CELLULOSE CHEMISTRY AND TECHNOLOGY

ENERGETIC VIABILITY OF WHEAT STRAW FRACTIONATION BY ACETOSOLV PROCESS

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Recentadvances in the development of the Acetosolv process, particularly with respect to its industrial scale-up are presented. The main drawback that makes the process economically unfeasible up to now is its highprocess energy demand, which is determined by: (1) liquid flows required in the digestion, separation of dissolved lignin and hemicelluloses, and washing of acetic pulp, and (2) the amount of water fed into the distillation column. A continuous Acetosolv process was developed, in order to decrease the required liquid/solid ratio. In addition, pulp washing by ethyl acetate rather than by water and drying of the digestion liquor has been proposed to minimize the water feed in the distillation column. The processes under study have been modeled in ASPEN PLUS to calculate the mass balance of each subsystem and the energy requirement of principle subsystems, as well as of the overall process. The overall energy requirement was reduced dramatically.

Keywords: Acetosolv process, wheat straw, scale-up, energy demand, simulation

INTRODUCTION

The selective dissolution of lignin with organic solvents has been known for over 100 years.[1]The use of acetic acid is particularly attractive as it is a widely availablelow-cost solvent, present as an intermediate in many biological processes that, under appropriate conditions, can be highly selective towards lignin. There exist numerous studies evaluating diverse raw materials, suitable reaction conditions and characteristics of the main products.[2]

Most of the developments to date reproduce works on a laboratory scale. The first pilot plant based on carboxylic acids was built in 1987 in southern Germany for the company Kunz Holding. Based on the Acetosolv Process, wood chips of *Pinus sylvestris* were processed in a carrousel type reactor with concentrated acetic acid and hydrochloric acid as catalyst. The plant was later remodeled by the consortium VebaOel, implementing the alternative Acetocell Process.[3] This considered a batch reactor of 800 L, which could operate at a temperature of 190 °C. More than 6 tons (dry basis) of pulp was produced, which was washed in a closed circuit that consisted in two consecutive dilution sequences with acetic acid and drainage in an extrusion press. Subsequently, the pulp was subjected to ozone bleaching in high consistency acetic medium and hydrogen peroxide in alkaline aqueous medium.[4]

In the early 90s, the KCl institute and Kemira constructed and operated a MiloxProcess based pilot plant in Oulu, Finland. This involved three stages of digestion: with formic acid and hydrogen peroxide at 80 °C, with formic acid at 100-140 °C and again with formic acid and hydrogen peroxide. 84 digestions with birch and several trials with annual plants were carried out.[5]

A third pilot plant based on the CIMV Process developed by the University of Toulouse[6] was built in the northeast of France. This plant was designed to process 100 kg/h of annual plants with formic and acetic acid under atmospheric pressure and a temperature near the normal boiling point of the mixture. The batch reactor is a belt conveyor reactor, commonly used for sugar extraction.[7]

A fourth pilot plant was implemented at the University of Concepcion in southern Chile. The first version of the process was very similar to the plant operated by VebaOel in Germany in the 80s-90s; softwoods (*Pinus radiata* D. Don), hardwoods (*Eucalyptus globulus*) and wheat straw (*Triticum aestivum*) were processed with acetic acid to 87% (w/w) at temperatures of 190, 165 and 160 °C, respectively. Wheat straw also was processed under atmospheric pressure, replacing a part of acetic acid by formic acid.[8] Cellulose fibers with a Kappa number of 14 were obtained by digesting the biomass with 87% (w/w) acetic acid solution at 160 °C for 120 min. The main drawbacks of the batch process,which make it economically unfeasible, are the high energy consumption during digestion, evaporation of liquor and separation of the solvents.

Conventional Acetosolv Process

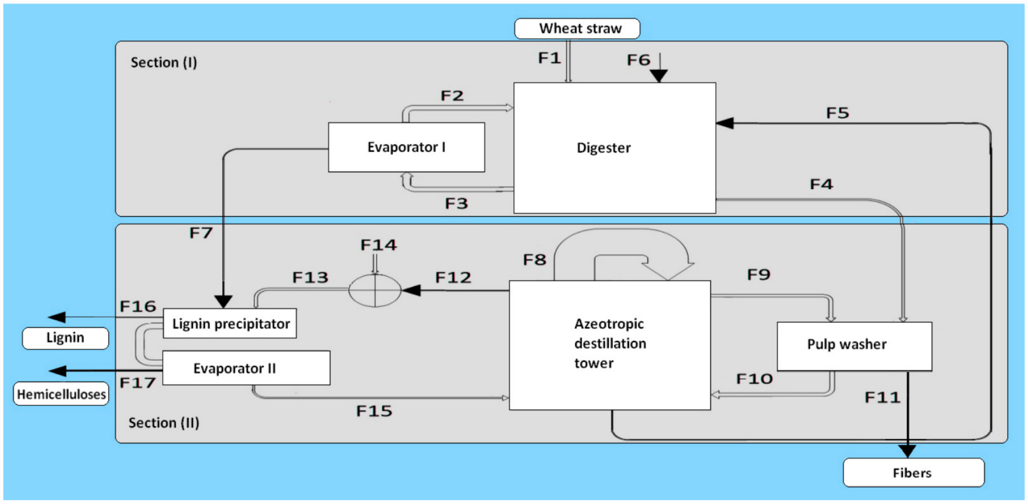
The initial configuration conceived for the separation of the components of the wheat straw is shown in Figure 1.The overall process can be divided into two subsections: Section 1, which involves delignification of the wheat straw and concentration of the resulting liquor, and includes delignification reactor and evaporator; Section 2, which involves the following: separation of lignin and hemicelluloses, washing of the pulp and separation of the solvents. The overall process in each section mentioned is described below.

Delignification of the wheat straw

The process involves a batch digester with a processing capacity of 1 ton/h of biomass and solid to liquid ratio of 1:10, where the biomass is digested in 87% (w/w) acetic acid solution at 160°C, for 120 min. The resulting fibers are washed in countercurrent with fresh acid and are drained to 40% solids. The liquor from the delignification reaction is fed to an evaporator where it is dried to contain 50% solids by weight to reintegrate the acid in the reactor, as the condensate from the evaporator has nearly the same acetic acid content as the initial feed in the digester. The batch digester available in UDT of the University of Concepcion is shown in Figure 2(a).

Separation of lignin and hemicelluloses

The concentrated liquor is diluted to contain approximately 20% acetic acid, as it has been proved that the lignin solubility at such concentration is low enough to precipitate the maximum amount of the lignin present in the diluted sugar solution. The precipitated lignin is washed and dried at reduced pressure at 50ºC to conserve its integrity. The diluted liquor that is composed of aqueous solution of soluble sugars and acid is evaporated to contain 50% solid by weight.



Flows	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14	F15	F16	F17
Biomass	1000	0	600	400	0	0	600	0	0	0	400	0	0	0	0	200	400
Water	82	1037	1105	195		76,4	68	0	2400	1878	599	682	5310	687	1204	10	157
Acetic acid	0	6265	7395	1305	540	10,7	1129	0	0	521	0,28	0	0	0	26	0	9,8
Et. acetate	0	0	0	0	0	0	0	2700	0	0	0	0	0	0	0	0	0
Total	1082	7302	9100	1900	548	87	1797	2700	2400	2400	1000	682	5310	687	1230	210	567

Figure 1: Simplified flow sheet and simulation results of the mass balance in conventional Acetosolv process

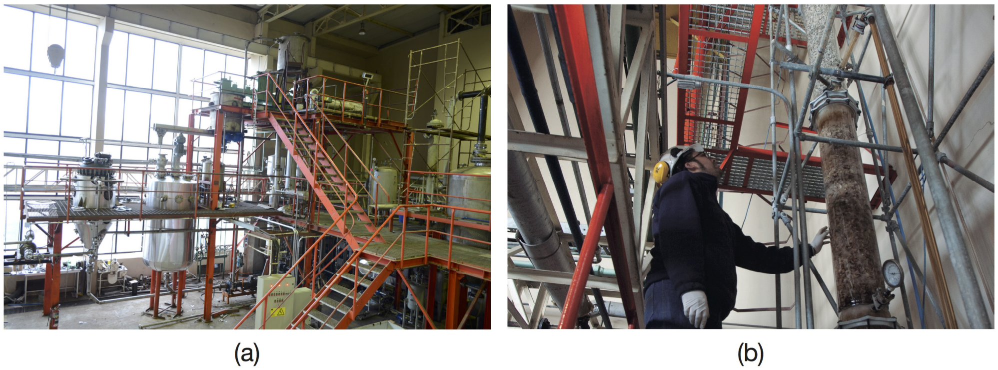


Figure 2: Main equipment employed in the conventional delignification process in UDT; a) Batch digester, b) Azeotropic distillation column

Acetic acid removal from the pulp

The acetic pulpresulting from delignification is washed in a three stage countercurrent washer by water to displace the acid in the fibers. The dilution factor of 2.4 is considered for the process.

Separation of the solvents

The dilute acid solutions obtained from evaporation, fiber washing and lignin washing are then fed to a continuous azeotropic distillation tower that uses ethyl acetate as entrainer. The distillation products are recycled back to the process. Figure 2(b) shows the azeotropic distillation tower present in UDT.

The main drawback of the process is the high energy consumption. To overcome this drawback, the batch process has been modified and several alternatives to recover acetic acid from the pressed washed fibers and the concentrated digestion liquor were simulated and evaluated.

EXPERIMENTAL

Process simulation

Aspen Plus, widely used in academic and industry simulation, was used to model the processes. There is no built-in model for the reactor used for delignification, a common approach would be to develop a complete model in FORTRAN, taking into account complex phenomena of heat and mass transfer, their properties and kinetics of delignification and link it to Aspen Plus as a separate subroutine, which is not the objective of the present work.

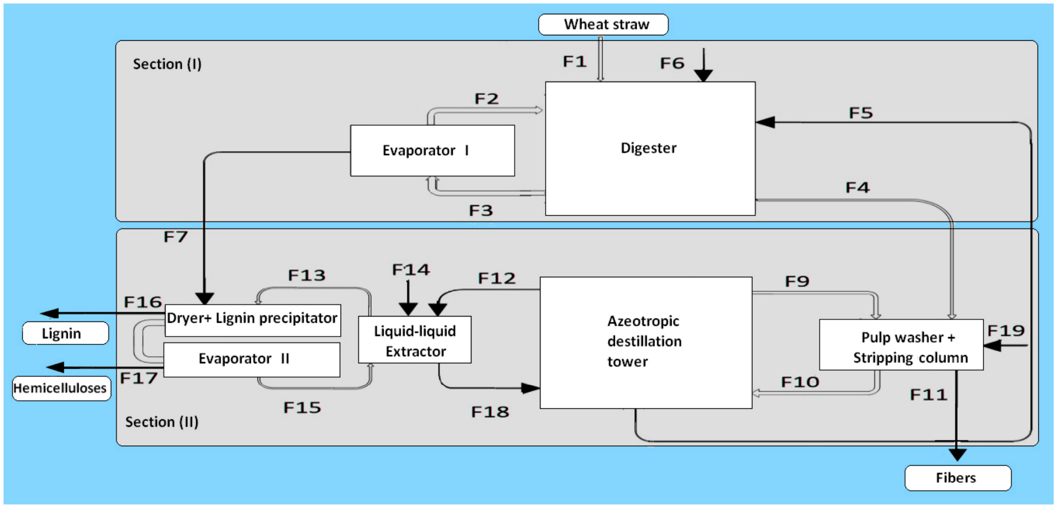
With reference to Figure 3, the stream biomass is fed into the “digester” block that simulated a continuous delignification reactor, along with 87% acetic acid. The biomass stream composition and thermodynamic conditions were specified as conventional solids, using NREL physical properties database.[9]Since the reaction kinetics and other transport properties for the reactor are unknown in this case, the continuous reactor is modeled using a Yield reactor with an approximate conversion of biomass to its split components, which was obtained in the pilot plant. The dryers used in the process were modeled with simple flash drums at very low pressure and relatively high temperature, which is according to the process requirements, where vacuum dryers are used, as very high temperature could negatively affect the physical properties of the solids under study. All liquid-liquid and liquid-vapor equilibriums in the process are modeled using UNIQUAC-HOC activity coefficient model, as can be used for VLE and LLE for non-ideal chemical systems. Another important point to be noted is the modeling of the washing unit, which was done using a wash system available in the unit operation blocks in three countercurrent stages, with a mixing efficiency of 1 in both cases. The ideal behavior of the system is assumed. The energy consumption being studied is only a preliminary version of the heat required in the principal energy consuming equipment. Heat integration, through which theenergy requirements of the overall process are expected to decrease, has not been performed. The process simulations have fully converged with all recycle streams closed.

RESULTS AND DISCUSSION

A simplified flow sheet of the conventional delignification process described earlier and the simulation results of its mass balance are shown in Figure 1. Among the various alternative systems evaluated, the flow sheet of the least energy consuming set-upis shown in Figure 3.

The conceptual design of the continuous process is mainly based on the experimental results obtained at the laboratory and an operating pilot plant in the Technological Development Unit (UDT). The main changes made in the conventional process are: Section 1: the discontinuous batch delignification has been replaced by a continuous delignification process;

Section 2: drying of liquor has been proposed prior to lignin precipitation and water has been replaced by ethyl acetate to wash the acetic pulp.



Flows	F1	F2	F3	F4	F5	F6	F7	F9	F10	F11	F12	F13	F14	F15	F16	F17	F18	F19
Biomass	1000	0	600	400	0	0	600	0	0	400	0	0	0	0	206	394	0	0
Water	82	483	442	78	0	0	4	0	78	140	0	970	400	978	10	386	8	140
Acetic acid	0	2930	2958	522	540	10	28	0	521	1	0	0	0	20	0,2	8	20	0
Et. acetate	0	0	0	0	0	0	0	1000	1000	0	85	0	0	0	0	0	85	0
Total	1082	3368	4000	1000	540	10	636	1000	1599	542	85	970	400	997	216	788	112	140

Figure 3: Schematic representation of the modified process for separating components of wheat straw in acetic acid medium (simplified diagram) and simulation results of the mass balance

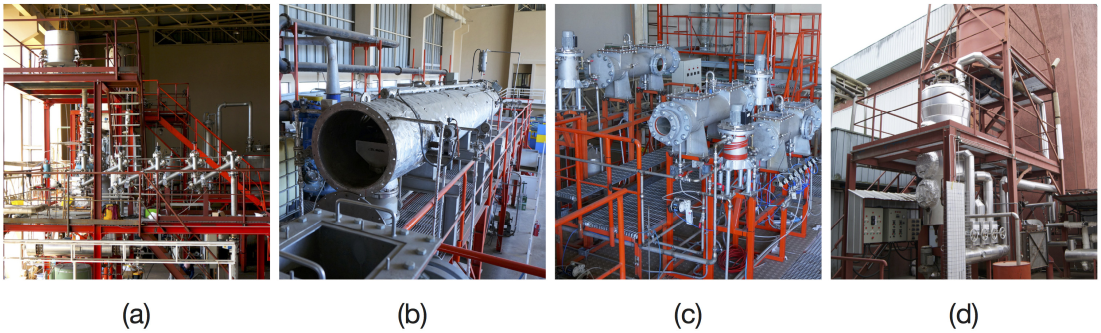

(a) (b) (c) (d)

Figure 4: Main equipment of the continuous pilot plant in UDT; (a) Continuous digestion reactor, (b) Vacuum belt dryer, (c) Mixer-settler type liquid-liquid extractor; (d) Desolventizer

Delignification

Continuous digestion is essential for the processing of annual plants, due to the low density of the material. Moreover, some restrictions are to be considered; among them, the tendency of biomass to agglomerate, avoiding uniform permeation of the material and to retain a great part of the solvent, due to hydrophilic properties of the biomass, making it difficult to extract the solubilized components.

In accordance with this, a continuous pilot plant (patent in preparation) has been designed and constructed, which is now in the initial phase of its operation. It consists of three sequenced stages, each stage with one vertical section for the biomass feed and one oblique section for the solid transport, the next step in countercurrent with liquid (see Figure 4a). It was established that the solid/liquid relation can be reduced from 1/10 to 1/4 (w/v), without affecting negatively the lignin and hemicelluloses recovery through preliminary pilot plant tests and simulation results.

Separation of lignin and hemicelluloses

Given the hydrophobic character of lignin and the hydrophilic character of carbohydrates, they can be separated by dilution of the concentrated acetic acid solution containing these components. Experiments have been carried out and it was found feasible to solubilize carbohydrates from evaporated and dried liquor with water, and separate lignin by filtration (see the vacuum belt dryer in Figure 4b). Therefore, the concentrated liquor after evaporation is dried and subsequently dissolved in water to separate the insoluble lignin from water soluble sugars. The lignin is further filtered and dried. The residual acetic acid in the aqueous sugar solution is recovered through liquid-liquid extraction with ethyl acetate(seethe mixer-settler in Figure 4c), and subsequently the mixture of ethyl acetate and the acetic acid is fed in the azeotropic distillation column. The recovery of residual acetic acid though liquid-liquid extraction is an important step in the process as it minimizes the entry of water to the distillation column.

Acetic acid removal through pulp washing

It has been demonstrated that the separation of acetic acid from the digested fibers is performed more effectively by ethyl acetate than by water. The reason is the high affinity of acetic acid to ethyl acetate, and the fact that the cellulose fibers retain less than 50% by mass of the ester compared to water. Therefore, it is assumed that the dilution factor of 2.4, taken in water, can be lowered to 1 in the case of washing with ethyl acetate.

Another important consequence is that the resulting solution is a mixture of ethyl acetate and acetic acid instead of acetic acid diluted with water, which is not only easier to separate through azeotropic distillation, but also less energy consuming compared to the distillation of the mixture of acetic acid with water.

The ethyl acetate remaining in the fibers after washing can be easily removed by steam stripping. This is done on a pilot plant level in a desolventizer (see Figure 4d). The direct stripping of ethyl acetate with saturated steam, on the one hand removes the residual ethyl-acetate from the fibers and on the other conserves the integrity of the fibers, the latter being subjected to moisture. The main equipment used for the modified process is shown in Figure 4.

Mass balance

Maintaining the operation parameters constant, it is seen that the loss of acetic acid and water in the final sugar solution and dried lignin is lower in the modified process compared to that of the conventional process. It helps not only to reduce the acetic acid loss in the final sugar solution, but also to reduce the use of ethyl acetate as entrainer in the distillation column to separate the solvents. This, evidently, has a positive impact on the process economy.

Energy analysis

There is a direct relation between the solid to liquid ratio fed into the process and the overall process energy requirement. The energy required by both processes is mainly supplied by thermal energy. The energy requirement for the conventional process amounts to 153.803 MJ/ton of dry biomass, while it descends to 16.593 MJ/ton of dry biomass in the proposed continuous process. The energy demands calculated are in close agreementwith those calculated for similar organosolv process.[10]The energy consumption in each section has been summarized in Table 1.

Table 1
Energy consumption of the main subsystems in the Acetosolv Process

Section	Subsystems	Energy requirements (MJ/kg)	
		Conventional process	Continuous process
1	Digester	2.288	932
	Evaporator 1	1.230	456
2	Dryer	0	274
	Evaporator 2	4.299	1. 025
	Washer + stripping	0	203
	Azeotropic distillation	145.987	13.703
Total		153.804	16.593

CONCLUSION

- Processing of annual plants is convenient in a continuous delignification reactor, to decrease the required volume of the solvent and, therefore, the energy requirement during the evaporation of liquor.
- The energy requirement of the distillation column decreases dramatically when the separation of lignin and hemicelluloses is done by washing out the carbohydrates of dried liquor.
- Washing of acetic fibers by ethyl acetate is much more effective than by water: it reduces the dilution factor during washing and diminishes the energy requirement for the separation of the components, due to the replacement of water by ethyl acetate in the feed of distillation column.
- The modified process being proposed allows decreasing the energy requirements from 153.803MJ to 16.593 MJ per kg of dry biomass processed (only the main energy consumption and no energy integration are considered).

ACKNOWLEDGEMENTS: The authors acknowledge the funding obtained from CONICYT, through the projects FONDEF IDEA IT 13I10060 and PROGRAMA DE FINANCIAMIENTO BASAL PFB-27.

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