Optimization of process variables for production of dissolving pulps from wheat straw and hemp

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ABSTRACT: Statistical methods of experimental planning were used to determine the optimum conditions for producing dissolving pulp from Hungarian wheat straw and hemp. Good fits were obtained between calculated and experimental values for bleached pulp yields, and several polynomial models were obtained. Produced under optimum processing conditions, dissolving pulps from wheat straw and hemp are suitable raw materials for production of cellulose derivatives.

KEYWORDS: Alkaline pulping, bleaching, dissolving pulps, experimental design, hemp, optimization, wheat straw.

The production and chemical modification of cellulose from reed and eucalyptus dissolving pulps have been extensively studied and reviewed *(1, 2)*. The objective of the present work was to establish the optimum pulping and bleaching conditions for producing dissolving pulp from Hungarian wheat straw and hemp.

Previous studies

Pulping

The presence of sodium sulfide in alkaline pulping of pulpwood facilitates the removal of lignin by the formation of low-molecular-mass thiolignin fractions, increasing the rate of delignification and producing marked changes in the yield and in the chemical and physical characteristics of the pulp *(3)*. In the case of agricultural residues, sodium sulfide also results in favorable effects *(4–8)*.

A few studies have been performed on delignification of lignocellulosic materials with alkaline hydrogen peroxide. Gould *(9)* found that approximately half the lignin present in agricultural residues, such as wheat straw, could be solubilized when the residue was treated at 25°C with an alkaline solution of hydrogen peroxide. Delignification was most effective at pH 11.5. McDonough *et al. (10)* studied the delignification of southern pine kraft pulp with alkaline hydrogen peroxide. They also found that approximately half of the lignin present in the pulp could be removed.

Hata *(11)* investigated soda pulping and soda–oxygen pulping of manila hemp. Cunningham and coworkers *(12)* treated another hemp-type annual plant (*Crotalaria juncea*), a potentially suitable source for papermaking. Sulfate pulping resulted in 53–54% yield. The pulp was bleached with 5.7% effective chlorine to 78% brightness. Quality of the fibrous raw material obtained was the same as that of hardwood pulps.

Bosia and Nisi *(13)* investigated the utilization of whole hemp stems of *Cannabis sativa*, which is the same as the Hungarian hemp species. They analyzed the chemical composition of bast fibers and woody elements and found that woody elements contain less (approximately by 80%) cellulose and about 2.5 times more (34.6%) hemicellulose than bast fibers. They also found that the lignin content of the woody elements was approximately four times higher (18.4%) than the bast fibers. Woody

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and bast fibers were thus separated with a rotating screening drum before pulping. Bast fibers were treated with alkaline oxygen pulping. Woody elements were pulped mechanically and chemimechanically (applying 2% NaOH and 2% H_2O_2).

Felton *(14)* investigated the use of alkaline sulfite to pulp such agricultural residues as hemp and flax. He produced good-quality cigarette papers from the high-freeness pulps. Mita *(15)* pulped hemp in NaOH and H_2O_2, applying EDTA (ethylene-diamine tetraacetic acid) and anthraquinone as additives. Hernadi and Rusznàk *(16)* pulped hemp stems of various chopped sizes with sulfate, alkaline anthraquinone, and alkaline peroxide methods. Marpirello *(17)* pulped whole hemp stems with an acidic sulfite process.

Bleaching

The objective in bleaching is to produce a white pulp of stable color at reasonable cost and with a negligible deleterious effect on the physical and chemical properties of the pulp. Two principal reactions take place in bleaching. The first is the solubilization and removal of colored matter. The second is the transformation of colored matter to a colorless form that should be as stable as possible to light and heat. Lignin is the main offender as far as color is concerned. Cellulose and hemicelluloses are inherently white *(18)*.

In a sense, the chlorination and caustic-extraction stages in multistage bleaching are purifying rather than bleaching operations, since the lignin is removed as alkali-soluble chlorolignins and the pulp is made no whiter. During these stages, the loss in carbohydrate content is very small (less than 1%), while lignin removal is about 9.5% in chlorination and 4% in caustic extraction *(19)*. On the other hand, in bleaching with peroxide, the lignin is mostly decolorized without removal. The loss in yield can vary from 1% or less in peroxide bleaching of mechanical pulp to 10–20% in multistage bleaching of semichemical pulps. Normally, the loss is 3–10% of the original moisture-free wood for the bleaching of regular chemical wood pulps.

The cost of removing lignin is less in the cooking process than in the bleaching process. For this reason, it is generally more economical, when making high-brightness pulps, to cook to an "easy bleaching" pulp than to attempt to bleach a raw or undercooked pulp.

In one sense, bleaching can be considered to be a continuation of the cooking process, since both are concerned with purification. Excessive bleaching can cause chemical degradation of cellulose, so bleaching conditions must be chosen to hold degradation to a minimum. In general, chemical wood pulps are bleached with chlorine compounds, either direct chlorine plus hypochlorite, hypochlorite alone, or chlorine dioxide. Semichemical pulps can be bleached with chlorine compounds

I. Characteristics of wheat straw and hemp

*Characteristics**	*Wheat straw*	*Hemp (whole stem)*
Moisture content, %	13.29	12.70
Solubility in benzene:ethyl alcohol (2:1), %	2.80	5.76
Lignin content, %	20.77	17.50
Alpha-cellulose content, %	46.41	54.50
Pentosan content, %	21.45	25.10
Holocellulose content, %	78.35	79.60
Ash content, %	6.50	3.40

*Determined by TAPPI Test Methods *(20–26)*

II. Bleaching sequence for the wheat straw and hemp pulps

Stage no.	*Bleaching agent, and other chemicals*	*Concentration of the bleaching agent, or the chemicals*	*Other bleaching parameters*
First	Hydrogen peroxide (as solution)	15 g H_2O_2/100 g pulp	pulp conc.=4% temp.=80°C time=60 min pH=10–11
	Prestogen® catalyst	0.2 g/100 g pulp	
Second	Same as first stage	Same as first stage	Same as first stage
Third	alkali extraction (by NaOH)	3.5 g/100 g pulp	pulp conc.=4% temp.=25°C time=60 min
Fourth	acidification (by 98% H_2SO_4)	10 g/100 g pulp	pulp conc.=4% temp.=60°C time=60 min

III. Coded and experimental values of process variables

Coded level	Operating temperature, °C	Time at operating temperature, h	Active alkali, % (as Na_2O)
−1.682	160	2.0	10
−1.0	165	2.5	12
0.0	170	3.0	14
+1.0	175	3.5	16
+1.682	180	4.0	18

IV. Sequence of experiments according to central composite design for wheat straw and hemp pulping processes

Experiment no.	Coded variables			Real variables		
	X_1	X_2	X_3	Temp., °C	Time, h	Active alkali, % (as Na_2O)
1	−1	−1	−1	165	2.5	12
2	+1	−1	−1	175	2.5	12
3	−1	+1	−1	165	3.5	12
4	+1	+1	−1	175	3.5	12
5	−1	−1	+1	165	2.5	16
6	+1	−1	+1	175	2.5	16
7	−1	+1	+1	165	3.5	16
8	+1	+1	+1	175	3.5	16
9	−1.682	0	0	160	3.0	14
10	+1.682	0	0	180	3.0	14
11	0	−1.682	0	170	2.0	14
12	0	+1.682	0	170	4.0	14
13	0	0	−1.682	170	3.0	10
14	0	0	+1.682	170	3.0	18
15	0	0	0	170	3.0	14
16	0	0	0	170	3.0	14
17	0	0	0	170	3.0	14
18	0	0	0	170	3.0	14
19	0	0	0	170	3.0	14
20	0	0	0	170	3.0	14

or with peroxide. Groundwood pulps are generally bleached with peroxide, but hardwood and groundwood pulps can be bleached with hypochlorite.

Experimental

Characteristics of raw materials

Before carrying out the pulping experiments, an approximate chemical analysis of the wheat straw and hemp was performed in accordance with TAPPI Test Methods *(20–26)*. **Table I** lists the characteristics of the wheat straw and hemp used in this study.

The following characteristics of the experimentally produced dissolving pulps also were determined:

- Permanganate number of the unbleached pulp *(27)*
- Alpha-cellulose content of the bleached pulp *(23)*
- Degree of polymerization of the bleached pulp *(28)*.

Pulping conditions

Chips were hand cut to lengths of 1–2 cm and pulped in an electrically heated, stainless-steel, rotatable digester. The normal charge was 100 g of moisture-free chips (basis of calculation). Chemicals were mixed to reach the calculated charge of active alkali at 25% sulfidity. All chemicals were added to chips in an aqueous solution. The liquor-to-chips ratio was adjusted to 5 cm^3 liquor to 1 g chips. This ratio of liquor to pulp was maintained at a constant 5:1 throughout all experiments.

After chips and chemicals had been placed in the digester, the lid was closed and the electrical heater and motor were switched on. Thermometer readings were recorded every 5 min until they reached the set value. The time of heating up was about 1 h. At the end of the cook, the digester pressure was reduced to atmospheric level and the digester was left to cool. The cooled pulp was collected on a muslin cloth and washed with tap water.

The pulp was disintegrated in a three-bladed mixer for 3 min at a pulp consistency of 1.5%. The pulp was then screened on a vibrating flat-plate screen with 0.2-mm slots. The screened yield was determined by weighing the air-dried pulp and measuring its moisture content. Rejects were dried in an oven and weighed.

Bleaching conditions

Pulp was bleached using a four-stage chlorine-free process (PPEA). Bleaching conditions are listed in **Table II**. After each stage of bleaching, the pulp was washed thoroughly with hot water. In the final stage of bleaching, the pulp was washed with distilled water.

Experimental design and nonlinear regression

Three parameters, among others, strongly influence the delignification process. These are the temperature, the time at cooking temperature, and

V. Coded and real variables and the corresponding fiber characteristics for kraft pulping of wheat straw

Exp. no.	Coded variables X_1	X_2	X_3	Real variables: Temp., °C	Time, h	Active alkali, % (as Na_2O)	Permanganate No. before bleaching	Yield, % Unbleached	Yield, % Bleached	Alpha cellulose, %	DP	Ash, %
1	−1	−1	−1	165	2.5	12	11.91	53.61	32.12	94.34	1699	2.70
2	+1	−1	−1	175	2.5	12	14.82	56.49	30.23	90.67	1617	1.60
3	−1	+1	−1	165	3.5	12	18.53	54.57	30.52	93.67	1971	2.74
4	−1	−1	−1	165	2.5	16	9.07	46.27	28.41	94.99	1948	2.68
5	+1	+1	−1	175	3.5	12	11.42	45.15	29.80	90.02	1667	0.99
6	+1	−1	+1	175	2.5	16	7.20	49.71	33.81	92.77	1194	1.95
7	−1	+1	+1	165	3.5	16	7.01	59.81	29.34	89.89	1648	2.49
8	+1	+1	+1	175	3.5	16	10.32	41.45	30.43	90.22	1850	1.03
9	−1.682	0	0	160	3	14	8.83	41.94	29.60	88.37	1549	1.56
10	+1.682	0	0	180	3	14	14.42	32.86	28.32	87.27	1100	3.78
11	0	−1.682	0	170	2	14	9.31	34.92	27.02	86.78	2023	2.14
12	0	+1.682	0	170	4	14	11.40	34.51	28.85	87.68	1579	0.63
13	0	0	−1.682	170	3	10	11.21	40.14	36.37	90.68	2014	2.03
14	0	0	+1.682	170	3	18	8.62	36.06	32.34	88.89	1251	1.26
15	0	0	0	170	3	14	7.5l	40.76	32.61	93.36	2010	0.06
16	0	0	0	170	3	14	9.12	40.15	32.28	89.28	1800	2.89
17	0	0	0	170	3	14	7.41	39.78	32.56	88.39	1980	0.77
18	0	0	0	170	3	14	9.22	39.08	33.67	94.68	1959	1.02
19	0	0	0	170	3	14	9.90	39.48	32.84	88.39	2093	2.38
20	0	0	0	170	3	14	10.12	39.92	33.26	93.58	2038	3.95

VI. Coded and real variables and the corresponding fiber characteristics for kraft pulping of hemp

Exp. no.	Coded variables X_1	X_2	X_3	Real variables: Temp., °C	Time, h	Active alkali, % (as Na_2O)	Permanganate No. before bleaching	Yield, % Unbleached	Yield, % Bleached	Alpha cellulose, %	DP	Ash, %
1	−1	−1	−1	165	2.5	12	17.11	51.63	42.28	89.00	565	0.67
2	+1	−1	−1	175	2.5	12	20.00	42.86	39.13	91.00	560	0.59
3	−1	+1	−1	165	3.5	12	17.01	50.45	40.63	86.51	493	0.51
4	−1	−1	+1	165	2.5	16	12.30	46.67	37.56	87.61	554	0.71
5	+1	+1	−1	175	3.5	12	12.60	53.30	38.25	90.21	585	0.89
6	+1	−1	+1	175	2.5	16	10.10	44.70	38.66	91.77	585	0.21
7	−1	+1	+1	165	3.5	16	8.60	46.57	40.00	86.71	495	0.71
8	+1	+1	+1	175	3.5	16	7.81	46.86	37.44	92.00	563	0.78
9	−1.682	0	0	160	3	14	13.00	50.26	42.90	90.01	567	0.35
10	+1.682	0	0	180	3	14	11.31	51.83	38.33	91.20	570	0.31
11	0	−1.682	0	170	2	14	13.27	50.51	40.36	89.90	538	0.90
12	0	+1.682	0	170	4	14	14.41	56.00	37.01	86.31	516	0.63
13	0	0	−1.682	170	3	10	17.01	51.00	40.00	86.38	530	0.37
14	0	0	+1.682	170	3	18	13.20	45.50	39.59	92.10	590	0.12
15	0	0	0	170	3	14	14.81	51.30	43.50	90.11	560	0.62
16	0	0	0	170	3	14	14.00	48.60	43.99	91.10	550	0.68
17	0	0	0	170	3	14	11.80	51.60	42.41	92.60	560	0.77
18	0	0	0	170	3	14	14.42	50.70	39.30	90.01	563	0.12
19	0	0	0	170	3	14	15.81	51.11	40.60	89.21	540	0.32
20	0	0	0	170	3	14	13.81	46.43	40.91	89.70	555	0.55

the concentration of active alkali (as Na_2O).

These three parameters were optimized in a program of experiments designed using the central composite rotatable design method *(29)*. The first step in designing the experiments was to specify the range of variables. Thus,

$$X_1 = (T-170)/5 \quad (1)$$

$$X_2 = (t-3)/0.5 \quad (2)$$

VII. Calculated and experimental optimum conditions and product characteristics

Results	Process conditions X_1 Temp, °C[a]	X_2 Time, h[b]	X_3 AA, %[c]	Characteristics Bleached pulp yield, %	Alpha-cell., %	DP[d]
			Wheat straw			
Calculated	0.0 (170)	0.0 (3)	−1.682 (10)	35.24	92.45	1662
Experimental	0.00 (170)	0.0 (3)	−1.682 (10)	36.32	90.62	2014
			Hemp			
Calculated	−1.103 (164)	−0.046 (3)	−0.381 (13.24)	42.51	88.69	540
Experimental	−1.103 (164)	−0.046 (3)	−0.381 (13.24)	40.99	92.67	595

[a]Maximum pulping temperature
[b]Time of treatment at maximum temperature
[c]Active alkali (as Na_2O), % based on moisture-free wood
[d]Average degree of polymerization of bleached pulp

VIII. Characteristics of dissolving pulps from wheat straw, hemp, and bleached cotton linters (standard cellulose required for nitration)

Characteristics	Wheat straw pulp	Hemp pulp	Cotton linters
Aspect	white*	white*	white*
Moisture content, % *(33)*	5.68	5.34	<8
Ash content, % *(34)*	0.26	0.21	<0.3
$CaCO_3$, NaOCl, and sulfate content	trace	trace	trace
Alpha-cellulose, % *(23)*	90.62	92.67	>90
Dimethyl ether extract, % *(35)*	0.24	0.20	<0.25
Copper number *(36)*	0.27	0.36	<0.50
Viscosity, mPa·s *(37)*			
(1% dissolved in CUOXAM)	37.81	26.81	>10.90
(0.5% dissolved in CUOXAM)	10.89	7.12	>4.40
Alkali solubility, % *(38)*	7.59	5.95	<5.00

*No mechanical impurities

$$X_3 = (AA-14)/2 \quad (3)$$

where

T = maximum pulping temperature, °C

t = time of pulping at maximum temperature, h

AA = active alkali (as Na_2O), % based on moisture-free wood.

The values of variables are coded as shown in **Table III.** The number of different levels for each of the variables was always five (regardless of the number of variables). A preliminary step was setting up the three corresponding real process variables, X_j, for each coded level, where j=1, 2, and 3. The calculations were based on Eqs. 1, 2, and 3.

This experimental design of variables resulted in a schedule of 20 experiments, which were carried out in the sequence shown in **Table IV.**

The results of these experiments were used to develop mathematical models for alpha-cellulose, bleached pulp yield, and degree of polymerization (DP) as functions of the three process variables (X_j) under investigation. The form of this relationship is given by Eq. 4:

$$Y = b_0 + b_i X_i + b_{ii} X_i^2 + b_{ij} X_i X_j \quad (4)$$

The b values are constants, computed by the least-squares method.

Results and discussion

Regression analysis

Tables V and VI summarize results of kraft pulping of wheat straw and hemp, respectively. Alpha-cellulose content, degree of polymerization, and bleached pulp yield are shown as functions of the three process parameters.

Computer-assisted second-order polynomial analysis of bleached pulp yield, alpha-cellulose content, and the average degree of polymerization led to the following equations for wheat straw and hemp *(30)*.

Wheat straw.

$$\text{Bleached pulp yield, \%} = 32.62 + 0.11X_1 - 0.08X_2 - 0.55X_3 - 0.37X_1X_2 + 1.15X_1X_3 - 0.09X_2X_3 - 1.23X_1^2 - 1.61X_2^2 + 0.61X_3^2 \quad (5)$$

$$DP = 1946.44 - 207.16X_1 - 88.20X_2 - 20.25X_3 - 50.36X_1X_2 - 162.81X_1X_3 - 138.01X_2X_3 - 221.21X_1^2 - 52.78X_2^2 - 112.34X_3^2 \quad (6)$$

Alpha-cellulose, % = $90.35 - 1.02X_1 - 0.81X_2 - 0.53X_3 + 0.03X_1X_2 + 0.39X_1X_3 - 1.34X_2X_3 - 0.23X_1^2 - 0.45X_2^2 + 0.43X_3^2$ (7)

Hemp.

Bleached pulp yield, % = $41.80 - 1.07X_1 - 0.51X_2 - 0.53X_3 - 0.35X_1X_2 + 0.50X_1X_3 + 0.47X_2X_3 - 0.48X_1^2 - 1.17X_2^2 - 0.77X_3^2$ (8)

DP = $554.64 + 15.56X_1 - 11.71X_2 + 7.17X_3 + 17.37X_1X_2 + 1.87X_1X_3 - 3.62X_2X_3 + 3.08X_1^2 - 9.64X_2^2 + 2.02X_3^2$ (9)

Alpha-cellulose, % = $89.81 + 1.26X_1 - 0.74X_2 + 0.79X_3 + 0.33X_1X_2 + 0.45X_1X_3 + 0.34X_2X_3 + 0.30X_1^2 - 0.58X_2^2 - 0.21X_3^2$ (10)

The F-values of these equations are 5.964, 4.420, 2.215, 5.023, 4.354, and 3.215, respectively. All six equations exceed the tabulated F-value of 2.2 determined for 10 degrees of freedom and 95% confidence limits *(31)*.

The estimated standard deviation values were found to be 1.245, 1.475, 1.099, 1.548, 1.832, and 1.411, respectively. Therefore, Eqs. 5–10 adequately describe the process behavior through the region studied.

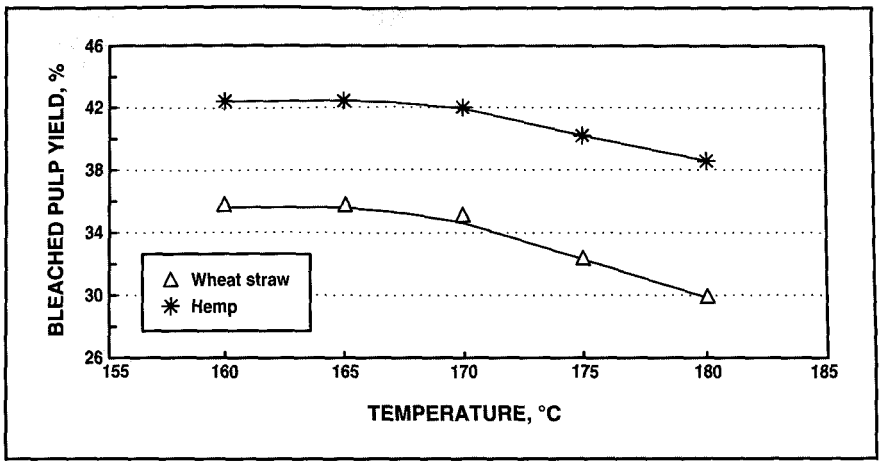
Process optimization

Based on the described regression analysis, the optimization problem could be formulated as follows:

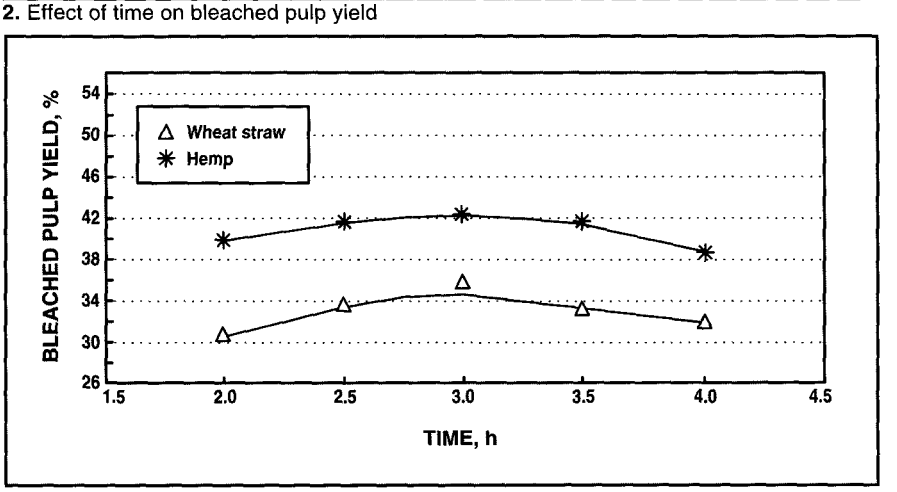
The bleached pulp yield (objective function), i.e., $Y = f_1(X_1,X_2,X_3)$, should be maximized as depicted by Eqs. 5 and 8, subjected to the degree of polymerization and alpha-cellulose content constraints, i.e., to DP = $f_2(X_1,X_2,X_3)$, as depicted by Eqs. 6 and 9, and to alpha-cellulose = $f_3(X_1,X_2,X_3)$, as depicted by Eqs. 7 and 10.

These equality constraints have been investigated by Rosenbrock's method *(32)* in an effort to locate the optimum process-control parameters. The applied "hill climbing" technique is efficient for optimizing nonlinear functions. Computer programs were set up to generate solutions for this optimization problem using regression equations. **Table VII** presents the calculated results that define the optimum pulping conditions. These calculated data were later confirmed experimentally, and

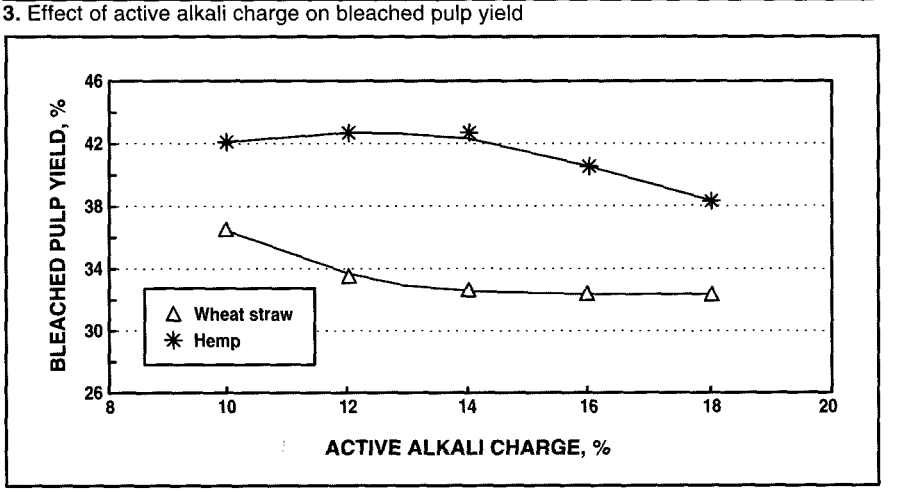
1. Effect of temperature on bleached pulp yield



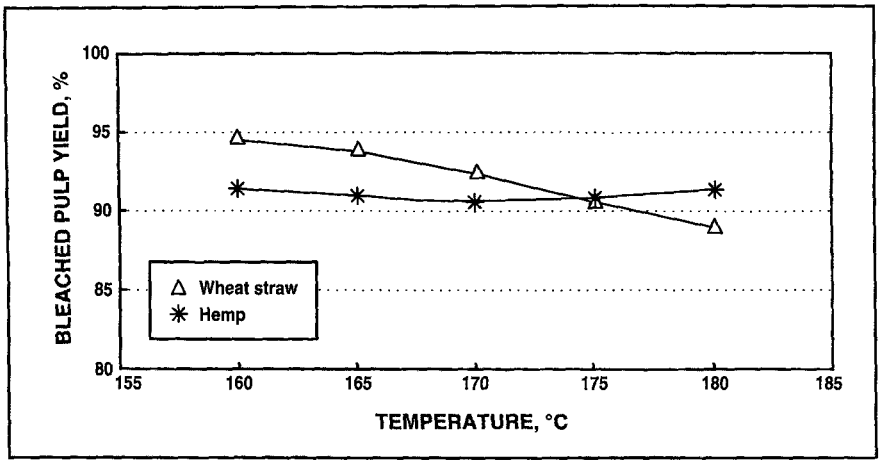
2. Effect of time on bleached pulp yield



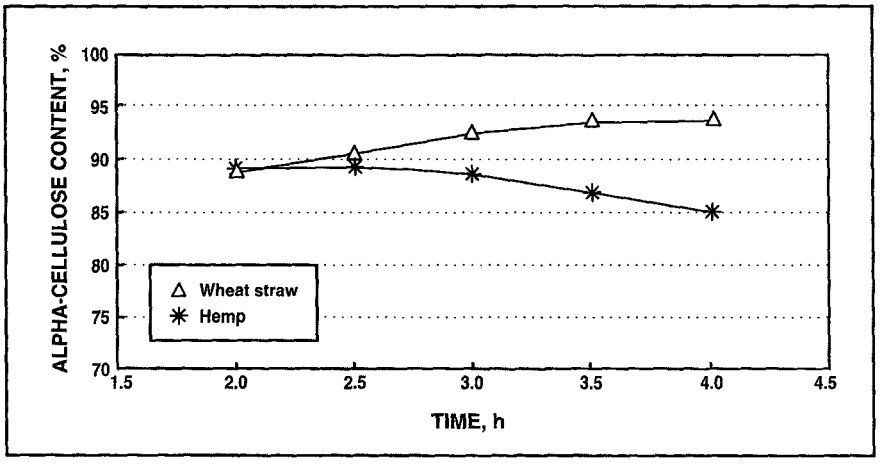
3. Effect of active alkali charge on bleached pulp yield



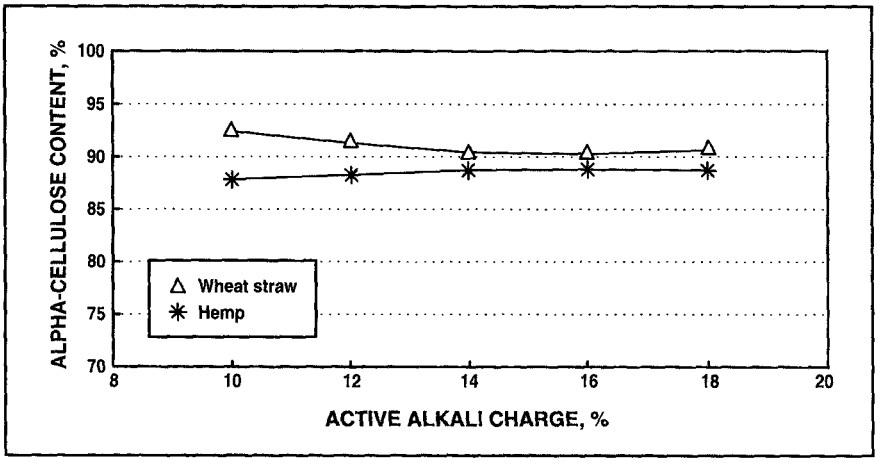
4. Effect of temperature on alpha-cellulose content



5. Effect of time on alpha-cellulose content



6. Effect of active alkali charge on alpha-cellulose content



these results are presented in Table VII as well. Satisfactory agreement is indicated between calculated and experimental optimal values.

The bleached pulp yield for hemp is clearly higher than that of the wheat straw. This is because the alpha-cellulose content of hemp is higher than that of the wheat straw (Table I).

The optimum conditions generated through Rosenbrock's method were confirmed experimentally (Table VII). Properties of dissolving pulps produced from wheat straw and hemp at these optimal conditions are presented in **Table VIII.** These properties compare favorably with the properties of a typical dissolving pulp produced from cotton linters, also presented in Table VIII.

Effect of process variables on bleached pulp characteristics

The nine figures presented in this article illustrate the effects of temperature, time of treatment, and concentration of active alkali on bleached pulp yield, alpha-cellulose content, and DP for wheat straw and for hemp.

Bleached pulp yield vs. temperature. At temperatures above 170°C, the bleached pulp yield of wheat straw and hemp pulps decreased with increasing temperature, as seen in **Fig. 1.** The relative loss in bleached pulp yield between pulping at 160°C and 180°C was 16.7% for wheat straw and 9.5% for hemp. The drop in bleached pulp yield is due to increased cellulose degradation at higher pulping temperatures. Pulping at high temperature also increases (a) dissolution of hemicelluloses and smaller molecular cellulose fractions in the alkaline pulping solution and (b) removal of solubilized lignin.

Bleached pulp yield vs. time of treatment. Increasing the time of treatment increased the bleached pulp yield for both wheat straw and hemp, as seen in **Fig. 2.** Maximum bleached pulp yield occurred at a treatment time of 3 h for both types of pulp. Longer pulping times caused a substantial loss in yield. Wheat straw showed a 20% increase in yield between the starting point and the optimum level, and yield suffered an

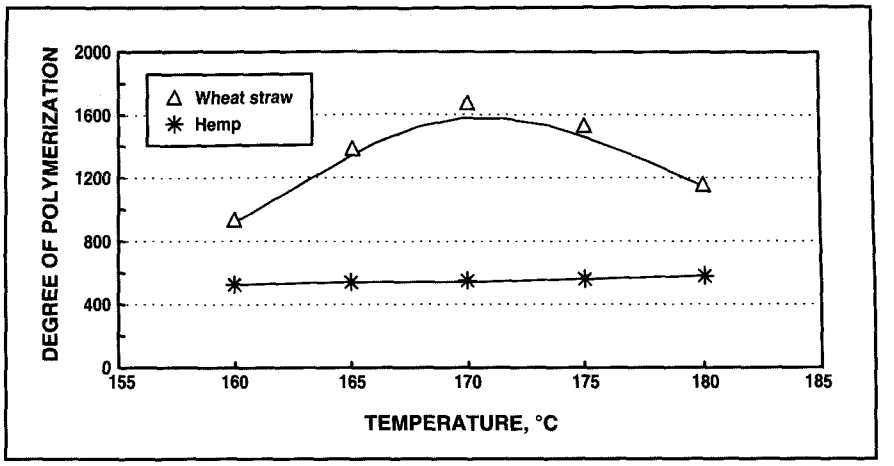
11% loss between the optimum and the endpoint of the curve. Hemp showed a 5% increase and a 7% drop in bleached pulp yield for the corresponding times of treatment. These phenomena reflect the effects of time and temperature on the rates of delignification and cellulose degradation.

Bleached pulp yield vs. active alkali charge. The bleached pulp yield of wheat straw decreased rapidly and then leveled off at active alkali concentrations above 14%, as seen in **Fig. 3.** In the case of hemp, the yield was constant initially and then decreased at alkali charges above 14%. The loss in yield for both pulps, between the starting and final value was 11%. At higher concentrations of sodium hydroxide solution, the degradation of cellulose and the solubilization of its fractions was faster.

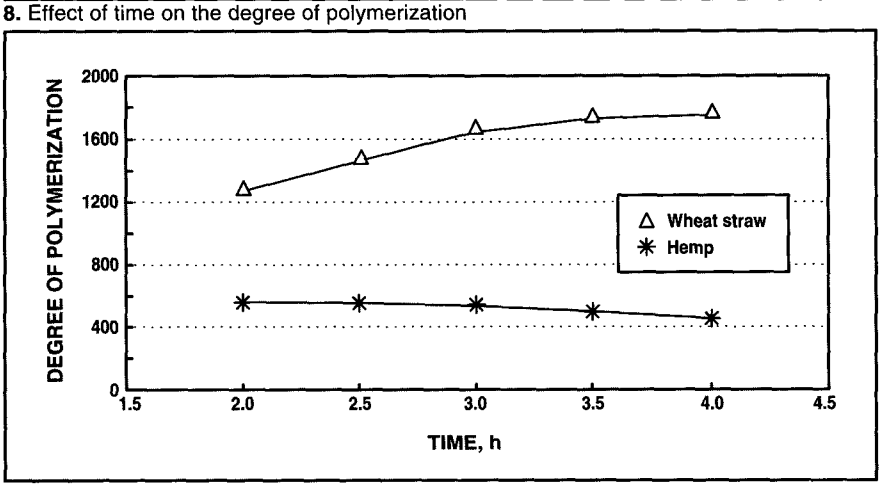
Alpha-cellulose vs. pulping temperature. As seen in **Fig. 4**, the initially high (95%) alpha-cellulose content of wheat straw pulp continuously decreased to 89% as the pulping temperature was increased. In contrast, the initially lower (91%) alpha-cellulose content of hemp pulp did not change over the range of pulping temperatures studied. The higher DP of wheat straw cellulose (1600–2000) was much more sensitive to alkaline degradation than the lower-DP hemp pulp. At higher temperature, the DP of wheat straw decreased to approach that of hemp as a limiting value. Consequently, more detectable amounts of alkali-soluble low-molecular-weight fractions were generated at the higher temperatures from wheat straw cellulose than from hemp cellulose.

Alpha-cellulose vs. pulping time. A completely different tendency was observed for changes in alpha-cellulose content with increasing pulping times. In the case of wheat straw at 170°C, the rate of delignification exceeded that of the alkaline cellulose degradation over the full range of treatment times.

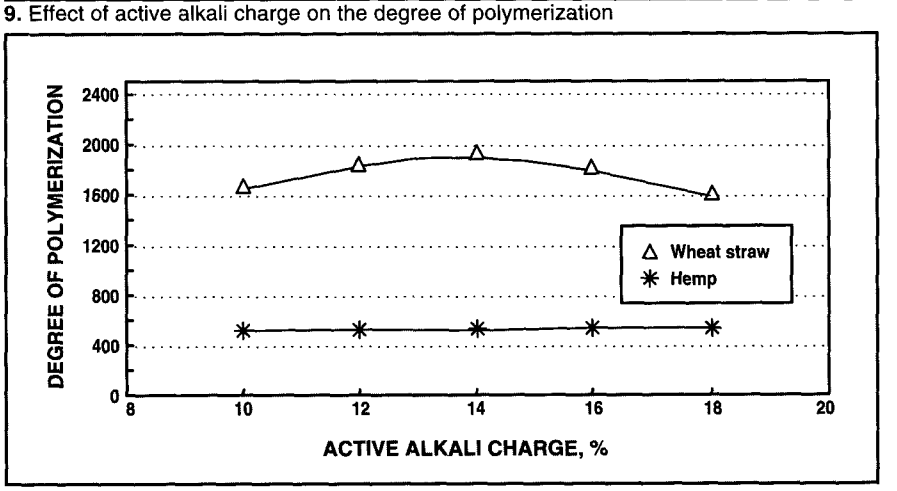
7. Effect of temperature on the degree of polymerization



8. Effect of time on the degree of polymerization



9. Effect of active alkali charge on the degree of polymerization



Consequently, a 5% increase was observed in alpha-cellulose content over that range, as seen in **Fig. 5.** Hemp pulps responded differently. The rate of hemp delignification was relatively low at 170°C. Therefore, the 4.5% drop in alpha-cellulose content might be due to degradation of

alpha-cellulose by alkali for pulping time lasting longer than 3 h.

Alpha-cellulose vs. active alkali charge. An 80% increase in the active alkali charge produced only a small (3%) loss in the alpha-cellulose content of wheat straw pulp, as seen in **Fig. 6**. There was practically no change in the alpha-cellulose content of hemp under similar conditions.

Degree of polymerization vs. temperature. The DP of the cellulose in the wheat straw pulp increased by 73% as pulping temperature was increased from 160°C to 170°C, as seen in **Fig. 7**. At higher temperatures (170–180°C), DP decreased continuously but still remained 21% higher than the values obtained at 160°C (DP=950). The DP of the cellulose in hemp pulp (DP=580) increased slightly over the full range of pulping temperatures studied (160–180°C).

Degree of polymerization vs. time. The DP of wheat straw pulp cellulose increased by 40% over the range of pulping times, as seen in **Fig. 8**. Maximal DP was achieved and leveled off after pulping for 3h. The DP of hemp pulp cellulose decreased by 14% as pulping time increased from 2 h to 4 h. However, no significant drop in DP occurred until pulping time exceeded 3 h.

Degree of polymerization vs. active alkali charge. The DP of cellulose in wheat straw pulp increased by 18% over the 10–14% range of active alkali charge, as seen in **Fig. 9**. DP reached a maximum at 14% and then decreased with higher alkali concentrations. The active alkali concentration of the pulping liquor did not affect the DP of the hemp pulp cellulose.

Conclusions

Optimized pulping conditions

A central composite rotatable experimental design was used to establish the optimum pulping and bleaching conditions for producing dissolving pulp from Hungarian wheat straw and hemp. The experiment focused on the effects of three key process variables: pulping temperature, time at temperature, and active alkali charge. The results show that the maximum bleached pulp yield for wheat straw is obtained by pulping at 170°C for 3 h with an active alkali charge of 10%. For hemp, maximum yield is obtained by pulping at 164°C for 3 h with an active alkali charge of 13.24%.

The validity of the calculated process variables was verified by pulping experiments performed at the identified optimum conditions. The differences between the experimentally obtained and the calculated bleached pulp yields were insignificant.

The properties of dissolving pulps produced from wheat straw and hemp were comparable with those of a cotton linters dissolving pulp. This indicates that wheat straw and hemp are adequate raw materials for production of cellulose derivatives.

Effect of optimized variables on pulp characteristics

Bleached pulp yield. Bleached pulp yield of hemp greatly exceeded that of wheat straw.

Wheat straw. Of the three process variables, pulping temperature had the greatest effect on bleached pulp yield, followed by alkali charge and pulping time.

Hemp. The three process variables showed a similar pattern for the hemp pulp, with the effects of temperature > active alkali > pulping time.

Alpha-cellulose content. The alpha-cellulose content in wheat straw pulp was noticeably higher than in hemp pulp.

Wheat straw. Temperature had the greatest effect on alpha-cellulose content, followed by pulping time and alkali charge.

Hemp. Pulping time had the greatest effect on alpha-cellulose content. Neither temperature nor active alkali charge affected the alpha-cellulose content.

Degree of polymerization. DP of wheat straw was much higher than that of hemp.

Wheat straw. Pulping temperature influenced the DP of cellulose from wheat straw pulp, with DP increasing up to 170°C and then falling at higher temperatures. It is likely that at higher temperature, the increased rates of dissolution of hemicellulose and low molecular fractions of cellulose were significantly higher than the rate of cellulose degradation.

Pulping time also influenced the DP of cellulose from wheat straw pulp, with DP increasing at longer pulping times. Apparently, the rate of dissolution of hemicellulose and depolymerized cellulose exceeded the rate of cellulose degradation over the range of pulping time studied.

The active alkali charge also influenced the DP of cellulose from wheat straw pulp. DP increases at low concentrations of active alkali because of the fast dissolution of low-molecular-weight depolymerized products and the simultaneous slow degradation of cellulose. However, higher alkali concentrations generate faster depolymerization of cellulose, causing the DP to decrease.

Hemp. Pulping temperature did not influence the DP of cellulose from hemp pulp. This independence of hemp pulp cellulose DP from pulping temperature might be due to (a) its lower initial DP (less sensitive to hot alkaline degradation at that range of molecular mass) and (b) the higher solubility of hemicellulose and depolymerized cellulose at 160°C (the lowest pulping temperature used in this study).

Pulping time did not influence the DP of cellulose from hemp pulp. This independence of hemp pulp cellulose DP from pulping time might be due to (a) the significantly higher initial depolymerization of cellulose (pulping for less than 2h) and/or (b)

the presence of less-sensitive types of hemicellulose in hemp.

The hemp pulp, which is initially more depolymerized than the wheat straw pulp, appears to be stable to further alkaline depolymerization over the range of alkali charge applied in this study (10–18%).

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