyptus nitens* is able to bear the same temperatures and to grow enduring between 50 and 150 frosts per year. In comparison with *E. globulus*, previous studies (Tejedor, 2004) have demonstrated that *E. nitens*, in general, is less affected by pests and diseases previously mentioned, especially in altitudes higher than 300 meters above sea level. There are also important differences between provenances of *E. nitens* for disease resistance.

Additionally, the growing data of both species for the region of Cantabria, 24-29 m^3/ha/year for *E. nitens* and 13-17 m^3/ha/year for *E. globulus* (Forest Patrimony of Sniace group), gives an idea of how the productivity in the whole process from the forest to the factory can increase. Therefore, *E. nitens* presents better forestry characteristics according to the purpose of this work.

2.2 Density

Density is one of the most important properties of wood and pulping processes because it is related to mechanical resistance and to cellulosic and energetic flair. Optimal density is a function of end-use of wood.

Table 18 shows the density values obtained by other authors and those of this work. First, what attracts attention is that the density of *Eucalyptus nitens* is slightly lower than *Eucalyptus globulus*. In Cantabrian forests, the results are 475-650 Kg/m^3 for adult trees of *E. globulus* and 460-520 Kg/m^3 for *E. nitens*. *E. globulus* presents more density than *E. nitens* in all cases; however, the studied interval of variation is wider in the case of *E. globulus*. Density is a parameter which is very dependent on other factors such as the genetics of the tree (provenance, family, clone…), the age of trunk, the position inside the trunk and the forest location.

Table 20. ***E. globulus*** **and** ***E. nitens*** **density values (Kg/m^3)**

	E. globulus	*E. nitens*
Cotterill (1997)	533	463
Evans (2000)	-	471.1
Monteoliva (2002)	549	-
Paz (2003)	554.5	499
This work	532	485

2.3 Composition

Composition knowledge is very important to evaluate the wood for pulping and valorization options. Between hardwoods and softwoods, generally the first kind has a higher proportion of holocellulose and less lignin although a greater percentage of extractives. However, among different species of hardwoods there are differences that make them suitable or non-suitable for a fixed pulping process. For dissolving pulp, higher contents of cellulose and lower of lignin are more interesting. Thus, the results obtained by different authors and those of this work are shown in tables 21 and 22.

The first parameter in both tables is related to the percentage of extractives, which has very different values due to the use of different solvents such as acetone (this work), ethanol (Paz, 2003), ether (Alonso, 1976), ethanol-benzene (Alonso, 1976) or a mixture of dichloromethane, ethanol and water (Esteves, 2008; Pereira, 1988). The second parameter is ash. Very similar results have been obtained for both species.

Table 21. ***E. globulus*** **composition values (%)**

	Alonso (1976)	Pereira (1988)	Cotterill (1997)	Paz (2003)	This work
Extractives*	0.42/1.4	4.9	-	1.18	1.5
Ash	0.48	0.40	-	-	0.35
Lignin	21.24	23.1	27	20.85	23.28
Alpha-cellulose	-	54**	45	50.65	51.3
Holocellulose	79.47	-	-	84.1	80.5

* Different solvents employed by each author

** Total content of cellulose

Table 22. ***E. nitens*** **composition values (%)**

	Alonso (1976)	Cotterill (1997)	Paz (2003)	This work
Extractives*	0.31/0.76	-	1.57	1.98
Ash	0.24	-	-	0.31
Lignin	21.33	27	21.41	25.43
Alpha-Cellulose	-	43	47.33	51.2
Holocellulose	83.14	-	83.27	78.4

* Different solvents employed by each author

According to other parameters such as alpha-cellulose, it can be said that *E. nitens*, which presents similar values to *E. globulus*, theoretically looks suitable at the same level as *E. globulus* in order to obtain pulp. Regarding lignin, its slightly higher content in the case of *E. nitens* can make the process a little more complicated; however, this content can increase the valorization options of the byproducts oriented to a biorefinery.

2.4 Pulping

In order to evaluate the suitability of both species to produce pulp and the development of valorization options, an analysis of the cooking stage has been done in two steps: the study of the impregnation step and the study of the behavior of both species in pulping.

Impregnation Step

The non-uniformity of pulp has unfavorable effects on the cooking and bleaching steps. To obtain a uniform pulp, the cooking liquor must be equally distributed into the wood chips, that is, to achieve a uniformly impregnated wood in the minor possible time (Gullichsen and Sundqvist, 1995; Gustafsson, 1988). This is why the impregnation step has an important role in the whole process because it is the first and can have a bearing on the improvement of the delignification and penetration times of liquor into wood. The effect of the quality of the impregnation has been studied by other authors (Gullischen and Sundqvist, 1995; Hart et al., 2011; Kazi et al., 1998; Malkov et al., 2004).

Some impregnation trials were carried out at laboratory scale. The impregnation value in each trial is obtained taking into account the difference of liquor volume among the input and the output, and using an average value of liquor density of 1054 kg/m^3 obtained in a previous work (Rueda et al., 2015). Therefore, the final impregnation value is given in mg/g dried matter (DM).

Once the impregnation is obtained in mg/g, the percentage of impregnation can be calculated in every period of time taking into account the impregnation at that time and the maximum value that the wood can be impregnated for each specie (shown in table 23). Based on the experience of the mill, an 80% of impregnation is considered to be enough in this type of process.

In order to obtain a representative curve of the impregnation, data were represented by first order exponential equations according to equation 19; where *y* represents impregnation in mg/gDM and *a, b* are constants. The obtained parameters are shown in table 23 and the curves in figure 28.

$$y = a\,(1 - e^{(-bx)}) \qquad (19)$$

Table 23. Obtained parameters for both types of wood

	E. globulus	*E. nitens*
a (mg/gDM)	558.56	764.68
b (min^{-1})	0.01292	0.009350

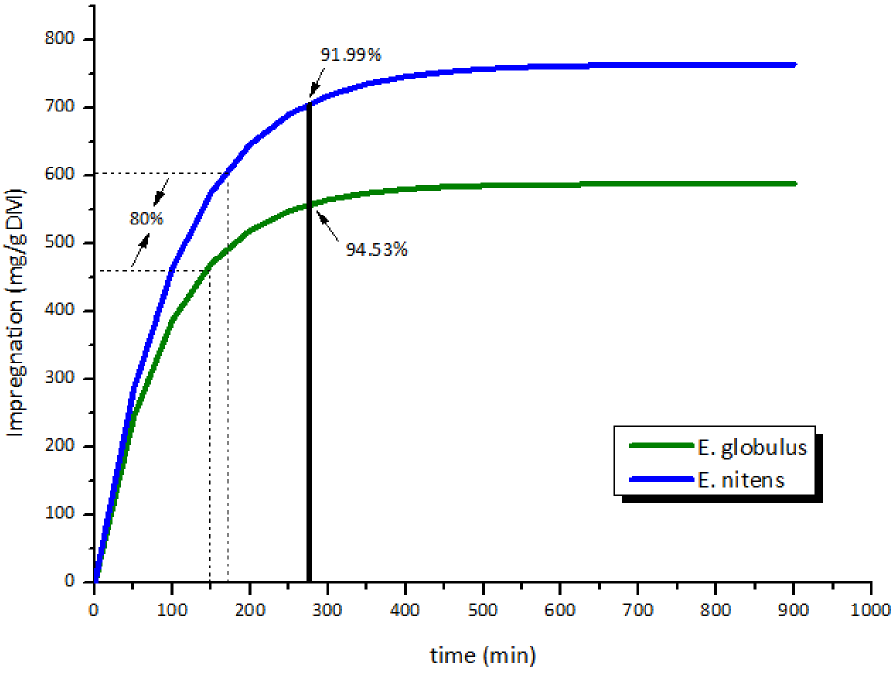

Figure 28. Tendency of impregnation stage of *E. globulus* and *E. nitens*, in mg/gDM and in impregnation percentage.

As can be seen in table 23 and figure 28, *E. nitens* has a higher maximum impregnation value, which means that for the same conditions at certain times, it will impregnate more milligrams per grams of available dry wood; however, it will be less impregnated than *E. globulus* because it needs more time to reach the same percentage of impregnation. Furthermore both types of wood fulfill the requirement of an impregnation of 80%. Focusing on time employed in the existing mill, the impregnation obtained for *Eucalyptus globulus* represents a 94.53% of the available wood versus 91.99% for *Eucalyptus nitens*. Both values exceed the 80% declared as enough, therefore *E. nitens* could be used without big modifications in the existing process.

Cooking Step

A literature search was carried out focusing on the pulping behavior of these two types of wood in different processes. The aim is to evaluate the yields and the properties of both in pulp and byproducts, to get better products and higher valorization opportunities.

All the literature consulted refers to alkaline processes and not to sulfite processes. On one hand, the study of Paz (Paz, 2003) shows that *Eucalyptus globulus* (~54%) has a little more yield than *Eucalyptus nitens* (~52.7%) for a final kappa closest to 14±1. Escalona et al. (Escalona et al., 2000) affirms that *E. globulus* has the best pulping yield and furthermore *E. nitens* consumes more energy in cooking to reach a similar grade of delignification (kappa 16±1). On the other hand, Clarke (2000) affirms that the yields of the samples that are used in his work are compared favorably to those reported for *Eucalyptus globulus*.

In order to check some of the statements of the literature, some laboratory tests have been carried out and the properties of the resultant products after the cooking process have been analyzed.

The experiments were carried out as was mentioned in the epigraph 1.2, fixing the liquid/solid ratio at 20:1 L/Kg in order to avoid the diffusion and to study only the effect of the cooking stage, as the impregnation stage was previously studied.

Figure 29 shows the evolution of lignosulfonates and total monomer content of spent sulfite liquor of *E. nitens* and *E. globulus* digestion. The *E. nitens* showed a higher delignification grade since a higher content of lignosulfonates was found in the spent sulfite liquor. Furthermore the total sugar content is slightly lower in the spent liquor obtained using *E. nitens* than in the one obtained by *E. globulus* digestion. This indicates that *E. nitens* spent liquor would reach a greater degree, better for lignosulfonates valorization purposes than sugars.

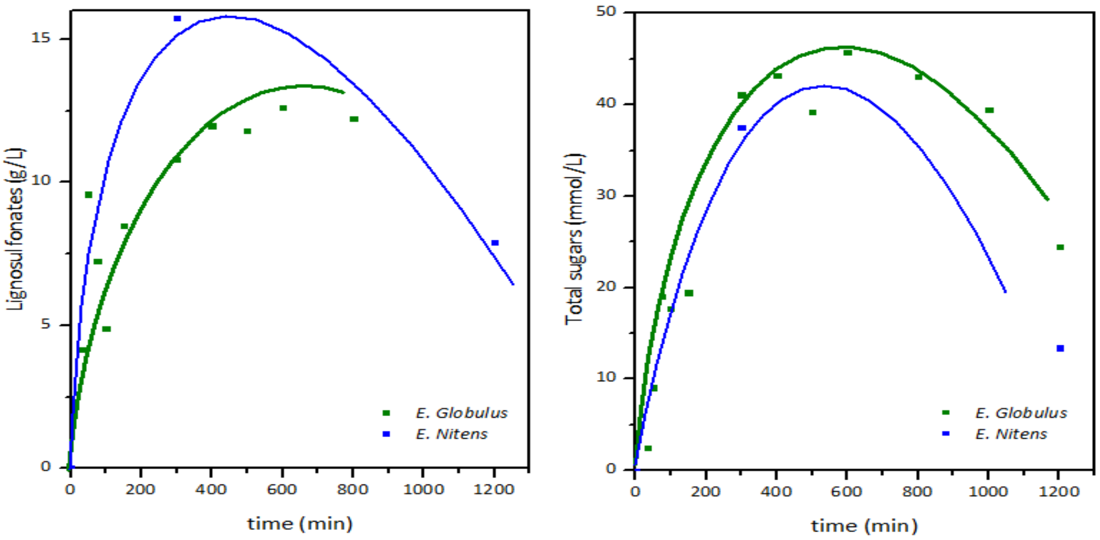

Figure 29. Evolution of lignosulfonates and total sugar content in spent sulfite liquor with time for *E. globulus* and *E. nitens* digestion.

Taking a cooking time of 300 minutes, the properties of the obtained pulp have been determined and shown in table 24.

Table 24. Kappa number and viscosity for different samples

TIME (min)	Kappa		Viscosity (mL/g)	
	E. globulus	*E. nitens*	*E. globulus*	*E. nitens*
300	7.57	10.87	578.19	374.40

Regarding the pulp properties, it seems that the digestion process in the case of *E. nitens* is more aggressive and it is able to isolate the lignin and hemicellulose from cellulose; however, the degradation of sugar could be too accused, turning their transformation into other decomposition products such as furfural or HMF in the spent liquor. This means that the process could be carried out at a lower temperature which involves an important decrease in the energy costs.

Based on the obtained results and the biorefinery purposes, *E. nitens* shows better results in terms of lignin valorization; however, the optimization of the pulping process using *nitens* is needed in order to increase the hemicellulosic content in the hydrolyzate (spent liquor).

3. INFLUENCE OF THE COOKING ACID

The cooking acid modifies two of the three major "driving forces" of the conventional sulfite process, the pH and the SO_2 concentration. By means of changing the base of the fresh liquor or modifying the combined SO_2, an increase of the pH can be achieved. This affects the reaction rates of the pulping (as it was mentioned in the general introduction, epigraph 2.2), obtaining with calcium the slowest and with magnesium the second fastest rate behind ammonium. However, the characteristics of the obtained pulp after the cooking stage can be worse because of the higher SO_2 consumption.

3.1 Effect of the pH of the cooking liquor

In order to study the influence of the pH of fresh liquor in the digestion process, this variable has been varied up to 2 with the addition of dolomite and SO_2 gas without varying the SO_2 content of the fresh liquor. This pH value was the maximum achieved without precipitating dolomite.

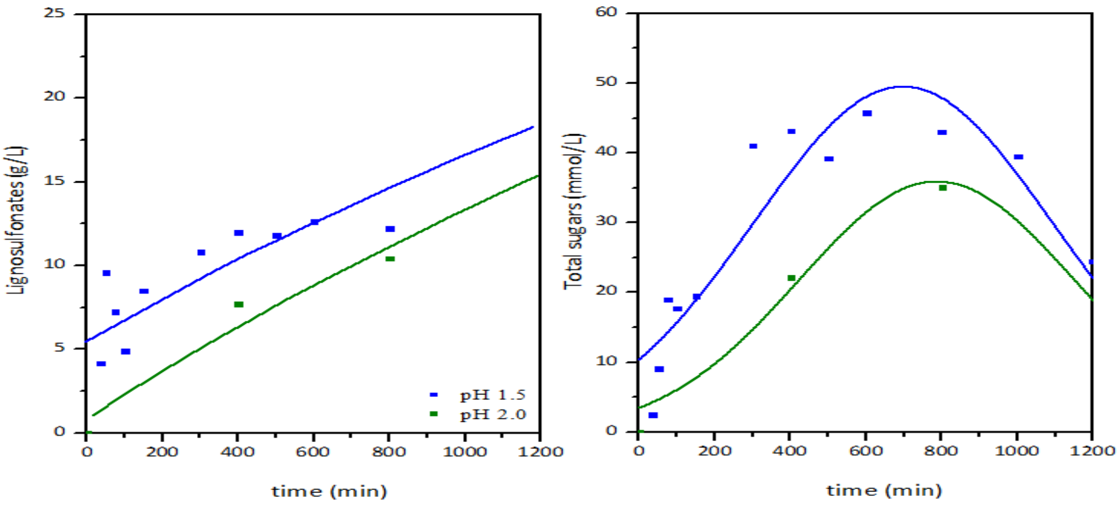

Figure 30. Evolution of lignosulfonates and total sugar content in spent sulfite liquor with time for different pH of fresh liquor

In figure 30 the evolution of lignosulfonates and total sugar content of spent sulfite liquor are represented for the base case, pH 1.5, and the experiments with fresh liquor with pH 2. The increase of pH gives a reduction of lignosulfonates and total sugar content in spent sulfite liquor.

The results of kappa index and intrinsic viscosity of the obtained pulp are shown in table 25. These results show that an increase of the time is necessary when the pH is 2 in order to obtain a pulp with similar quality.

Table 25. Kappa number and viscosity for different samples

TIME (min)	Kappa		Viscosity (mL/g)	
	pH=1.5	pH=2	pH=1.5	pH=2
400	9.91	16.2	138.96	627.51
800	-	12.26	-	190.62

Based on the obtained results, the lowest pH, which showed higher values of lignosulfonates and sugars in the spent liquor, benefits the valorization of this byproduct. Furthermore in terms of pulp, an increase in time is necessary to reach a pulp with the desired quality parameters. Thus, the variation of pH does not involve improvements at the process.

3.2 Effect of the base of the cooking liquor

Dissolving pulp production by means of the acid sulfite process can be carried out using cooking liquor made up with different bases. The commonly used bases are ammonium, sodium, magnesium and calcium. The ammonium based liquor process is known as the fastest (Casey, 1990; Smook, 2002) and the calcium based process as the worst in terms of process integration mainly due to the high tendency to produce inlays by its precipitation, furthermore the fact that the spent liquor is not suitable for burning since the recovery of the base is quite difficult (Casey, 1990) does not foster process integration. Another case, the magnesium based process, presents low level to produce inlays and also a relatively simply system of SO_2 absorption and it looks suitable for burning even with the recovery of the base (Casey, 1990). In this work, two different bases have been chosen: calcium and magnesium.

In figure 31 it can be seen that while the magnesium based digestion showed higher delignification grade due to the higher content of lignosulfonates in spent sulfite liquor, the total sugar content was lower than the obtained for calcium based digestion. This could be due to a higher degradation of the monomers into aldehydes, like furfural and hydroxymethylfurfural. This fact can be corroborated looking at the properties of the obtained pulp for different times, shown in table 26.

Table 26. Kappa number and viscosity for different samples

TIME (min)	Kappa		Viscosity (mL/g)	
	Ca	Mg	Ca	Mg
150	16.95	14.18	777.27	862.11
300	7.57	9.06	578.19	651.48

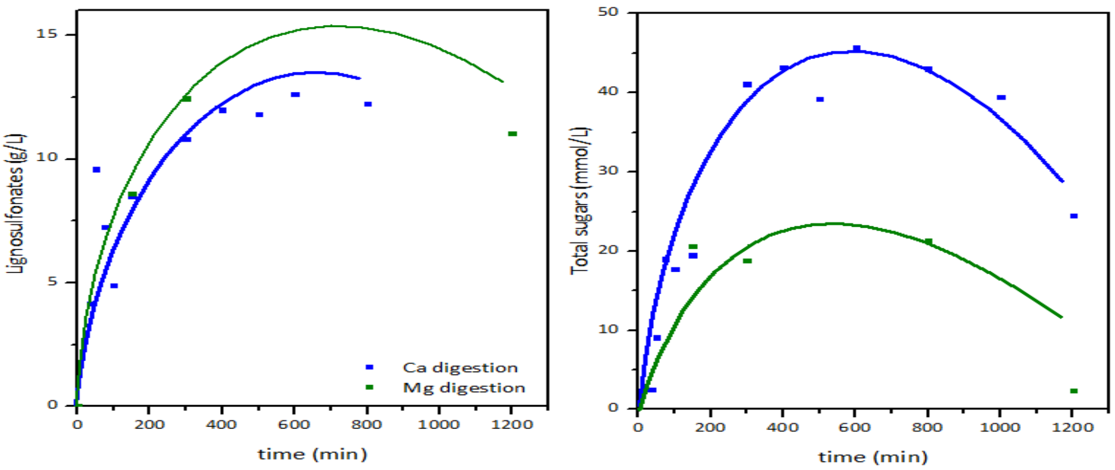

Figure 31. Evolution of lignosulfonates and total sugar content in spent sulfite liquor with time for calcium and magnesium based digestion

The results of table 26 show that the magnesium based digestion is faster in the delignification of wood but not in the separation of the cellulose from the hemicellulose. That is, it requires more time to obtain pulp with the desired quality. This explains the existence of less sugar in the spent liquor because they remain with the pulp.

Based on the obtained results comparing the two different bases, calcium based liquor looks to be much better alternative for sugar valorization on the spent liquor than magnesium. Furthermore a calcium base benefits the production of pulp with the desired characteristics. Thus, these modifications do not improve the process.

4. CONCLUSIONS

In this chapter, two of the variables that affect sulfite cooking, wood chips and cooking acid, have been assessed to verify that the available quantity of sugars in the spent liquor can be increased for biorefinery purposes.

Regarding wood chips, *Eucalyptus globulus* is commonly used in northern Spain and the Iberian Peninsula to produce pulp. However it has been afflicted in recent years by some pests and diseases that affect its availability. For this reason, the evaluation of other species needs to be done in order to complete the consumption of *E. globulus* with them. *Eucalyptus nitens* was selected to be compared with *E. globulus* in terms of general properties as well as chemical composition and behavior inside sulfite pulping.

Relating to forestry characteristics, *E. nitens* is less affected by pests and diseases and also less sensitive to frosts. Furthermore it has higher growing data. Another important characteristic is the wood density which in the studied case is lower for *E. nitens*. However, *E. nitens* can make a difference with higher growth and occupying areas where *E. globulus* does not withstand; which means that it could be planted successfully in these areas.

Concerning the chemical composition of both species, *E. nitens* presented in the studied case a higher content of lignin and similar content of alpha-cellulose than *E. globulus*, which theoretically would mean that *E. nitens* is a good candidate for producing dissolving pulp and furthermore it would produce more byproducts, valid for biorefinery purposes. To verify this, some laboratory tests were carried out showing that in the first part of the process, the impregnation step, *E. nitens* needs a bit more time to reach the desired impregnation of the wood. However, in the second step of the process, the cooking stage, *E. nitens* gives a higher concentration of lignin in the spent liquor with only a little decrease in the sugar content and worse results of the quality parameters in the dissolving pulp. A decrease of the temperature of the digestion is recommended in this case in order to improve the properties of pulp and decrease other decomposition products in the hemicellulose fraction of the spent liquor, giving more productivity in the process.

All of these results allow us to conclude that *E. nitens* can be used to produce dissolving pulp and other byproducts, which can be valorized by means of different biorefinery processes, making some modifications in the current process.

Regarding cooking acid, two parameters have been assessed: the pH and the base used for cooking.

The increase in the pH of the cooking liquor denoted that higher values of sugars can be obtained in the spent liquor but also of lignosulfonates, which benefit its valorization. However, in terms of pulp, an increase of the cooking time is required to obtain the same quality.

The comparison of the results using two bases, calcium and magnesium, showed that calcium based liquor looks to be a much better alternative for sugar valorization on the spent liquor than magnesium. Furthermore calcium based digestion fulfils the required parameters of the dissolving pulp.

All of these results allow us to conclude that the modifications done in terms of pH and base of the cooking acid do not improve the actual process.

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CONCLUSIONS AND FUTURE WORK

1. CONCLUSIONS

The conclusions of this doctoral thesis can be summarized in the following points:

- The physico-chemical characterization of the industrial spent liquor from an acid sulfite pulping process has been carried out in the context of the implementation of a biorefinery. Two cases have been considered, before the evaporation plant and after. The main components present in the liquor are lignosulfonates (47.32 g/L before evaporation and 427.05 g/L after) and sugars (25.01 g/L prior to concentration and 138.24 g/L after) and lesser amounts of acids, decomposition products and SO_2.

  Several process options from the literature compatible with the spent liquor composition, were analyzed in order to establish the case studies for the valorization of the spent liquor into value-added products. The selected valorization options for the analyzed spent liquor were the production of lignosulfonates, xylitol, ethanol, polyhydroxybutyrate, polybutylene-succinate, furfural and hydrogen as the most feasible options and other minority alternatives such as acetic acid, methanol and vanillin. Taking into account the market size, the costs and the amount of the appropriate sugar substrate available in the spent liquor, furfural, xylitol and ethanol have been selected for further studies.

- Taking into account the physico-chemical characteristics of the spent liquor and the possible valorization options, the techno-economic assessment of three biorefinery scenarios, furfural, xylitol and ethanol has been carried out. The software Aspen Plus has been used for the design and simulation of the processes.

  Different detoxification and purification techniques were analyzed. Considering the results obtained, ion exchange using anionic resins was selected as the most cost effective technique.

  Furfural, xylitol and ethanol, production processes with respective capacities of 19.9, 15.8 and 14.6 ton/d from 1970 ton/d of spent liquor were proposed. An economic evaluation was performed, the fixed capital invested (FCI) and the manufacturing costs (COM) for each process were computed. The FCI values are 4.25 M€ for the furfural plant, 5.13 M€ for the xylitol plant and 6.01 M€ for the ethanol plant. The values obtained for the COM, are 3.59 M€, 4.83 M€ and 4.20 M€ for furfural, xylitol and ethanol respectively. These values are quite close.

Two profitability indicators, Return Period (RP) and Net Present Value (NPV) were computed for each project. On the basis of these values and taking into account the key parameters (estimated costs, selling price, market potential and technical barriers), the implementation of a xylitol biorefinery into the existing mill was proposed.

- The possibility to increase the sugar content of the spent liquor to optimize the existing process without damaging the quality of the pulp was considered. For this purpose the kinetic study of the carbohydrates degradation within the cooking stage was carried out.

  Three different temperatures were tested (130°C, 140°C and 150°C). Kinetic models were posed considering different reaction schemes. In all cases, kinetic equations of first or higher order were considered using Aspen Custom Modeler. The results show that the transformation of polysaccharides into monosaccharides is better described by a reaction order close to 3 while the transformation of monosaccharides into decomposition products can be described with a kinetics of 1. The conversion of acetyl groups into acetic acid has also been considered as a parallel reaction giving first order kinetics results.

  The kinetics showed that higher temperatures increases the rate of sugars production. However, more decomposition products are also produced and, therefore, less than maximum sugar conversion is attained. Thus, 130°C appears to be the best temperature to carry out the process. The maximum sugar conversion is 33.91 mol% and the formation of decompositions products is 13.81 mol%.

- Another way to increase the available quantity of sugars in the spent liquor is to do some modifications on the wood chips and of the cooking acid. The effect of *Eucalyptus globulus* and *Eucalyptus nitens* species over the resulting pulp and spent liquor quality has been investigated.

  Eucalyptus nitens is less affected by pests and diseases, less sensitive to frosts and has a higher growing rate. However, its density is lower than that of *Eucalyptus globulus*. As a result *E. nitens* can overtake occupying areas where *E. globulus* is less adapted. Both species have a similar alpha-cellulose content. However, *E. nitens* analyzed in this work has a higher content of lignin. This is an advantage for pulping and for biorefinery purposes as well. This fact has been corroborated by several laboratory tests performed on the impregnation step prior to cooking and on the cooking itself. In the first study the results indicated that *E. nitens* requires more time to reach the desired impregnation of the wood. Furthermore, *E. nitens* gives a higher concentration of lignin in the spent liquor with a light decrease in sugar content and inferior quality results of dissolving pulp. This indicates that the operating temperature in the case of *E. nitens* is too high. However, lower temperature will yield less decomposition products in the spent liquor, therefore producing a better substrate for the biorefinery processes.

These results globally support the conclusion that *E. nitens* can be used to produce dissolving pulp and other byproducts, which can be valorized by various biorefinery processes, if some modifications in the current process are executed.

- Modifying of the pH and the base of the cooking liquor has also been studied. The increased pH produces more sugars and lignosulfonates in the spent liquor. However, a longer cooking time is required to obtain pulp with these desired characteristics. Also the effect of the change from calcium based to magnesium based cooking acid, was investigated. The obtained results showed that the calcium based liquor is a superior alternative for sugar valorization from the spent liquor than magnesium. Furthermore calcium based digestion produces the required properties of the dissolving pulp.

  All of these results support the conclusion that the modifications performed in terms of pH and base of the cooking acid do not improve the process.

2. FUTURE WORK

The following items should be undertaken to implement the conversion of the mill into an integrated forest biorefinery:

- Design and development of laboratory tests to assess the feasibility of xylitol production from the spent liquor. This study will facilitate the enhancement of the mass and energy transport processes. Furthermore, the proposal of a scale up and the improvement of the process costs for the purpose of getting better results of simulation and modeling of the biorefinery, ensuring its profitability.

- To carry out the cooking process at pilot scale, with similar equipment to those used in the mill, rather than standard as was used in this work and that allow the operation at the same L/S ratio as in the industrial mill. The purpose of this step is to produce reliable pilot data representative of industrial data.

The following studies should be undertaken to improve the biorefinery options influencing the pulping stage:

- Development of a kinetic model for the lignin degradation into lignosulfonates in order to complete the study of the digester and the cooking stage. These results will provide valuable information to determine the new parameters of the optimized process prior to the implementation of a biorefinery, using the sugar and lignin platforms and to increase the opportunities in the lignin platform.

- The study of the process kinetic and the simulation of the xylitol production from *Eucalyptus nitens* including a complete characterization of this specie in the Cantabrian forest in order to formulate recommendations for the substitution of *E. globulus* in the mill.

- Other techno-economic assessments of different biorefinery scenarios identified in this work such as biopolymers like polyhydroxybutirate, polybutylene-succinate or biofuels like hydrogen should be carried out to identify biorefinery options other than the xylitol process.

- Integration of a customized model for the studied mill into Aspen Custom Modeler so Aspen users can have access to a model of the acid sulfite digestion in the library of the program. This model will be very useful to be integrated in further simulations of this pulp mill or any other that use this kind of process.

CONCLUSIONES Y TRABAJO FUTURO

1. CONCLUSIONES

Las principales conclusiones de esta tesis doctoral pueden ser resumidas en los siguientes puntos:

- Se ha llevado a cabo la caracterización físico-química del licor gastado industrial de cocción con vistas a procesos de biorrefinería, antes y después de la planta de concentración. Los principales componentes presentes en él son lignosulfonatos (47,32 g/L antes de evaporación y 427,05 g/L después de evaporación) y azúcares (25,01 g/L y 138,24 g/L antes y después de concentración respectivamente), seguidos de menores cantidades de ácidos, productos de descomposición y SO_2.

  Basándose en la composición del licor obtenida anteriormente, se realizó un análisis bibliográfico y se encontraron diferentes opciones potenciales para valorizar este subproducto en productos de valor añadido. De acuerdo a las referencias analizadas y a las características del proceso existente, las principales opciones de valorización detectadas son la producción de lignosulfonatos, xilitol, etanol, polihidroxibutirato, polibutileno-succinato, furfural e hidrógeno como opciones más factibles y además otras alternativas minoritarias como ácido acético, metanol y vainillina. Debido al mercado, el precio y la disponibilidad del substrato de azúcares en el licor gastado, se seleccionaron furfural, xilitol y etanol como opciones para ser desarrolladas en profundidad.

- Teniendo en cuenta las conclusiones anteriores, se llevó el análisis tecno-económico de tres escenarios de biorrefinería, furfural, xilitol y etanol, utilizando el software Aspen Plus para el diseño y simulación de los procesos.

  En primer lugar, se analizaron diferentes técnicas de detoxificación/purificación. Considerando los resultados obtenidos, se seleccionó intercambio iónico con resinas aniónicas como la mejor técnica.

  Se obtuvieron procesos de producción de furfural, xilitol y etanol de 19,9, 15,8 y 14,6 t/día respectivamente a partir de 1970 t/día de licor gastado. A continuación se desarrolló la evaluación económica de los escenarios y se calcularon los parámetros de capital fijo invertido y costes de operación. Los valores de capital fijo invertido son 4,25 M€ para la planta de furfural, 5,13 M€ para la de xilitol y 6,01 M€ para la de etanol. Los valores de costes de operación obtenidos son 3,59 M€, 4,83 M€ y 4,20 M€ para furfural, xilitol y etanol respectivamente.

A continuación se calcularon dos indicadores de rentabilidad para cada proyecto, el periodo de retorno (RP) y el valor actual neto (VAN). Basándose en los resultados obtenidos y de acuerdo a los costes estimados, precio de venta, potencial de mercado y barreras técnicas; se ha determinado que la mejor opción es la implementación de una biorrefinería para producir xilitol.

- Por otro lado, una opción para incrementar el contenido de azúcares en el licor gastado es la optimización del proceso existente sin dañar la calidad de la pasta. Con este propósito se ha desarrollado el estudio cinético de la degradación de carbohidratos en la etapa de cocción.

  Se testearon tres temperaturas (130ºC, 140ºC y 150ºC). A partir de los resultados obtenidos se propusieron los modelos cinéticos considerando diferentes modelos de reacción. En todos los casos se utilizaron ecuaciones de orden n utilizando Aspen Custom Modeler. Los resultados muestran que la transformación de los polisacáridos en monosacáridos se describe mejor con una reacción de orden cercano a tres, mientras que la transformación de los monosacáridos en productos de descomposición puede ser descrita por una cinética de orden uno. Además la conversión de los grupos acetilo en ácido acético se consideró como una reacción paralela, dando una cinética de primer orden.

  La cinética mostró que temperaturas más altas favorecen la obtención más rápida de azúcares. Sin embargo se obtienen más productos de descomposición y por tanto menos conversión máxima de azúcares. Por ello, 130ºC parece la mejor temperatura para llevar a cabo el proceso, dando una conversión máxima de azúcares de 33,91 mol% y 13,81 mol% para la formación de productos de descomposición.

- Otros puntos considerados en esta tesis para incrementar la cantidad disponible de azúcares en el licor gastado son los chips de madera y el licor de cocción. Los primeros en términos de especie (*Eucalyptus globulus* y *Eucalyptus nitens*), para ver su efecto sobre la pasta y el licor gastado resultantes; y el segundo mediante la modificación del pH y la base del licor de cocción.

  Con respecto a los chips de madera: en términos de plantación el *E. nitens* se ve menos afectado por pestes y enfermedades, además es menos sensible a las heladas y tiene un crecimiento mayor. Sin embargo su densidad es menor que la del *Eucalyptus globulus*, hecho que el *E. nitens* puede mejorar ocupando áreas donde el *E. globulus* no puede resistir.

  Referente a la composición química, ambas especies presentaron un contenido de alfacelulosa similar. Sin embargo el *E. nitens* analizado en esta tesis tiene un mayor contenido en lignina. Por eso, parece bueno para pasteado así como para metas de biorrefinería. Este hecho ha sido corroborado mediante diversos ensayos de laboratorio, primero para la etapa de impregnación previa a la cocción y después para la cocción en sí misma. En el primer estudio los resultados indicaron que el *E. nitens* necesita más tiempo para alcanzar la impregnación deseada de la madera. Además cuando se analizó la etapa de cocción, el *E. nitens* dio una mayor concentración de lignina en el licor gastado con un ligero decremento en el contenido de azúcares y peores resultados en cuanto a los parámetros de calidad de la pasta. Esto significa que la temperatura de operación en el caso del *E. nitens* es demasiado alta. Sin embargo este hecho indica que una temperatura más baja dará menos productos de descomposición en el licor gastado, lo que significaría un substrato mejor para los procesos de biorrefinería.

Todos estos resultados permiten concluir que el *E. nitens* puede ser utilizado para producir pasta *dissolving* y otros subproductos, que pueden ser valorizados mediante diferentes procesos de biorrefinería realizando pequeñas modificaciones en el proceso actual.

Referente al ácido de cocción, el incremento de su pH mostró que un pH más alto es mejor para obtener más azúcares y lignosulfonatos en el licor gastado. Sin embargo se requiere más tiempo de cocción para obtener la pasta con las características deseadas.

También se analizó el efecto del cambio de la base cálcica por la magnésica. Los resultados obtenidos mostraron que la base cálcica constituye una mejor alternativa para la valorización de azúcares en el licor gastado. Además la base cálcica completa los parámetros requeridos para la pasta *dissolving*.

Todos los resultados anteriores permiten concluir que las modificaciones realizadas en materia de pH y base del licor de cocción no mejoran el proceso.

2. TRABAJO FUTURO

Basándose en los objetivos y los resultados presentados en esta tesis doctoral, se han considerado varios puntos:

Con el fin de estudiar la transformación de la fábrica en una biorrefinería forestal integrada,

- Diseñar y desarrollar experimentos a escala laboratorio que permitan el estudio de la producción de xilitol a partir del licor gastado. Este trabajo permitirá mejorar el conocimiento sobre los balances de materia y energía. Además con el propósito de conseguir mejores resultados de simulación y modelado de la biorrefinería, proponer el escalado y la mejora de los costes de proceso que mejoren su rentabilidad.

- Llevar a cabo el proceso de cocción a escala piloto con similar equipamiento al que se usa en la fábrica, que no consiste en tanques de mezcla y que permite operar al mismo ratio L/S que la planta industrial. En este sentido se obtendrán datos fiables tanto para escala piloto como para escala industrial.

Con el fin de mejorar las opciones de biorrefinería influyendo en la etapa de pasteado:

- Desarrollar un estudio cinético para la degradación de la lignina en lignosulfonatos y así completar el estudio dentro del digestor en la etapa de cocción. Estos resultados proveerán de información útil para establecer los nuevos parámetros de un proceso optimizado antes de la implementación de la biorrefinería, utilizando no solo las plataformas de azúcares y lignina sino también incrementando las posibilidades en la plataforma de lignina.

- El estudio del proceso cinético y la simulación de la producción de xilitol en el caso de utilizar *E. nitens* junto con una caracterización completa de esta especie en los bosques de Cantabria, con el fin de recomendar la sustitución del *E. globulus* en el proceso industrial.

- Otros estudios tecno-económicos de diferentes escenarios de biorrefinerías señalados en esta tesis como biopolímeros (polihidroxibutirato o polibutileno-succinato) o biocombustibles (hidrógeno). Esto permitirá determinar si otras opciones aparte de la propuesta en este trabajo (xilitol) son posibles.

- La integración de un modelo customizado para el proceso industrial estudiado, programado en Aspen Custom Modeler y utilizando un modelo de Aspen Plus, de modo que el usuario de Aspen pueda tener una "caja negra" del proceso de digestión al sulfito ácido en la librería de modelos del programa, y poder así integrarla en posteriores simulaciones de esta fábrica o de cualquier otra que use este tipo de procesos.

APPENDIX. DISSEMINATION OF RESULTS

APPENDIX. DISSEMINATION OF RESULTS

The complete references of the scientific papers and international congress communications directly related to this doctoral thesis are presented next. Cristina Rueda is in all cases the first author:

SCIENTIFIC PAPERS:

Paper 1. Rueda C., Calvo P. A., Moncalian G., Ruiz G., Coz A. (2015) Biorefinery options to valorize the spent liquor from sulfite pulping. Journal of Chemical Technology and Biotechnology, 90(12), 2218-2226 [JCR IF 2014: 2.349; Chemical Engineering Q2].

Paper 2. Rueda C., Marinova M., Paris J., Ruiz G., Coz A. (2015) Integrated forest biorefinery to produce value added products from spent sulfite liquor. Journal of Chemical Technology and Biotechnology, DOI: 10.1002/jctb.4868. [JCR IF 2014: 2.349; Chemical Engineering Q2].

Paper 3. Rueda C., Fernández-Rodríguez J., Ruiz G., Llano T., Coz A. (2015) Monosaccharide production in an acid sulfite process: Kinetic modeling. Carbohydrate Polymers, 116, 18-25 [JCR IF 2014 : 4.074; Applied Chemistry, Organic Chemistry and Polymer Science Q1].

Paper 4. Rueda C., Tejedor C., Quijorna N., Andrés A., Coz A. (2015) Influence of input variables over the wood digestion in a sulfite pulp mill for biorefinery purposes. Journal of Biology and Life Science, 6(2), 160-171.

INTERNATIONAL CONGRESS COMMUNICATIONS:

Conference 1. Rueda C., López-Álvarez J., Llano T., Quijorna N., Blanco A., Viguri J.R., Coz A. (2011) Physico-chemical characterization of a spent sulfite liquor oriented to its valorization options. *16th International Symposium on Wood, Fibre and Pulping Chemistry - ISWFPC 2011.* China.

Conference 2. Rueda C., Llano T, Quijorna N., Ruiz G., Coz A. (2011) Study of acid hydrolysis conditions of a lignocellulosic industrial waste on the sugar content for bioethanol production. *12th Mediterranean Congress of Chemical Engineering.* Spain.

Conference 3. Rueda C., Llano T., Tejedor C., Quijorna N., Andrés A., Coz A. (2012) Characterization of species of *Eucalyptus* and comparison of its behavior as a lignocellulosic biomass in a pulp process. *4th International Conference on Engineering for Waste and Biomass Valorisation.* Portugal.

Conference 4. Rueda C., Ruiz G., Rafione T., Marinova M., Coz A. (2013) A kinetic model for wood pulping and polysaccharide production in an acid sulfite process. *3rd EPNOE International Polysaccharide Conference.* France.

Conference 5. Rueda C., Rafione T., Marinova M., Paris J., Coz A. (2014) Furfural production from the spent liquor of an acid sulfite process. *4th International Forest Biorefinery Symposium.* Canada.

Conference 6. Rueda C., Quijorna N., Ruiz G., Andrés A., Coz A. (2014) Valorization options of a lignocellulosic waste: influence of raw materials used in pulping. *4th International Conference Industrial and Hazardous Waste Management.* Greece.

Conference 7. Rueda C., Ruiz G., Marinova M., Paris J., Quijorna N., Coz A. (2015) Design and simulation of biorefinery processes from an acid sulfite pulping mill. *COST FP1306 Meeting: Lignoval. First Workshop & Second MC Meeting. Belgrade.*

In addition, the participation in the following papers and congress communications:

Paper 5. Llano T., Rueda C., Quijorna N., Blanco A., Coz A. (2012) Study of the delignification of hardwood chips in a pulping process for bioethanol production. Journal of biotechnology 162:422-429 [JCR IF 2014: 2.871; Chemical Engineering Q1].

Paper 6. Coz A., Llano T., Rueda C., Quijorna N., Maican E. (2015) Hydrolysis and separation of lignocellulosic biomass in a sulphite process to valorise the main fractions within the biorefinery concept. ISB-INMA TEH' 2015 International Symposium. Romania.

Conference 8. Llano T., Rueda C., Blanco A., Andrés A., Coz A. (2010) Design of a laboratory for the study of the digestion of hardwood chips in order to obtain pulp and sugars for bioethanol production. *Third international symposium on energy from biomass and waste.* Italy.

Conference 9. Quijorna N., Llano T., Portilla A.I., Rueda C., Blanco A., Andrés A., Coz A. (2011) Comparison of sugar content of two pulping processes in order to produce bioethanol of 2nd generation. *Wastes 2011*. Portugal.

Conference 10. Llano T., Quijorna N., Rueda C., Mendivil R., Galán B., Coz A. (2011) Analysis of sugars and inhibitors obtained by the digestion of hardwood chips for bioethanol production. *ECCE/ECAB 2011.* Germany.

Conference 11. Llano T., Rueda C.**,** Quijorna N., Galán B., Blanco A., Coz A. (2012) Influence of the digestion variables on a pulping process to maximize all of the lignocellulosic waste options. *4th International Conference on Engineering for Waste and Biomass Valorisation.* Portugal.

Conference 12. Coz A., Quijorna N., Llano T., Portilla A.I., Rueda C., Andrés A., Galán B., Ruiz G., Viguri J. (2013) Study of sulphite process to obtain dissolving pulp and other valorisation options from spent liquor. *COST FP1205 Meeting: Dissolution and regeneration of cellulose*. Sweden.

Conference 13. Quijorna N., Llano T.**,** Fernández-Rodríguez J., Rueda C.**,** Blanco A., Coz A. (2013) Production of sugar substrate and lignosulphonates in a pulping process for bioproducts: study of the main operation digestion variables. *3rd EPNOE International Polysaccharide Conference.* France.

Conference 14. Coz A., Quijorna N., Rueda C.**,** Llano T., Portilla A.I., Blanco A., Andrés A., Galán B., Ruiz G., Viguri J. (2013) Valorization of a lignocellulosic waste from a sulfite pulp mill in bioproducts. *3rd International Forest Biorefinery Symposium.* Canada.

Conference 15. Quijorna N., Rueda C., Llano T., Andrés A., Galán B., Ruiz G., Viguri J., Coz A. (2014) Simulation and Optimization of sulfite process to obtain dissolving pulp and valuable products from spent sulfite liquor. COST FP1205 Meeting: WG2: Science and uses of nanocellulose and WG3: Cellulose foams and films, Bangor, UK.

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