Hydrothermal pretreatment of wheat straw for the production of pulp and paper

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ABSTRACT

A chemical-free pretreatment process for the production of pulp is described. By treating wheat straw biomass with hot compressed liquid water (e.g, 200°C, 22 bar), almost all the hemicellulose and up to 62% of the lignin are extracted from the lignocellulosic matrix. The remaining solid residue, the pulp, consists of cellulose and residual lignin. Several modes of operation (percolation, recirculation, and combined modes) in a 10-L pilot plant were used for this investigation. The combined recirculation-percolation process is advantageous because of its low water and energy consumption. Bleaching was carried out by alkaline extraction and by using hydrogen peroxide only. Indications as to how bleaching can be improved are given. With unbleached pulp, paper tensile strengths of over 3 km were reached. Bleaching increased this value by approximately 1 km.

Application:

In this way, it is possible to produce technical-grade paper without the use of chemicals. With chlorine-free bleaching, pulps for different and higher requirements can be obtained. In addition, the biomass in the water extract can serve as chemical raw material, e.g., for saccharification and fermentation.

THE PRODUCTION OF HIGH-quality pulp from lignocellulosic plant material requires removal of the lignin. This is commonly carried out by treating the plant material with sulfur-containing chemicals. To reduce environmental pollution, these processes are usually performed in closed circuits, and all the chemicals and reaction products in this process are recycled. Increased environmental consciousness led to the development of alternative procedures in research laboratories and the pulp industry. Especially, pretreatment methods using only water in the form of steam or in the liquid phase, as well as mixtures of water with organic solvents, are of growing interest. All these processes are operated at approximately 200°C, thereby dissolving and sometimes decomposing the hemicellulose as, for example, in steam explosion *(1–4)* and steam extraction *(5)*. Varying amounts of lignin can also be extracted by these procedures, depending on the liquid phase formed during operation *(6, 7)*.

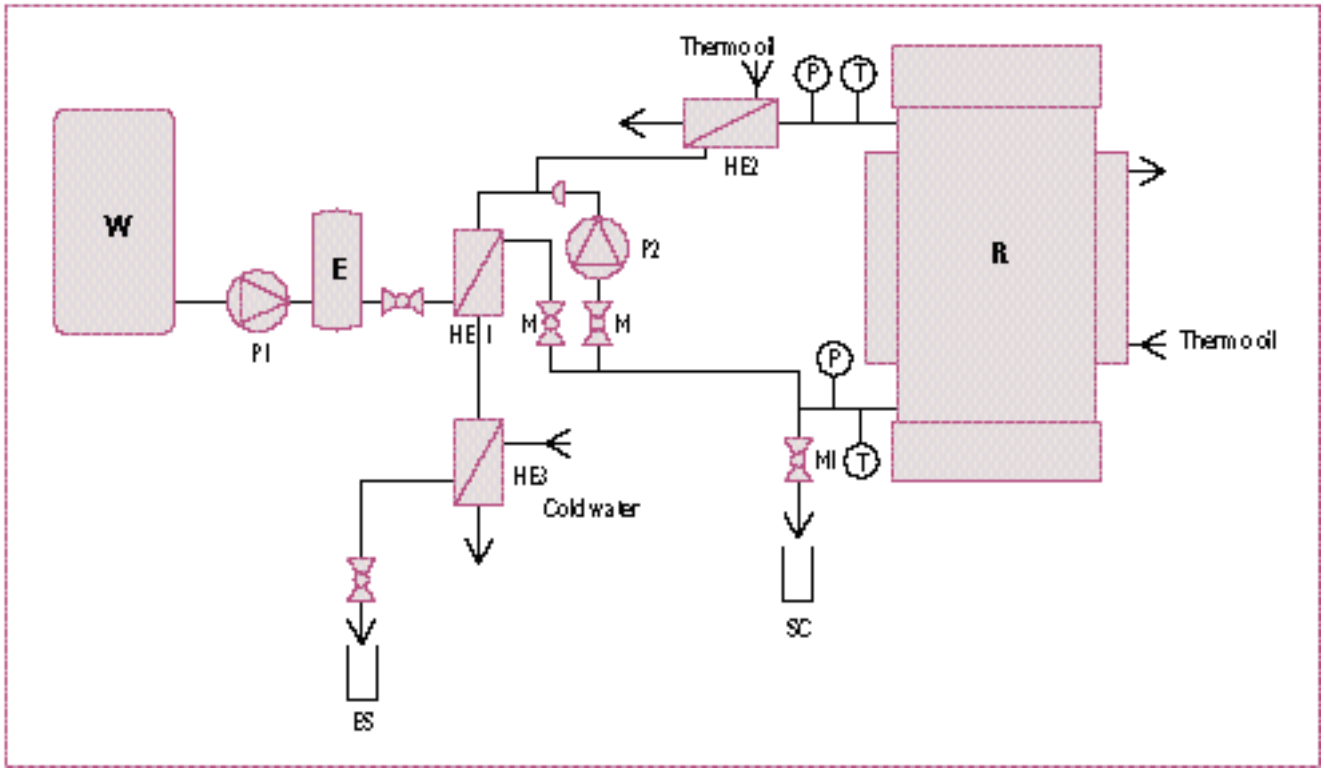
The organosolv process, for example using 50% ethanol and 50% water, was introduced in 1931 by Kleinert *(8)* and further developed in recent years *(9)*. The closure in 1993 of the 350-tons/day plant *(10)* in Kehlheim, Germany, after one year of operation was a severe drawback for this process.

Hydrothermal pretreatment (hydrothermolysis) was introduced in 1968 *(11)*. In this case, hot compressed water (e.g., 180–220°C at 1.1–2.4 MPa) is led through the biomass-filled reactor, thereby extracting 30 to 60% of the plant biomass *(6, 12–14)*. The process is also called "Aquasolv," and practically all the hemicellulose and a considerable part of the lignin are dissolved *(15)*. According to the relevant experiments *(12, 15, 16)*, the amount of biomass extracted can be prognosed with relatively high accuracy; this favors hydrothermolysis in comparison with steam extraction.

Organosolv renders results very similar to those of the hydrothermal treatment, as long as both processes are operated in a direct percolation mode *(6)*. Using wheat straw, the dissolved, extracted part of the biomass is, in the case of hydrothermolysis, even somewhat higher than in organosolv *(12)*. Organosolv, however, is mainly carried out by recirculating the liquid until the hemicellulose and the dissolved lignin are degraded and therefore lost as chemical raw material. In the case of hardwood, the slightly higher dissolving power of organosolv in comparison with hydrothermolysis *(12)* probably does not compensate for the higher additional costs of the extracting liquid, fireproof installations, and other environmental precautions.

The purpose of this paper is to evaluate different hydrothermal process modes using wheat straw as biomass. Thereby the high water- and energy-consuming percolation (direct flow-through), the recirculation that leads to severe biomass degradation when carried out too long, and a combined process had to be investigated, especially in regard to their ability to produce a pulp that gives good paper properties.

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1. Hydrothermal pretreatment equipment: high-pressure pump (P1), recirculation pump (P2), heat exchangers (HE1, HE2, HE3), water storage tank (W), expansion vessel (E), reaction vessel (R), extract storage tank (ES), sampling valve (M1), and sample collector (SC)

EXPERIMENTAL

Hydrothermal extraction experiments

The hydrothermolysis experiments were carried out using a pilot plant with a reactor volume of 10 L, made according to our specifications. Figure 1 depicts the schematic flow diagram of the apparatus. The plant material is held in the cylindrical reactor by means of two sieve plates, which are connected with the upper and lower screw cap. The biomass, chopped wheat straw (2–5 cm), is fed batchwise into the reaction vessel. The amount of straw filling in the reactor was usually in the region of 0.9–1.0 kg, calculating the biomass as dry matter. Pressure and flow rate are controlled by a sensor and a regulation valve, respectively.

Percolation (PC)

In this operational mode, fresh water is led from a 1500-L water storage tank (W in Fig. 1) by the high-pressure pump (P1) through an expansion vessel (E) and the heat exchangers (HE1 and HE2) into the reaction vessel (R). From there, the liquid flows over the heat exchangers (HE1 and HE3) and is collected in the extract storage tank (ES). The second heat exchanger (HE2) brings the water to the chosen reaction temperature using an electrical heating unit with thermo-oil. The reactor itself is covered with a heating mantle that is also operated by thermo-oil. Samples for analysis can easily be taken from the valve leading to the extraction storage tank (ES). The flow rate of the extracting water through the reaction vessel was 3–4 L/min.

Recirculation (RC)

The liquid eluate is pumped from the reaction vessel over the heat exchanger (HE2) and back into the reactor by means of a recirculation pump (P2). Small samples can be collected (SC) through valve M1 and a cooler not indicated in Fig.1. This recirculation method requires only one volume of water and therefore saves energy. The residence time of the biomass at the reaction temperature in both the recirculation and percolation modes was 15–50 min at flow rates of 3–9 L/min.

Combined recirculation and percolation (RC + PC)

In this combined operation, first recirculation is applied until the desired reaction temperature is reached, and then this mode is continued for approximately 10 min until a high concentration of dissolved biomass is obtained in the liquid. Afterwards, the percolation mode is used. In this combined process, the hemicellulose can be

Bleaching step:	E	P
Consistency, %	7	9
Residence time, min	120	120
Temperature, °C	70	80
pH at start	-	12.0
pH at end	-	10.3
Peroxide, %	-	4
NaOH, %	3	2
Na_2SiO_3, %	-	9
$MgSO_4$, %	-	0.05
EDTA or DTPA, %	-	0.5

*The applied RC+PC process was carried out at about 187°C, the cooking yield was 60%, the delignification was 49.5%, and the reaction time after recirculation was 15 min. The breaking length was 3.1 km, and the brightness was 32.7%.

I. Bleaching conditions for hydrothermally pretreated wheat straw (WS 21) (E=alkaline extraction, P=peroxide bleaching). The amount of chemicals added is related to the ovendry material.*

Exp. no.	Approx. reaction temp., °C	Reaction time, min	Delignification, %	Cooking yield, %
WS 8	182	25	34.4	70.5
WS 20	190	10	50.6	58.1
WS 13	192	15	49.5	61.8
WS 5	195	15	58.0	61.5
WS 15	200	30	44.4	58.0
WS 11	204	30	53.4	51.1

II. Delignification and cooking yields of hydrothermally treated wheat straw at different temperatures. The reaction times are counted after the initial recirculation mode. For all experiments, the combined process (recirculation and percolation) was applied.

recovered from the eluate with very little degradation.

Pulp bleaching

The residual solid biomass is transferred to a specially made 45-L vessel provided with a heating system. Then the pulp is diluted to 4% consistency and unraveled for 30–60 min at 60–70°C with 700 rpm. Subsequently, totally chlorine-free (TCF) peroxide bleaching is carried out at 5–10% consistency under stirring (700–1400 rpm) for 1–2 hours. The bleaching was terminated by transferring the pulp into a vessel provided with a sieve and washed with water.

In these experiments, only two simple bleaching processes were applied: alkaline extraction (E) and peroxide treatment (P). An example of the bleaching conditions is given in Table I.

Analysis and paper testing

The wheat straw raw material and the solid residue (pulp) were analyzed according to TAPPI Test Methods, but only the lignin values are relevant in this context (TAPPI T 222 om-88). The dry matter content (DM) of the solution and the cellulosic residue were determined after drying at 105°C.

For the paper and pulp parameters, the air-dried pulp samples were soaked in water to reach 2% consistency. Standard test sheets and their investigation were prepared according to TAPPI Test Methods.

RESULTS

The separation of cellulose and hemicellulose is achieved by hydrothermal treatment with relatively short residence times (10–20 min) and moderate temperatures (approx. 200°C). This enables a subsequent utilization of both the cellulosic residue and the liquid eluate containing the hemicellulose. Lignin is distributed approximately equally between the liquid and the solid phase. The combined process (190–204°C) rendered delignification values between 44.4 and 58.0%. The lowest reaction temperature (approx. 182°C), however, yielded only 34.4% delignification (Table II).

As this table shows, the cooking yields in the combined process are from 51.1 to 70.5%. The lowest reaction temperature resulted in a surprisingly high yield but was accompanied by relatively low delignification. Generally, approximately 30–60% of the original amount of material (on a dry matter basis) is solubilized during hydrothermolysis in the investigated temperature region of 180–230°C *(6, 12)*. Depending on the mode of operation, a higher concentration of dissolved material in the liquid eluate or a higher degree of delignification in the solid cellulosic residue can be adjusted. For most purposes, a combined mode of recirculation and subsequent percolation may be applied to obtain the desired products.

Due to the fast dissolution of hemicellulose and part of the lignin, hydrothermolysis does not produce ultra-high pulping yields as does steam explosion with Na_2SO_3-impregnated wood chips *(17, 18)*. This advantage of steam explosion, however, is due to a significant 8–16% sulfite addition.

Hydrothermal process parameters

In the *percolation mode*, fresh water is pumped over the heat exchangers and through the reactor loaded with wheat straw. Figure 2 shows a percolation experiment (elution profile). With the equipment used, the rise in temperature to reach the final value of 195°C takes approximately 20 min. The maximum concentration in the liquid eluate (DM = dry matter) coincides with the minimum pH value of the solution. The solubilized mater-

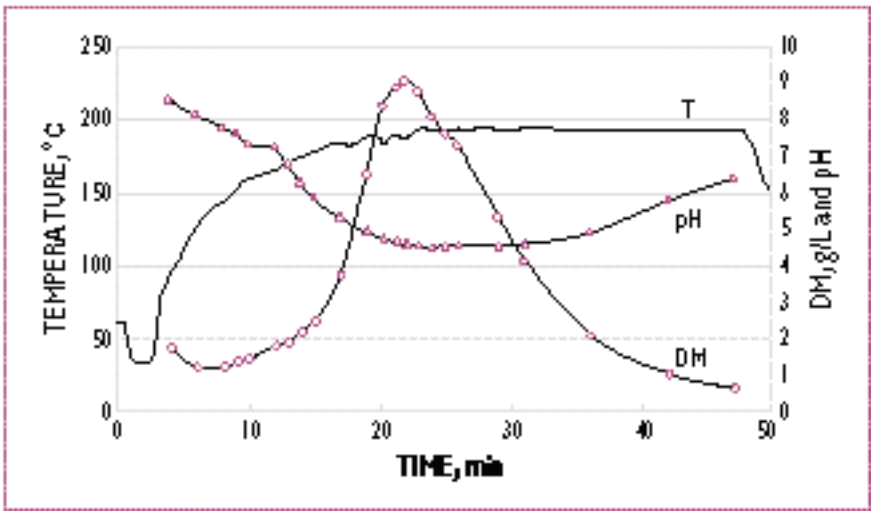
ial reaches 9.1 g/L at the peak, thereby decreasing the pH value to 4.5. The flow rate applied in this experiment was 3 L/min. If only the solution with the main dry matter peak (20 min) were to be collected for further usage, 60 L of water would be used, and the dissolved 0.39 kg of biomass would give a 0.65% concentrated solution. This low concentration makes an economical use of the dissolved hemicellulose and lignin rather difficult.

The cooking yield of the percolation experiments in the range of 190–230°C can be mathematically approximated by including earlier measurements *(12)* using the following linear relation:

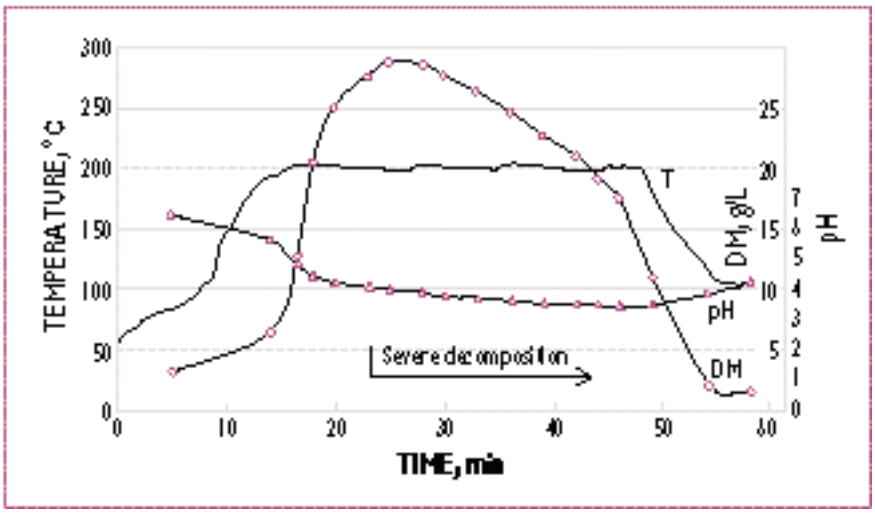
$$Y = 130 - 0.38T \qquad (1)$$

where Y is the cooking yield (%) and T is the cooking temperature in degrees C. In a series of experiments carried out with wheat straw, reaction temperatures and times were varied from 183 to 205°C. The reaction time was always long enough for the biomass concentration in the extracting water to become very low, thereby dissolving the maximum amount of hemicellulose and lignin. Thus it was not necessary to take the reaction time into account in Eq. 1. High degrees of delignification were obtained with the pure water treatment (up to 62%). This makes the process suitable for technical paper grades, e.g., paperboard.

The evaluation of these experiments gives valuable information on the physical chemical background of the hydrothermal process: Only an 11% decrease of the molecular weight of the cellulose was measured after a 32-min treatment at 195°C *(19, 20)*, which seems very moderate. The hemicellulose is almost completely dissolved and degraded only so far that solubility in water is reached *(15)*. Lignin is partially transformed to smaller soluble aggregates *(21)*.

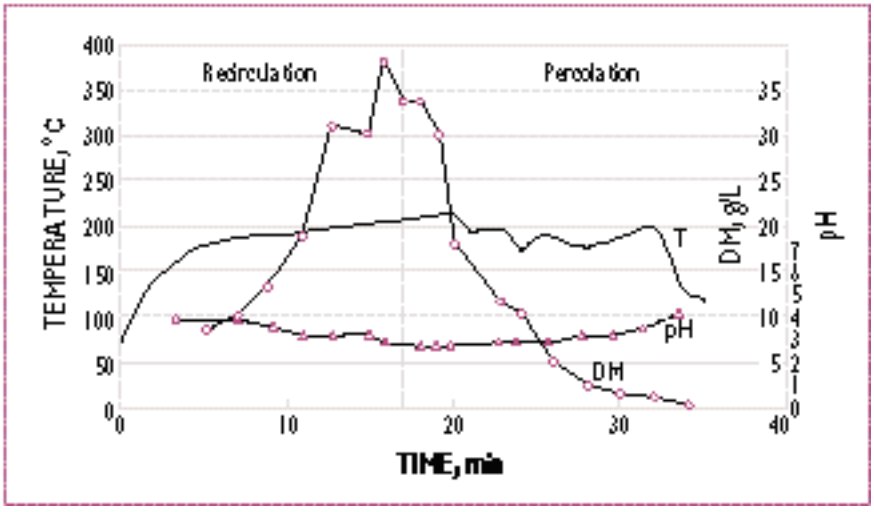


2. Hydrothermal percolation experiment (PC) using wheat straw as biomass (elution profile). DM=dry matter in solution (g/L), pH is that in solution, T=temperature (°C) in the reaction vessel.



3. Hydrothermal recirculation experiment (RC) using wheat straw as biomass (extraction profile). DM=dry matter in solution (g/L), pH is that in solution, T=temperature (°C) in the reaction vessel.

Recirculation. The situation changes if the process is carried out by recirculating the eluate repeatedly through the reactor by means of a recirculation pump. Equation 1 is no longer directly applicable. But this process mode is advantageous for energy- and water-saving reasons, and the reaction temperature can be achieved more quickly, as demonstrated in Fig. 3. It takes only 15 min to reach the final temperature, and by recirculating the eluate, the maximum concentration of solubilized material can be more than tripled from 9.1 g/L in Fig. 2 to 28.8 g/L in Fig. 3.



4. Combined hydrothermal process (RC+PC) using wheat straw as biomass (extraction and elution profile). Up to 27 min, the operation mode is recirculation; after this time, percolation is applied. DM=dry matter in solution (g/L), pH is that in solution, T=temperature (°C) in the reaction vessel.

Exp. no.:	WS 2		WS 4		WS 5	
Process mode	RC		RC		RC+PC	
Reaction temperature, °C	204		202		192	
Reaction time, min	50		30		15	
Yield (*Y*), %	59.2		52.0		60.1	
Klason lignin, %	21.2		20.4		14.5	
Delignification, %	39.2		48.7		58.0	
Freeness, °SR	30	50	30	50	30	50
Thickness, mm	0.305	0.209	0.317	0.224	0.280	0.186
Density, kg/m^3	250	381	247	377	278	459
Breaking length, km	0.93	1.63	1.11	2.06	2.31	3.35
Bursting index, kPa·m^2/g	0.63	0.66	0.61	0.94	1.13	2.21
Tearing index, mN·m^2/g	2.01	1.58	4.11	3.89	5.60	6.28

III. Comparison of process parameters and pulp properties of three unbleached hydrothermally pretreated wheat straw samples. Process modes: RC=recirculation and RC+PC=combined process.

On the other hand, the process should not be carried out for too long, since reactive low-molecular hemicellulose and lignin degradation products can deteriorate the fiber properties by recondensation reactions. This situation is also shown in Fig. 3: After about 25 min reaction time, the concentration in the recirculated liquid decreases strongly. Obviously, recondensation occurs, and the water-insoluble products are adsorbed by the straw biomass. These are lignin-like substances, which considerably reduce the final degree of delignification *(22)*. In this experiment, the delignification was only 19%. The maximum concentration in the extracting liquid can only be kept for a limited time.

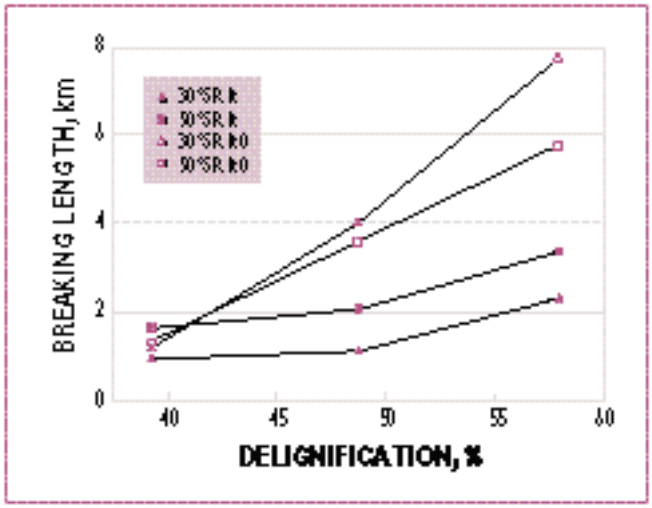
Combined process. To utilize the advantages of recirculation and percolation, a combined mode was set up. During the stage of heating the system and the biomass, recirculation was chosen. Only one reactor volume of water is necessary to reach the final temperature, thereby making sure that a high energy reduction is obtained in this mode. After the temperature is reached and held for approximately 10 min, the system is switched to operate by percolation (Fig. 4). The highest concentration of undegraded solubilized material is obtained if the process mode is switched when the pH minimum is reached. In this way, both recondensation and degradation reactions are considerably reduced. The whole process is finished after 30 min; from this time on, only negligible amounts of solubilized material are eluated. This period of 30 min could certainly be reduced in a technical plant by shortening the heating time and by faster elution in the percolation state.

Remarkably low Klason lignin contents in the cellulosic residue of 14.5–15.5% were found in the temperature range of 192–194°C and 14–16 min reaction time. Consequently, with a combined process, it is possible to obtain maximum delignification and minimum decomposition of the dissolved material.

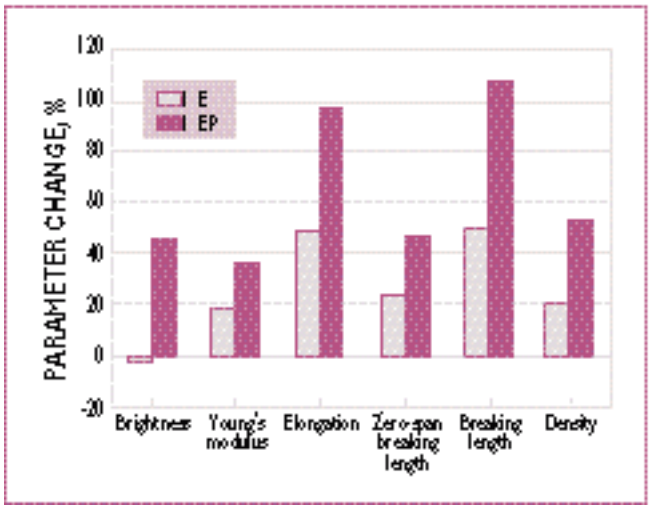
Pulp and paper properties

Unbleached pulp. With paper pulps, the fiber length, mechanical properties, and chemical composition play an important role. It was not until recently that mainly long fiber pulps were used for the production of paper. Short fiber pulps, as from deciduous woods and annual plants, are being increasingly used for this purpose, because these materials are beaten more easily.

Hydrothermal pulps have properties related to those of mechanical ones. The pulps were beaten to a freeness of 30° and 50° Schopper-Riegler, which equals 435 mL and 227 mL CSF, respectively.



5. Influence of delignification (DL in %) and beating (in °SR) on the breaking length of hydrothermally treated wheat straw. lt=breaking length, lt0=zero-span breaking length. The process data are depicted in Table III.



6. Changes of parameters after E and EP bleaching. Wheat straw (WS 21) was treated by the combined RC+PC process at 187°C. Reaction time was 15 min, cooking yield obtained was 59.9%, and breaking length after bleaching (Table I) was 3.1 km.

KEYWORDS
Alkali extraction, bibliographies, biomass, circulation, hemicelluloses, lignins, paper properties, percolation, peroxide bleaching, pretreatment, pyrolysis, recycling, wheat straw.

Table III shows a comparison of the properties of three unbleached hydrothermal pulps, two obtained in the recirculation process (WS2 and WS4) and the other in the combined process (WS5). The combined process is clearly superior to recirculation; the yield is higher, the lignin content is lower, and the delignification and paper strength properties are better. In addition, these positive results are obtained at a lower reaction temperature and in a shorter reaction time. The degree of delignification and the freeness have a most significant influence on the mechanical properties (Fig. 5). The zero-span breaking lengths are more influenced by the degree of delignification, but the breaking lengths of the test sheets also increase with increasing delignification. Both results indicate that the combined process (RC+PC) produces better paper qualities than the lignin-richer RC process. In addition, a lower lignin content leads to an increase of the tearing resistance and the bursting strength of the paper. The delignification (DL in %) was calculated according to Eq. 2:

$$DL = 100\left(1 - \frac{KL \cdot Y}{100 \cdot KL_0}\right)$$

where KL_0 is the Klason lignin content of the straw raw material (KL_0= 20.67%), KL is the Klason lignin percentage of the hydrothermally pretreated straw, and *Y* is the cooking yield in percent.

Bleached pulp. To compare hydrothermal pulps with pulps obtained from other processes, the cellulosic residue was bleached with a TCF bleaching sequence (Table I). By using a low-concentration peroxide bleaching and a beating to 40°SR, a brightness of 32.7% and a breaking length of 3.1 km were reached. The mechanical fiber properties were determined after beating and compared with the unbleached pulp samples. A distinction can be made between the bleaching sequences regarding whether the pulp was only extracted with alkali or subsequently bleached with peroxide. Except for the brightness, every mechanical parameter is improved (Fig. 6).

In an EPP bleaching process (one alkaline and two peroxide steps) *(23)* with very high peroxide concentrations (e.g., 20 and 30% on a dry pulp basis), the brightness values were increased from 20 to 80%. A new high-temperature alkaline extraction step *(24)* has been developed. This considerably more economical process, tested on small hydrothermal 10-mL laboratory percolation equipment, enables high delignification. At 175°C, a 5% alkaline solution was able to remove an additional two-thirds of the lignin from hydrothermally pretreated straw. This alkaline treatment reduced the 16–18% Klason lignin value to a 6% content.

CONCLUSIONS

Of the three hydrothermal processes investigated [direct percolation (PC), recirculation (RC), and the combined process (RC + PC)], the latter demonstrated several advantages: (a) the water consumption, and with it the energy requirements, were relatively low, (b) the straw could be beaten in a very short time *(25),* and (c) the liquefied hemicellulose and part of the lignin can be recovered in a fairly high concentration and used as chemical raw material [e.g., for saccharification *(26)*].

The combined process gives a pulp with a content of approximately 16–19% lignin. With a low alkaline extraction and peroxide-bleaching process, brightnesses of about 33% can be obtained. Hot alkaline extraction *(24)* and $NaOCl_2$ treatments *(25)* improve the bleaching conditions considerably.

The highest breaking length for unbleached samples (3.4 km) and slightly bleached test sheets (4.3 km) were also achieved with the combined process. TJ

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