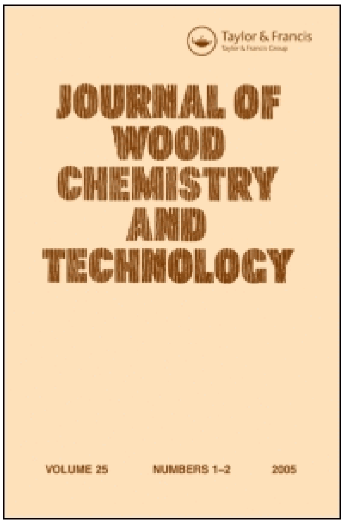

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SIMULATION OF ACETOSOLV PULPING OF *Eucalyptus* WOOD

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ABSTRACT

Experiments on the Acetosolv pulping of *Eucalyptus globulus* wood have been carried out under a variety of operational conditions. Catalyst (HCl) concentration, liquor/solid ratio, temperature and reaction time have been considered as operational variables. Mathematical models have been developed to describe the dependence of both the composition of pulps (measured by their contents in cellulose, hemicelluloses and lignin) and the concentration of hemicellulose-decomposition products (monosaccharides and furfural) in pulping liquors. The pulp yields were calculated on the basis of the pulp composition. The overall mathematical simulation of the Acetosolv pulping was achieved with a limited set of regression coefficients. The validity of the models was confirmed by comparison of experimental and calculated data.

INTRODUCTION

The Acetosolv process, based on the utilization of concentrated acetic acid for wood delignification,[1] shows interesting properties as an alternative to conventional pulping technologies. Acetosolv pulping can reach extensive delignification at good pulp yield with excellent selectivity towards cellulose degradation. In this kind of operation, hemicelluloses can be almost completely removed, whereas the sulphur-free lignin fragments can be insolubilized by water addition. On the other hand, some process byproducts (such as acetic acid from acetyl group cleavage and furfural from pentose decomposition) have commercial value and may complement the overall economic balance.

Both uncatalyzed and catalyzed acetic acid-based media have been assayed for wood processing. Uncatalyzed media have been employed for processing hardwoods,[2] whereas HCl-catalyzed media have been used for delignification of both hardwoods and softwoods.[1, 3-8] HCl-catalyzed media allow selective delignification at temperatures near the normal boiling point of solutions.

Previous work of our research group resulted in a preliminary engineering analysis of the Acetosolv process,[7] as well as in the kinetic modeling of the hemicellulose behavior.[8] Based on these findings, this work deals with an improved simulation of *Eucalyptus globulus* wood fractionation in HCl-catalyzed acetic acid media. Experimental data were obtained under a wide range of operational conditions and used for modeling the following phenomena: i) polysaccharide (including cellulose and hemicelluloses) degradation, ii) lignin removal and repolymerization, and iii) byproduct generation from polysaccharides. Pulp yield was calculated from the contribution of the various wood fractions. The overall calculation procedure involved less regression parameters than previous studies[7] and was succesfully applied to a wider range of operational conditions, including assays at various liquor/solid ratios. An exhaustive comparison of experimental and calculated data proved the ability of the calculation scheme proposed for providing a reliable interpretation of results.

RESULTS AND DISCUSSION

Acetosolv Processing of Wood

Based on previous studies on the Acetosolv pulping of *Eucalyptus*,[4] the

TABLE 1
Operational Conditions Used in the Chemical Processing of Wood

Variable	Nomenclature	Units	Variation range
Temperature	T	°C	110-130
Liquor/solid ratio	LSR	g/g	7-10
Catalyst conc.	CaCo	g HCl/100 g liquors	0.2-0.4
Reaction time	t	min	0-100

concentration of acetic acid in pulping liquors was fixed in 95 weight percent, and HCl was chosen as a catalyst. The operational variables and their variation ranges are shown in Table 1.

Table 2 shows the operational conditions considered, which were selected by combination of the values of variables shown in Table 1. The set of experiments 1-16 of Table 2 has a centered, factorial structure with minimum dead volume.[9] Replications in the central point of the design were included to allow an evaluation of the reproducibility of experimental data.

In each experiment, operation was stopped at the beginning of the isothermal period (that was considered time zero) or at selected reaction times (10, 20, 20, 45, 60, 75 or 100 min), and the experimental values of the following variables were determined:

a) Variables measuring the composition of pulps. The variables considered, their nomenclature and units are as follows: hemicellulose content of pulps (HC, expressed as g hemicelluloses/100 g pulp, oven-dry basis); cellulose content of pulps (CC, expressed as g cellulose/100 g pulp, oven-dry basis); Klason lignin content of pulps (LC, expressed as g lignin/100 g pulp, oven-dry basis).

b) Variables measuring the composition of liquors. The variables considered, their nomenclature and units are as follows: hemicellulose-derived sugar concentration in liquors (HSC, expressed as g sugars/kg liquor); furfural concentration in liquors (FC, expressed as g furfural/kg liquor).

TABLE 2
Operational Conditions Used in Experiments

Experiment.	Temperature, T (°C)	Liquor/Solid Ratio, LSR (g/g)	HCl conc., CaCo (%)
1	110	7	0.3
2	110	8.5	0.2
3	110	8.5	0.4
4	110	10	0.3
5	120	7	0.2
6	120	7	0.4
7	120	8.5	0.3
8	120	8.5	0.3
9	120	8.5	0.3
10	120	10	0.2
11	120	10	0.4
12	130	7	0.3
13	130	8.5	0.2
14	130	8.5	0.4
15	130	10	0.3
16	120	10	0.3

c) Pulp yield (variable PY), measured as the weight percent of the solid residue respect to the untreated wood, oven-dry basis.

The next sections describe the fundamentals of the mathematical modeling of Acetosolv pulping.

Hemicellulose Decomposition

The kinetic modeling of hemicellulose decomposition during the acetolysis of *Eucalyptus* wood was considered in a previous work of our research group,[8] and it was based on the following hypotheses:

a) The hemicellulose fraction of *Eucalyptus* is made up of two different fractions with different susceptibility toward hydrolysis. A similar idea was previously used for modeling the hydrolysis of hemicelluloses in acid-catalyzed, aqueous media.[10-14]

b) The contribution of the "non susceptible" fraction of hemicelluloses to the hydrolysis process is negligible.

c) A parasitic pathway leading to hemicellulose consumption with formation of unknown, non-sugar compounds exists. This idea was formerly used by Mok et al.[15] in their study on the dilute acid-catalyzed hydrolysis of cellulose.

d) Sugars are generated from hemicelluloses, and then degraded to furfural. It can be noted that the main hemicellulosic sugar in *Eucalyptus* wood is xylose, whereas arabinose appears in limited proportion.[13] Both xylose and arabinose are pentoses able to give furfural upon dehydration.

e) Furfural was also directly generated from the end sugar units of hemicellulose chains.

f) Furfural-consuming reactions give condensation products (CP).

g) All the reactions are of pseudohomogeneous, first-order kinetics.

These assumptions are summarized in the mechanism shown in Figure 1 considering the direct conversion of susceptible hemicelluloses into furfural (dashed line).

In this work, we have considered a wider range of operational conditions in experimentation. The liquor/solid ratio was included as a new operational variable. In a first approach, we applied the above ideas to the new working conditions, but the mechanism shown in Figure 1 with a dashed line was unable to accurately predict the time course of the concentrations of all the fractions. For example, the concentrations of hemicelluloses, hemicellulosic sugars and an overall term including the sum of the concentrations of non-valuable byproducts (NSC and CP) were correctly predicted in all cases, but then the furfural concentrations were overestimated in the first part of the reaction and underestimated at prolonged reaction times. Based on these findings, and considering the sigmoidal shape of the experimental curves describing the time course of the furfural concentration, we studied a modified mechanism, in which the generation of furfural from

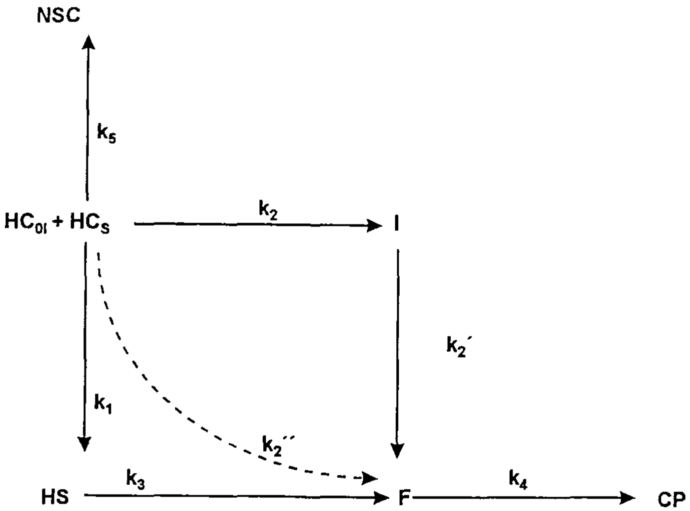

FIGURE 1. Mechanisms for hemicellulose degradation. a) Mechanism with direct generation of F from HC_S (dashed line) proposed in a previous study[8]. b) Mechanism studied in this work, with generation of F from the intermediate I (solid line)

Nomenclature: HC_{0I}=non-susceptible fraction of hemicelluloses; HC_S= fraction of hemicelluloses susceptible to be degraded; NSC= non-sugar compounds; HS=hemicellulosic sugars; I= reaction intermediate; F=furfural; CP=condensation products; $k_1 \ldots k_5$= pseudo-first order kinetic coefficients

hemicelluloses was assumed to proceed through the generation and consumption of a reaction intermediate (I). This assumption required a new kinetic coefficient (k_2') and led to the mechanism shown in Figure 1 with a solid line, which provided a good interpretation of results (see below).

Cellulose Behaviour

Cellulose showed little variation during all the experiments performed, confirming the high selectivity of the Acetosolv process. A single, pseudohomogenoeus, first order reaction of cellulose to glucose, according to the reaction:

$$\text{Cellulose} \xrightarrow{k_6} \text{Glucose}$$

gave an adequate interpretation of results.

Lignin Degradation

A qualitative analysis of the experimental data showed that the time course of the lignin content of samples was closely related to that observed for other Kraft and Organosolv processes.[3,5,16,17] The increased lignin content of samples observed in assays performed under harsh conditions proved the existence of recondensation reactions. These experimental trends were interpreted on the basis of a mechanism involving two-sequential reactions (degradation/repolymerization), both of them being of pseudofirst order. The reaction scheme is as follows:

$$L_N \xrightarrow{k_7} L_S \xrightarrow{k_8} L_R$$

where:

L_N= native lignin, L_S=solubilized lignin and L_R=repolymerized lignin.

Pulp Yield

The Acetosolv treatments of the raw material caused a variety of effects, the major ones being delignification and polysaccharide degradation. On the other hand, lignin repolymerization reactions took place under harsh conditions, increasing the overall weight of the solid phase. Finally, other fractions such as acetyl groups, extractives, acid-soluble lignin, oligomers derived from hemicelluloses, etc. also contribute to the overall pulp yield. In a previous work,[7] the modeling of pulp yield was carried out on the basis of a pseudo-first order reaction involving two regression parameters. In this case, the availability of detailed models describing the time course of the main fractions involved in fractionation allowed a direct calculation of pulp yield without introducing new regression coefficients (see below).

Mathematical Simulation of the Overall Process

In order to allow an easier calculation procedure, the variables measuring the pulp composition (HC, CC and LC) were used to obtain a new set of parameters (denoted HCE, CCE and LCE) that are expressed in different units (g/kg liquor). HCE and CCE have been defined as "sugar equivalents" by introducing the corresponding hydration factors. The interrelationships between these two sets of variables are given by the following equations:

$$HCE=[(HC.PY/10)/(LSR+1-PY/100)].(150/132) \qquad [1]$$

$$CCE=[(CC.PY/10)/(LSR+1-PY/100)].(180/162) \qquad [2]$$

$$LCE=(LC.PY/10)/(LSR+1-PY/100) \qquad [3]$$

In the same way, a similar variable (FCE) was defined to measure the furfural concentration as a "sugar equivalent",

$$FCE=FC.(150/96) \qquad [4]$$

The initial values of variables HCE, CCE, LCE, HSC and FCE (denoted HCE_0, CCE_0, LCE_0, HSC_0 and FCE_0, respectively) were directly calculated from the experimental data. For calculation purposes, the concentration of the intermediate I expressed as a sugar equivalent was denoted ICE. It can be noted that the zero time was taken at the beginning of the isothermal stage of the reaction, and that the substrate may have reacted in some extent at this moment.

An additional variable (the "susceptible fraction of hemicelluloses", denoted α) was employed in the kinetic modeling. This parameter is defined as:

$$\alpha = HCE_{S0}/HCE_0 \qquad [5]$$

where HCE_{S0} and HCE_0 are the initial contents of raw wood in "susceptible hemicelluloses" and total hemicelluloses, respectively. It can be followed that the insoluble hemicellulose fraction HC_{0I} can be calculated as

$$HCE_{0I} = HCE_0.(1-\alpha) \qquad [6]$$

and

$$HCE = HCE_{0I} + HCE_S \qquad [7]$$

According to the mechanism shown in Figure 1, the differential equations describing the time course of the above variables are:

$$-d(HCE_S)/dt = (k_1+k_2+k_5).HCE_S \qquad [8]$$

$$d(HSC)/dt = k_1.HCE_S - k_3.HSC \qquad [9]$$

$$d(ICE)/dt = k_2.HCE_S - k_2'.ICE \qquad [10]$$

$$d(FCE)/dt = k_2'.ICE + k_3.HSC - k_4.FCE \qquad [11]$$

The total hemicellulose content can be calculated as the sum of the contributions of the susceptible and non-susceptible fraction:

$$HCE = HCE_s + HCE_0.(1-\alpha) \qquad [12]$$

On the other hand, the joint contribution of the terms NSC, CP and I to the overall balance in terms of sugar equivalents as g/kg liquor (variables denoted NSCE, CPE and ICE) can be directly calculated from the following conservation equation:

$$NSCE + CPE + ICE = HCE_0 - HCE - HSC - FCE \qquad [13]$$

The time depedence of the variables involved in equations 8 to 11 has been calculated by numerical solving of differential equations using a 4th order Runge-Kutta method. In a first run of calculations, both the values of the "susceptible fraction" α and those of the kinetic coefficients corresponding to the various experiments were calculated using an optimization algorithm similar to that described elsewhere.[8] Equation 13 allowed the calculation of (NSCE + CPE + ICE), which measures the fraction of initial hemicelluloses converted into compounds different from polysaccharides, pentoses or furfural. It can be noted that the right hand of the equation can be directly calculated from the experimental data for each reaction time in each assay, and that the left hand of equation 13 can be evaluated when the respective kinetic coefficients are known. In this part of the calculations, a narrow variation range was observed for the parameter α (0.74-0.84), with an average value (0.792) that provided a fair interpretation of results under all the conditions examined. Because of that, α was fixed in its average value and a new calculation procedure was made for recalculating the kinetic coefficients involved in hemicellulose-decomposition reactions (see Figure 1).

The cellulose content of samples CC was directly calculated assuming an exponential decrease:

$$CCE=CCE_0.\exp(-k_6.t) \qquad [14]$$

where CCE_0 is the initial value of CCE.

The Klason lignin content of pulp accounted for both the "native lignin" remaining in wood and the "repolymerized" lignin. Taking into account that the time course of the soluble lignin (expressed in terms of LCE_S) follows the expression:

$$d(LCE_S)/dt = k_7.LCE_N - k_8.LCE_S \qquad [15]$$

(where LCE_N refers to native lignin), it can be inferred that the sum of non-solubilized and repolymerized lignin (LCE) follows the expression:

$$LCE = LCE_0.\{1\text{-}k_7.[(\exp(-k_7.t)-\exp(-k_8.t)]/(k_8-k_7)\} \qquad [16]$$

where LCE_0 can be calculated from the experimental data.

As a first approach, the pulp yield can be calculated on the basis of the contributions of: a) non-degraded cellulose, b) residual hemicelluloses and c) overall lignin content (including both residual native lignin and repolymerized lignin). Pulp yield should also include several fractions that have been not measured systematically, such as acetyl groups, pulp extractives, acid-soluble lignin, oligomers derived from polysaccharides, ashes, etc. The joint contribution of all these factors has been assumed to be a constant proportion of the pulp weight (denoted contribution of other fractions, COF, g/g treated pulp) (see below). According to these ideas, the overall pulp yield can be calculated using the following equation:

$$PY=100.[CCE.(LSR+1-PY/100).(162/180).(1/1000) + HCE.(LSR+1-PY/100).$$
$$(132/150).(1/1000)+LCE.(LSR+1-PY/100).(1/1000)+COF.PY/100] \qquad [17]$$

Validation of the Mathematical Simulation

Table 3 shows the results obtained for the regression coefficients included in the kinetic equations. An overall comparison between calculated and experimental pulp yields showed that COF=0.10 g/g treated pulp provided a fair interpretation of results of all the assays. In order to provide a qualitative confirmation of the contribution of term involving the parameter COF to the pulp yield, additional experimentation was done using 5 pulps from selected experiments (data not shown). The additional determinations carried out and the variation ranges obtained were: ethanol extractives of samples (0.02-0.05 g/g pulp), acid-soluble lignin (0.007-0.014 g/g pulp) and acetyl group content (0.04-0.07 g/g pulp, which were measured as a function of the acetic acid concentration in the liquors from the quantitative acid hydrolysis of ethanol-extracted pulps). It can be noted

TABLE 3
Regression Parameters Obtained in Calculations for α=0.792
(k_1 to k_8 in min^{-1})

Exper.	k_1	k_2	k_2'	k_3	k_4	k_5	k_6	k_7	k_8
1	0.0035	0.0082	0.0555	0.0003	0.0000	0.0332	0.0015	0.0453	0.0041
2	0.0032	0.0127	0.0661	0.0006	0.0038	0.0255	0.0008	0.0388	0.0031
3	0.0042	0.0255	0.0125	0.0045	0.0180	0.0092	0.0012	0.0421	0.0037
4	0.0050	0.0124	0.1174	0.0006	0.0000	0.0331	0.0009	0.0477	0.0031
5	0.0032	0.0098	0.0666	0.0008	0.0007	0.0346	0.0012	0.0341	0.0042
6	0.0122	0.0322	0.5606	0.0060	0.0030	0.0870	0.0007	0.0594	0.0064
7	0.0099	0.0228	0.2813	0.0098	0.0052	0.0541	0.0005	0.0655	0.0058
8	0.0093	0.0236	0.2607	0.0079	0.0043	0.0552	0.0009	0.0609	0.0052
9	0.0093	0.0234	0.1975	0.0077	0.0043	0.0530	0.0005	0.0630	0.0058
10	0.0058	0.0109	0.2297	0.0073	0.0000	0.0394	0.0015	0.0470	0.0054
11	0.0053	0.0199	0.5474	0.0079	0.0072	0.0297	0.0009	0.0621	0.0063
12	0.0044	0.0183	0.4772	0.0005	0.0008	0.0438	0.0017	0.0760	0.0058
13	0.0088	0.0243	0.6160	0.0018	0.0001	0.0519	0.0024	0.0723	0.0049
14	0.0097	0.0497	0.6295	0.0028	0.0048	0.0688	0.0022	0.1070	0.0078
15	0.0111	0.0577	0.0971	0.0054	0.0073	0.0600	0.0026	0.1307	0.0079
16	0.0122	0.0760	0.0444	0.0032	0.0098	0.0373	0.0014	0.0688	0.0055

that the sum of these contributions to the pulp yield agreed fairly with the value 0.10 g/g selected for COF.

The set of regression parameters listed in Table 3 and the fixed value of COF selected above allowed the mathematical simulation of the whole set of variables measuring the pulping process. Figures 2 to 5 show the experimental and predicted time courses of selected operational variables for four representative assays. In order to check exhaustively the validity of the calculation framework, the following dimensionless variables measuring the main effects caused by the Acetosolv processing of wood were defined: percent of hemicellulose removal (PHR), percent of cellulose recovery (PCR), percent of lignin removal (PLR), percent of hemicellulose conversion to sugars (PHCS) and percent of hemicellulose conversion to furfural (PHCF). The interrelationships of the new variables with the previous ones are:

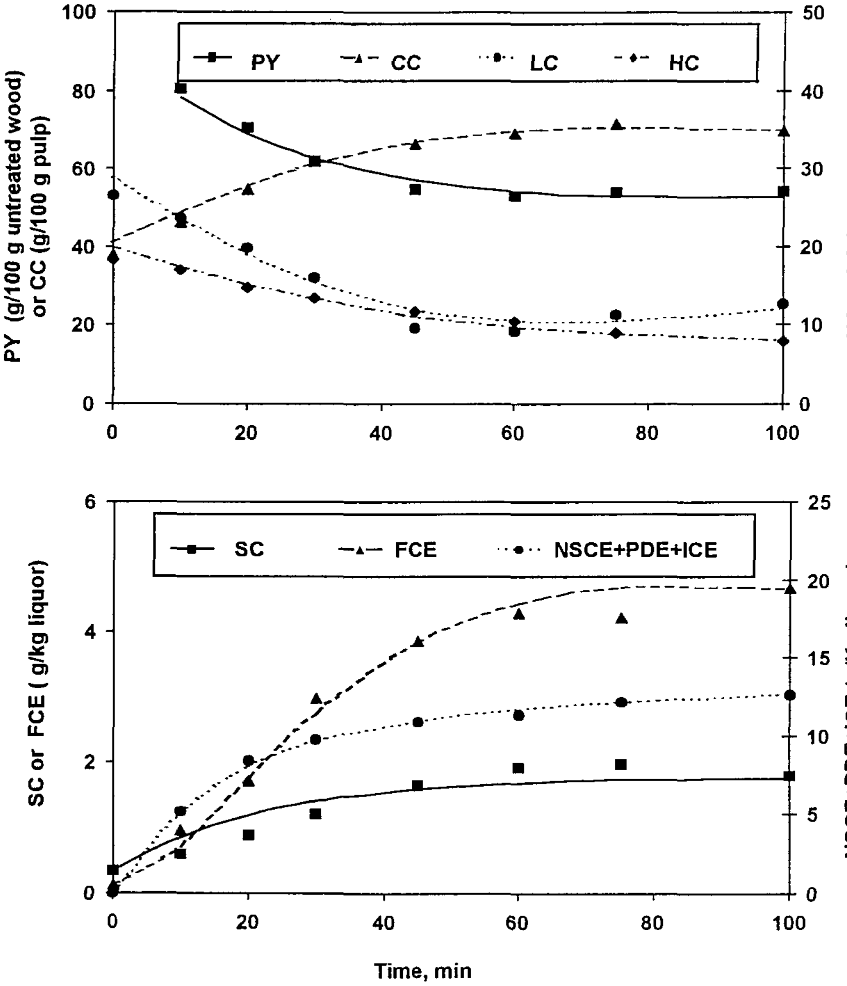

FIGURE 2. Time course of experimental and predicted values of pulp yield (PY, percent of untreated wood), cellulose content of pulps (CC, %), lignin content of pulps (LC, %), hemicellulose content of pulps (HC, %), sugar concentration (SC), equivalent furfural concentration (FCE) and equivalent concentration of other hemicellulose-derived fractions (NSCE+PDE+ICE) corresponding to Experiment 2 of Table 2. Nomenclature: NSCE, PDE and ICE: equivalent xylose concentrations of non-sugar compounds, decomposition products and intermediate I.

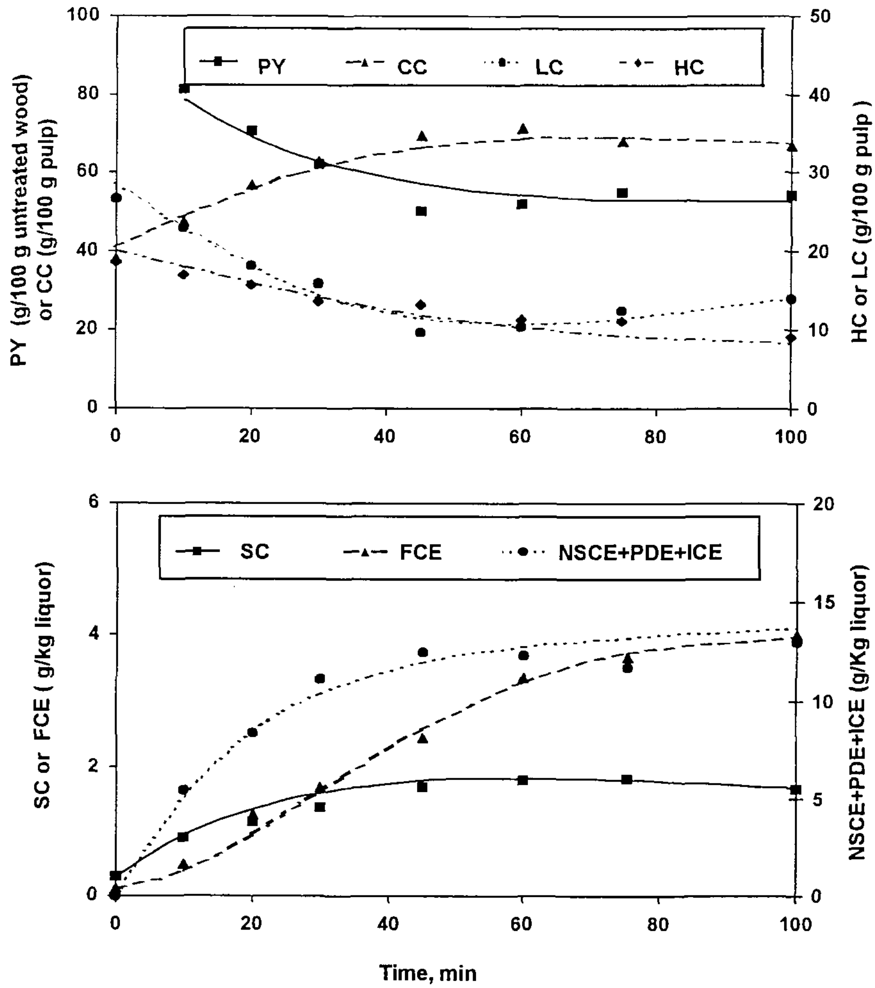

FIGURE 3. Time course of experimental and predicted values of pulp yield (PY, percent of untreated wood), cellulose content of pulps (CC, %), lignin content of pulps (LC, %), hemicellulose content of pulps (HC, %), sugar concentration (SC), equivalent furfural concentration (FCE) and equivalent concentration of other hemicellulose-derived fractions (NSCE+PDE+ICE) corresponding to Experiment 3 of Table 2. Nomenclature: NSCE, PDE and ICE: equivalent xylose concentrations of non-sugar compounds, decomposition products and intermediate I.

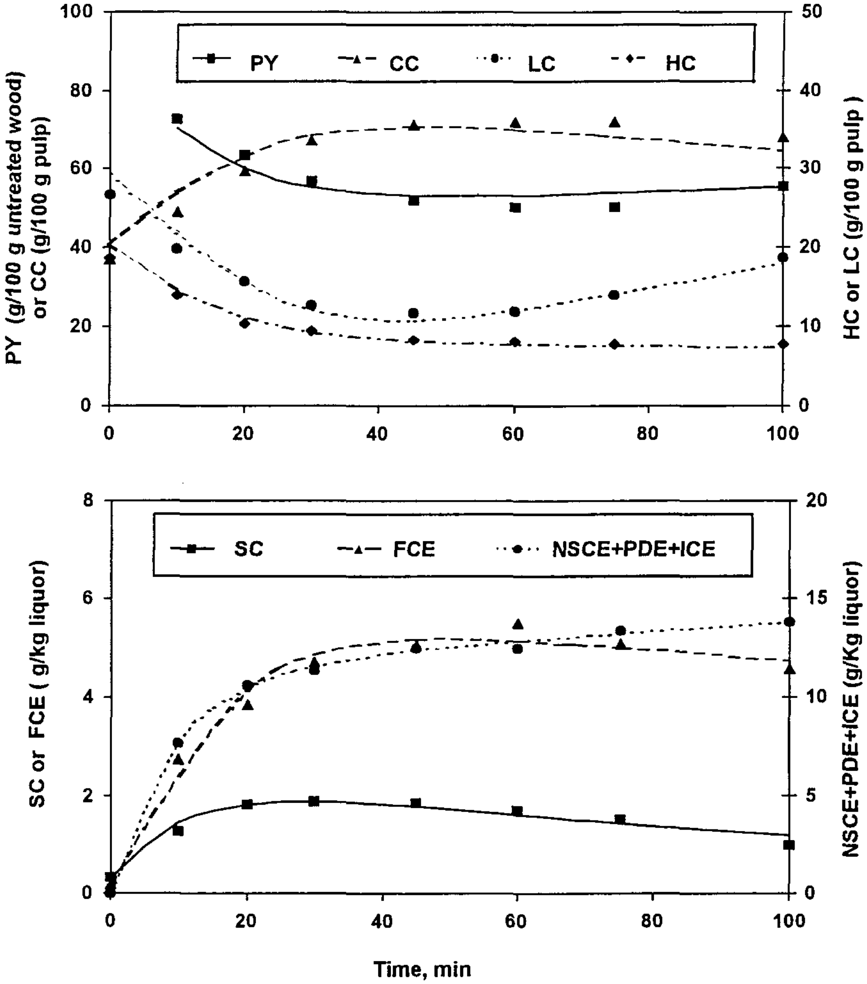

FIGURE 4. Time course of experimental and predicted values of pulp yield (PY, percent of untreated wood), cellulose content of pulps (CC, %), lignin content of pulps (LC, %), hemicellulose content of pulps (HC, %), sugar concentration (SC), equivalent furfural concentration (FCE) and equivalent concentration of other hemicellulose-derived fractions (NSCE+PDE+ICE) corresponding to Experiment 8 of Table 2. Nomenclature: NSCE, PDE and ICE: equivalent xylose concentrations of non-sugar compounds, decomposition products and intermediate I.

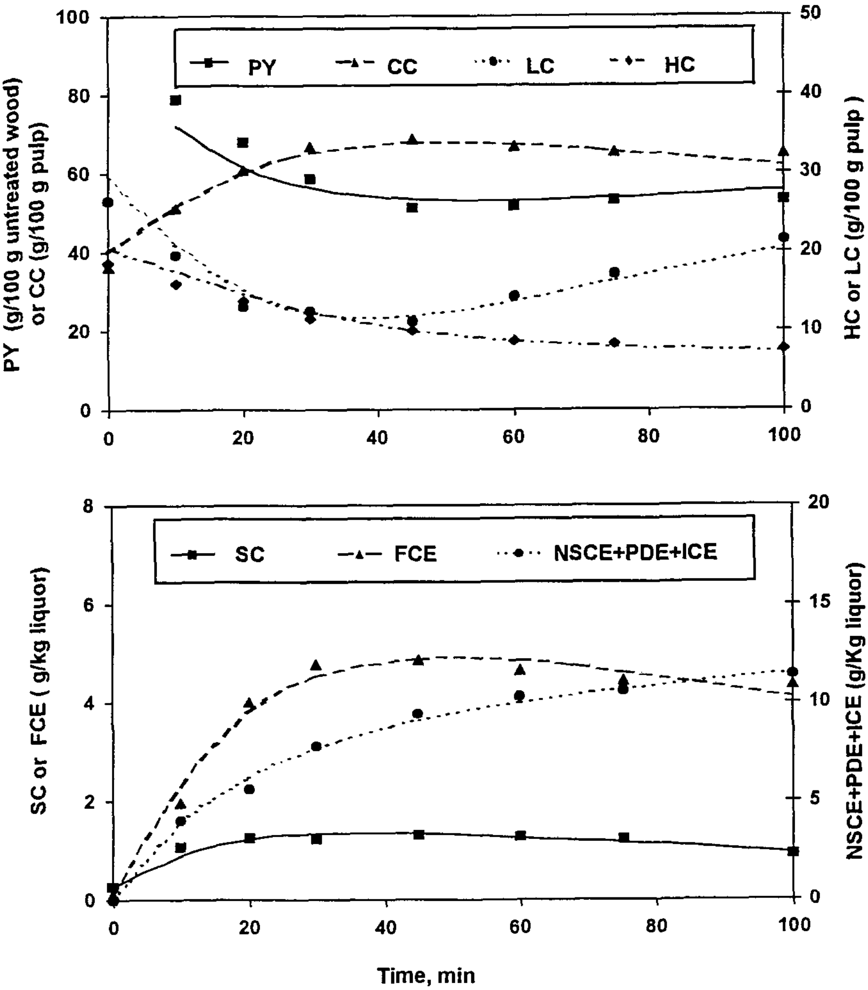

FIGURE 5. Time course of experimental and predicted values of pulp yield (PY, percent of untreated wood), cellulose content of pulps (CC, %), lignin content of pulps (LC, %), hemicellulose content of pulps (HC, %), sugar concentration (SC), equivalent furfural concentration (FCE) and equivalent concentration of other hemicellulose-derived fractions (NSCE+PDE+ICE) corresponding to Experiment 11 of Table 2. Nomenclature: NSCE, PDE and ICE: equivalent xylose concentrations of non-sugar compounds, decomposition products and intermediate I.

$$PHR=100.(1-HCE/HCE_0) \qquad [18]$$

$$PCR=100.(CCE/CCE_0) \qquad [19]$$

$$PLR=100.(1-LCE/LCE_0) \qquad [20]$$

$$PHCS=100.(HSC/HCE_0) \qquad [21]$$

$$PHCF=100.(FCE/HCE_0) \qquad [22]$$

Figures 6 and 7 show the agreement between experimental and predicted values of these dimensionless variables, as well as the same comparison for pulp yield (calculated from equation 17). The excellent agreement between experimental and calculated results confirms the validity of the mathematical simulation proposed.

CONCLUSION

A sound understanting of the kinetics of organosolv pulping processes is a key factor affecting their future development at an industrial scale. In this field, a novel mechanism for the Acetosolv pulping of *Eucalyptus* wood is proposed and validated. A set of consecutive and parallel reactions, which were assumed to be of pseudohomogeneous, first order, allowed the deduction of equations describing the time course of pulp composition and composition of pulping liquors. Based on material balances, a procedure for the calculation of pulp yield is proposed. Nonlinear regression was used to calculate the set of regression parameters from experimental data. These results provide the basic information needed for an evaluation of the Acetosolv process in economic terms.

EXPERIMENTAL

Raw Material

Eucalyptus globulus wood samples from a local factory were milled,

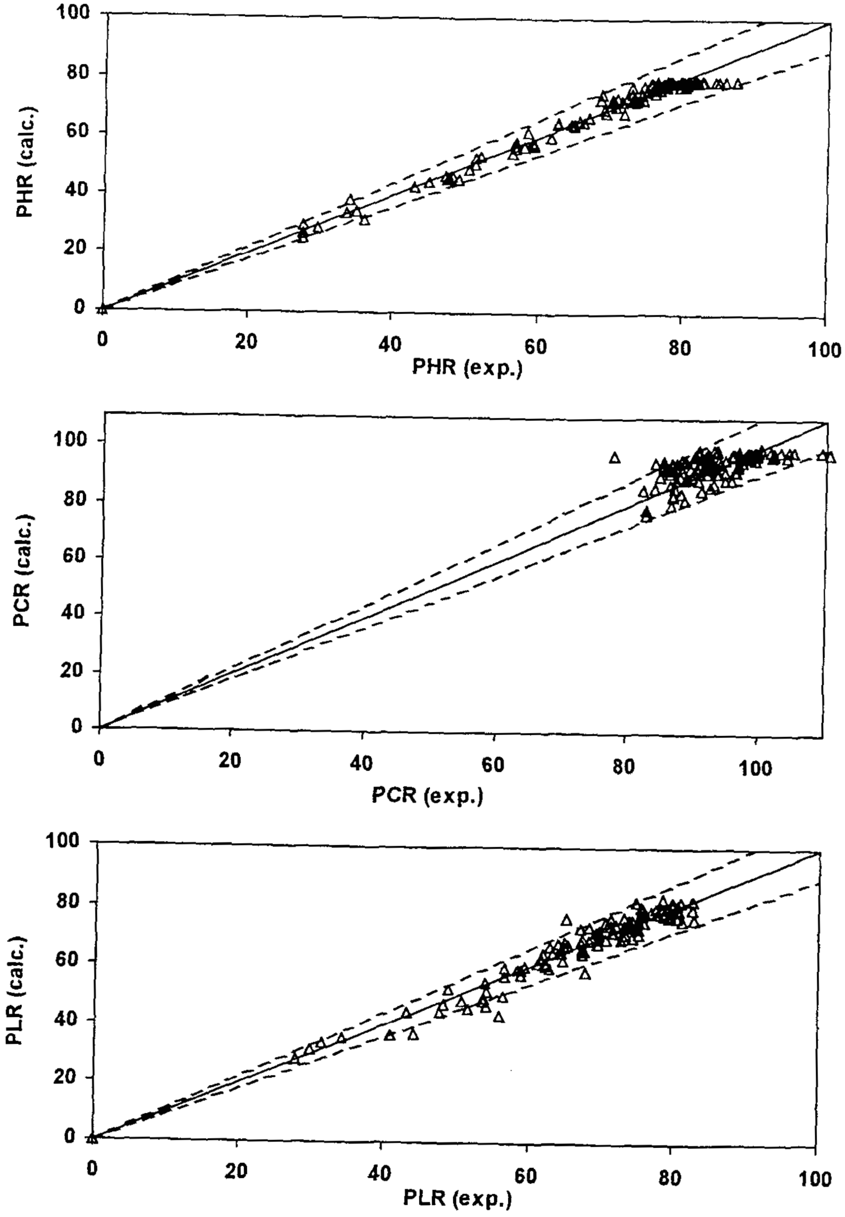

FIGURE 6. Comparison of experimental and calculated data of variables PHR (percent of hemicellulose removal), PCR (percent of cellulose recovery) and PLR (percent of lignin removal) in experiments 1-16 of Table 2. Solid line: experimental=calculated; dashed lines= 10% deviation

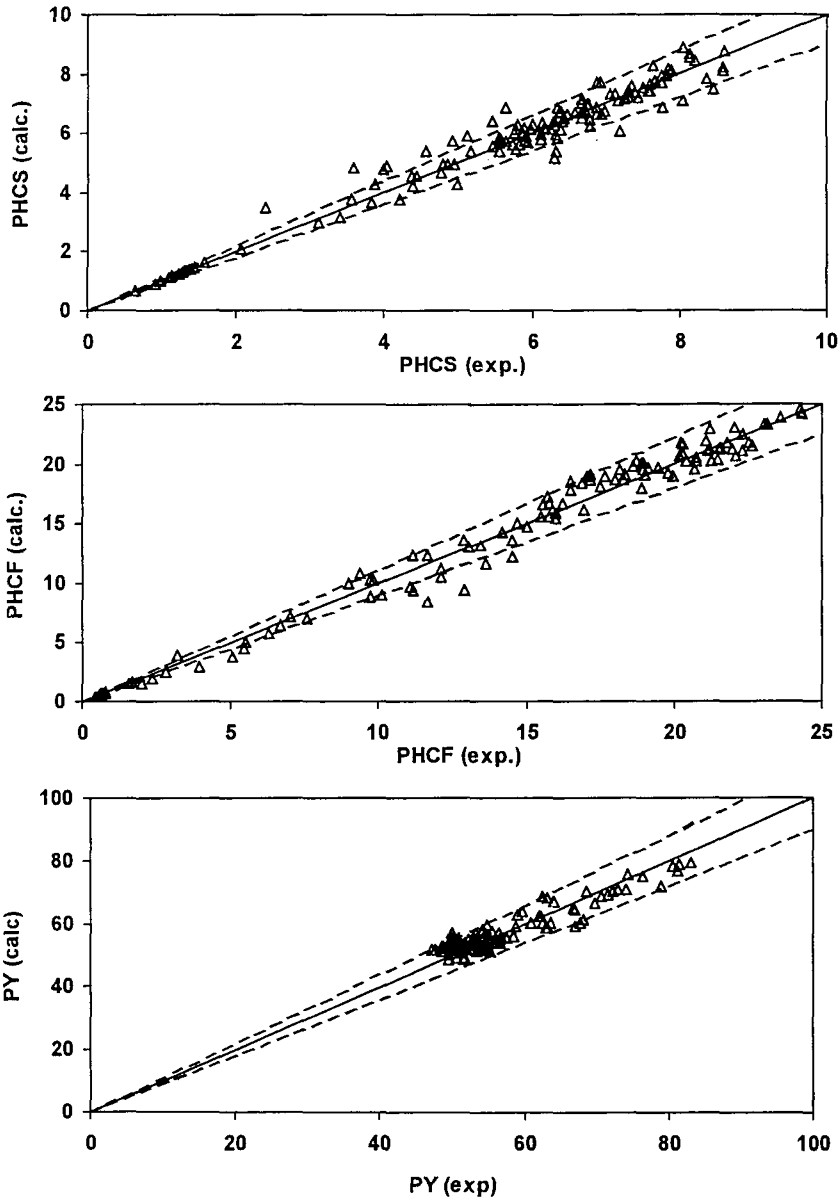

FIGURE 7. Comparison of experimental and calculated data of variables PHCS (percent of hemicellulose converted to sugars), PHCF (percent of hemicellulose converted to furfural) and PY (pulp yield, g/100 w wood) in experiments 1-16 of Table 2. Solid line: experimental=calculated; dashed lines: 10% deviation.

screened to select the fraction of particles with a size between 0.25 and 1 mm, air-dried, homogenized in a single lot to avoid differences in composition, and stored.

Analysis of Wood

Aliquots from the homogenized wood lot were subjected to moisture determination and to quantitative acid hydrolysis with 72% sulfuric acid following standard methods.[18] The solid residue after hydrolysis was considered as Klason lignin. The monosaccharides and acetic acid contained in hydrolyzates were determined by spectrophotometry or by the HPLC method with RI detection used in previous studies.[7] HPLC analysis with UV detection (280 nm) was employed for furfural determination in same assays carried out for sugars.

Pulping of Wood Samples

Wood chips, acetic acid, concentrated HCl solutions and water were adjusted to the desired liquor/wood ratio. The moisture of wood was considered as water in the material balances. The pulping stage was performed as described elsewhere.[7] At the end of treatments, the solid residues were recovered by filtration, washed with acetic acid and acetone, air-dried and subjected to quantitative saccharification. The acid-insoluble residue was considered as lignin. Aliquots from the pulping liquors were taken before filtration, mixed with water (1:10), and centrifuged to separate the lignin fraction as a precipitate. Aliquots from supernatants were filtered through 0.45 μm membranes and analyzed by HPLC for monosaccharides and furfural.[8]

Ethanol Extractives

Extractives in pulp were determined by Soxhlet extraction according to Browning.[18]

Soluble Lignin

Soluble lignin was spectrophotometrically determined as *per* Maekawa.[19]

Fitting of Data

The experimental data were fitted to the proposed equations using commercial software with a built-in Newton's optimization routine.

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