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Combined organosolv and ultrafiltration lignocellulosic biorefinery process

M. González Alriols, A. García, R. Llano-ponte, J. Labidi*,[1]

Chemical and Environmental Engineering Department, University of the Basque Country, Escuela Politécnica de San Sebastián, Plaza de Europa, 1, 20018, Donostia-San Sebastián, Spain

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ABSTRACT

Non-woody lignocellulosic feedstock (*Miscanthus sinensis* L.) was fractionated by a biorefinery process to obtain cellulose, different molecular weight lignin fractions and an hemicelluloses enriched liquor following economically and environmentally sustainable criteria. An integrated process composed by ethanol organosolv pre-treatment followed by a membrane ultrafiltration system was used to extract the different fractions. Products physico-chemical characterization (FTIR, GPC, ^{1}H NMR) was done to evaluate their potential possible industrial applications. Obtained experimental data were used to develop a simulation of the process using Aspen Plus software in order to establish mass and energy balances and optimize the process in terms of yield, solvent recovery and energy consumption. Finally, production costs of the obtained ultrafiltrated lignin were estimated resulting in 52 €/tonne of lignin for the studied process conditions.

1. Introduction

In the last decades, renewed interest has been put on biomass as an alternative to fossil fuels to produce products and energy. While the former may be produced from several alternative sources and technologies, wind, sun, water, biomass or nuclear energies, substances obtaining depends basically on biomass [1]. Nevertheless, in order to become an actual alternative to fossil fuels and petroleum derivate products, biorefinery processes must face the challenge of being competitive and cost-effective, which is highly dependent on raw materials costs. The 'Whole Crop Biorefinery', based on processing cereals or grain (maize), uses expensive feedstock with fluctuant prices; the 'Green Biorefinery' system, process green grass and immature cereal whether the 'Lignocellulose Feedstock Biorefinery' makes use of 'nature-dry' raw material such as wood, straw and forest or agricultural lignocellulosic residues. The latter group is predicted to have the highest success due to the abundance (estimated annual worldwide production of 10–50 billion dry tonnes, accounting for about half of the global biomass yield) and variety of available raw materials and the good position of the conversion products on the market [1,2].

Another clue point in the process profitability is the selection of the technology required to alter the structure of lignocellulosic biomass, where native cellulose is protected by lignin and hemicelluloses [3]. Several bioconversion schemes have been proposed, including enzymatic fractionating by cellulases or chemical hydrolysis (with hot water and dilute or concentrated acid), steam explosion, alkaline treatment and organosolv processes [4]. The latter group, which consists on using mixtures of water and organic alcohols or acids to fractionate the biomass, is well known in the pulp and paper industry. These processes allowed overcoming some of the main drawbacks of traditional pulping processes by using sulphur free delignifying agents, which could be recovered by distillation after the pulping process [5,6].

Ethanol organosolv process, already used biofuel production and in the pulp and paper industry as the Alcell® process [7], has gained new relevance for biomass biorefining (Lignol process). This technology has been successfully applied to fractionate softwoods [4] and hardwoods [8] allowing the obtaining of multiple co-products (cellulose, lignin, hemicelluloses and extractive components of the lignocellulosic biomass) with versatile uses.

Cellulose obtained from biomass as a solid fraction presents many interesting applications: paper and board production, anticake agent, emulsifier, stabilizer, dispersing agent, thickener or gelling agent, although its main industrial use is to produce water-soluble derivatives with pre-designed and wide-ranging properties dependent on involved groups and the degree of derivatization [9]. Furthermore, hydrolytic enzymes can be used to convert the cellulose in lignocellulosic biomass to glucose for fermentation and ethanol production.

Lignin structure, an intricate combination of phenyl propanoid units linked by different ether and carbon–carbon linkages, is

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* Corresponding author. Tel.: +34 943017166; fax: +34 943017140.
E-mail addresses: maria.gonzalez@ehu.es (M.G. Alriols), jalel.labidi@ehu.es (J. Labidi).
[1] Tel.: +34 943017178; fax: +34 943017140.

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highly dependent on its origin and the method used for its extraction [10]. Organosolv lignins present low molecular weight values and high solubility in most common solvents [11]. The high percentage of phenolic hydroxyl groups and oxidized groups present in their composition allow their use for polymer formulation and their chemical modification [12]. Hardwood Alcell lignins, extracted through acidic ethanolysis, have been successfully transformed into filament form suitable for carbon fibres without any chemical modification [13] and Alcell lignin/poly(vinyl chloride) composites have been reported to present higher mechanical properties than kraft or sodium lignosulphonate-based materials [14]. Within their ability to undergo chemical modification, organosolv lignins have been found to be an appropriate raw material for producing LMW compounds [15] like vanillin, widely used in cosmetics, simple and hydroxylated aromatics, quinones, aldehydes, aliphatic acids and many others, for which the economic feasibility is being studied [16].

Furthermore, oligomers and monomers hydrolyzed from the hemicelluloses as well as the degraded hemicellulosic polymers are associated with specific properties and diverse applications, as films and coatings, polyelectrolytes, food emulsifiers or rheology modifiers, as well as drugs [17,18].

In this study, organosolv ethanol treatment was combined with membrane ultrafiltration technology to treat non-woody biomass feedstock (*Miscanthus sinensis*). Organosolv technology enabled the fractionation of the raw material in different products (cellulose hemicellulose-derived sugars and lignin) allowing the subsequent recovery of the solvents by distillation with high yields and low energy consumption. Membrane ultrafiltration was used to obtain specific molecular weight lignin fractions as it proportioned excellent fractionation capability with low chemicals consumption and low energy requirements.

The combination of the abovementioned technologies present the novelty of allowing to obtain lignin with defined properties, particularly specific molecular weight and low polydispersity, which could be used in high added value applications, as polymer formulation or low molecular weight compounds.

In order to maximize process efficiency, a simulation of the biorefinery process based on experimental laboratory results was carried out using Aspen Plus software. Solvent consumption recovering section was designed to recycle ethanol and water to the different process units reducing their fresh input. Mass balance and stream compositions were calculated and adjusted as well in order to minimize the operation costs of the process and reduce its environmental impact.

2. Materials and methods

2.1. Materials

Characterization of original *M. sinensis* fibres was done according to standard methods (see Table S1 in the Supporting Information Section).

2.2. Biorefinery process

M. sinensis biorefinery process (Fig. 1) consisted of several stages: raw material organosolv ethanol pre-treatment, solid fraction (SF) washing and separation, membrane ultrafiltration of the liquid fraction (LF), lignin precipitation and isolation and solvents recovery. This last step consisted on the evaporation of an ethanol–water stream which was sent to a distillation column to separate and reuse both components and the obtaining of a concentrated liquid fraction enriched in hemicelluloses.

2.3. Laboratory experiments

2.3.1. Ethanol organosolv pre-treatment

Lignocellulosic raw material was milled and treated in aqueous ethanol, in a laboratory scale 20 L batch reactor with temperature and pressure control. Experimental conditions (selected after an extensive series of laboratory experiments) used were defined as follows: solvent concentration: ethanol–water 60/40 w/w; temperature: 160 °C; reaction time: 90 min; liquid/solid ratio: 6:1. Contents were stirred by rotating the reaction vessel via motor connected through a rotary axle to the control unit. After cooking, the reactor content was cooled to room temperature. SF and LF were then separated using a nylon mesh. The former was washed three times with 5 L aqueous ethanol (60/40 w/w) at 40 °C and the filtrates were mixed with the LF from the reactor forming the total liquid fraction (TLF) stream. SF was separated from uncooked material by screening through a sieve of 1 mm mesh.

2.3.2. Membrane ultrafiltration unit

Ultrafiltration module used to fractionate the TLF was a Pall Membralox XLab5 pilot unit equipped with a 3L 316 stainless steel tank with water jacket for temperature control, a recirculation pump and a set of tubular ceramic membranes of different cut-offs in the interval 5–15 kDa manufactured by IBMEM (Industrial Biotech Membranes, Germany). Four different cut-off fractions were obtained: less than 5 kDa fraction; 5–10 kDa fraction; 10–15 kDa fraction and more than 15 kDa fraction. The diameter of the membrane tubes was 6 mm, the length was 250 mm and the area of each membrane tube was 110 cm^2. The retentate and permeate were recirculated to the feed tank for 2 h before samples of permeate and retentate were withdrawn. The pressure was measured at the inlet and at the outlet of the membrane tube. As the pressure on the permeate side was atmospheric, the TMP is the average of the inlet and outlet pressure on the feed side. The experiments were done at the following experimental conditions: TMP: 300 kPa; cross-flow velocity: 5.6 m/s and temperature: 60 °C.

2.3.3. Organosolv lignin

Lignin contained in the obtained ultrafiltrated fractions was precipitated by dilution with 1.5 volumes of acidified water (pH 3) [19]. Precipitated lignin samples were allowed to settle over a 24-h period, centrifuged at 3500 rpm for 12 min, washed with water twice to remove sugar and other impurities and finally dried in a vacuum oven at 65 °C and −60 cmHg. Lignin concentration was then calculated gravimetrically, and isolated lignin samples were stored for subsequent characterization.

2.4. Process simulation

Aspen Plus was used to design and simulate the process on the basis of experimental results in order to optimize solvents recovery and calculate stream material balances and compositions. Lignin, cellulose and hemicelluloses were defined by their chemical structure and physical properties which were obtained from the National Renewable Energy Laboratory (NREL) database (NREL/MP-425-20685; task number BF521004), whereas other conventional components were selected from the ASPEN PLUS data bank. NRTL-RK (Non-Random, Two Liquids—Redlich-Kwong) model was used to simulate the thermodynamic properties of solutions. This route includes the NRTL equation, obtained by Renon and Prausnitz, for the liquids activity coefficients calculation, Henry's law for the dissolved gases and RKS (Redlich-Kwong-Soave) equation of state for the vapour phase.

The simulation process was developed using the following inlet streams to the reactor: 1000 kg/h of dry raw material with the abovementioned composition and 6000 kg/h of ethanol–water