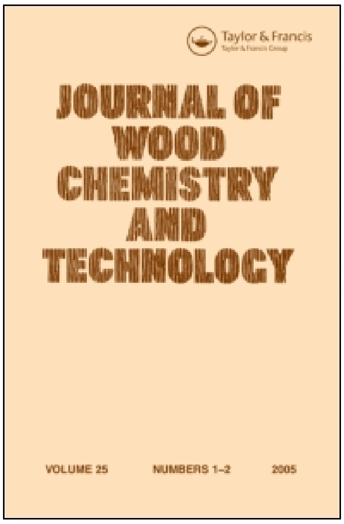

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FORMIC ACID-PEROXYFORMIC ACID PULPING OF *Fagus sylvatica*

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ABSTRACT

Beech *(Fagus sylvatica)* wood samples were subjected to two-stage treatments following the philosophy of the Milox process. By means of incomplete, second-order, factorial designs, the effects of selected operational variables on the composition and on the technical properties of pulps were assessed for optimization purposes. Under the best conditions assayed, a pulp with 5.5% lignin, 86.3% cellulose and 4.3% xylan was obtained at 46.6% pulp yield. The selected pulp showed good technical properties (*kappa* number = 25, SCAN viscosity higher than 1000 mL/g, R-10 test for alkaline resistance = 88.9%, R-18 test for alkaline resistance = 91.8%), showing potentiality to be used as feedstock for dissolving pulp production after TCF bleaching.

INTRODUCTION

Altenative pulping processes based on the utilization of carboxylic acids (such as formic acid or acetic acid) are free from sulphur-containing chemicals, and the whole pulping can be carried out in media containing only carbon, hydrogen, and oxygen.[1] Acetic acid and/or formic acid are the solvents employed in the Acetosolv, Acetocell, Formacell and Milox processes, all of them allowing the fractionation of lignocellulosic raw materials into cellulose, hemicellulose-degradation products (mainly sugars) and lignin-degradation products.

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Formic acid was proposed as an agent for delignification as early as 1917,[2] but no systematic studies were made until the 80's. Formic acid pulping was patented in 1982.[3] In this field, the Milox pulping and bleaching process (*Mil*ieu Pure *Ox*idative, 1984) was developed at the "Finnish Pulp and Paper Research Institute" (KCL) and is based on the action of formic acid and peroxyformic acid (obtained by reacting formic acid and hydrogen peroxide). Since 1991, the Milox process has been studied on the pilot scale by Kemira Oy and KCL. The cellulosic fraction from the Milox process is suitable for the production of textile fibers, plastics, microcrystaline cellulose, and various cellulose derivatives.[4] As for other organosolv processes, the role of by-products is of major significance in this process.

Treatments in formic acid media have been reported to be suitable for pulping softwoods,[5,6-8] hardwoods,[9,10-11] and nonwoody plants.[11-13] Pine (*Pinus sylvestris*), birch (*Betula sp.*), and spruce (*Picea abies*) have been the main wood species used in Milox pulping. Using wood as a raw material, three-stage processing leads to good results in terms of degree of delignification, consumption of chemicals and pulp quality. Three-stage operation is carried out by sandwiching a formic acid stage between two peroxyformic acid stages.[9] This operational procedure has been modified in some cases. For example, Obrocea and Cimpoesu[7] proposed a single peroxyformic acid stage for sprucewood pulping (at temperatures in the range 80-110°C with reaction times up to 4 hours), whereas Da Silva et al.[11] replaced the third stage by an alkaline extraction in the processing of *Eucalyptus grandis* wood and sugarcane bagasse. Non-woody materials (such as *Common red* or *Phragmites comunis*) behave differently than wood, and the optimum conditions for them depend on the species considered. Two-stage Milox pulping (including cooking with formic acid alone, followed by reaction in media made up with formic acid and hydrogen peroxide) has been reported to be more effective than the three-stage cooking in some cases because the overall cooking time is shorter, yields are higher, and the pulping procedure is easier in practice because of the better impregnation.[12,13]

This work deals with the two-stage pulping of beech wood, one of the most important hardwoods in northern and central Europe. The effects of selected operational variables on the composition and technical properties of pulps are established by means of empirical models, providing information useful for assessing the selection of the operational conditions.

RESULTS AND DISCUSSION

The first and second stages of Milox delignification are affected by a number of operational variables. In order to reduce the experimental deal to a reasonable limit, preliminary experiments (data not shown) were carried out to indentify the most influential operational variables. In the same way reported in literature, [7,11,13] it was found that isothermal operation in the first stage was a reasonable strategy. For this reason, temperature was kept constant at 70°C in all the experiments. Table 1 shows the set of fixed and experimental variables considered in the first part of this study, as well as their values or variation ranges. The same Table includes the definitions of the dependent variables selected to characterize both pulps and pulping liquors. The set of experiments 1-16 involves 3 independent variables measured at 3 different levels, its structure corresponding to an optimized, incomplete, centered, second order factorial design of experiments.[14] This methodology has been successfully applied to the empirical modelling of organosolv pulping.[15-19]

Table 2 presents the operational conditions and the experimental results obtained for variables y_1 to y_{11} corresponding to experiments 1-22. The experimental results of experiments 1-16 can be correlated with the independent, dimensionless operational variables by means of empirical models in which the dependent variables were evaluated as the sum of the linear, interaction and second-order terms, according to the generalized expression:

$$y_j = b_{0j} + b_{1j}x_1 + b_{2j}x_2 + b_{3j}x_3 + b_{12j}x_1x_2 + b_{13j}x_1x_3 + b_{23j}x_2x_3 + b_{11j}x_1^2 + b_{22j}x_2^2 + b_{33j}x_3^2 \quad [1]$$

TABLE 1
Variables Considered in the First Set of Experiments

a) Fixed variables

Formic acid concentration: 80 weight percent of liquors

Temperature of the first stage : 70°C

Duration of the first stage (t_1) : 60 min

Temperature of the second stage: normal boiling temperature.

b) Operational variables

Wood to liquor ratio (WLR): 8, 12 or 16 g wood (o.d. basis)/ 100 g liquors

Hydrogen peroxide concentration (HPC): 1, 3 or 5 g/100 g wood (o.d. basis)

Duration of the second stage (t_2): 90, 135 or 180 min

c) Dependent (experimental) variables

Pulp yield (y_1), g pulp/100 g wood, o.d. basis

Variables used to measure the composition of pulps:

Cellulose content (y_2), g cellulose/100 g treated sample, o.d. basis

Xylan content (y_3), g xylan/100 g treated sample, o.d. basis

Lignin content (y_4), g lignin/100 g treated sample, o.d. basis

Acid-soluble lignin content (y_5), g acid-soluble lignin/100 g treated sample, o.d. basis

Acetyl group content (y_6), g acetyl group/100 g treated sample, o.d. basis

Viscosity (y_7), mL/g (SCAN viscosity)

R-10 test for alkaline resistance (y_8), % weight of pulp

R-18 test for alkaline resistance (y_9), % weight of pulp

Variables used to measure the composition of liquors:

Concentration of xylose in pulping liquors (y_{10}), g /L

Concentration of furfural in pulping liquors (y_{11}), g /L

TABLE 2

Operational Conditions and Experimental Results Obtained in Experiments 1-22 Expressed in Terms of the Dependent Variables y_1-y_{11} Defined in Table 1.

Exp.	Indep.variables			Dependent variables										
	WLR (g/100 g)	HPC (% wood)	t_2 (min)	y_1 (pulp yield)	y_2 (% cellulose)	y_3 (% xylan)	y_4 (% lignin)	y_5 (% ac. solub. lignin)	y_6 (% acetyl groups)	y_7 (viscosity, mL/g)	y_8 (R-10,%)	y_9 (R-18,%)	y_{10} (xylose conc., g/L)	y_{11} (furfural conc., g/L)
1	8	1	135	48.5	81.7	3.9	8.4	0.5	0.5	997	90.3	93.1	13.6	0.4
2	8	3	90	49.0	80.2	4.7	7.9	0.7	1.0	1013	88.9	93.2	12.8	0.3
3	8	3	180	47.0	84.3	4.0	5.6	0.5	1.8	968	88.6	94.6	13.4	0.6
4	8	5	135	46.9	84.3	4.1	7.7	0.7	1.6	975	90.1	93.8	13.0	0.4
5	12	1	90	50.3	77.9	4.4	10.0	0.6	0.7	982	89.4	91.9	18.1	0.3
6	12	1	180	47.5	79.4	3.3	5.8	0.5	0.5	978	90.6	93.9	13.8	0.6
7	12	3	135	48.4	81.8	4.1	7.0	0.5	0.9	1011	88.5	92.7	16.0	0.6
8	12	3	135	47.6	82.4	4.3	7.3	0.6	0.7	1017	89.2	93.4	20.0	0.6
9	12	3	135	48.6	81.6	4.3	7.3	0.6	0.6	1013	89.2	91.2	17.9	0.5
10	12	5	90	49.8	79.8	4.6	7.7	0.6	0.8	960	88.8	89.6	18.3	0.4
11	12	5	135	47.4	83.6	5.0	4.9	0.7	0.7	976	88.6	90.4	20.5	0.5
12	12	5	180	46.6	86.3	4.3	5.5	0.6	0.6	1016	88.9	91.8	21.6	0.8
13	16	1	135	49.1	81.3	4.5	8.4	0.8	0.6	1035	89.3	91.7	25.1	0.8
14	16	3	90	49.1	82.0	4.9	8.5	0.6	1.1	979	87.7	91.3	22.4	0.5
15	16	3	180	47.2	85.4	4.1	6.6	0.5	0.8	1008	89.2	94.0	24.5	1.0
16	16	5	135	48.4	84.5	4.8	6.6	0.6	1.1	988	87.8	92.8	21.6	0.6
17	12	5	300	46.2	80.0	3.3	5.2	0.5	0.4	830	90.4	93.2	n.d.[1]	n.d.[1]
18	12	7.5	240	48.3	75.8	4.3	5.2	0.8	3.0	809	87.5	92.3	n.d.[1]	n.d.[1]
19	12	7.5	240	47.6	85.3	3.9	5.0	0.7	1.8	814	89.6	93.8	n.d.[1]	n.d.[1]
20	12	10	180	49.3	77.9	6.3	6.9	0.9	2.9	893	n.d.[1]	n.d.[1]	n.d.[1]	n.d.[1]
21	12	10	240	44.7	76.0	3.3	5.7	0.8	1.8	772	90.8	91.4	n.d.[1]	n.d.[1]
22	12	10	300	44.2	80.9	3.5	4.8	0.5	0.3	741	87.6	n.d.[1]	n.d.[1]	n.d.[1]

[1] n.d.: result not determined

where y_j is the dependent variable considered; b_{0j}....b_{ikj} are regression coefficients, calculated from the experimental data by multiple regression by the least-squares method; x_1 is the dimensionless wood to liquor ratio; x_2 is the dimensionless hydrogen peroxide concentration and x_3 is the dimensionless reaction time of the second stage.

Variables x_1 to x_3 are defined as:

$$x_1 = 2\ (WLR_i - WLR_{med})/(WLR_{max} - WLR_{min}) \qquad [2]$$

$$x_2 = 2\ (HPC_i - HPC_{med})/(HPC_{max} - HPC_{min}) \qquad [3]$$

$$x_3 = 2\ (t_{2i} - t_{2med})/(t_{2max} - t_{2min}) \qquad [4]$$

The nomenclature used in these equations corresponds to the definitions of Table 1, whereas the subscript i refers to the number of the experiment considered, and the subscripts med, max and min refer to the central point, upper limit and lower limit of the variables′ variation range, respectively.

Table 3 lists the regression coefficients obtained for the models describing the behaviour of selected variables measuring the composition of pulps and liquors. The same Table includes the statistical parameters measuring both the correlation and the statistical significance of the models.[20, 21]

Pulp yield (variable y_1) was principally affected by the hydrogen peroxide concentration (HPC) and the reaction time of the second stage (t_2). Figure 1 shows the model predictions for pulp yield as a function of these variables for media containing 12 g wood/100 g liquor (WLR = 12). The yield decreased almost linearly when either the hydrogen peroxide concentration or the reaction time of the second stage were increased. The lowest pulp yield (46.5%) was obtained in experiment 12, which was performed under the harsher conditions assayed for both hydrogen peroxide concentration and reaction time. Despite the narrow variation range of pulp yield, the empirical model provided a good interpretation of the experimental data, as it can be confirmed by comparing the results of Table 2 with the model predictions for the corresponding conditions (see Figure 1).

TABLE 3

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 ,y_4, and y_8

Parameters	**j=1** **y_1(pulp yield)**	**j=2** **y_2(% cellulose)**	**j=3** **y_3(% xylan)**	**j=4** **y_4(% lignin)**	**j=8** **y_8 (R10,%)**
b_{0j}	48.16**	81.99**	4.32**	6.98**	88.9**
b_{1j}	0.30	0.33	0.20*	0.06	-0.48**
b_{2j}	-0.51**	-1.85**	0.27**	0.83**	-0.53**
b_{3j}	-1.23**	-1.96**	-0.36**	1.32**	0.31
b_{12j}	0.24	0.16	0.01	-0.29	-0.32
b_{13j}	0.04	-0.18	-0.02	0.10	0.43
b_{23j}	-0.10	1.26**	0.21	0.49	-0.29
b_{11j}	-0.18	1.49**	0.11	0.43	-0.14
b_{22j}	0.19	-0.51	-0.06	0.20	0.59*
b_{33j}	0.16	-0.59	-0.06	-0.12	-0.12

* Significant coefficients at the 90% confidence level

** Significant coefficients at the 95% confidence level

Statistical Results Measuring the Correlation (R^2 Coefficient) and Significance (Fischer's F Parameter) of Models

Model for variable	y_1	y_2	y_3	y_4	y_8
R^2	0.8950	0.9679	0.8439	0.8378	0.8550
F exp	5.68	20.10	3.60	3.44	3.92
Significance level (based on the F test)	>97%	>99%	>93%	>92%	>94%

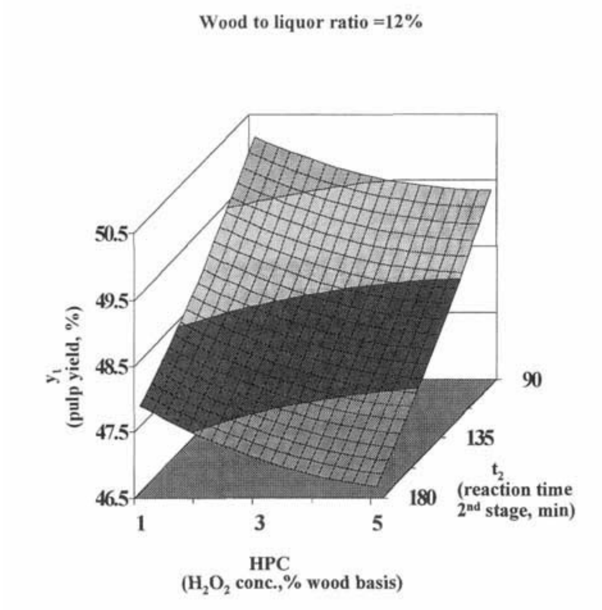

FIGURE 1. Calculated dependence of pulp yield on the hydrogen peroxide concentration and on the duration of the 2nd stage.

Figure 2 presents the calculated dependence of the cellulose content of pulps on the most influential variables (hydrogen peroxide concentration, HPC and reaction time of the second stage, t_2) for media containing the intermediate wood to liquor ratio considered. The surface response confirms that the major effects on the cellulose content of pulps was caused by HPC. The pulp with the highest cellulose content (86.3%) was obtained in experiment 12, in which both the hydrogen peroxide concentration and the reaction time of the second stage were kept in their highest values. On the basis of the experimental data concerning wood composition, pulp yield and cellulose content of pulp, it can be calculated that over 95% of the cellulose contained in wood was retained in pulps, confirming the excellent selectivity of the process.

The xylan content of pulps (variable y_3) was mainly affected again by the hydrogen peroxide concentration (HPC) and the reaction time of the second stage

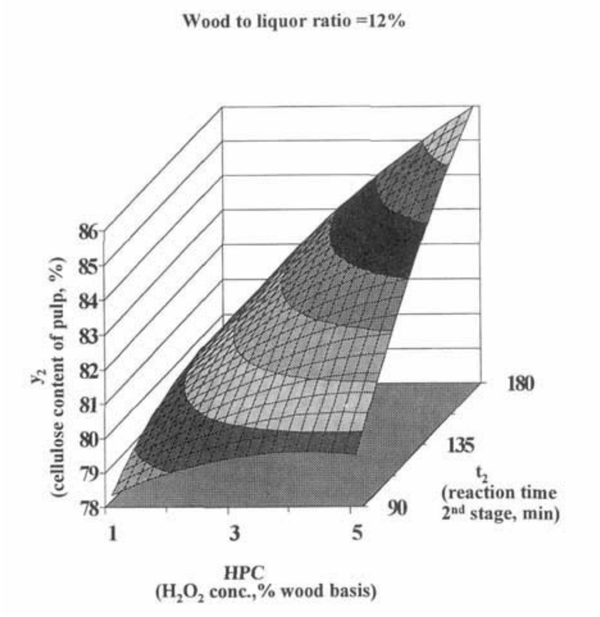

FIGURE 2. Calculated dependence of the cellulose content of pulps on the hydrogen peroxide concentration and on the duration of the 2nd stage.

(t_2) (see Table 3), and its values varied in a narrow range (3.3-5.0%). Considering the composition of the raw material and the pulp yields, it can be inferred that high percents of xylan removal (in the range 86.1-91.1%) were achieved in experiments, confirming the remarkable ability of the process for obtaining pulps with high cellulose content.

The hydrogen peroxide concentration and the reaction time of the second stage were the major variables affecting the Klason lignin content of pulps (variable y_4). The surface response (see Figure 3) shows that the Klason lignin content of pulps decreased when either the hydrogen peroxide concentration or the reaction time of the second stage were increased, but the relative influence of the hydrogen peroxide concentration decreased at prolonged reaction times. From the

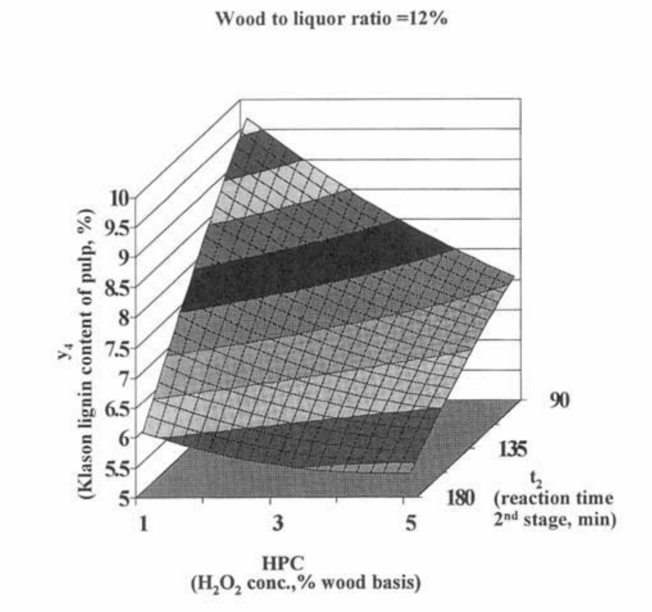

FIGURE 3. Calculated dependence of Klason lignin content of pulps on the hydrogen peroxide concentration and on the duration of the 2nd stage.

experimental data, it can be calculated that over 85% of the initial lignin can be removed under a variety of experimental conditions which also lead to both extensive hemicellulose solubilization and low cellulose degradation. A systematic analysis of lignin removal can be carried out considering the empirical models developed for y_1 and y_4. This operational way confirmed the low influence of the hydrogen peroxide concentration for experiments whose second stage lasted 135-180 min.

A fair linear interrelationship between the Klason lignin percents with the *kappa* number of pulps (with a variation range of 22.3-31.1) was observed, with an average ratio of 0.272 units of Klason lignin percent *per* unit of *kappa* number. The most important finding is that bleachable pulps can be obtained under operational conditions defined by HPC>3% and t_2>135 min.

Owing to the limited variation range and to the incidence of the experimental error, a *non-significant* dependence of variables y_5 (percent of acid-soluble lignin in pulps), y_6 (percent of acetyl groups in pulps) and y_7 (SCAN viscosity of pulps, mL/g) on the operational variables was found. The results determined for the acid-soluble lignin content (0.5-0.8%) showed that this variable lacked of importance for the selection of operational conditions, a similar situation being observed for the percent of acetyl groups in pulps (variation range, 0.5-1.8%). On the contrary, the SCAN viscosity (variable y_7) was of primary importance for measuring the quality of pulps derived from the process. All the experiments led to satisfactory viscosities, which were distributed within a narrow variation range (960-1035 mL/g). The best result was found in experiment 13 at WLR = 16 g/100 g liquor, HPC = 1% and intermediate values of reaction time of the second stage (t_2). The lowest value (960 mL/g) was determined in experiment 10, carried out with 12% of wood to liquor ratio and the maximum hydrogen peroxide concentration assayed.

On the basis of the above results concerning cellulose degradation, hemicellulose removal, delignification and viscosity, the Milox process can be considered a promising technology for dissolving pulp production from *Fagus sylvatica* wood. In order to check the quality of pulps for this purpose, the R-10 and R-18 tests for alkaline resistance were included in the experimental plan as dependendent variables, the first of them (variable y_8) being correlated with the operational conditions by means of a statistically significant model (see Table 3). Even if the most influential variables on R-10 were the wood to liquor ratio and the hydrogen peroxide concentration (as it can be inferred from the significance of the regression coefficients involved in models), its limited variation range (87.7-90.6%) hinders a detailed discussion on their effects. The limits determined for the assay R-18 (variable y_9, with values in the range 90.4-94.6%) confirmed the favourable distribution of molecular weights of the cellulose contained in pulps. It can be noted that even if formic acid is the main component of the reaction media (this compound being able to give ester groups leading to decreased alkaline resistance), the experimental results showed that this possibility has no practical importance.

In order to assess the generation of valuable byproducts from hemicelluloses, the concentrations of xylose and furfural in liquors (variables y_{10} and y_{11}, respectively) were considered in the experimental plan as dependent variables. The experimental results show that xylose was the main degradation product, and its comparatively high concentrations (which account as average for more than 84% of the initial xylan) adds a new interesting feature to the studied process. Owing to its low concentrations, furfural does not contribute to the economic feasibility of the process.

The empirical models developed for pulp yield and for variables measuring the composition of pulps suggested that further improvements could be reached under harsher operational conditions. For this purpose, a new experimental plan (assays 17-22 of Table 2) was carried out in media containing 12 g wood/ 100 g liquors, and only the most relevant operational variables were measured. Together with experiment 12, assays 17-22 corresponded to an experimental design allowing the development of empirical models which included linear terms in x_1 and x_2 and an additional interaction term. The models developed for pulp yield, cellulose content and xylan percent of pulps (variables y_1, y_2 and y_3) were not significant at the 90% confidence level owing to their narrow variation range and to the incidence of the experimental error. For the assays 17-22 of Table 2, the results obtained for pulp yield, cellulose content and xylan percent were closely related to those obtained under the severest conditions considered in experiments 1-16, even if the marginal improvements of the results suggested that the amount of hydrogen peroxide was too high. The *kappa* number of pulps corresponding to experiments 12 and 17-22 varied in the range 23-42 and presented a good correlation with the Klason lignin content of pulps, with a fairly linear dependence on both the hydrogen peroxide concentration and the reaction time of the second stage. For this set of assays, an average ratio of 0.229 units of Klason lignin percent *per* unit of *kappa* number was determined.

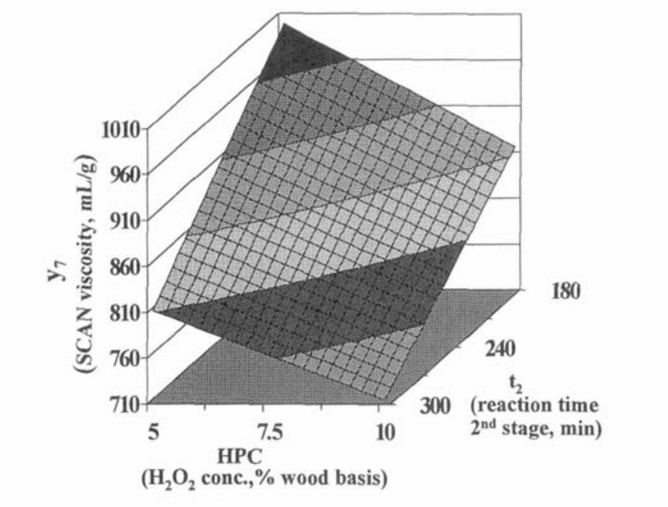

FIGURE 4. Calculated dependence of viscosity on the hydrogen peroxide concentration and on the duration of the 2nd stage.

As it was stated above, the results determined for both the acid-soluble lignin content of pulps (variable y_5) and the percent of acetyl groups (variable y_6) were not relevant for the purposes of this work.

Statistically significant models can be developed for Klason lignin content (variable y_4) and SCAN viscosity (variable y_7) from the experimental data corresponding to experiments 12 and 17-22. In this case, viscosity provided the most relevant information. The model predictions for the dependence of y_7 on both hydrogen peroxide concentration (HPC) and reaction time of the second stage (t_2) are shown in Figure 4, in which a continuous decrease of viscosity with the severity of the operational conditions is observed. The decrease of viscosity was linear with the two selected operational variables along their entire variation range. Considering the predicted values for viscosity under the severest conditions shown in Figure 4, it can be concluded that no harsher operational conditions should be assayed in further experiments. On the basis of the surface-response shown in Figure 4, and assuming 800 mL/g as the lower viscosity for unbleached pulps suitable for dissolving pulp production, the optimal conditions for pulping in this stage of our study were considered to correspond to $t_2 = 180$ min and HPC = 5% (experiment 12).

Further assessment on the operational conditions affecting the second stage of delignification

As a possible way to improve the above results, a new set of experiments was developed to study the behaviour of pulping when the reaction time of the first stage was decreased to 45 min and the second stage was carried out in autoclave at 120°C. The variation ranges of both the wood to liquor ratio (WLR) and the hydrogen peroxide concentration (HPC) were the same used in the first set of experiments, whereas the limits for the reaction time of the second stage (t_2) were 60 and 180 min. The structure of the experimental design (experiments 23-38 of Table 4) was similar to the first one described in this study. Therefore, empirical models following the generalized expression shown in eq. 1 can be developed as above. Even if statistically significant models can be deduced for the most important dependent variables, a quantitative discussion is omitted owing to the technical characteristics of pulps obtained (see below).

A qualitative comparison of the experimental data listed in Tables 2 and 4 suggested that high temperature operation in the second stage allowed an improved xylan removal at a similar pulp yield, but no significant improvements in delignification and cellulose content were observed. Other dependent variables (including acid-soluble lignin, acetyl group content, tests for alkaline resistance and conversions of polysaccharide into sugars) did not provide additional relevant information for assessing the selection of the operational conditions. For this purpose, viscosity (variable y_7) provided again the most valuable criterium: assuming that a viscosity of 800 mL/g is a threshold under which the unbleached pulps are not easily utilizable for dissolving pulp production (owing to the limited

TABLE 4

Operational Conditions and Experimental Results Obtained in Experiments 23-38 Expressed in Terms of the Dependent Variables y_1-y_{11} Defined in Table 1.

Exp.	Independent variables			Dependent variables								
	WLR (g/100 g)	HPC (% wood)	t_2 (min)	y_1 (pulp yield)	y_2 (% cellulose)	y_3 (% xylan)	y_4 (% lignin)	y_5 (% ac. solub. lignin)	y_6 (% acetyl groups)	y_7 (viscosity, mL/g)	y_8 (R10,%)	y_9 (R18,%)
23	8	1	120	48.3	84.7	3.2	6.1	0.6	1.2	729	88.7	92.0
24	8	3	60	49.0	88.8	3.1	6.9	0.7	0.9	721	90.5	90.4
25	8	3	180	46.8	82.1	2.8	6.2	0.5	0.8	826	90.6	91.9
26	8	5	120	47.4	72.6	2.8	6.2	0.6	2.1	591	89.7	99.6
27	12	1	60	48.1	81.5	4.2	8.1	0.7	1.1	852	89.6	93.3
28	12	1	180	48.3	74.0	3.9	7.0	0.6	2.9	602	89.6	90.3
29	12	3	120	48.7	77.7	3.6	7.6	0.7	2.7	686	87.9	91.2
30	12	3	120	48.7	78.0	3.5	7.6	0.8	1.5	655	90.1	92.7
31	12	3	120	48.6	76.5	3.5	7.8	0.8	2.2	667	89.8	92.1
32	12	5	60	47.9	75.5	4.6	7.7	0.7	0.6	918	89.5	91.8
33	12	5	120	45.8	74.7	3.4	6.2	0.7	2.8	940	91.2	94.1
34	12	5	180	47.8	79.6	4.1	8.4	0.7	2.2	993	89.3	89.6
35	16	1	120	48.0	84.8	3.2	7.4	0.6	0.6	920	88.4	92.6
36	16	3	60	49.9	81.5	4.1	7.8	0.7	4.6	774	87.7	89.8
37	16	3	180	48.0	85.5	3.1	6.7	0.6	1.9	596	89.0	89.4
38	16	5	120	45.4	87.9	3.6	4.4	0.6	2.4	814	91.8	91.8

viscosity loss allowable during the bleaching stages), only 7 experiments of Table 4 met this specification. Among them, experiment 38 is interesting owing to its limited Klason lignin content (4.4%, corresponding to a *kappa* number of 22.7), even if the correspondent viscosity (814 mL/g) is near the lower limit acceptable. Alternatively, experiments 32 to 34 (which were carried out in media containing 12 g wood/100 g liquors and 5% hydrogen peroxide during 60, 120 and 180 min, respectively) and experiment 35 (which was carried out with 1% hydrogen peroxide during 120 min in media containing 16 g wood/100 g liquors) led to viscosities higher than 900 mL/g, but their comparatively low contents in cellulose, their proportion in Klason lignin (6.2-8.4%, corresponding to *kappa* number of 31-36) as well as the values of the parameter R-10 were not favourable.

In conclusion, the surface-response methodology applied in this study allowed the identification of operational conditions leading to bleachable Milox pulps from *Fagus sylvatiyca* wood in two-step treatments. The best pulps corresponded to experiments whose second stage was carried out at normal pressure. For example, experiment 12 of Table 2 was characterized by a *kappa* number = 25 at 46.6% pulp yield, with viscosity higher than 1000 mg/L and good alkaline resistance. These results show the potentiality of the technology considered in this study for dissolving pulp production from beech wood after TCF bleaching.

MATERIALS AND METHODS

Raw material

Beech *(Fagus sylvatica)* wood chips were kindly provided by Dr. Sixta and Dr. Harms (Lenzing A. G., Lenzing, Austria). Wood chips were screened to select a fraction of particles with size below 2 mm, homogenized in a single lot to avoid compositional differences and stored.

Analysis of wood and pulps

The composition of wood and pulps was determined using the following methods: moisture, ISO 638:1978; cellulose (as glucan), xylan, araban and acetyl groups, by HPLC determination of the glucose, xylose, arabinose and acetic acid contained in hydrolysates from a quantitative acid hydrolysis carried out according to the TAPPI T13m assay;[22,23] acid-soluble lignin as *per* Maekawa et al;[24] *kappa* number, ISO 302:1981 method; SCAN viscosity, SCAN C15:62 method; alkaline resistance (R-10 and R-18), ISO 699:1982 method. The composition of the wood lot used, expressed as the average of three replicate determinations and expressed in terms of weight percent (o.d. basis), was as follows: cellulose, 39.6%; xylan, 17.4%; araban, 0.21%; acetyl groups, 5.6%; Klason lignin, 23.7%; acid-soluble lignin, 2.7%; water extractives, 1.15%; ethanol extractives, 0.57% and ethanol-benzene extractives, 0.49%.

Milox processing of wood

Delignification experiments were carried out in stirred glass reactors with temperature control under a variety of operational conditions in 80% formic acid media (see below). Pulps were successively washed with warm 80% formic acid and water until pH = 7, treated in a UltraTurrax T-50 defibrator (IKA Labortechnik, Germany) for 30 s at 5000 rpm and air-dried before analysis. Experiments 1-22 were performed at normal pressure. The first stage of experiments 23-38 was also performed at normal pressure, but the second stage was carried out in autoclave at 120°C.

HPLC analysis of monosaccharides

Samples from pulping liquors and from quantitative acid hydrolyses were analysed for glucose and pentoses (xylose and arabinose) using a Hewlett Packard HPLC with refractive-index detector. The operational conditions were: column Transgenomic™ ICSep ICE-ION-300 (300 x 7.8 mm); column temperature 55°C; flow rate 0.4 mL/min; mobile phase 0.006N H_2SO_4.

Fitting of data

The experimental data were fitted to the proposed models by non-linear regression using commercial sofware (Statistica® 6.0, StatSoft).

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