Simulation of an Organosolv Pulping Process: Generalized Material Balances and Design Calculations

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The economic feasibility of organosolv pulping depends on the efficiency of solvent and byproduct recovery, as well as on the market price of pulping byproducts. Computer simulation of organosolv pulping is a valuable tool for assessing key points of the process (including the degree of solvent recovery, analysis of possible strategies for stream integration, and specification of mass flows for products and byproducts). Based on experimental data for Acetosolv pulping (carried out in a HCl−water−acetic acid medium), a flowsheet has been proposed for a possible industrial plant, and generalized material balances have been carried out using commercial simulation software. The material balances enabled the calculation of the mass flows of pulp and pulping byproducts, as well as the specification of the composition of streams in which they are included. The calculations predicted 97.6% of acetic acid recovery and 91.7% of HCl recovery.

Introduction

The commercial pulping processes (kraft and sulfite technologies) lead to high-quality pulps, but fractions such as lignin and hemicelluloses (accounting for about 50% of the dry weight of wood) are converted into waste fractions or employed in low-added-value applications such as power generation.

In this field, organosolv pulping (based on the utilization of organic solvents as delignification media) allows the fractionation of the feedstocks to give sulfur-free lignin and valuable hemicellulose reaction products (including sugars, furfural, and acetic acid from acetyl groups), providing a superior approach from the point of view of the feedstock utilization.[1,2] The easy recovery of solvent and the efficient pollution control are important features of these kinds of processes. On the other hand, the lack of expensive heat-recovery furnaces for black liquor processing enables the design of plants smaller than the minimum size needed to reach profitability in kraft facilities.[3,4]

Some organosolv processes (such as Acetosolv, Acetocell, and Formacell) are based on the utilization of concentrated acetic acid, which shows an excellent ability for causing both extensive and selective delignification and is generated during pulping by hydrolysis of acetyl groups, decreasing the need for fresh solvent addition. In the Acetosolv process, the pulping medium is made up of concentrated acetic acid, and HCl is added as a catalyst to promote the hydrolytic degradation of lignin and hemicelluloses under mild operational conditions. Acetosolv pulps show good chemical properties[5] and are susceptible toward bleaching, enabling the production of fully bleached pulps by totally chlorine-free technologies.[6] As in other organosolv technologies, xylose, furfural, and sulfur-free lignin fractions are valuable pulping byproducts.

Computer simulation of chemical processes enables a fast and cheap analysis of suitable flow diagrams, providing a valuable assessment on technical problems.

Commercial software applications useful for the above purposes are available. In some of them, built-in routines for aspects such as the prediction of physical properties and design as well as extensive databases are included. To obtain valid simulation predictions, special attention must be paid to the reliable prediction of physical properties.[7]

Simulation software has been used in the literature for a variety of purposes, including biomass processing.[8,9] Some simulators allow a modular approach to process design, include built-in modules for standard unit operations, permit the implementation of user-written routines for additional calculations, and show the ability to deal with "nonconventional compounds" which cannot be characterized by standard thermodynamic properties.

This work deals with the assessment of the recovery of solvent and byproducts from Acetosolv pulping liquors through the formulation of generalized material balances. Based on experimental data, the main units of a possible Acetosolv processing plant have been studied by computer simulation.

Experimental Section

Raw Material. Chips of *Eucalyptus globulus* wood were collected in a local pulp mill (ENCE, Pontevedra, Spain). The chips were passed through a two-roll mill fitted with a 2-mm screen, homogenized, and subjected to pulping.

Pulping. Pulping assays were carried out for 3 h at 130 °C in an autoclave, using a liquor-to-wood ratio of 10 kg/kg (oven dry wood basis), in media containing 90% acetic acid and 0.2% HCl. These conditions were selected from reported results.[2]

Analysis of Raw Material and Pulp. Analytical assays were performed according to the following procedures: moisture, ISO 638:1978 method; quantitative acid hydrolysis, TAPPI T13m method; Klason lignin, by gravimetric determination of the residue from the TAPPI T13m assay; cellulose (as glucan), by high-performance liquid chromatography (HPLC) determination (IR detection) of the glucose contained in hydro-

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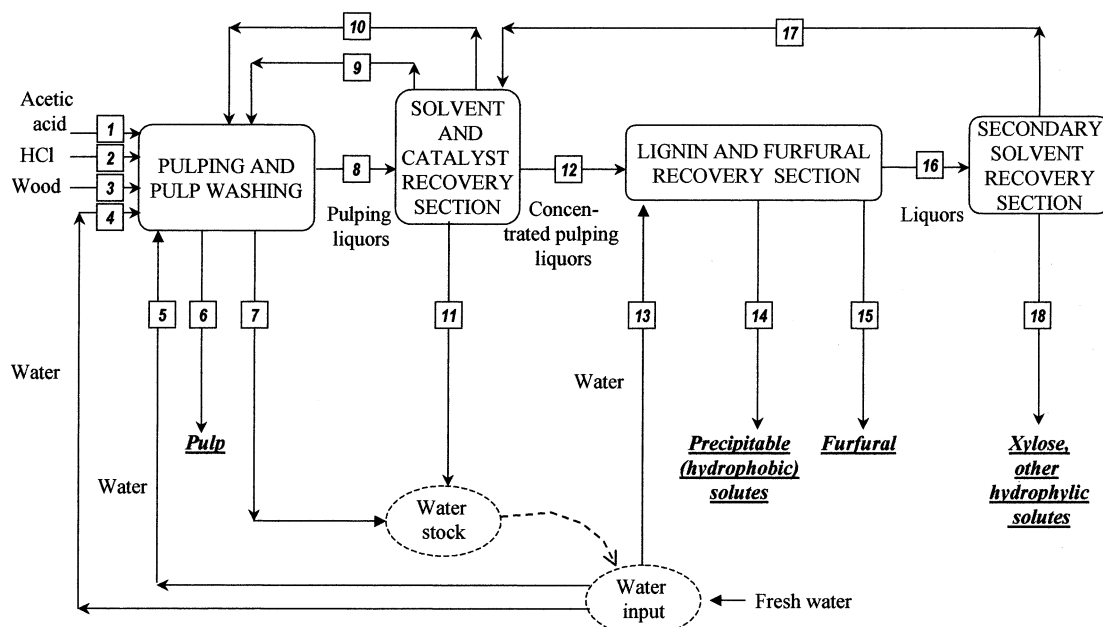
Figure 1. General idea of the proposed process.

lyzates from the TAPPI T13m assay;[2] hemicelluloses, by HPLC determination (IR detection) of the nonglucose sugars contained in same hydrolyzates; acetyl groups, by HPLC determination (IR detection) of the acetic acid present in hydrolyzates.

Composition of Pulping Liquors. As a simplification, the hemicellulose-derived sugars (which were determined by direct HPLC analysis of the supernatant obtained after water addition and centrifugation) were considered as xylose. The furfural content of pulping liquors was measured by HPLC analysis of the same supernatant, using diode array detection (DAD).

Liquor Holdup in Pulp Filtration. Suspension aliquots from the pulping medium were weighed and processed in a laboratory centrifugal filter (25 cm diameter, 2800 rpm), and the filtered solids were thoroughly washed with warm 90% acetic acid and water. The liquor retained by pulp was calculated after oven-drying of washed pulp.

Concentration of Pulping Liquors and Determination of Nonvolatile, Dissolved Solids (NVDS) and Precipitable NVDS. To assess the solvent-recovery stage, aliquots of pulping liquors were vacuum-concentrated at the desired proportion using a rotary evaporator. The composition of concentrated liquors was assayed by HPLC as described above for pulping liquors. The content of NVDS was determined by vacuum-drying of liquor aliquots to reach a constant weight. For determination of the content of precipitable NVDS, aliquots of concentrated pulping liquors were poured into centrifuge tubes with the desired amount of water, mixed, and centrifuged (6000 rpm, 10 min). The vacuum-dry weight of the precipitate measured the content of precipitable NVDS (corresponding to hydrophobic solutes). Aliquots of precipitable NVDS were subjected to quantitative acid hydrolysis (using the same methods employed for wood and pulp) in order to measure the contents of insoluble sugar oligomers and polymers.

Computer Simulation. A commercial simulation software package (Aspen Plus; Aspen Technology, Inc., Cambridge, MA) was used to assess the alternatives selected for solvent, catalyst, and furfural recovery from

pulping liquors. Both built-in modules and Fortran flowsheeting were employed in calculations.

Results and Discussion

Structure of the Process. To simplify the problem to a reasonable limit, only the relevant units for material balance calculations are included in the process flow diagram. Other necessary units (heat exchangers, storage facilities allowing the implementation of the batch reactor with the continuous operation of the recovery sections, etc.) are not considered in this study. In the same way, water effluents are sent to a virtual water stock, which would be employed to decrease the need for fresh process water.

Figure 1 shows the general idea of the process. Wood is mixed with the pulping reagents and recycle streams and pulped in the reactor. The resulting suspension is sent to the separation and washing section, where a part of the liquors is separated by filtration and the rest of them is retained by pulp. Pulp is washed with water in a percolation unit, displacing the pulping liquors (which are sent to the solvent- and catalyst-recovery section together with the liquors coming from the main pulp filter), and both additional water from the washing unit and water-containing pulp leave the process.

In the solvent- and catalyst-recovery section, liquors and a recycle stream from the secondary recovery section are processed by flash evaporation, stripping, and distillation to recover catalyst and solvent (which are recycled), water (which is sent to the virtual water stock), and concentrated liquors that are sent to the next section.

In the lignin- and furfural-recovery section, the concentrated liquors (containing nonvolatile fractions of wood such as lignin-degradation products, hemicellulosic sugars, furfural, and furfural-degradation products) are mixed with water, enabling the precipitation of hydrophobic solutes, which are recovered by centrifugal filtration. The liquors from the lignin-precipitation unit are subjected to heteroazeotropic distillation to give a head stream that is rectified to obtain almost pure

Table 1. Mass Flows of Components Corresponding to Streams of the Mixing and Presoaking Unit (See Figure 2)

		mass flow, kg/h					
	component	stream 1	stream 2	stream 3	stream 4	stream 9	stream 10
solid phase	cellulose	0	0	23 730.00	0	0	0
	hemicelluloses	0	0	8 689.00	0	0	0
	lignin	0	0	11 636.00	0	0	0
	acetyl groups	0	0	1 778.00	0	0	0
	OCSP[a]	0	0	4 980.00	0	0	0
liquid phase	acetic acid	10 494.80	0	0	0	18 818.30	428 004.0
	water	0	169.33	25 407.00	13 676.61	3 275.68	7 268.37
	HCl	0	84.67	0	0	931.59	0
	xylose	0	0	0	0	0	0
	furfural	0	0	0	0	2.05	92.79

[a] OCSP = other compounds in the solid phase.
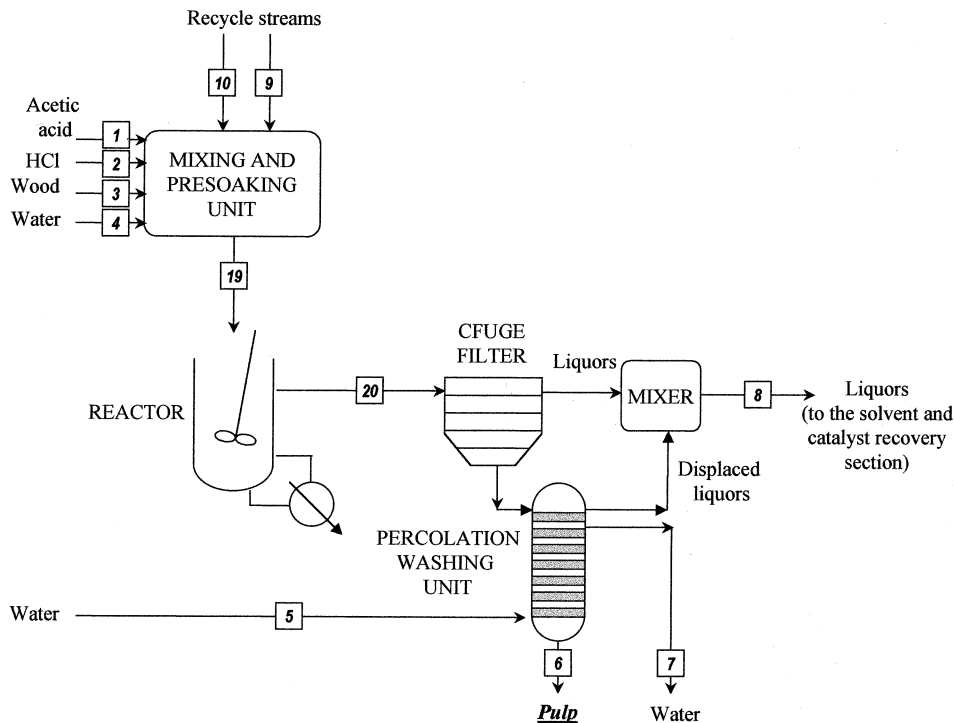
Figure 2. Flow diagram of the pulping and pulp-washing section.

furfural and a bottom stream that is processed in the next section.

In the secondary solvent-recovery section, the above liquors are evaporated to separate the nonvolatile solutes (xylose and other nonvolatile compounds which remained in solution after lignin recovery) as a concentrated solution, whereas the vapor is recycled.

Simulation of the Pulping Stage. To facilitate the understanding of data and calculation procedures, material balances were formulated in terms of mass flows. For this purpose, operation was assumed to occur in an industrial plant having a processing capacity of 6×10^5 t of *E. globulus* wood (as received)/year, the same as a kraft mill existing in our country. For the purposes of this work, oven-dry wood is considered to be made up of cellulose, hemicelluloses (xylan), lignin (Klason lignin), acetyl groups, and other components in the solid phase (denoted OCSP, which include fractions such as acid-soluble phenolics, extractives, and ashes). On the basis of experimental data, the moisture content of wood was assumed to be 50% of its oven-dry weight. Wood moisture was considered as water in the material balances.

After debarking and chipping, wood is sent to a mixing and presoaking unit together with recycle streams

containing acetic acid and catalyst. HCl (as a commercial aqueous solution), concentrated acetic acid, and water are fed to achieve the composition desired for the reaction medium (90% acetic acid, 9.8% water, and 0.2% HCl).

Considering 328 work days/year, the apparent mass flows of every component present in the feed can be calculated from the plant capacity, wood composition, and moisture content. Table 1 shows the corresponding data using the stream notation presented in Figures 1 and 2. For calculation purposes, streams involving solids were considered to be made up of two substreams: the oven-dry solid (wood or pulp) was considered as a "nonconventional" solid phase, and the other components (moisture, reagents, or liquors) are assumed to be a virtual "liquid" phase. This operational procedure has been followed in reported studies dealing with components in the solid phase that are not characterizable by normal molecular properties, such as molecular weight, and critical properties.[8]

In the pulping stage, a variety of effects are caused including the following: (i) lignin is depolymerized by cleavage of α- and β-aryl ethers to give soluble oligomeric components; (ii) extractives are removed from the solid phase; (iii) hemicelluloses are depolymerized and

Table 2. Mass Flows of Components Corresponding to the Reactor Feed Stream and Product Stream (See Figure 2)

		mass flow, kg/h	
	component	stream 19	stream 20
solid phase	cellulose	23 730.00	23 730.00
	hemicelluloses	8 689.00	1 042.68
	lignin	11 636.00	1 097.56
	acetyl groups	1 778.00	1 371.95
	OCSP[a]	4 980.00	197.15
liquid phase	acetic acid	457 317.10	457 884.30
	water	49 796.99	49 796.99
	HCl	1 016.26	1 016.26
	xylose	0	863.82
	furfural	94.84	2 228.98
	NVDS[b]	0	19 808.80

[a] OCSP = other compounds in the solid phase. [b] NVDS = nonvolatile, dissolved solids.

converted into sugar oligomers and hemicellulosic sugars, which can be dehydrated to give furfural; (iv) furfural reacts to give condensation products, which may react with lignin; (v) acetyl groups are split off from hemicelluloses by reaction with water, giving acetic acid as a reaction product; (vi) cellulose can be esterified by acetic acid, to give new acetyl groups.

Other chemical reactions of minor importance (for example, generation of methyluronic monomers, production of methanol from either *O*-methyluronic units or lignin, methanol sterification to give methyl acetate, or neutralization of ashes) are not considered in this study. In a similar way, reported studies on biomass organosolv processing neglected the influence of minor components (for example, extractives) in material balances.[10,11]

The composition of pulping liquors is measured by their contents of acetic acid, water, HCl, xylose, furfural, and NVDS, which may have a hydrophobic or hydrophilic nature depending on their behavior upon water addition: hydrophobic solutes are precipitated, whereas hydrophilic solutes remain in solution. The relative proportions of precipitable and nonprecipitable NVDS were measured in experiments (see below).

Based on experimental data for pulp yield (54%) and pulp composition, the mass flows of components of stream 20 leaving the reactor (see Figure 2) are presented in Table 2. Owing to the selectivity of delignification in an acetic acid medium (a well-known feature of the Acetosolv process), cellulose is not significantly degraded in pulping, and its mass flow is not affected by processing.[2] The pulp contents of lignin (4.0 wt %, corresponding to about 90% lignin removal) and hemicelluloses (3.8 wt %, corresponding to about 88% hemicellulose removal) are in agreement with reported data.[2]

The composition of the liquid phase cannot be exactly determined from the available data, owing to the occurrence of side reactions involving water (for example, reactions leading to water consumption, such as hydrolysis of lignin, hemicelluloses, and uronic acids, or reactions leading to water generation, such as furfural formation from xylose, furfural condensation, and esterification reactions). In this context, Girard and Van Heiningen[12] have been pointed out that a fundamental error of all mass balance closures in pulping processes is that the net amount of reaction water formed during cooking is not considered. Based on the small error introduced when the net formation or consumption of water are neglected, the mass flow of water has been considered to be constant in the pulping stage.

In the pulping media, reactions involving both acetic acid generation (hydrolysis of acetyl groups of hemicelluloses) and acetic acid consumption (acetylation of pulp) occur. The mass flow of acetic acid leaving the reactor was calculated on the basis of the net balance of hemicellulose deacetylation and pulp esterification, which resulted in the formation of 11.16 kg of acetic acid/t of wood, an important finding contributing to the feasibility of the process.

In organosolv pulping media, xylan is decomposed in part to give xylose and furfural. In material balances to ethanol pulping,[10,11] the formation of furfural was negligible, but in our case, a significant amount of furfural (42 kg/t of wood) is generated in pulping. Assuming that the hemicelluloses of *E. globulus* wood are made up of xylose units, and considering the corresponding stoichiometric factors, the experimental data show that about 33.7% of the initial xylan is converted into furfural, 8.7% of the initial xylan is hydrolyzed to xylose, and 12% of the initial xylan remains in wood. That means that more than 45% of the initial xylan is converted into sugar oligomers and/ or in furfural-decomposition products, which may react with lignin (see below). In terms of material balances, these compounds are included in the NVDS fraction.

The influence of the catalyst (HCl) in the material balances is also of minor importance, owing to its limited concentration. Although a part of HCl could be consumed by neutralization with ashes, the presence of a huge amount of acetic acid (which can also act as a neutralizing agent) supports the hypothesis that HCl is not significantly affected in the reaction stage.

Separation and Washing of Pulp. The suspension leaving the reactor (stream 20) is filtered in a centrifugal filter to separate liquors from a solid phase embedded in pulping liquors. Experimental data showed a holdup of 3 kg of liquors/kg of oven-dry pulp, enabling the calculation of the corresponding mass flows. The liquors from the filtration stage are sent to the solvent- and catalyst-recovery section, and the solid is washed in a percolation unit. For simplicity, the existence of two washing periods has been considered. In the first one, the pulping liquors retained by pulp are displaced by water in a perfect plug operation without longitudinal mixing. With this assumption, the liquid mass flows of streams 8 and 20 are identical. The displaced liquors are mixed with the liquors separated in filtration (which have identical composition) for further processing. In the second washing period, the washing effluent is essentially pure water at a mass flow adjusted to give a washing ratio of 5 kg of water/kg of oven-dry pulp. The washing liquor from the second period is sent to the water stock for further utilization in the process. The washed pulp leaves the process to be processed by totally chlorine-free bleaching for dissolving pulp production.[1,5] The data concerning the material balances to the separation and washing of pulp are summarized in Table 3.

Recovery of Solvent and Catalyst. Figure 3 shows the management of pulping liquors in the solvent- and catalyst-recovery section, and Table 4 lists the mass flows of components present in the corresponding streams. The pulping liquors (stream 8) are flashed to atmospheric pressure, allowing the separation of a vapor phase (stream 9, containing acetic acid, water, and HCl), which is directly recycled to the mixing and presoaking unit (see Figure 2). Preliminary vapor−liquid equilibria
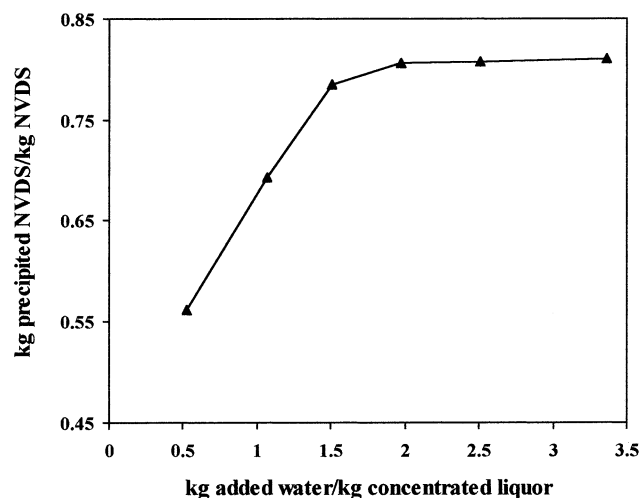
Table 3. Mass Flows of Components Corresponding to Streams 5−8 (Corresponding to the Separation and Washing of the Pulp Section; See Figures 1 and 2)

		mass flow, kg/h			
	component	stream 5	stream 6	stream 7	stream 8
solid phase	cellulose	0	23 730.00	0	0
	hemicelluloses	0	1 042.68	0	0
	lignin	0	1 097.56	0	0
	acetyl groups	0	1 371.95	0	0
	OCSP[a]	0	197.15	0	0
liquid phase	acetic acid	0	0	0	457 884.30
	water	219 515.00	82 318.00	137 197.00	49 796.99
	HCl	0	0	0	1 016.26
	xylose	0	0	0	863.82
	furfural	0	0	0	2 228.98
	NVDS[b]	0	0	0	19 808.80

[a] OCSP = other compounds in the solid phase. [b] NVDS = nonvolatile, dissolved solids.

Figure 3. Flow diagram of the solvent- and catalyst-recovery sections.

Table 4. Mass Flows of Components Corresponding to Streams Involved in the Solvent- and Catalyst-Recovery Sections (See Figures 1 and 3)

	mass flow, kg/h						
component	stream 8	stream 9	stream 21	stream 22	stream 10	stream 11	stream 12
acetic acid	457 884.30	18 818.30	439 066.00	411 654.00	428 004.00	7.80	27 412.00
water	49 796.99	3 275.68	46 521.31	45 755.41	7268.37	102 270.06	765.90
HCl	1 016.26	931.59	84.67	84.67	0	84.67	0
xylose	863.82	0	863.82	0	0	0	863.82
furfural	2 228.98	2.05	2 226.93	29.74	92.79	16.81	2 197.19
NVDS[a]	19 808.80	0	19 808.80	0	0	0	19 808.80

[a] NVDS = nonvolatile, dissolved solids.

prediction runs were carried out assuming either that the NVDS corresponded to a syringyl polymer (a model structure for lignin-derived compounds) or that the NVDS did not affect the equilibrium conditions. Because negligible differences were observed between both hypotheses, the second approach was assumed. For the operational conditions employed in flashing (feed temperature, 130 °C; pressure = 1 atm), the simulation predicted 91.67% HCl recovery in stream 9 (see Table 4). The liquid phase from the flash unit (stream 21) has a reduced HCl content (HCl mass fraction = 1.7×10^{-4}), an important fact considering the corrosion caused by

this compound in an acetic acid medium. With this approach, only the main reactor, the units dealing with solids (filter and washing percolator), and the flash unit have to be built in highly corrosion-resistant materials (one of the main disadvantages of the Acetosolv process).

The liquors leaving the flash evaporator (stream 21) are sent to a stripper made up of three equilibrium stages operating at a head pressure of 1 atm to give a vapor phase containing 89.9% acetic acid at a mass flow equivalent to 90% of the feed stream (22) and a bottom stream (12) containing xylose, NVDS, almost all of the furfural contained in stream 8, and additional acetic

Figure 4. Dependence of the mass ratio between precipitable and total NVDS on the amount of added water (measured as the mass ratio of water to concentrated liquor).

Table 5. Mass Flows of Components Corresponding to Streams Involved in Lignin Recovery (See Figures 1 and 5)

component	mass flow, kg/h			
	stream 12	stream 13	stream 14	stream 23
acetic acid	27 412.00	0	9624.14	17 787.86
water	765.90	102 096.00	36 114.74	66 747.16
HCl	0	0	0	0
xylose	863.82	0	303.29	560.53
furfural	2 197.19	0	771.43	1 425.76
NVDS[a]	19 808.80	0	17 366.55	2 442.25

[a] NVDS = nonvolatile, dissolved solids.

acid and water, which is further processed in the lignin- and furfural-recovery section. Stream 22 is fed to the 20th plate of a distillation column operating at a head pressure of 1 atm containing 25 equilibrium stages (including reboiler and condenser) and operating at reboiler and condenser ratios of 5, to increase the acetic acid concentration in the bottom stream (stream 10) to a level (>98 wt %) suitable for recycling to the mixing and presoaking unit. This distillation column also receives an input (stream 17) from the secondary solvent-recovery section, which is fed to the 15th plate. The head stream from the column (stream 11) is made up of almost pure water, which is sent to the water stock for further utilization in the process.

Lignin Recovery. The hydrophobic solutes (corresponding mainly to lignin-degradation products) can be precipitated from the concentrated pulping liquors (stream 12) by water addition.[13] Experimental work was carried out as described in the Experimental Section to assess the effect of the relative amount of water employed for lignin precipitation. For this purpose, in a laboratory evaporator at the same proportion as that corresponding to the mass flows ratio of streams 12 and 22 to confirm the absence of precipitation and viscosity-related problems and mixed with water in several proportions. The experimental data shown in Figure 4 show that no additional precipitation of hydrophobic solutes was achieved when using more than 2 kg of water/kg of concentrated liquors. Under these conditions, 81 wt % of the nonvolatile solutes was recovered as a precipitate after centrifugal filtration and 63 wt % of the whole precipitate corresponded to embedded liquors. With these results, the mass flows of streams 13, 14, and 23 can be calculated (see Table 5). In the literature, 51.6–56.6% lignin recovery by water precipitation has been reported for methanol pulping, in comparison with 63–69% for ethanol pulping and 77.9% for the same process after acidification of the medium.[11]

Comparing the mass flow of solubilized lignin with the mass flow of precipitable solutes, it can be inferred that the weight increase of lignin-derived fractions owing to the stoichometry of hydrolysis reactions is not enough to justify the difference between both results and that other unknown reactions (such as lignin acetylation and/or reactions of acid-insoluble lignin with a variety

of products, including oligosaccharides, hemicellulosic sugars, furfural, extractives, acid-soluble lignin, etc.) participate in the overall process.

To obtain further information on the chemical nature of precipitable and nonprecipitable solutes, both fractions were subjected to quantitative saccharification to release the sugar monomers, making part of the oligosaccharides possibly present in these fractions.[14] The further determination of reducing sugars in the corresponding hydrolyzates showed that the joint contribution of mono- and oligosaccharides accounted for 0.015 kg/kg of precipitable solutes and 0.223 kg/kg of nonprecipitable solutes. However, because xylose accounts for 0.187 kg/kg of nonprecipitable solutes, it can be inferred that the contribution of oligosaccharides (measured as a xylose equivalent) was only 0.036 kg/kg of nonprecipitable solutes. The experimental content of precipitable solutes in Klason lignin (89.7%) was in close agreement with reported results.[14]

Furfural Recovery. The hydrophilic phase coming from the lignin precipitation section (stream 23 of Table 5) contains furfural, a valuable chemical that must be recovered for both economic and environmental reasons.

Figure 5 shows the structure of the furfural-recovery section: stream 23 (containing acetic acid, water, and furfural as volatile compounds) is fed to a distillation column. The bottom stream from the column (stream 16, containing water, acetic acid, xylose, and nonprecipitable NVDS) is sent to the secondary solvent-recovery section, whereas the head stream is totally condensed and settled in a decanter, to separate the aqueous phase (stream 25) from the organic phase (stream 26). The aqueous phase is recycled and used for reflux in the previous column, and the furfural-rich fraction (stream 26) is distilled to recover almost pure furfural (stream 15) whereas the head stream (containing water and furfural) is recycled to the decanter.

The study of furfural recovery from the process liquors by heteroazeotropic distillation needs reliable data on the liquid–vapor equilibrium of the furfural–acetic acid–water system, which presents a complex behavior owing both to its azeotropic nature and to the dependence of solubility on temperature. The UNIQUAC method showed a satisfactory ability to reproduce the experimental data available for this system.[15] Figure 6 shows the map of residual curves calculated for operation at 1 atm. Considering the composition of the feed stream, it can be seen from the residual curves that the head product tends to reach the concentration of the azeotrope and that a decrease in the temperature results in immiscible phases.[16,17] The occurrence of phase separation under the process conditions has been confirmed in the laboratory.

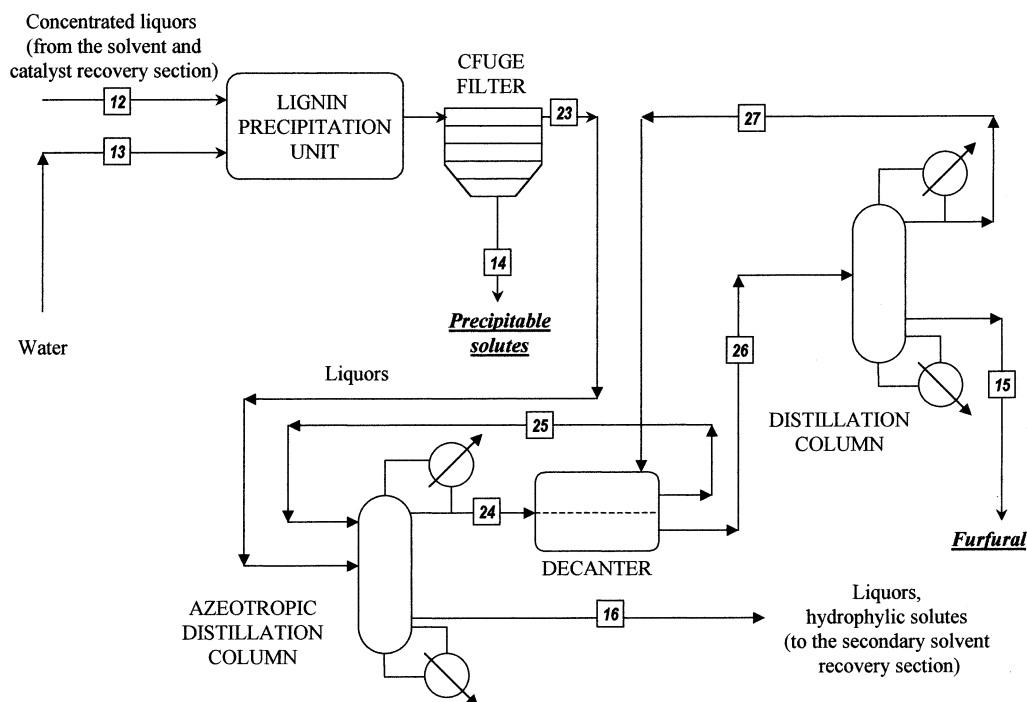The azeotropic distillation column is made up of 10 equilibrium stages and fitted with a total condenser.

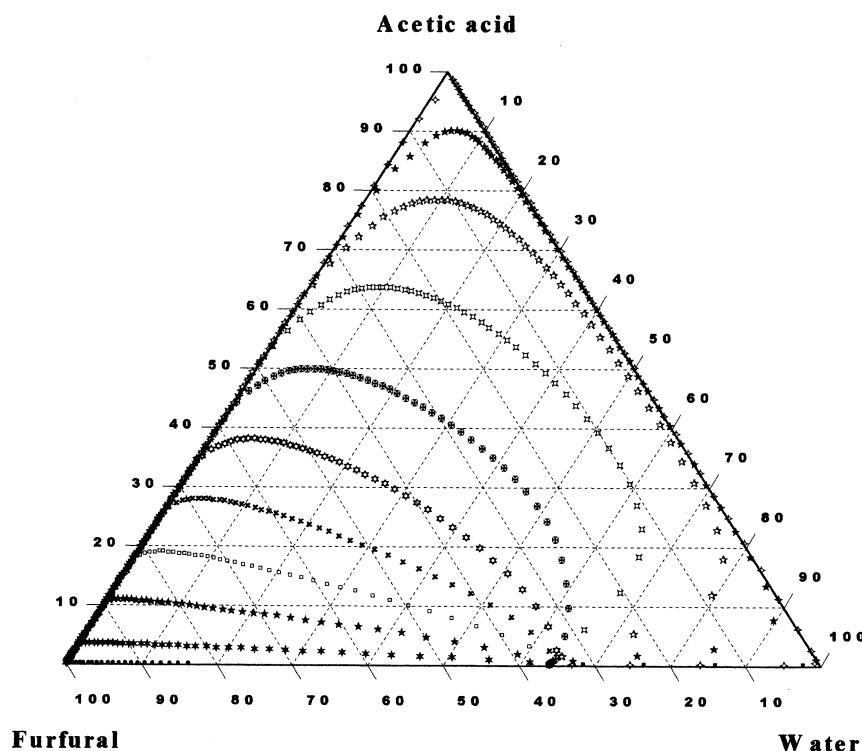**Figure 5.** Flow diagram of the lignin- and furfural-recovery section.

Figure 6. Predicted data for the equilibrium of the ternary system acetic acid−water−furfural ($P = 1$ atm).

Operation was assumed to occur at atmospheric pressure with reboiler and reflux ratios of 0.75 and 10, respectively, whereas the settler operated at 90 °C. Streams 25 and 23 enter to the second and seventh plates, respectively.

The heavy phase from the decanter is sent to the fourth plate of a dehydration column made up of five equilibrium stages operating at 1 atm at reboiler and reflux ratios of 3 and 6, respectively. The bottom stream is made up of almost pure furfural (which leaves the process), and the head stream is recycled to the decanter. The results of the material balances listed in

Table 6 show that 94% of the fed furfural is recovered in this section.

Secondary Solvent-Recovery Section. To recover acetic acid, the aqueous effluent from the furfural-recovery unit is sent to an evaporator (see Figure 7), where 91.5% of the feed is converted into vapor (see material balances in Table 7), leaving a liquid phase containing xylose, nonprecipitable NVDS (hydrophilic solutes), acetic acid, and water. The vapor phase is recycled to the solvent- and catalyst-recovery sections, and the liquid phase leaves the process for further utilization. This point is not considered in our work

Table 6. Mass Flows of Components Corresponding to Streams Involved in Furfural Recovery (See Figures 1 and 5)

component	mass flow, kg/h					
	stream 15	stream 23	stream 24	stream 25	stream 26	stream 27
acetic acid	0.41	17 787.86	2.17	1.76	0.41	0
water	6.50	66 747.16	4425.65	4419.15	135.21	128.71
HCl	0	0	0	0	0	0
xylose	0	560.53	0	0	0	0
furfural	1335.42	1 425.76	1806.57	471.15	1456.36	120.94
NVDS[a]	0	2 442.25	0	0	0	0

[a] NVDS = nonvolatile, dissolved solids.
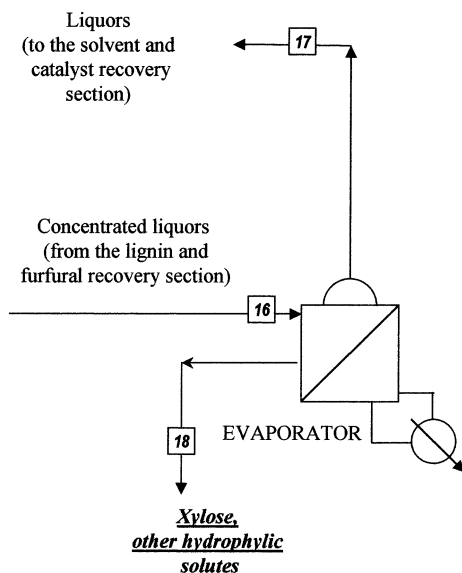
Figure 7. Flow diagram of the secondary solvent-recovery section.

Table 7. Mass Flows of Components Corresponding to Streams Involved in the Secondary Solvent-Recovery Section (See Figures 1 and 7)

component	mass flow, kg/h		
	stream 16	stream 17	stream 18
acetic acid	17 787.45	16 357.80	1429.65
water	66 740.66	63 783.02	2957.64
HCl	0	0	0
xylose	560.53	0	560.53
furfural	90.34	79.86	10.48
NVDS[a]	2 442.25	0	2442.25

[a] NVDS = nonvolatile, dissolved solids.

because the necessary experimental data are not available. Experimental work is underway to assess this point.

Conclusions

This study provides valuable insight into the feasibility and key technical problems of the Acetosolv process, including the identification and evaluation of suitable separation technologies, determination of working conditions, suitability of strategies for an efficient utilization of the raw material, assessment on the concentrations of streams, degree of byproduct recovery, and identification of bottlenecks and new points where additional research is needed. The computer simulation of the integrated process, including recycle streams, provides a sound information assessing the recovery of acetic acid, HCl, and reaction byproducts from pulping liquors. According to the material balances, the proposed process allowed 97.6% of acetic acid recovery and 91.7% of HCl recovery, whereas almost pure 99.5% furfural is obtained as a commercially valuable byproduct.

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