CHEMICAL ENGINEERING TRANSACTIONS Volume 21, 2010
Editor J. J. Klemeš, H. L. Lam, P. S. Varbanov
ISBN 978-88-95608-05-1 ISSN 1974-9791
DOI: 10.3303/CET1021113

Lignocellulosic Biorefinery Approach: A Challenge for a New World

Ana Toledano, Itziar Egües, María Angeles de Andrés, Rodrigo Llano-Ponte, Jalel Labidi*
Chemical and Environmental Engineering Department, Univerity of the Basque Country, Plaza Europa 1, 20018 San Sebastian, Spain
jalel.labidi@ehu.es

Today’s life is based on petroleum energy and derivative products. At the rate of nowadays consume, reserves will run out of the precious fossil fuel in a short time. The environmental impact of our way of life is tremendous. Society and governments concern the uncertain world we are building and that is why renewable energies are emerging so strongly. Biomass is a promising renewable energy that could replace products, at present, produced by petroleum industry.

Biorefinery concept lies on an economically feasible processing to achieve a complete utilization of most of the biomass components. The utilization of agricultural residues as raw materials is a promising alternative to fossil resources for production of energy and high value added products. Pulp/paper industry can be considered as a primitive biorefinery. The drawbacks that this business has to deal with are environmental laws, high energy and water consumption and forest resources scarcity. Facing these weaknesses as challenges, pulp and paper industry could easily become a biorefinery trying to fulfil current environmental demands and competitiveness. The utilisation of assorted lignocellulosic feedstock as agricultural and forestry wastes, the exploitation of different interesting fractions, apart from cellulose, as lignin and hemicelluloses, and the recovery of used solvents can improve the efficiency and profitability of these processes.

Organic alcohols and acids have been used in the pulp and paper industry (organosolv technology) and they are gaining new relevance for biomass biorefining as they allow the obtaining of multiple co-products (cellulose, lignin, hemicelluloses and extractive components of the lignocellulosic biomass) with versatile uses (Serrano et al., 2010).

In the present work, a scheme of a lignocellulosic biorefinery is presented. Among the existent lignocellulosic materials pretreatments, hydrolysis is one of the processes that presents high yield of dissolved hemicellulosic sugars under mild operation conditions. According to the environmental point of view of the biorefinery, organosolv pulping process was considered as the solvent can be easily recovered at the end of the process and the sulphur-free nature allows the obtaining of interesting co-products from the black liquors. The most important substance present in the black liquor is lignin. Lignin fractionation is a promising way to obtain specific molecular weight lignin fractions that can be used to produce high value added products. Membrane ultrafiltration technology

Please cite this article as: Toledano A., EgüesI. , Andrés A., Llano-Ponte R. and Labidi J., (2010), Lignocellulosic biorefinery approach: a challenge for a new world, Chemical Engineering Transactions, 21, 673-678, DOI: 10.3303/CET1021113.

provides excellent fractionation capability with low chemicals consumption and low energy requirements.

1. Materials and Methods

1.1 Raw material

Miscanthus sinensis used in the experiments was kindly supplied by the company Straw Pulping Engineering (SPE), S.L. (Zaragoza, Spain). Characterization of original *M. sinensis* fibres was done according to TAPPI standard methods (www.tappi.org). Moisture content (5.8 wt. %) was determined after drying the samples at 105 ◦C for 24 h (TAPPI T264 cm-97). Chemical composition, given on an oven dry weight basis, was the following: 1.8±0.1 % ash (TAPPI T211 om-93), 16±0.9 % aqueous NaOH soluble matter (TAPPI T212 om-98), 4.2±0.4 % hot water soluble matter (TAPPI 207 om-93), 2.0±0.5 % ethanol–benzene extractives (TAPPI T204 cm-97), 20±0.1 % lignin (TAPPI T222 om-98), 73±1.0 % holocellulose (Wise method) and 45±0.2% α-cellulose (Rowell method).

Once dried, it was ground in a hammer mill and sieved to obtain the 1 – 3 cm size fraction, free of impurities such as stones, sand and dust.

1.2 Organosolv treatment

The raw material was processed under organosolv 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. Solid fraction (SF) and liquid fraction (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 1mm mesh. The diagram of the biorefinery process suggested is shown in Figure 1 (Alriols et al., 2010).

1.3 Fractionation process

Ultrafiltration process was applied to the liquid fraction obtained after the organosolv treatment. The UF module used in the present work was supplied by IBMEM – Industrial Biotech Membranes (Frankfurt, Germany). The membranes (5, 10 and 15 kDa) were made of ceramic material (TiO_2), tubular and multichannel type, with an external and hydraulic diameter of 10 and 2 mm, respectively, and a surface of 110 cm^2. Two stainless steel filtration modules placed in series were used. The black liquor solution was filtered successively increasing the membrane cut-off.

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

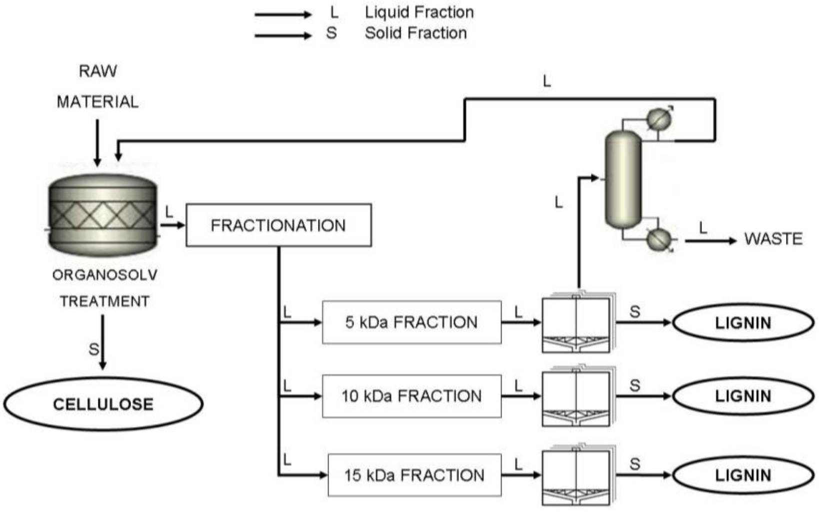

Figure 1: Diagram of the biorefinery suggested for lignocellulosic biomass

1.4 Solid fraction characterization

All the solid fractions resulted for each treatment applied were characterized using the TAPPI standard methods: moisture content (TAPPI T264 cm-97), ash content (TAPPI T211 om-93), NaOH soluble matter (TAPPI T212 om-98), hot water soluble matter (TAPPI 207 om-93), ethanol - benzene extractives (TAPPI T204 cm-97), Klason lignin (TAPPI T222 om- 98), holocellulose (Wise method) and α-cellulose (Rowell method).

1.5 Lignin characterization

Lignin ultrafiltrated fractions were analyzed by Thermogravimetric Analysis (TGA) and Size Exclusion Chromatography (SEC).

A thermogravimetric analysis was developed in a TGA/SDTA RSI analyzer of Mettler Toledo. The samples of 5 mg (approximately) were heated from 25 º C up to 800 º C at a rate of 10º C/min. A constant nitrogen flow was used, which provided an inert atmosphere during the pyrolysis and allowed extracting the gaseous and condensable products that could cause secondary interactions in vapor phase.

The Size Exclusion Chromatography (SEC) was carried out in a Perkin-Elmer instrument equipped with an interface (PE Nelson Series 900). Three Waters Styragel columns (HR 1, HR 2, HR 3) ranging from 100 to 5·105 and a refractive index detector (Series 200) were employed with a flow rate of 1 mL/min.

2. Results and Discussion

2.1 Solid fractions characterization

Lignin content in pulp was 10.8±0.3 % and hollocellulose 72.3±0.1 % (cellulose: 55±0.3 %, hemicelluloses: 17.3±0.3 %), results given on an oven dry solid fraction weight basis. Lignin and hemicelluloses percentages on the solid fraction were considerably lower than in the raw material composition (lignin: 20 %; hemicelluloses:

32 %) indicating a considerable removal of lignin and hemicelluloses during organosolv treatment process which were recovered in the water-soluble stream. The solid fraction cellulose percentage (55 %) was, as a consequence, higher than in the raw material (48 %). High cellulose and low lignin contents in the solid fraction made this material optimal to apply enzymatic hydrolysis to convert cellulose in glucose and obtain ethanol by further fermentation of the latter. Higher lignin percentages (about 27 %) in solid fractions resulted in very low hydrolysis performances due to the enzymes impediment to attack cellulose in lignin presence (Pan et al., 2005).

2.2 Lignin characterization

The TG curves and their derivatives (DTG curves) of ultrafiltrated lignin fractions are shown in Figure 2. For all the fractions it can be observed that there are three zones of weight losses which means that three components are present in the obtained lignin fractions.

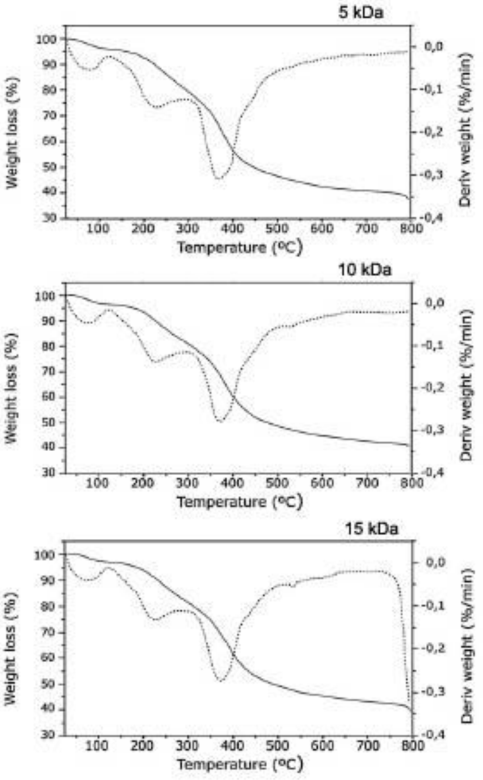

Figure 2: Lignin fractions thermogravimetric curves and their derivatives (DTG)

A peak representing weight loss can be observed around 90 °C, which corresponds to absorbed water evaporation. The peak around 225 °C is related to hemicelluloses content in the samples. These components have a degradation temperature between 200 and 300 °C (Sun et al., 1998). It can be observed that hemicelluloses content in samples is low. The most important degradation peak appears around 400 °C being assigned to lignin degradation (Domínguez et al., 2008). The residual mass fraction that remained at 800º C was found to be from 30 to 45 % for the studied samples. This non-volatile fraction was related to the creation of highly condensed aromatic structures during thermal degradation.

Molecular weight (MW) distribution: weight average MW (Mw), number average MW (Mn) and polydispersity (Mw/Mn) of lignin samples analyzed by SEC are shown in Table 1. Obtained values were in the range of organosolv lignin MW published data (Sun et al., 1997) and lower than those reported for Kraft and soda lignins (Tejado et al., 2007). The ultrafiltrated lignin fractions presented low polydispersity, especially the 5 kDa fraction, suggesting that the membrane filtration system would allow the purification of narrower lignin fractions with similar molecular weights which could be used in specific industrial applications as polymer formulation or as antioxidants.

Table 1: Molecular weight distribution of the different ultrafiltrated lignin fractions.

	M_w	M_n	M_w/M_n
5 kDa Fraction	1380	1043	1.3
10 kDa Fraction	1793	1281	1.4
15 kDa Fraction	1927	1273	1.5

3. Conclusions

Organosolv treatment was proved to be a good treatment for delignification of the raw material reaching a liquid fraction rich in lignin and a solid fraction rich in cellulose. Ultrafiltration allowed the fractionation of the liquid fraction where the lignin was dissolved making possible the obtaining of different lignin fractions. Therefore, it has been proved that the biorefinery approach suggested produces lignin fractions with different molecular weight distribution that can be used in their most appropriate and effective use taking into account their different properties.

As a drawback of the process suggested, lignin fractions showed hemicelluloses contamination as it was observed in the thermogravimetric analysis. Hemicelluloses are one of the main components of the lignocellulosic biomass and have a promising future uses as a component in biopolymer formulations, biofuel production. In order to reduce the contamination of lignin fraction and to make hemicelluloses a profitable stream, we propose another biorefinery process approach (Figure 3) including a pretreatment, hydrolysis. The idea is to extract the hemicelluloses as pure as it is possible so they can be transformed into high added value products and then to maximize the yield of cellulose and lignin by applying organosolv treatment. Lignin is a promising precursor for chemicals production but the main drawback is that lignin obtained immediately from the black liquor is very heterogeneous. Fractionation process suggested (ultrafiltration) allows obtaining different lignin fractions with homogenous properties.

Acknowledgements

The authors would like to thank the Spanish Ministry of Science and Innovation (CTQ2007-65074-C02-02) and the Diputación Foral de Guipuzcoa for financially supporting this research project.

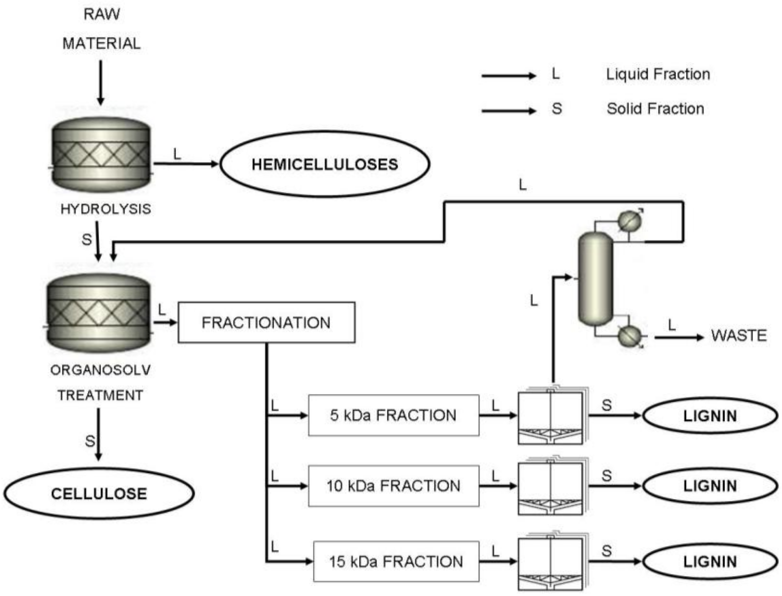

Figure 3: Diagram of the biorefinery suggested to make hemicelluloses a profitable stream and to reduce lignin contamination.

References

Serrano L. , Egües I., González Alriols M., Llano-Ponte R., Labidi J., 2010, Miscanthus sinensis fractionation by different reagents. Chemical Engineering Journal, 156 (1) 49-55

TAPPI Standard Test Methods. <www.tappi.org> (last access 02/07/20101).

Alriols M.G., García A., Llano-Ponte R., Labidi J., 2010, Combined organosolv and ultrafiltration lignocellulosic biorefinery process. Chemical Engineering Journal 157 113 ‑ 120.

Pan X., Arato C., Gilkes N., Gregg D., Mabee W., Pye K., Xiao X., Zhang X., Saddler J., 2005, Biorefining of softwoods using ethanol organosolv pulping: preliminary evaluation of process streams for manufacture of fuel-grade ethanol and co-products, Biotechnol. Bioeng. 90 (4) 473 ‑ 481.

Sun R.C., Fang J.M., Rowlands P., Bolton J., 1998, Physicochemical and thermal characterization of wheat straw hemicelluloses and cellulose, J. Agric. Food Chem. 46 (1998) 2804–2809.

Domínguez J.C., Oliet M., Alonso M.V., Gilarranz M.A., Rodríguez F., 2008, Thermal stability and pyrolysis kinetics of organosolv lignins obtained from Eucalyptus globulus, Ind. Crops Prod. 2 (7) 150 ‑ 156.

Sun R.C., Lawther J.M., Banks W.B., Xiao B., 1997, Effect of extraction procedure on the molecular weight of wheat straw lignins, Ind. Crops Prod. 6 97 ‑ 106.

Tejado A., Peña C., Labidi J., Echeverria J.M., Mondragon I., 2007, Physicochemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis, Biores. Technol. 98 1655 ‑ 1663.