Comparison of lignin extraction processes: Economic and environmental assessment

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HIGHLIGHTS

- Four different lignin production processes are evaluated and compared.
- Economic and environmental technical evaluations are performed.
- Importance of the quality of lignin for high value-added products.

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ABSTRACT

This paper presents the technical–economic and environmental assessment of four lignin extraction processes from two different raw materials (sugarcane bagasse and rice husks). The processes are divided into two categories, the first processes evaluates lignin extraction with prior acid hydrolysis step, while in the second case the extraction processes are evaluated standalone for a total analysis of 16 scenarios. Profitability indicators as the net present value (NPV) and environmental indicators as the potential environmental impact (PEI) are used through a process engineering approach to understand and select the best lignin extraction process. The results show that both economically and environmentally process with sulfites and soda from rice husk presents the best results; however the quality of lignin obtained with sulfites is not suitable for high value-added products. Then, the soda is an interesting option for the extraction of lignin if high quality lignin is required for high value-added products at low costs.

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1. Introduction

Important compounds such as cellulose, hemicellulose and lignin in lignocellulosic materials are nowadays platforms to obtaining several chemical products. Lignocellulosic biomass is the most abundant renewable source with an estimated annual production of 1×10^{13} tons worldwide (Alvira and co-workers, 2010). Different residues, including rice straw and hulls (Karimi and co-workers, 2006), cotton stalks (Silverstein and co-workers, 2007), sugarcane bagasse (Adsul and co-workers, 2004) and coffee cut-stems (Triana and co-workers, 2011), urban residues (Cardona and co-workers, 2004), among others have been studied as potential sources of cellulose as main product without considering the lignin as possible raw material for obtaining value-added products.

Usually lignin is a byproduct in the pretreatment and saccharification of biomass as well as a co-product in the pulp industry. It uses and specific functionalization processes within the biomass refinery makes the lignin a potential source of value-added products in chemical, food, pharmaceutical, textile and cosmetic research fields (Kamm and co-workers, 2012). Currently, approximately 5% of the worldwide lignin production has been marketed for the formulation of adhesives, dispersants, surfactants, antioxidants and rubbers, while the remaining 95% is mostly used to produce energy through cogeneration systems (Laurichesse and Avérous, 2013).

Lignin is one of the three main components of the lignocellulosic biomass and it is considered the main aromatic renewable resource in the world (Cotana and co-workers, 2014). Lignin can be found in different forms and can be isolated by different extraction processes such as mechanical, physical, chemical and enzymatic treatments, among others (Zakzeski and co-workers, 2010). Some processes mainly used to isolate lignin from lignocellulosic matrix are divided in two main categories: sulfur lignins and sulfur free lignin.

Soda process is a hydrolytic treatment with alkali solutions such as ammonium, sodium and calcium hydroxide, among others. This pretreatment is carried out for different temperatures, soda

concentration and reaction times. According to Sipponen and co-workers (2013) corn cabs are treated at 20 °C and sodium hydroxide (NaOH) concentration of 0.5 M during 24 h. However sugarcane bagasse in Jonglertjunya and co-workers (2014)) is treated with a temperature of 90 °C and NaOH concentration 40% (w/w) for 4 h. Finally lignocellulosic material can be treated in extreme conditions, with temperatures of 140 °C, NaOH concentration 10% (w/w) during 10 h as it is reported by Li and Ge (2012). Some pretreatments with solvents are applied also for lignocellulosic materials and wood components using ethanol, formic acid, methanol, hexane, acetic acid among others (Doherty and co-workers, 2011). Organosolv process has some advantages compared with kraft and sulfite process since lignin can be isolated easily from the lignocellulosic matrix and the recoverability of the solvent by different routes (precipitation and distillation) is achieved at lower environmental impacts. On the other hand, kraft pulping process is the most used in the world to produce cellulose pulp with approximately 85% of worldwide production (Dos Santos and co-workers, 2014). Kraft process uses mainly wood and forest residues and the hydrolytic treatment is performed with high pH with sodium hydroxide and sodium sulfide (Na_2S) for temperatures 170 °C (Chakar and Ragauskas, 2004). Finally sulfite processes are widely used for pulp production of more than 1 million tons per year and using a sulfur aqueous solution (SO_2) and a calcium, sodium, magnesium and ammonium base. Some research has been performed for this kind of process, however the lignin quality involves traces of sulfur as sulfonate groups present in the aliphatic chains (Gosselink, 2011).

The aim of this work is to present an economic and environmental assessment of fourth extraction processes used to isolate lignin from lignocellulosic matrix for two kinds of raw materials with high lignin contents in the Colombian context (rice husk and sugarcane bagasse). The results show the distribution cost, cost per kilogram of lignin and net present value for soda, kraft, organosolv and lignosulfonate processes. Additionally for the environmental assessment eight categories of potential environmental impact are evaluated.

2. Materials and methods

2.1. Raw materials

Sugarcane bagasse and Rice husk are characterized in terms of moisture (measurement: moisture balance MOC-120H, Shimadzu equipment), holocellulose (α-cellulose and hemicellulose) (ASTM Standard D1104), lignin (TAPPI T222), extractives (NREL/TP-510-42619), ash (NREL/TP-510-42622). All procedures are performed for triplicate and based on Norms and Standards reported by NREL (National Renewable Energy Laboratory, Golden, CO, USA) and ASTM (American Society for Testing and Materials).

2.2. Simulation process

The extraction processes scheme and the flowsheet synthesis was carried out using process simulation tools. The objective of this procedure is to generate the mass and energy balances for calculating the raw materials, consumables, utilities and energy requirements. The main simulation tool used is the commercial package Aspen Plus v8.2 (Aspen Technology, Inc., USA).

The kinetic model used for calculating the hydrolysis step is reported by Jin and co-workers (2011). The yield used for soda extraction process is calculated based on the information reported by Nikzard and co-workers (2013). Furthermore, in the solvent extraction process (organosolv) the yield used to calculate is taken from Jim and co-workers (2006). Also the yield in kraft extraction process is calculated taking into account the data reported by Zhao

and co-workers (2011). Finally for the sulfite extraction process data are taken from Xu and co-workers (2015) to calculate the yields, that are used in the process simulation.

The Non-Random Two-Liquid (NRTL) thermodynamic model is applied to calculate the activity coefficients of the liquid phase. Also the UNIFAC-DORTMUND and Soave Redlich Kwong models for liquid and vapor phases are needed when the NRTL model did not predict the properties (e.g. Liquid–Liquid separations and distillation columns) and Henrýs law to calculate dissolved gases (García and co-workers, 2010; López and co-workers, 2009).

2.3. Cases description

2.3.1. Lignin extraction processes with a preliminary acid hydrolysis

In the lignin extraction processes with a preliminary acid hydrolysis the lignocellulosic material (sugarcane bagasse and rice husk) enters to mix tank (1) where it is contacted with a sulfuric acid solution 2% (v/v) in a solid ratio of 1:10, there the mixture is heated (2) to a temperature of 90 °C to subsequently enter a stirred tank reactor (3) at an operational conditions of 110 °C and 1 bar. The mixture is cooled in a heat exchanger (4) at a temperature of 90 °C to be filtered (5) and then to recover the liquid fraction rich in xylose that is cooled at 25 °C (6) to be mixed with a calcium hydroxide ($Ca(OH)_2$) (7) to neutralize the sulfuric acid in a detoxification tank. (8) In this tank there are produced solid compounds such as calcium sulfate (Gypsum) that are filtered (9) to separate the xylose liquor, while the solid fraction is a mixture of cellulose, hemicellulose and lignin which is the feed stream to the lignin extraction processes. The lignin stream enters a mixing tank (10) where it is contacted with a delignifying agent as sodium hydroxide, organic solvents or mixtures of sodium hydroxide with other compounds such as bisulfites or sulfides. Each lignin extraction process is performed separately for a total of fourth processes: Soda, organosolv, kraft and sulfite. Then, the mixture is brought to a heat exchanger (11) in order to adapt to the operating conditions of each process to complete in stirred tank reactor (12) where the delignification is carried out. Finally treatments were performed for the isolation of lignin mixture that is passed to a heat exchanger (13) in order to lower temperature until about 25 °C and sent to final filtration step. (14) Finally the pulp is washed in a tank. (15) In the Fig. 1 it is observed the process flow diagram related with the lignin extraction process with a preliminary acid hydrolysis.

2.3.2. Lignin extraction processes without a preliminary acid hydrolysis

In the Fig. 2 is observed the lignin extraction process without a preliminary acid hydrolysis. Lignocellulosic material enters to a mix tank (1) where is contacted with a delignifying agent. There fourth lignin extraction processes are carried out: Soda, organosolv, kraft and sulfite. Successively the mixture is brought to a heat exchanger (2) in order to adjust the mixture to required operating conditions for each of the processes. Then the stream is entered into a stirred tank reactor (3) where is performed the delignification process and lignin is separated from the lignocellulosic matrix. The resulting stream is cooled (4) at a temperature of 25 °C and is separated by filtration. (5) Finally the pulp is washed in a tank. (6) Given the fact that the present work is based on the lignin recovery, it is assumed here that all the hemicellulose remains together with cellulose in the solid fraction. After extractions, small fractions of sugars (1.1% wt of hexoses and 1.3% wt of xylose) are considered in the lignin liquor stream when no hydrolysis steps are involved as recommended by Dhepe and Sahu (2010) and Mousavioun and Doherty (2010).