PULPING OF ASPEN WOOD IN ACETIC ACID MEDIA: EFFECT OF OPERATING CONDITIONS ON YIELD AND PULP PROPERTIES

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ABSTRACT

Populus tremula* tremuloides *wood samples were processed in acetic acid–water–HCl media. The effects of selected operating variables on pulp yield and pulp composition were assessed using empirical models valid for optimization. Under the best conditions analyzed, a pulp containing 1.5% lignin, 81.8% cellulose, and 6.2% xylan was obtained at 49% pulp yield. The selected pulp showed good SCAN viscosity (796 mL/g) and reduced kappa number (5). The values of the parameters measuring the alkali resistance (R-10 = 79.2%, R-18 = 86.5%) were affected by the acetyl group content of the samples.*

APPLICATION STATEMENT

This work provides information allowing the technical evaluation of acetic acid-based pulping. The experimental protocols, the design of experiments, and the methodology used for data analysis allowed a complete description of the overall pulping, particularly in terms of pulp yield, pulp quality, and by-product generation. This information is of primary importance for the simulation and evaluation of the studied process.

INTRODUCTION

As an alternative to the kraft process, a variety of organosolv-based technologies have been considered in the literature. In this field, catalyzed or uncatalyzed acetic acid media have been successfully applied for pulping both hardwoods and softwoods *(1, 2, 3, 4, 5, 6)*.

Pulping in HCl-catalyzed acetic acid media can achieve extensive delignification under mild operating conditions. Simultaneously, hemicelluloses are degraded to sugars, furfural, and condensation products *(7)*. The phenolic fraction can be separated from the liquors by concentration and water addition *(1)*, leading to a "fractionation" of the lignocellulosic raw materials into separate streams.

This work deals with the optimization of aspen wood pulping in HCl-catalyzed acetic acid media. In two sets of experiments (performed at different temperatures), the effects of selected

operating variables (reaction time, catalyst concentration, and liquor-to-wood ratio) on both pulp yield and chemical composition of pulps were assessed by means of incomplete, second-order, centered, factorial designs. The experimental results allowed the selection of the best operating conditions. Based on these results, the effects caused by a new operating variable (acetic acid concentration of the pulping media) were assessed. Finally, the best pulps were analyzed for further characterization (including acetyl group content, SCAN viscosity, kappa number, and alkali resistance), measuring their potential for use as feedstocks in the production of dissolving pulp.

EXPERIMENTAL

Raw material

Chips of *Populus tremula* tremuloides* wood were kindly provided by the Federal Research Centre of Forestry and Forest Products, Institute of Wood Chemistry and Chemical Technology of Wood, Hamburg, Germany. The chips were passed through a two-roll mill fitted with a 2-mm screen and homogenized in a single lot to avoid compositional differences among aliquots. Screened chips were stored for use in the experiments.

Pulping

Pulping experiments were carried out under a variety of operating conditions in glass reactors with temperature control or in autoclave (see Tables I and II). Pulps from experiments 1–32 (see Table II) were sequentially washed with cold 90% acetic acid and water and then Soxhlet-extracted with ethanol. The pulps obtained in experiments 33–38 of Table IV were sequentially washed with warm 90% acetic acid and warm water, treated during 30 s at 5000 rpm in an UltraTurrax T-50 defibrator (IKA Labortechnik, Germany), and finally washed with acetone before determination of viscosity and alkali resistance.

Analytical characterization of raw material and pulp

The analyses were performed according to the following procedures: moisture, ISO 638:1978; quantitative acid hydrolysis, TAPPI T 13 m; Klason lignin, by gravimetric determination of the residue from the acid hydrolysis; cellulose (as glucan), by HPLC determination of the glucose contained in hydrolyzates from the acid hydrolysis; xylan and araban, by HPLC determination of the xylose and arabinose contained in hydrolyzates from the acid hydrolysis *(4)*; acetyl groups, by HPLC determination of acetic acid in hydrolyzates from the acid hydrolysis; furfural and sugars in pulping liquors, by direct HPLC determination after dilution with water and centrifugation *(4)*; kappa number, ISO 302:1981; viscosity, SCAN C 15:62; extractives, according to the operating procedure outlined in TAPPI T 13 m; alkali resistance (R-10 and R-18), ISO 699:1982.

RESULTS

Chemical composition of aspen wood

The results obtained for the chemical composition (expressed as weight percent on ovendry basis) are as follows: extractives, 3.22 wt.%; cellulose (as glucan), 47.0 wt.%; xylan, 17.6 wt.%; araban, 0.16 wt.%; acetyl groups, 3.64 wt.%; Klason lignin, 21.4 wt.%.

Experimental design

Table I shows the value fixed for the acetic acid concentration as well as definitions for the three independent variables (reaction time *t*, HCl concentration CC, and liquor/wood ratio LWR) and the seven dependent variables (y_1 through y_7, which measure pulp yield, pulp composition, and composition of liquors) considered in the experiments. The sets of experiments 1–16 or 17–32 of **Table II** involve three independent variables explored at three levels and correspond to incomplete, centered, second order, factorial designs of experiments. This methodology was previously used to model organosolv pulping *(3, 5, 8, 9)*, and it has proved to be a useful tool for this kind of application. For calculation purposes, Table II also lists the operating conditions expressed in terms of the dimensionless, normalized variables (x_1, x_2, and x_3) with variation ranges (–1 to 1) that are linearly related to the corresponding independent variables.

			Value or range	
Variable	**Definition and units**	**Label**	**Normal boiling point**	**Operation at 120 °C**
Fixed	Acetic acid concentration, % weight of liquor	…	90	90
Independent	Reaction time, min	*T*	30–70	10–40
	HCl concentration, % weight of liquor	CC	0.1–0.4	0.1–0.4
	Liquor/wood ratio, g/g o.d. wood	LWR	6–10	6–10
Dependent	Pulp yield, g pulp/100 g o.d. wood	y_1	…	…
	Cellulose content, g cellulose/100 g o.d. pulp	y_2	…	…
	Xylan content, g xylan/100 g o.d. pulp	y_3	…	…
	Lignin content, g lignin/100 g o.d. pulp	y_4	…	…
	Cellulose conversion to glucose in liquors, %	y_5	…	…
	Xylan conversion to xylose in liquors, %	y_6	…	…
	Xylan conversion to furfural in liquors, %	y_7	…	…

Table I. Fixed and operating variables considered in experiments.

DIMENSIONAL INDEPENDENT VARIABLES								DIMENSIONLESS (NORMALIZED) INDEPENDENT VARIABLES			
	Normal boiling point				Operation at 120°C						
Expt. No.	t, min	CC, %	LWR, g/g	Expt. No.	t, min	CC, %	LWR, g/g	Expt. Nos.	x_1	x_2	x_3
1	30	0.1	8	**17**	10	0.1	8	**1 or 17**	–1	–1	0
2	30	0.25	6	**18**	10	0.25	6	**2 or 18**	–1	0	–1
3	30	0.25	10	**19**	10	0.25	10	**3 or 19**	–1	0	1
4	30	0.4	8	**20**	10	0.4	8	**4 or 20**	–1	1	0
5	50	0.1	6	**21**	25	0.1	6	**5 or 21**	0	–1	–1
6	50	0.1	10	**22**	25	0.1	10	**6 or 22**	0	–1	1
7	50	0.25	8	**23**	25	0.25	8	**7 or 23**	0	0	0
8	50	0.25	8	**24**	25	0.25	8	**8 or 24**	0	0	0
9	50	0.25	8	**25**	25	0.25	8	**9 or 25**	0	0	0
10	50	0.4	6	**26**	25	0.4	6	**10 or 26**	0	1	–1
11	50	0.4	10	**27**	25	0.4	10	**11 or 27**	0	1	1
12	70	0.1	8	**28**	40	0.1	8	**12 or 28**	1	–1	0
13	70	0.25	6	**29**	40	0.25	6	**13 or 29**	1	0	–1
14	70	0.25	10	**30**	40	0.25	10	**14 or 30**	1	0	1
15	70	0.4	8	**31**	40	0.4	8	**15 or 31**	1	1	0
16	50	0.4	8	**32**	25	0.4	8	**16 or 32**	0	1	0

Table II. Operating conditions analyzed in experiments 1–32, expressed in terms of the independent variables defined in Table I (reaction time t, HCl concentration CC, and liquor/wood ratio LWR) and in terms of the dimensionless, normalized, independent variables x_1, x_2, and x_3.

On the basis of both the structure of the experimental design and the experimental results obtained for variables y_1 to y_7 in experiments 1–16 or 17–32 (see Table II), empirical models describing the interrelationships among variables were derived. In these models, the dependent variables were evaluated according to the generalized expression:

$$y_j = b_{0j} + \Sigma_i b_{ij} x_i + \Sigma_i \Sigma_k b_{ikj} x_i x_k \qquad (1)$$

where y_j denotes the dependent variable considered; x_i or x_k (i or k: 1 to 3, $k \geq i$) are the dimensionless, independent variables; and $b_{0j} \ldots b_{ikj}$ are the regression coefficients, calculated from the experimental data by multiple regression using the least-squares method.

Pulping at atmospheric pressure (normal boiling point)

Table III shows the regression coefficients obtained for the models describing the behavior of the four main variables involved in pulping (pulp yield y_1, cellulose content of pulps y_2, xylan content of pulps y_3, and Klason lignin content of pulps y_4), as well as their significance and parameters measuring the correlation and statistical significance of the models *(10, 11)*.

Variable	Normal boiling point (Expts. 1–16)				Operation at 120°C (Expts. 17–32)			
	j=1 (y_1, pulp yield)	*j*=2 (y_2, % cellulose)	*j*=3 (y_3, % xylan)	*j*=4 (y_4, % lignin)	*j*=1 (y_1, pulp yield)	*j*=2 (y_2, % cellulose)	*j*=3 (y_3, % xylan)	*j*=4 (y_4, % lignin)
REGRESSION COEFFICIENTS AND SIGNIFICANCE								
b_{0j}	58.2	74.6	8.30	3.35	56.6	75.4	7.02	2.08
b_{1j}	–2.62**	2.24**	–0.84**	–1.67**	–3.38**	3.66**	–1.49**	–1.78**
b_{2j}	–6.11**	5.50**	–1.60**	–3.47**	–6.66**	6.92**	–2.37**	–2.91**
b_{3j}	–2.40**	2.04*	–0.47**	–0.86**	–3.27**	2.20**	–0.35**	–0.33
b_{12j}	0.28	–0.96	–0.03	0.66**	0.86	–0.54	–0.39**	1.61**
b_{13j}	0.17	–0.09	0.07	0.15	0.90	0.47	0.08	0.15
b_{23j}	1.39**	–0.42	0.53**	0.55**	1.53*	–1.48	0.19	1.65**
b_{11j}	1.13**	–0.45	0.23	1.02**	0.78	0.92	0.34**	0.86**
b_{22j}	3.59**	–3.23**	0.50**	1.90**	3.85**	–1.95**	0.86**	2.71**
b_{33j}	0.58	–0.34	0.30	0.47*	0.75	–0.07	0.59**	0.82**
STATISTICAL RESULTS MEASURING CORRELATION (R^2 COEFFICIENT) AND SIGNIFICANCE (FISCHER'S *F* PARAMETER) OF MODELS								
R^2	0.99	0.91	0.98	0.99	0.98	0.97	0.99	0.99
F	77	7	39	118	43	23	175	65
Significance level, %	>99	>98	>99	>99	>99	>99	>99	>99

* Significant coefficients at the 90% confidence level

** Significant coefficients at the 95% confidence level

Table III. Regression coefficients and significance (based on a t-test) and statistical parameters measuring the correlation and significance of models obtained for variables y_1, y_2, y_3, and y_4 in the sets of experiments 1–16 and 17–32.

The empirical model developed for pulp yield (variable y_1) proved that the reaction time (t) and the catalyst (HCl) concentration (CC) were the most influential factors. **Figure 1** shows the

calculated dependence of pulp yield on the selected operating variables (*t* and CC) when the liquor-to-wood ratio was held at 8 g/g. The variation range and the general trends of the experimental results were well interpreted by models (see Table III and Fig. 1). Nearly constant pulp yields were predicted for prolonged reaction times (*t* > 50 min) and high catalyst concentrations (CC > 0.25%).

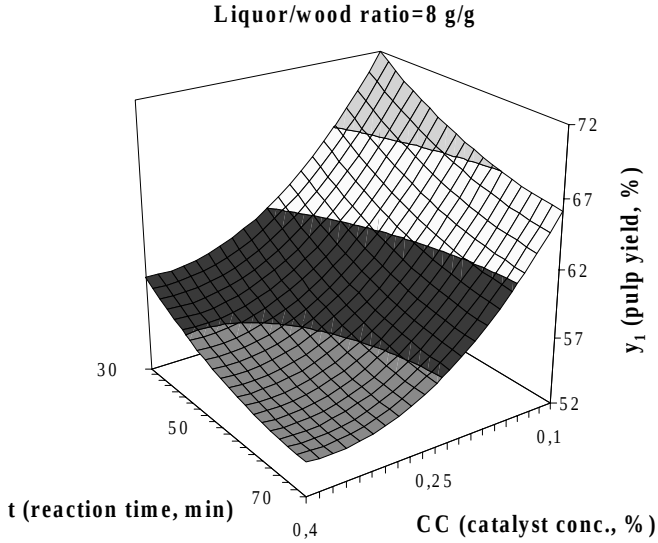


Figure 1. Predicted dependence of pulp yield (y_1) as a function of reaction time (t) and catalyst concentration (CC) for operation at the normal boiling point (LWR = 8 g/g).

Figure 2 shows the calculated dependence of pulp cellulose content (variable y_2) on the most influential independent variables (*t* and CC) when the liquor-to-wood ratio was held at 8 g/g. The highest cellulose contents were predicted for conditions near the highest values assayed for the experimental variables. Little variations in the cellulose content (76–78%) were predicted for conditions near the upper limits assayed for the operating variables. After treatments, 87.6–97.6% of the initial cellulose was retained in pulps.

Figure 3 shows the dependence of pulp xylan content (y_3) on the reaction time and on the catalyst concentration when the liquor-to-wood ratio was held at 8 g/g. During the experiments, 51–79.7% of the initial xylan was removed. The minimum xylan content (6.6%) was reached under the severest experimental conditions (experiment 15). These results demonstrate the ability of the process to remove hemicelluloses.

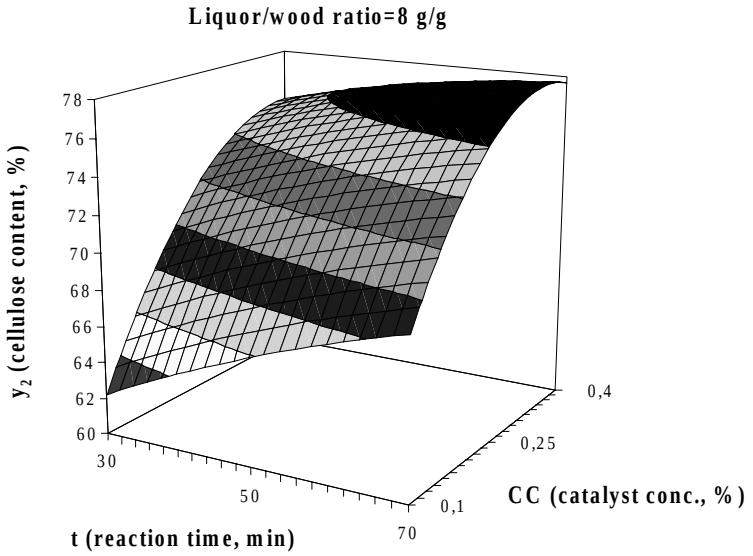


Figure 2. Predicted dependence of pulp cellulose content (y_2) as a function of reaction time (t) and catalyst concentration (CC) for operation at the normal boiling point (LWR = 8 g/g).

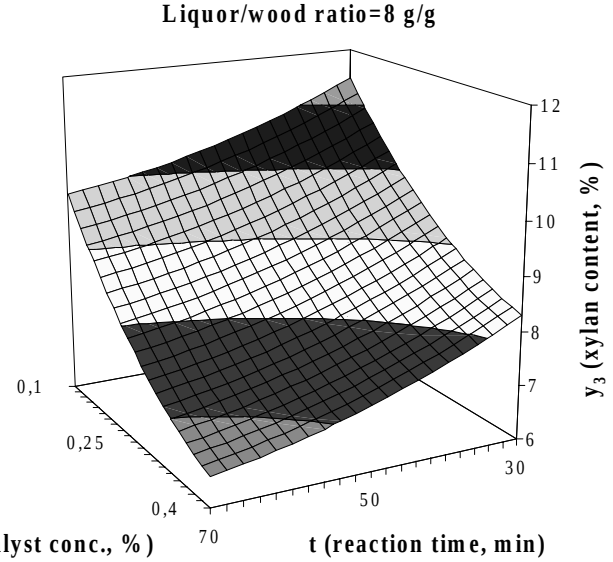


Figure 3. Predicted dependence of pulp xylan content (y_3) as a function of reaction time (t) and catalyst concentration (CC) for operation at the normal boiling point (LWR = 8 g/g).

The lignin content of pulps (variable y_4) was mainly affected by reaction time and catalyst concentration. **Figure 4** shows the calculated dependence of pulp lignin content on both variables when the liquor-to-wood ratio was held at 8 g/g. A remarkable decrease in the lignin content of samples was predicted when the selected independent variables increased from their lower values up to the central point of their variation ranges, but further increases in time (from 50 to 70 min) and/or catalyst concentration (from 0.25 to 0.4%) caused only minor effects. Up to 95% lignin was removed under harsh operating conditions.

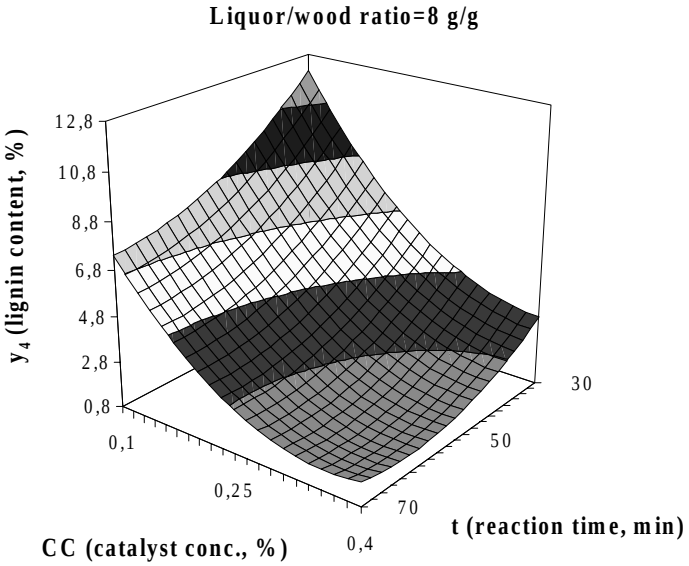


Figure 4. Predicted dependence of pulp lignin content (y_4) as a function of reaction time (t) and catalyst concentration (CC) for operation at the normal boiling point (LWR = 8 g/g)

The rest of the dependent variables considered in this study were selected to measure the composition of liquors. Variable y_5 (cellulose conversion into glucose) was introduced to check the reaction selectivity toward cellulose degradation. Similarly, xylose and furfural were measured in liquors to assess the generation of valuable by-products from hemicelluloses (variables y_6 and y_7). Low cellulose conversion into glucose (0.15–0.40%) was observed, whereas xylose and furfural accounted for 6.8–14.3% and 0–23.5% of the initial xylan, respectively.

Pulping at 120ºC (operation in autoclave)

This part of the study corresponds to experiments 17–32 of Table II. Based on the experimental results, the regression coefficients listed in Table III were calculated to establish the interrelationships between independent and dependent variables according to Eq. 1.

As in the experiments carried out at atmospheric pressure, the reaction time (t) and the catalyst concentration (CC) were the most influential factors on pulp yield (variable y_1). The most remarkable finding was that pulp yield was almost unaffected when both t and CC were higher than the middle point of their variation ranges.

The highest cellulose content of pulps (y_2 = 84%) was predicted for the longest time (40 min) and highest catalyst concentration (0.4%). The percentages of cellulose retained in solid phase (90.4–98.1%, with an average value of 93.9%) were in close agreement with those determined in operation at atmospheric pressure.

The trends for pulp xylan content (variable y_3) were similar to those determined for operation at the normal boiling temperature, but the results were significantly lower in this case. For example, pulps with 4.2% xylan were obtained under the severest operating conditions assayed (experiment 31), whereas the percentages of hemicelluloses removal in treatments were in the range 52.1–87.8%.

Pulp lignin content (variable y_4) at the higher operating temperature was also mainly affected by reaction time and catalyst concentration. Increased lignin contents are predicted for operation under harsh conditions (t > 25 min and CC > 0.25), a fact suggesting the participation of lignin repolymerization reactions. The percentage of lignin removal varied within the range 58.8–96.5%, the best results corresponding to severe operating conditions.

The low concentrations of glucose (corresponding to 0.22–0.64% of the initial cellulose) proved the excellent selectivity of delignification toward cellulose degradation. After stoichiometric correction, xylose and furfural accounted for 8.2–16.0% and 1.9–39.0% of the initial xylan, respectively. Material balances showed that 19.1–46.8% of the initial xylan is degraded to compounds different from sugars or furfural (such as oligosaccharides or condensation products).

Study on the effect of the acetic acid concentration

In order to assess the possibility of obtaining pulps with decreased hemicelluloses content, a new set of experiments was carried out considering the acetic acid concentration as sole operating variable. For this purpose, the composition of pulps obtained under the best conditions assayed — either at atmospheric pressure or at 120ºC — in media containing 90% acetic acid were measured in three replicate assays, and further experiments were carried out in media containing 80% or 85% acetic acid. The experimental results, presented in **Table IV,** showed no significant effects when acetic acid concentration of media was varied within the range considered.

Expt. No.	T, ºC	t, min	CC, %	LWR, g/g	Acetic acid in liquor, %	y_1 (pulp yield, %)	y_2 (cellulose, %)	y_3 (xylan, %)	y_4 (lignin, %)
33	NBT*	70	0.35	8.3	80	51.8	79.0	7.0	1.4
34	NBT*	70	0.35	8.3	85	52.9	79.0	7.0	1.1
35	NBT*	70	0.35	8.3	90	54.2	79.4	6.8	2.2
36	120	40	0.30	8.3	80	49.0	81.8	6.2	1.5
37	120	40	0.30	8.3	85	50.0	80.9	6.0	2.2
38	120	40	0.30	8.3	90	53.8	82.4	5.4	1.4

* NBT: normal boiling temperature

Table IV. Experimental results obtained in experiments 33–38 carried out to assess the influence of the acetic acid concentration on pulp yield and pulp composition.

On the basis of the above experimental results, the pulps obtained in experiments 33 and 36 were selected for further characterization in order to measure their potential as feedstocks for production of dissolving pulp. The kappa numbers (6.9 and 5, respectively) and the SCAN viscosities (809 and 796 mL/g, respectively) showed favorable values, but the alkali resistances (measured by the R-10 and R-18 tests) were lower than expected (R-10 of 79.8% and 79.2%; R-18 of 85.7% and 86.5%, respectively). This can be explained on the basis of the significant acetyl group content of samples (6.3% and 5.5%, respectively), which should be substantially reduced in further bleaching treatments (for example, by alkaline saponification). Based on this information, the pulp obtained in experiment 36 can be considered as the most promising one.

CONCLUSIONS

The empirical modeling of HCl-catalyzed pulping facilitated identification of optimal treatment conditions that promote extensive removal of both lignin and xylan at good pulp yield while maintaining a remarkable selectivity toward cellulose degradation. The best pulp (corresponding to experiment 36) showed a Klason lignin content as low as 1.5% (kappa no. 5) and cellulose content of 81.8%. While the SCAN viscosity of the pulp was reasonable (796 mL/g), its suitability for production of dissolving pulp was limited by its xylan content (6.2%) and particularly by its alkali resistance (R-10 = 79.2%, R-18 = 86.5%), which were in relation with its high acetyl group content. Additional reduction of xylan content and improvement of the alkali resistance would have to be accomplished in subsequent bleaching stages (e.g., alkaline TCF treatments).

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