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Lignocellulosic feedstock biorefinery processes. Analysis and design

González M., García A., Toledano A., Llano-Ponte R., de Andrés, M.A., Labidi J.
Chemical and Environmental Engineering Department
University of the Basque Country
Plaza Europa, 1, 20018, Donostia-San Sebastián, Spain
E-mail: jalel.labidi@ehu.es, Tel.:+34-943017178, fax: +34-943017140

A simulation of a sustainable biorefinery process based on experimental results was developed using Aspen Plus software. *Miscanthus Sinensis* was fractionated to obtain high quality cellulose and different molecular weight lignin fractions by an integrated process composed by an ethanol organosolv pre-treatment followed by a multiple membrane ultrafiltration system. Reactants used in the different units (reaction unit, solid fraction washing step and lignin precipitation step) were recovered at the end of the process by distillation and recycled to reduce the fresh input. Mass balance and streams composition were calculated and adjusted by the simulation process in order to minimize the operation costs of the process and reduce its environmental impact.

1. Introduction

Biorefinery technology, especially the 'Lignocellulose Feedstock Biorefinery', is becoming an actual alternative to petroleum based industry to produce energy, chemicals and products. The conversion of 'nature-dry' raw material (wood, straw, forest and agricultural lignocellulosic residues) into goods is getting more and more important due to the abundance and variety of available raw materials, its renewable nature and the good position of the conversion products on the market (Kamm and Kamm, 2004). Lignocellulose, the most abundant renewable biomass produced from photosynthesis, is a complicated natural composite with three main biopolymers (cellulose, hemicellulose and lignin), whose structures and compositions vary greatly, depending on plant species, growth conditions and the method used to treat biomass (Ding and Himmel, 2006). There are several technologies to fractionate lignocellulosic feedstock components: enzymatic fractionating, hot water or acid chemical hydrolysis, steam or ammonia fiber explosion, alkaline treatment and organosolv processes (Mosier et al., 2005).
Organosolv processes, based on using mixtures of water and organic alcohols or acids and particularly, ethanol organosolv process, gained new relevance for biomass pre-treatment in a biorefinery sense (Lignol process) as it allowed obtaining several high-value products (cellulose, lignin, hemicellulose, extractives) under mild reaction

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conditions by a cost-effective process in which solvents were recovered and recycled at the end of the process (Pan et al., 2005).

In this work, a non-woody raw material (*Miscanthus Sinensis*) biorefinery process based on ethanol organosolv pretratment followed by an ultrafiltration process in a multiple membrane system was carried out at laboratory scale in order to obtain data to develop a simulation using Aspen plus software. Reactants used in the different units were recovered at the end of the process by distillation and recycled to reduce the fresh input. Mass balance and streams compositions were calculated and adjusted by the simulation process 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 *Miscanthus Sinensis* fibres was done according to standard methods. Moisture content (6.1 wt %) was determined after drying the samples at 105 ºC for 24 h (TAPPI T264 cm-97). Chemical composition, given on an oven dry weight basis, was the following: 0.9±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), 79±1.0% holocellulose (Wise et al., 1946) and 42±0.2% α-cellulose (Rowell, 1983).

2.2 Biorefining process

Miscanthus Sinensis biorefinery process (Figure 1) consisted of several stages: raw material organosolv ethanol pretreatment, solid fraction (SF) washing and separation, membrane ultrafiltration of the liquid fraction (LF), lignin precipitation and isolation and solvents recovery by distillation from waste liquors.

2.2.1 Process simulation

Aspen Plus was used to design and simulate the process on the basis of experimental results. Lignin and cellulose were defined by their chemical structure and molecular weight, whereas other conventional components were selected from the ASPEN PLUS data bank. NRTL model was used to simulate the thermodynamic properties of solutions. The simulation process was done based on the following streams entering the reactor: 1000 kg/h of dry raw material with the abovementioned composition and 6000 kg/h of ethanol-water (60% w/w), which corresponded to a liquid/solid ratio (w/w) of 6. As solvents were recovered at the end of the process and recycled to reaction unit, solvent input to reaction stage was the sum of the recovered solvent stream and a fresh solvent stream.

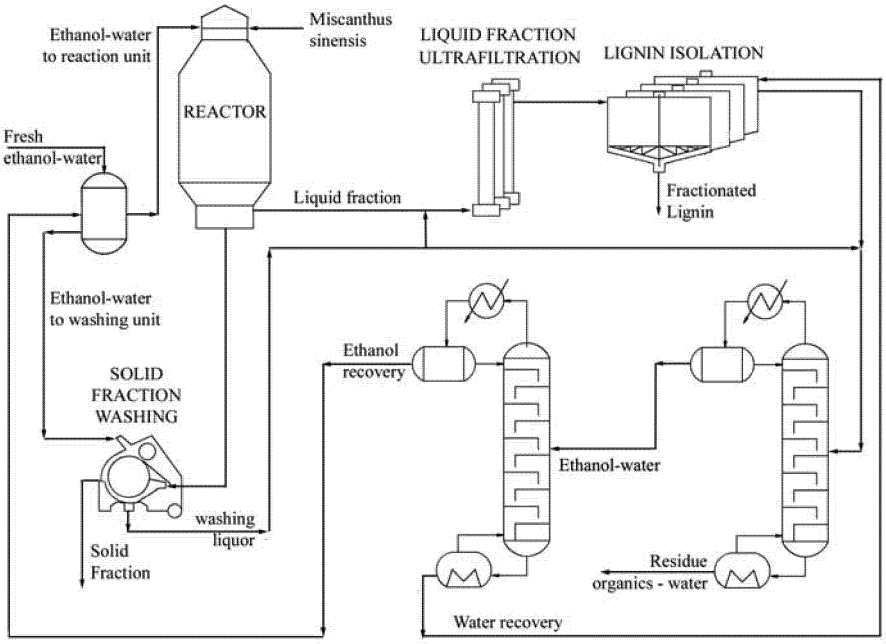

Figure1. Ethanol organosolv biorefinery process.

2.3 Laboratory experiments

2.3.1 Organosolv pretreatment

Miscanthus Sinensis was mixed with ethanol-water (ethanol concentration: 60% w/w), solid/liquid ratio: 6/1. Reaction temperature and time were 180ºC and 90 min respectively. After cooking, SF and LF were separated. The former was washed with aqueous ethanol (60/40 w/w) and the filtrates combined with LF from reactor (total LF). SF was separated from uncooked material by screening through a sieve of 1mm mesh. Final SF yield was 60%. Its composition, mainly cellulose, could be post-treated by several processes, as saccharification and fermentation to obtain ethanol or pulp for paper production by refining.

2.3.2 Membranes ultrafiltration system

Ultrafiltration module used 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. The diameter of the membrane tubes was 6 mm, the length 250 mm and the area of each membrane tube was 47 cm^2. The experiments were done at the following experimental conditions: trans-membrane pressure: 300 kPa; cross-flow velocity: 5.6 m/s and temperature: 60 ºC. Four LF streams were obtained at membrane modules exit: fraction>15KDa, 15KDa> fraction>10KDa, 10KDa> fraction>5KDa, fraction<5KDa.

2.3.3 Organosolv lignin

Lignin contained in the four LF streams (lignin fraction>15KDa, 15KDa>lignin fraction>10KDa, 10KDa>lignin fraction>5KDa, lignin fraction<5KDa) was precipitated by adding two volumes of water and conditioned (Ibrahim et al., 2004).

3. Results

3.1 Simulation results

3.1.1 Organosolv pretreatment

Tables 1 and 2 present obtained data (mass balances and mass fractions respectively) for organosolv pretreatment reaction unit.

Table 1 . *Mass balances of reaction unit (kg/h).*

Stream	Ethanol	Water	Cellulose	Lignin	Furfural	Acetic acid	Sugars	Others	Total
Miscanthus	0	60	395	188	0	0	273	84	1000
Solvent	3600	2400	0	0	0	0	0	0	6000
LF	2612	1710	0	112	3,8	9,5	158	36	4641
SF	988	742	395	76	1,2	3,2	108	48	2361

Table 2. *Mass fractions of reaction unit.*

Stream	Ethanol	Water	Cellulose	Lignin	Furfural	Acetic acid	Sugars	Others	Total
Miscanthus	0,000	0,060	0,395	0,188	0,000	0,000	0,273	0,084	1
Solvent	0,600	0,400	0,000	0,000	0,000	0,000	0,000	0,000	1
LF	0,563	0,369	0,000	0,024	0,000	0,002	0,035	0,007	1
SF	0,419	0,315	0,167	0,032	0,000	0,001	0,046	0,020	1

Liquid and solid fractions were separated after reaction and solid fraction sent to washing stage, where it was mixed with 1400 kg/h of washing solvent: WS (ethanol-water) which came from the solvent recovery stage at the end of the process. Thus, no fresh solvent was required in the solid fraction washing unit. Mass balances and mass fractions of washing stage are presented in Tables 3 and 4 respectively. Washing liquor (WL) exiting this stage were mixed with reaction LF and sent to ultrafiltration system.

Table 3. *Mass balances of solid fraction washing stage (kg/h).*

Stream	Ethanol	Water	Cellulose	Lignin	Furfural	Acetic acid	Sugars	Others	Total
SF	988	742	395	76	1,2	3,2	108	48	2361
WS	852	564	0	0	0	0	0	0	1416
Washed SF	980	692	395	25,6	0,51	1,26	65,7	21	2181
WL	860	614	0	50,1	0,69	1,94	42,3	27	1596

Table 4. *Mass fractions of solid fraction washing stage.*

Stream	Ethanol	Water	Cellulose	Lignin	Furfural	Acetic acid	Sugars	Others	Total
SF	0,419	0,315	0,167	0,032	0,000	0,001	0,046	0,020	1
WS	0,602	0,398	0,000	0,000	0,000	0,000	0,000	0,000	1
Washed SF	0,449	0,318	0,181	0,012	0,000	0,001	0,030	0,009	1
WL	0,539	0,386	0,000	0,032	0,000	0,001	0,026	0,016	1

3.1.2 Membranes ultrafiltration system

Total LF was fractionated into four streams (Table 5 presents ultrafiltration system mass balances) with the composition shown in Table 6.

Table 5 . *Mass balances of ultrafiltration system (kg/h).*

Stream	Ethanol	Water	Cellul.	Lignin	Furfural	Acetic acid	Sugars	Others	Total
Total LF	3472	2324	0	162	4,49	11,4	200	63	6237
LF<5KDa	170	116	0	8,1	0,25	0,63	16,1	4,01	315
5KDa< LF<10KDa	525	349	0	24,3	0,82	1,93	41,1	12,2	954
10KDa< LF<15KDa	868	581	0	40,5	0,97	2,47	32,8	10,3	1536
LF>15KDa	1909	1278	0	89,1	2,45	6,37	110	36,5	3432

Table 6. *Mass fractions of ultrafiltration system.*

Stream	Ethanol	Water	Cellul.	Lignin	Furfural	Acetic acid	Sugars	Others	Total
Total LF	0,557	0,371	0,000	0,026	0,000	0,001	0,033	0,011	1
LF<5KDa	0,541	0,367	0,000	0,026	0,000	0,002	0,052	0,012	1
5KDa< LF<10KDa	0,551	0,366	0,000	0,025	0,000	0,002	0,043	0,013	1
10KDa< LF<15KDa	0,565	0,379	0,000	0,026	0,000	0,002	0,021	0,007	1
LF>15KDa	0,557	0,373	0,000	0,026	0,000	0,001	0,033	0,010	1

3.1.3 Organosolv lignin

Lignin was precipitated from ultrafiltrated LF giving the yields presented in Table 7 (dry lignin kg/ dry lignocellulosic raw material kg). As it can be observed, the lowest molecular weight (MW) lignin fraction was obtained in less quantity finding higher lignin yields as lignin MW increased. Obtained lignin fractions were purified, acetylated and its MW distribution was characterized by GPC (Table 7). Obtained values were in the range of organosolv lignin MW published data (Sun et al, 1997, Tejado et al., 2007). Furthermore, low polydispersity was found, especially in the smallest MW fraction. This fact would suggest that the membrane filtration system allowed the obtaining of narrow MW lignin fractions which could be used in several industrial applications as polymer formulation (Kubo and Kadla, 2004) or as antioxidants (Pan et al, 2006).

Table 7. *Organosolv lignin yield obtained from ultrafiltrated LF (dry lignin kg/ dry lignocellulosic raw material kg). Weight average MW ($\overline{M}_w$), number average MW ($\overline{M}_n$) and polydispersity $\overline{M}_w / \overline{M}_n$ of acetylated lignin samples analysed by GPC.*

Lignin fraction	Lignin yield	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$
Lignin >15KDa	0,071	2370	1463	1.62
10KDa<Lignin<15KDa	0,022	2038	1315	1.55
5KDa<Lignin<10KDa	0,019	1870	1299	1.44
Lignin <5KDa	0,011	1509	1094	1.38

3.1.4 Solvents recovery

Solvents recovery section allowed reducing the fresh input of ethanol from 3600 kg/h to 900 kg/h (75%). Water required in the reaction section was 2400 kg/h and 9800 kg/h were needed to precipitate lignin fractions. Water recycling allowed an 80% reducing of this input (to 2100 fresh water kg/h) due to the high recovering yield in the distillation units.

4. Conclusions

Significant potential market value products (high quality cellulose and lignin) were satisfactorily obtained by a refining of non-woody biomass feedstock using organosolv and membranes filtration technologies. Process simulation allowed adjusting stream balances and compositions and high solvents recovery ratios maximized process effectiveness.

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