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Organosolv Pulping Processes Simulations

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Computer simulations of organosolv pulping processes using commercial simulation software (ASPEN PLUS) has been developed in order to design the process, to establish its key points (products and by-products mass flows balances, energy analysis and solvent by-products recovery) as well as to optimize the operation conditions. Ethanol and ethylene-glycol-water mixtures have been used as delignification agents and leucaena (*leucaena leucocephala*) as raw material for pulp production. Solvent, water and by-products recovery degree was determined for the proposed processes.

1. Introduction

The shortage of raw materials and the large energy and water consumptions are presently the main concerns of pulp and paper industry. Considerable research effort has been done trying to introduce alternative species as raw materials, like biomass from agricultural and forestry residues. Furthermore, it is of vital importance to maximize the efficiency of the process by recovering the by-products (lignin and hemicelluloses), which represent about 50wt% of the dry wood. In this context were developed organosolv processes, based on the use of organic solvents as delignification agents, in which it is possible to break up the lignocellulosic biomass to obtain cellulose fibres for paper making, high quality hemicelluloses and lignin degradation products avoiding emissions and effluents (Aziz and Sarkanen, 1989; Paszner, 1998; Sidiras et al., 2004). Several authors have reported studies in which different alcohols, glycols, acids, esters and others have been used as solvent agents (Gilarranz et al., 1998; Kleinert et al., 1931, 1977; Muurinen, 2000; Stockburger, 1993), trying to relate pulp quality and process variables (Jimenez et al., 2002; Vila et al, 2003).

In this study, computer simulations of organosolv pulping processes using ASPEN PLUS has been developed using laboratory experimental data. This study is focussed on the design and analysis of processes that allow the solvent and by-products recovery.

2. Materials and methods

2.1. Raw material

The chemical composition of leucaena, an alternative agro-alimentary raw material, was determined according to standard methods. After drying, the humidity was calculated: (TAPPI T264 cm-97): 6.6wt%. The chemical composition on an oven dry basis was: ash (TAPPI T211 om-93): 2.5%, 1% NaOH soluble matter (TAPPI T212 om-98): 18%, hot water soluble matter (TAPPI T264 cm-97): 4.0%, ethanol-benzene extractives (TAPPI T204 cm-97): 5.0%, lignin (TAPPI T222 om-98): 21%, holocellulose (Wise et al., 1946): 76%, α-cellulose (Rowell, 1984): 44%.

2.2. Experimental Process

In order to provide data for the simulations, several experiments have been carried out at laboratory scale. The experiment consists in a multi-step process involving raw material cooking, pulp separation, lignin precipitation, solvent recovery and by-products isolation. Two solvent mixtures were used: ethanol-water and ethylene-glycol-water. The first one, which corresponds to the largely investigated Kleinert process (Kleinert et al., 1931, 1977), has been demonstrated to be suitable for producing good quality pulp (Gilarranz et al., 1998) with a high solvent recovery degree. Ethylene-glycol-water pulping process belongs to the group of systems using higher boiling point solvents and has also provided good quality pulps (Nelson, 1977; Rutkowski et al., 1994; Stockburger, 1993; Uraki et al., 1999).

2.2.1. Pulping conditions

The experimental pulping conditions are summarized in Table 1. After cooking, the solid content was filtered and washed. The obtained pulp was separated from uncooked material by screening through a sieve of 1mm mesh and beat in a PFI refiner. The black liquors were also collected.

Table 1. Experimental pulping conditions.

Solvent		t (min)	T (ºC)	Dry basis raw matter (g)	Ratio Liquid/Solid (w/w)
Type	(% w/w)				
Ethanol-water	60	90	180	1000	6:1
Ethylene-glycol-water	60	90	180	1000	6:1

2.2.2. Black liquor characterization

The composition of obtained black liquors was determined as follows: lignin content was determined by gravimetric measurement after precipitation by acid dilution of black liquors in water (1:1.5 v/v, pH=2 by HCl adding). After lignin separation, sugars concentration were analysed in the filtrates by HPLC. Acetic acid was determined by titration with 0.1N sodium hydroxide until the titration end point. Finally, furfural concentration was calculated by UV absorbance. BL composition for both ethanol and ethylene glycol pulping processes is summarized in Table 2.

Table2. Black liquor composition (g/L of black liquor).

Solvent type	**Furfural**	**Acetic acid**	**Ash**	**Lignin**	**Sugars**
Ethanol	0.1	3.7	8.6	21.6	5.7
Ethylene-glycol	1.1	3.3	2.3	34.6	7.2

Ethanol black liquors pH and density are 4.3 and 0.958 g/cm^3 respectively, with ethanol content of 68wt% and 26wt% of water. Ethylene glycol black liquors pH is 4.5, density 1.084 g/cm^3 and ethylene glycol and water contents 54 wt% and 40wt% respectively.

2.2.4. Solvent recovery and by-products isolation

Black liquor's filtrate was distilled in the laboratory in order to calculate the solvent and by-products recovery degree. A batch distillation system was used to separate either ethanol or ethylene glycol and water. Ethanol-water filtrate was first distilled obtaining

distillate having most ethanol and 88wt% of water content and a residue stream containing the remaining water (12wt%) and all heavy components (sugars, lignin, furfural, acetic acid). After that, the former mixture was subjected to a new distillation step with the aim of separating ethanol from water. Two new streams, one containing 95wt% ethanol and 7wt% water and another one having 5wt% ethanol and 81wt% water, were obtained.

In ethylene glycol process a first distillation allowed the separation of 84wt% of water from the mixture and a second one to separate ethylene glycol from by-products. In this second step 80wt% of ethylene glycol mixed with furfural, acetic acid and 16wt% of the water content was separated leaving a residue composed by lignin, sugars and the remaining 20wt% of ethylene glycol.

3. Process Simulation

3.1 Ethanol-water process

As it is shown in Figure1, raw material and solvent (stream 10) are fed to a reactor that produces a pulp stream and black liquors (stream 1). This stream is diluted with water (stream 3) and acidified with HCl to precipitate the lignin. Solid lignin is separated by filtration (stream 5) and the filtrate black liquors (stream 4) go to the distillation units. The first column allows the separation of the stream in a mixture of by-products obtained at the bottom (stream 7), and distillate stream composed by ethanol and water, that is fed to the second column. In this unit ethanol is separated from water. The distillate is recycled as solvent to the digester unit. The residue (stream 9), mainly water, is used in the precipitation stage (stream 3) and to wash the pulp.

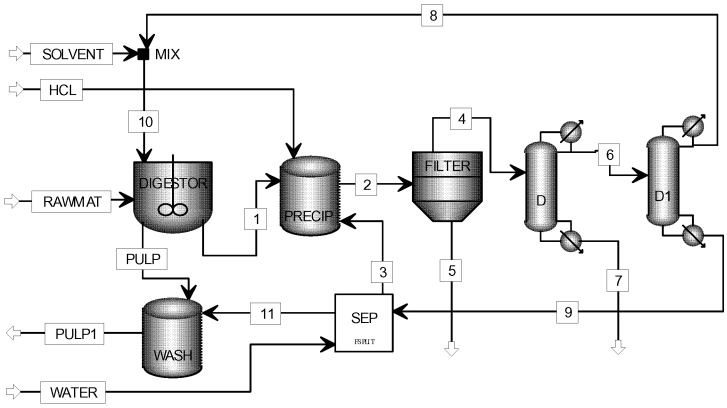

Figure 1.General flow sheet of the ethanol process.

3.2 Ethylene-glycol-water process

The flow sheet of ethylene glycol pulping process (Figure 2) presents some differences with the ethanol process in the distillation units due to the high boiling point of ethylene-glycol. As in ethanol scheme, the filtrate black liquors are fed to the first distillation unit, where the distillate (stream 6), mainly composed by water, is mixed with fresh water to feed the precipitation unit (stream 3) and the pulp-washing unit (stream 11). The residue stream (7) is fed to the second column obtaining a distillate rich in solvent (stream 8) and residue at the bottom containing most of by-products.

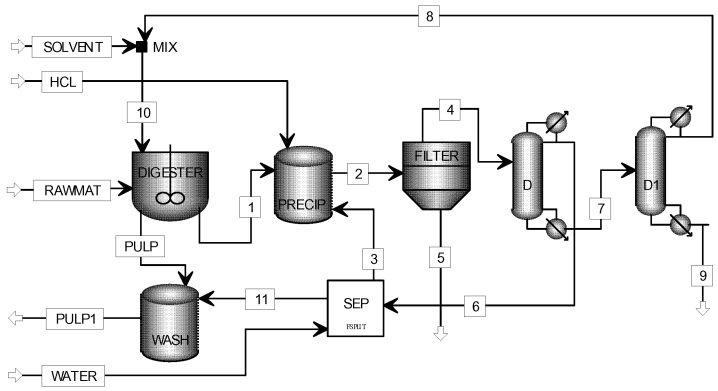

Figure 2.General flow sheet of the ethylene glycol process.

4. Results

4.1 Simulation results

4.1.1 Ethanol process

The results obtained from ethanol continuous process simulation are summarised in Tables 3 and 4.

Table 3. Mass balance for the Ethanol process (kg/h).

Stream	1	2	3	4	5	6	7	8	9	10	11
Ethanol	4256	4441	219	4441	0	4429	11.5	3886	543	4008	222
Water	1624	11197	8617	11196	0	9987	1210	424	9472	1912	2016
Lignin	158	1578	0	47.3	110.4	0	47.3	0	0	0	0
Furfural	5.06	5.06	0.004	5.06	0	0.005	5.062	0	0.005	0	0
Acetic acid	12.6	13.6	0.990	13.63	0	1.102	12.5	0	1.10	0	0
Sugars	61.3	61.3	0	61.3	0	0	61.3	0	0	0	0
Others	29.6	29.6	0	29.6	0	0	29.6	0	0	0	0
HCl	80	100	0	100	0	100	0	100	0	80	0
Total	6226	16005	8837	15893	110.4	14517	1377	4500	10016	6000	2237

Table 4. Mass fractions for the Ethanol process.

Stream	1	2	3	4	5	6	7	8	9	10	11
Ethanol	0.683	0.277	0.024	0.703	0.000	0.305	0.008	0.886	0.043	0.668	0.103
Water	0.261	0.700	0.975	0.277	0.000	0.685	0.879	0.092	0.956	0.319	0.897
Lignin	0.025	0.010	0.000	0.003	1.000	0.000	0.034	0.000	0.000	0.000	0.000
Furfural	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000
Acetic acid	0.002	0.001	0.001	0.006	0.000	0.000	0.009	0.000	0.001	0.000	0.000
Sugars	0.010	0.004	0.000	0.004	0.000	0.000	0.045	0.000	0.000	0.000	0.000
Others	0.005	0.002	0.000	0.002	0.000	0.000	0.021	0.000	0.000	0.000	0.000
HCl	0.014	0.006	0.000	0.005	0.000	0.010	0.000	0.022	0.000	0.013	0.000
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Process yield is 54wt%. Black liquor lignin separation ratio in the precipitation step is 69wt%, which means 53wt% of raw material content. By-products are isolated as residue in column 1 (stream 7: low molecular weight lignin: 22wt% of raw material content, furfural, acetic acid and sugars) and the ethanol-water mixture (stream 6). The second distillation column allowed the recovery of 90wt% of ethanol and 80wt% of water (stream 9). These results are in good concordance with those found in the laboratory analysis where in the batch distillation process 90wt% of ethanol was recovered in a stream with 7wt% of the water content.

4.1.2 Ethylene glycol process

The simulated process yield is 58wt%. Black liquors are treated to precipitate the lignin content (67wt% of high molecular weigh lignin from black liquors; 60 wt% of raw material lignin) and the filtrate (stream 4) is conducted to distillation units. 69wt% of total water content is introduced into the precipitation unit and 22wt% is used to wash the pulp. In the second column, the solvent recovery stream exits from the top (stream 8) containing 87wt% of ethylene glycol content that is recuperated and mixed to form stream 10, the solvent reactor input. At the bottom, by-products stream contains low molecular weight lignin (25wt% of raw material content) and sugars. In this system, in laboratory experiments 80wt% of ethylene glycol content was distilled, leaving the remaining quantity with the by-products of the process.

Table 5. Mass balance for the Ethyleneglycol process (kg/h).

Stream	1	2	3	4	5	6	7	8	9	10	11
Ethylene-glycol	3365	3365	0.012	3365	0	0	3365	2960	404.3	3365	0
Water	2510	12377	7879	12378	0	10422	1955	1955	0	2561	2543
Lignin	174.9	174.9	0	52.46	122.4	0	52.46	0.047	52.45	0.008	0
Furfural	26.49	26.50	0	26.50	0	0	26.50	26.47	0.031	21.15	0
Acetic acid	66.08	66.65	0.556	66.65	0	0.653	65.99	65.99	0	52.73	0.097
Sugars	84.78	84.78	0	84.78	0	0	84.78	0	84.78	0	0
Others	15.80	21.44	5.644	21.44	0	6.626	14.82	0	14.82	0	0.981
HCl	0	135.1	115.1	135.1	0	135.1	0	0	0	0	20.01
Total	6243	16251	8000	16129	122.4	10565	5565	5008	556.4	6000	2564

Table 6. Mass fractions for the Ethyleneglycol process.

Stream	1	2	3	4	5	6	7	8	9	10	11
Ethylene-glycol	0.538	0.208	0.000	0.209	0.000	0.000	0.641	0.592	0.727	0.561	0.000
Water	0.403	0.761	0.987	0.768	0.000	0.987	0.351	0.390	0.000	0.427	0.960
Lignin	0.028	0.011	0.000	0.003	1.000	0.000	0.009	0.000	0.094	0.000	0.000
Furfural	0.004	0.002	0.000	0.002	0.000	0.000	0.005	0.005	0.000	0.003	0.000
Acetic acid	0.011	0.004	0.000	0.004	0.000	0.000	0.012	0.013	0.000	0.009	0.000
Sugars	0.014	0.005	0.000	0.005	0.000	0.000	0.015	0.000	0.152	0.000	0.000
Others	0.002	0.001	0.003	0.001	0.000	0.000	0.003	0.000	0.027	0.000	0.000
HCl	0.000	0.008	0.010	0.008	0.000	0.013	0.000	0.000	0.000	0.000	0.040
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

5. Conclusions

Simulations of organosolv processes have been developed and contrasted with experimental results. In both cases, simulation study has permitted to establish a suitable process design and to determine the most convenient operation conditions. Process yield is 4wt% higher for ethylene glycol process. About 60wt% of lignin contained in raw material is dissolved in ethylene glycol black liquors (7wt% higher than ethanol process). Furthermore, 3wt% more of LMW lignin is obtained as well as 30wt% more of sugars. On the other hand, some upsets could be attributed to this system, such as a more difficult subsequent isolation treatment of by-products as they remain diluted in ethylene glycol instead of water (as in ethanol process) which is more convenient for further processing.

Solvent recovery ratio is 88 and 91%wt for ethylene glycol and ethanol processes respectively.

Fresh water supply is required for both processes into the digester and precipitator unit. Water recovery ratio is 81wt% and 89wt% in ethanol and ethylene glycol processes respectively. Around 20wt% of water is used to wash the pulp and the rest is recycled, reducing fresh water consumption of 80wt% and 92wt% respectively.

6. Acknowledgements

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