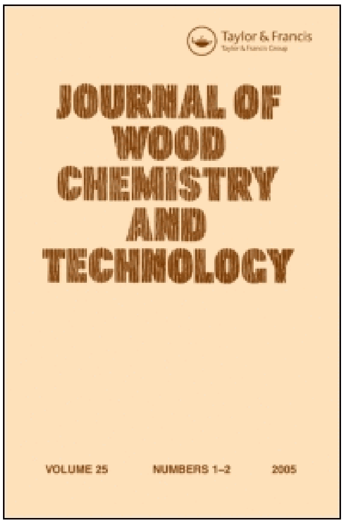

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# THE EFFECT OF SOLVENT ON THE OXYGEN OXIDATION OF POLYSACCHARIDES

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## KEYWORDS

Alcohols, aldonic acids, alkaline pulping, anthraquinone, cellobiose, end groups, ethanol, hydrocellulose, oxidation, oxygen, stabilization.

## ABSTRACT

The extent to which oxygen can stabilize polysaccharides against alkaline degradation was studied. The conversion of aldehyde end groups to aldonic acid groups (mainly arabinonic and erythronic acids) was accelerated markedly when cellobiose, hydrocellulose, or wood chips were treated in aqueous alkali with oxygen in the presence of anthraquinone monosulfonate. Change of the solvent to aqueous ethanol gave an even more pronounced effect without any additive. Other alcohols (methanol, *n*-propanol, *n*-hexanol, and ethylene glycol) gave a similar effect. After an oxidative pretreatment, the alkali stability of hydrocellulose (at 100 °C) was increased from about 50 % to more than 90 %. When the pretreated chips were pulped in soda-AQ liquor, the rate of delignification was substantially increased. The effect of oxidation on the stabilization of wood polysaccharides, however, was small because of the low stability of the aldonic acid end groups formed at higher temperatures.

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Based on the paper presented at the Ekman-Days 1981, The International Symposium on Wood and Pulping Chemistry, the Swedish Association of Pulp and Paper Engineers and the Swedish Forest Products Research Laboratory, co-sponsored with EUCEPA, TAPPI, and CPPA, Stockholm, June 9-12, 1981. SPCI report No. 38, Vol. 2, 90-93.

## INTRODUCTION

One of the most serious drawbacks of alkaline pulping processes is the extensive degradation of polysaccharides resulting in a low pulp (or carbohydrate) yield[1]. Although various treatments for the stabilization of polysaccharides have been proposed, none has proved very successful.

As found by Bach and Fiehn[2] the alkali stability of hydrocellulose can be markedly improved by treatment with an excess of anthraquinone-2-sulfonate (AMS) or other sulfonated anthraquinones in alkaline solutions. Later Ruoho and Sjöström[3] observed that the amount of AMS required can be substantially decreased in the presence of oxygen because the hydroquinone formed ($AMSH^-$) is reoxidized by oxygen, as shown in Fig. 1. Hydrogen peroxide, formed simultaneously, probably also plays an important role in the oxidation reactions.

The initial purpose of this study was to learn more about the possibilities of stabilizing carbohydrates with an oxygen-quinone system. Rather unexpectedly, it was observed that the carbohydrate stabilization was greatly improved when the oxidation was carried out in alcohol-water solutions instead of water alone. Consequently, additional experiments were performed to investigate the effect of the solvent.

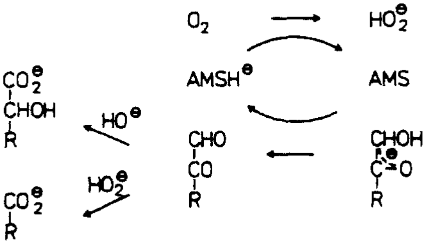

FIGURE 1. Formation of aldonic acids by AMS in the presence of oxygen. R is a carbohydrate residue.

## RESULTS AND DISCUSSION

The effect of oxidation on the alkali stability of hydrocellulose at 100 °C deserves a few comments. These alkali stability values are directly related to the introduction of aldonic acid end groups, which are essentially stable at this temperature. As can be seen from Fig. 2, hydrocellulose was stabilized effectively with AMS in the presence of oxygen and alkali, and only 0.5 % of AMS was needed to decrease the yield loss of hydrocellulose (DP 120) by 50 %. A corresponding treatment in nitrogen atmosphere resulted only in a minor improvement of alkali stability. A similar treatment with anthraquinone (AQ) instead of AMS gave almost no effect, obviously because of the low solubility of AQ in aqueous alkali solution.

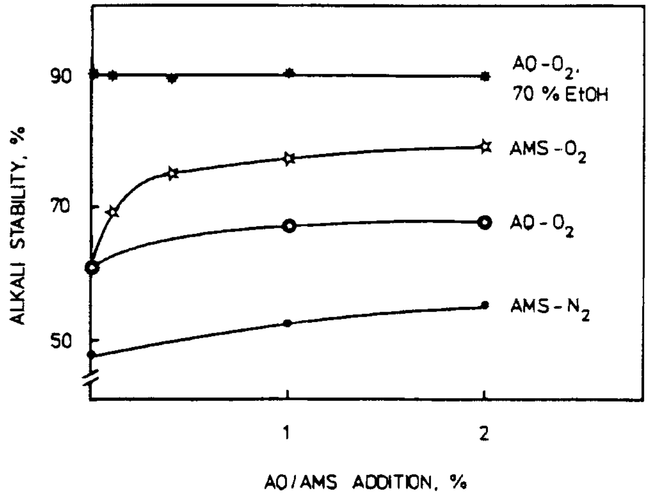

FIGURE 2. Effect of some pretreatments on the alkali stability of hydrocellulose; % AQ or AMS based on weight of hydrocellulose. Pretreatment conditions: 100 g hydrocellulose/dm$^3$ 0.2 M NaOH, $O_2$ or $N_2$-pressure 600 kPa, reaction temperature 70 °C (max.), reaction time 90 min, Mg(OAc)$_2$ addition 1 % on hydrocellulose (in the presence of oxygen). Alkali stability determination: 8 g hydrocellulose/dm$^3$ 1 M NaOH, 3 hours at 100 °C.

In order to increase the solubility of AQ, water was replaced by 70 % ethanol. The alkali stability of hydrocellulose was improved significantly. Further experiments, however, showed that this was because of the solvent; AQ had practically no influence on the stabilization of cellulose.

The effectiveness of the stabilization of cellulose in alcohol-water solution was further shown by the fact that an oxygen pressure of only 100 kPa was sufficient for maximum stabilization (Fig. 3). Experiments carried out at a temperature interval of 50-90 °C showed that the selectivity of the oxidation was slightly improved at lower temperatures. Increasing alkalinity also accelerated the oxidation up to pH 13.3 above which the selectivity decreased again (Fig. 4).

It was obvious from these experiments that the stabilizing effect of oxygen depended on the polarity of the solvent; Fig. 5 amplifies this observation. In the case of ethanol, the oxidation was still effective in 30 % concentration, whereas for *n*-propanol

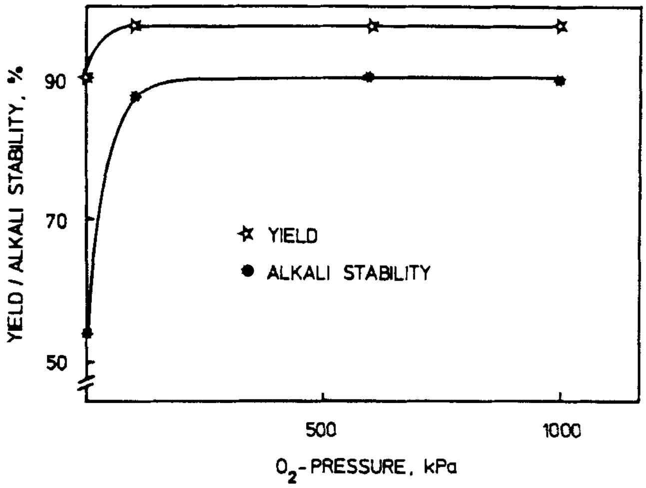

FIGURE 3. Effect of oxygen pressure on the oxidation of hydrocellulose in 70 % ethanol. Other reaction conditions as in Fig. 2.

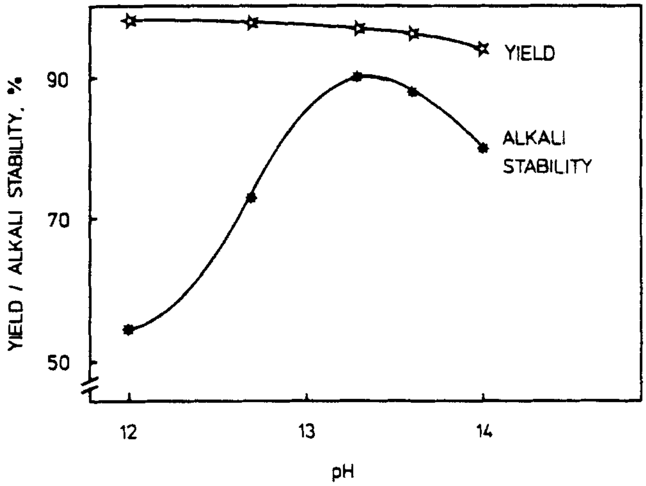

FIGURE 4. Effect of alkalinity on the oxidation of hydrocellulose in 70 % ethanol. Other reaction conditions as in Fig. 2.

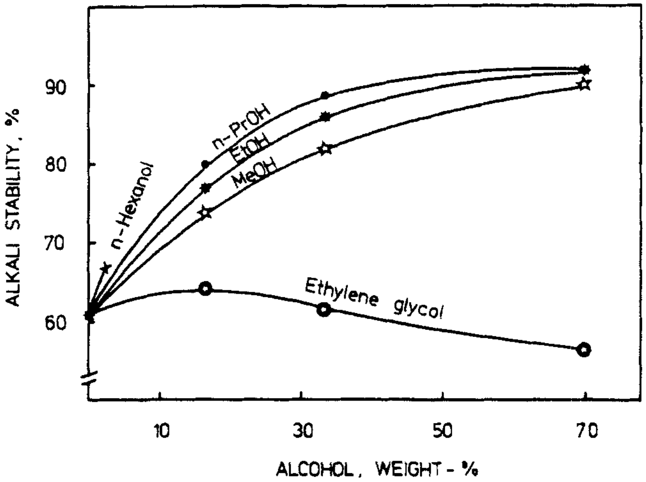

FIGURE 5. Effect of some alcohols on the oxidation of hydrocellulose. Other reaction conditions as in Fig. 2.

the corresponding concentration limit was about 25 %, and for methanol, about 40 %.

Table 1 shows the composition of acid end groups introduced into hydrocellulose after various oxidative treatments. After both AMS-oxygen and oxygen oxidations, the aldonic acid end groups were composed mainly of erythronic and arabinonic acids, and only small amounts of mannonic and gluconic acid end groups were present. The total amounts of acid end groups formed are in quite good agreement with the observed alkali stability data.

The arabinonic acid end groups were degraded extensively in alkali at 160 °C, in accordance with previous findings[4,5]. Surprisingly, however, erythronic acid end groups also showed low stability, contrary to earlier observations[4,5]. To study the extent to which an oxidative pretreatment of polysaccharides can

TABLE 1

Relative Composition (%) and Total Amount of the Acid End Groups Introduced into Hydrocellulose by Various Treatments. For Reaction Conditions, See Fig. 2.

| Acid | $O_2$ | $AMS-O_2$[a] | $EtOH-O_2$[b] | $EtOH-O_2$[b,c] |
|---|---|---|---|---|
| Erythronic | 55 | 44 | 49 | 9 |
| Arabinonic | 40 | 47 | 46 | 1 |
| Gluconic and mannonic | 5 | 9 | 5 | 12 |
| Metasaccharinic | d | d | d | 54 |
| 2-*C*-Methylglyceric | d | d | d | 24 |
| Total amount, mmol/kg | 10 | 23 | 39 | 15 |

[a] 1 % AMS
[b] 70 % EtOH
[c] After alkali stability determination at 160 °C
[d] Less than 1 %

prevent their degradation at higher temperatures, further alkali stability tests were performed above 100 °C. Hydrocellulose samples treated either with AMS–oxygen in aqueous alkali or with oxygen in 70 % ethanolic alkali were tested. As a reference, a hydrocellulose sample treated with sodium borohydride was included because of the high alkali stability of alditol end groups[4,5]. As could be expected from the amount of arabinonic acid end groups, a great deal of the stabilizing effect was lost after treatment at higher temperatures (Fig. 6). Even at 160 °C, however, the alkali stability of oxidized hydrocellulose was significantly higher compared with that of the untreated sample.

The effect of the solvent (alcohol) on the oxidation efficiency of hydrocellulose is probably the result of one or more of the following factors: (i) increased solubility of oxygen, (ii) increased rate of oxygen transfer from gaseous phase to liquid phase, (iii) increased rate of oxygen transfer from

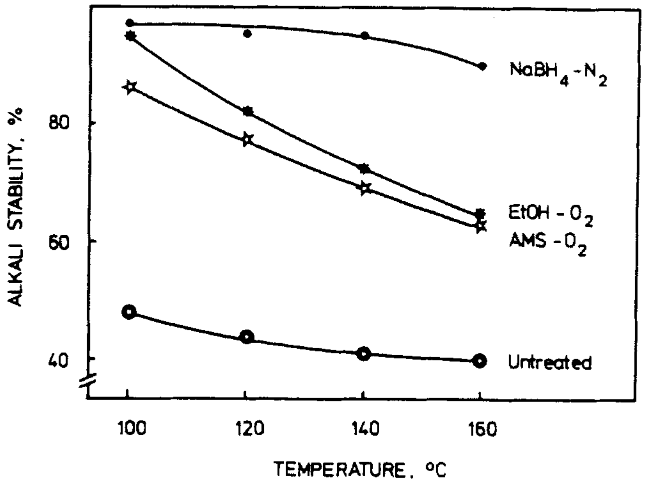

FIGURE 6. Effect of some pretreatments on the alkali stability of hydrocellulose. Pretreatment conditions: as in Fig. 2; NaBH$_4$ addition 5 %, AMS addition 1 %, 70 % ethanol. Alkali stability determination: 10 g hydrocellulose/ dm$^3$ 1 M NaOH, 4 hours.

liquid phase to solid phase, (iv) effect of the solvent on chemical reaction rates.

The importance of these factors is closely associated with the solubility of oxygen, which is markedly increased at higher ethanol concentrations[6]. The same tendency was also evident in the results reported here though the values are lower than the literature data because of the presence of alkali (Fig. 7).

The above experiments have shown that hydrocellulose is stabilized in 70 % ethanol at fairly low oxygen pressures. For example, the alkali stability of hydrocellulose treated at an oxygen pressure of 100 kPa was increased from 46 % (untreated sample) to 87 %. After a corresponding treatment in water solution at an oxygen pressure of 600 kPa, the alkali stability of hydrocellulose was only 62 % even if, in the state of equilibrium, the amount of oxygen dissolved is the same as in the ethanol-water case. The results are not directly comparable, because the actual solubility of oxygen in the reaction mixture

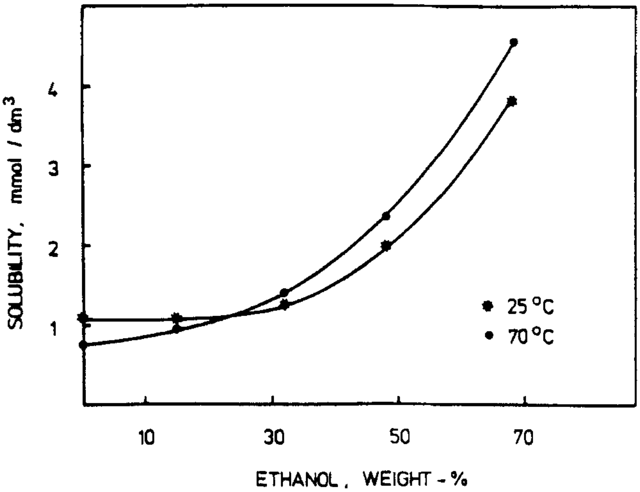

FIGURE 7. Solubility of oxygen in alkaline water-ethanol mixtures. Oxygen pressure 100 kPa, 0.2 M NaOH.

is also affected by the consumption of oxygen and the rate of oxygen transfer from the gas phase to the liquid phase. To eliminate these factors, additional experiments were carried out in both water and 70 % ethanol solution. Oxygen was continuously bubbled through the reaction mixture and the pressure was adjusted to give the same amount of dissolved oxygen in both cases ( 15 moles oxygen/mole of hydrocellulose, i.e., twice the amount consumed during the reaction). The alkali stabilities of the oxidized hydrocellulose samples were 66 % (after treatment in water) and 86 % (after treatment in 70 % ethanol). It can thus be concluded that the effect of the solvent on the oxidation rate of hydrocellulose is also affected by factors not connected with the solubility of oxygen and the rate of oxygen transfer from the gas phase to the liquid phase.

A simple calculation shows that when hydrocellulose was oxidized in 70 % ethanol, about 4 glucose units (on average) were peeled off from the cellulose chain before stabilization. In water solution, the corresponding number was 18. Thus, in 70 % ethanol, the selectivity of the oxidation of hydrocellulose is 18/4 or 4.5 times as high as that in water solution. When an equimolar amount of cellobiose was oxidized under similar conditions, the ratios of number of glucose units peeled to number of glucose units oxidized in 70 % ethanol and water solutions were 1 and 3, respectively, so the selectivity of the oxidation was 3 times as high in 70 % ethanol as in water solution (Table 2). According to these figures, the effect of the solvent is more pronounced for hydrocellulose, possibly because of the increased rate of oxygen transfer from the liquid phase to the surface of hydrocellulose.

In separate experiments, cellobiose was treated with oxygen in alkaline ethanol-water mixtures to determine the role of the solvent on the chemical reaction rates. The molar ratio of dissolved oxygen to cellobiose was 20 at the beginning of the reaction, and oxygen was continuously bubbled through the reaction

TABLE 2

Formation of Glucosylaldonic Acids from Cellobiose. Cellobiose 1.8 g/dm$^3$, 0.2 M NaOH, 90 min at 70 °C (max.).

| Ethanol, weight-% | Glucosylaldonic acids, % of cellobiose added |
|---|---|
| 0 | 26 |
| 15 | 31 |
| 32 | 45 |
| 70 | 51 |

mixture. As can be seen from Fig. 8, the overall reaction rate of cellobiose, as well as of glucose liberated, increased with ethanol concentration. Simultaneously, the proportion of oxidative reactions increased, as indicated by the amount of glucosylarabinonic and arabinonic acids formed. According to our recent studies, the changes in the overall reaction rates are due to the increased isomerization rates of carbohydrates[7]. For example, the alkaline isomerization rate of glucose to fructose in 50 % ethanol is twice that in water solution. This is also supported by our finding that the alkaline degradation of hydrocellulose, as well as of cellobiose, increased with increasing ethanol concentration of the solvent.

Finally, alkaline cooking experiments were carried out with pine chips pretreated either with AMS-oxygen in water solution or with oxygen in ethanol-water solution. With a constant cooking time, these pretreatments resulted in no significant increase in carbohydrate yield. The delignification rate, however, increased markedly, and the pretreated wood could be delignified to a lower lignin content (Table 3). Thus, compared at the same degree of delignification, the increase in carbohydrate yield was 2 to 3 % on wood. The viscosities of the pulps were decreased as a result

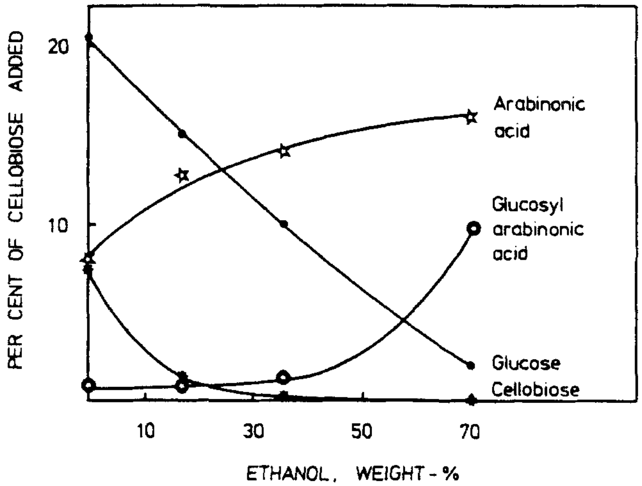

FIGURE 8. Effect of solvent on the oxidation of cellobiose. Treatment conditions: 0.2 M NaOH, dissolved oxygen 5.8 mmol/dm$^3$, cellobiose 0.28 mmol/dm$^3$, 90 min at 50 °C (max.).

TABLE 3

Effect of Some Pretreatments on AQ-Alkali Pulping of Pine Chips.

| Pretreatment | Cooking time, min | Kappa number | Lignin-free yield, % |
|---|---|---|---|
| - | 110 | 28.1 | 43.8 |
| $NaBH_4$ | 100 | 23.1 | 45.9 |
| AMS-$O_2$ | 70 | 25.8 | 44.8 |
| EtOH-$O_2$ | 70 | 23.6 | 44.3 |

of the oxidative pretreatments. For example, pretreated wood delignified to a kappa number of 20 had a viscosity of about 800 SCAN-units, whereas the viscosity of a reference AQ-alkali pulp was 900 SCAN-units at kappa number 30. The results of the cooking experiments will be discussed in detail in another paper[8].

## CONCLUSIONS

The reactions of cellulose catalyzed by alkali are outlined in Fig. 9. The reaction always starts by the isomerization of the glucose end group to a fructose end group, and the rate of this isomerization is increased with increasing alcohol concentration of the solvent. In the absence of oxidants, the fructose intermediate is mainly degraded through β-alkoxy elimination. In the presence of oxygen, the intermediate organic peroxide is further decomposed to yield mainly arabinonic and erythronic acid end groups. The oxidation efficiency of oxygen is increased with increasing alcohol concentration of the solvent; it can further be improved by adding a small amount of hydrogen peroxide, which retards decomposition of the organic peroxide to a glucosone end group which can undergo β-alkoxy elimination[7]. The same glucosone intermediate is formed when cellulose is treated with AMS. In the presence of oxygen, $AMSH^-$ is reoxidized, with the formation of hydrogen peroxide which oxidizes the glucosone intermediate via an organic peroxide mainly to arabinonic and erythronic acid end groups. The same oxidation products are formed when large amounts of AMS and

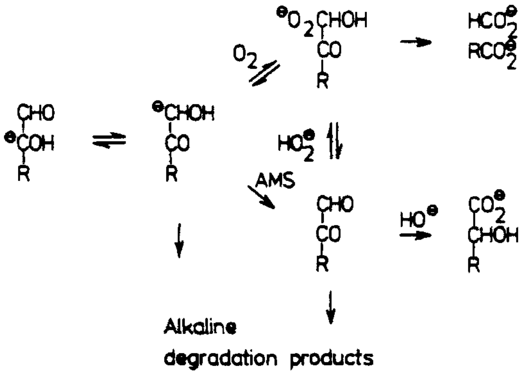

FIGURE 9. Reactions of the reducing end group of cellulose in alkaline solution. R is a cellulose residue.

hydrogen peroxide are used, as has been shown by our recent experiments[7].

The oxidation with oxygen at the conditions described results in relatively specific formation of aldonic acid end groups, which, however, are unstable at higher temperatures. Therefore, only a very limited stabilization of wood polysaccharides takes place when the pretreated chips are subjected to alkaline pulping. In addition, depolymerization of polysaccharides cannot be avoided.

Mainly mannonic acid end groups are formed when cellulose is oxidized with AMS in the absence of oxygen and hydrogen peroxide[9]. In this case, however, a large amount of AMS is needed, because the glucosone intermediate is preferentially decomposed through β-alkoxy elimination instead of the benzilic acid type of rearrangement. According to our calculations, only about 20 % of the glucosone end groups are rearranged to aldonic acid end groups. In normal AQ-alkali pulping of softwood, the increase in carbohydrate yield resulting from oxidative stabilization of polysaccharides is 1 to 2 % on wood[10]. The yield increase could be higher if a suitable catalyst for the benzilic acid type of arrangement could be found.

## EXPERIMENTAL

The determinations of oxygen solubility were based on Henry's law and carried out by using the equipment shown in Fig. 10. The solution was contained in a glass-lined autoclave (500 ml) immersed in a thermostated water bath. After adjusting to a suitable pressure (p, 600 kPa), preheated oxygen was bubbled (1 $dm^3$/min) into the solution through a fine glass sinter. After saturation (30 min), the oxygen stream was interrupted, and a sample of the solution was withdrawn in a graduated and gas-tight syringe (60 ml) through a cooler (T', ambient

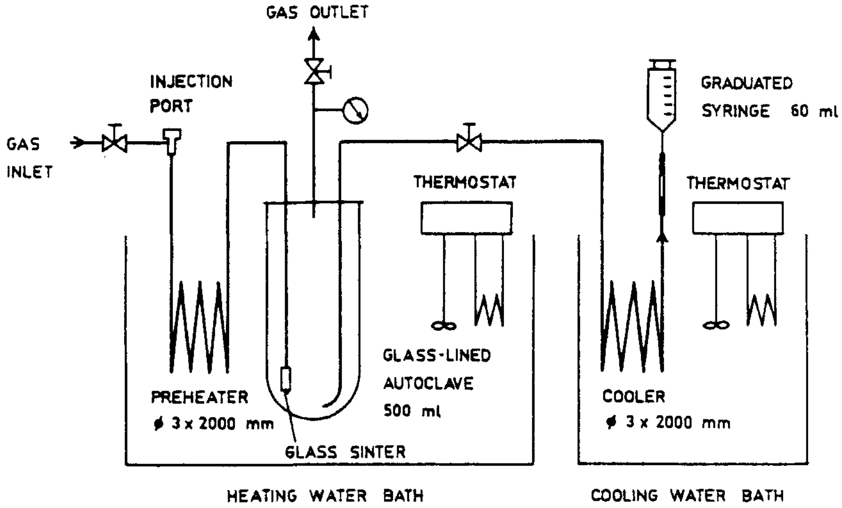

FIGURE 10. The equipment used in the solubility determinations.

temperature). The syringe was closed and shaken to establish an equilibrium between the liberated gas and the solution. The volumes of the gas phase ($V_g$) and the liquid phase ($V_l$) were read out. The solubility of oxygen at ambient temperature ($T=T'$) and under oxygen pressure of 100 kPa was calculated from following equation:

$$s' = \frac{V_g \cdot (p' - p'_s)}{v' \cdot V_l \cdot p'} \cdot \frac{100 \text{ kPa}}{p - p'} \qquad (1)$$

where $p'$ is atmospheric pressure

$p'_s$ is the vapor pressure of the solvent at $T'$[11]

$v'$ is the molar volume of the ideal gas at $T'$ and $p'$

The solubility of oxygen at any other temperature ($T$) was obtained from eq. 2:

$$s = \left\{ \frac{V_g \cdot (p' - p'_s)}{v' \cdot V_l \cdot p'} + s' \right\} \cdot \frac{100 \text{ kPa}}{p - p_s} \qquad (2)$$

where $p_s$ is the vapor pressure of the solvent at $T$[11]

The hydrocellulose was prepared by reacting cotton linters with 2 M HCl as described earlier[12]. The viscosity of the hydrocellulose and the corresponding degree of polymerization were determined according to SCAN-C15:62.

The oxidations were usually carried out in teflon-lined autoclaves (50 ml) equipped with magnetic stirring. The hydrocellulose concentration was 10 %, and the solution volume 25 ml. The pressurized autoclaves were placed in a thermostated polyglycol bath. The heating up time was 20 min to 66 °C, 30 min to 68 °C, and about 50 min to the maximum temperature (70 °C). After an appropriate reaction time, the autoclaves were cooled in cold water, and the hydrocellulose samples were washed successively with water and ethanol. When the solubility of oxygen was controlled, the experiments were carried out in the autoclave shown in Fig. 10. In this case, the hydrocellulose concentration was 0.5 %, and the reaction mixture was saturated with oxygen before thermostating. Oxygen was then bubbled (100 ml/min) into the reaction mixture throughout the reaction (90 min).

To determine alkali stability, a mixture of 1 g of hydrocellulose in 125 ml of 1 M NaOH was refluxed for 3 hours, after which the sample was washed with water and ethanol. The term alkali stability is used for the yield of hydrocellulose in this procedure. When the alkali stabilities were determined as a function of temperature, the treatments were carried out in teflon-lined autoclaves (50 ml) under nitrogen atmosphere. In this case, the concentrations of hydrocellulose and sodium hydroxide were 1.7 % and 1 M, respectively, and the reaction time was 4 hours.

The acid end groups of hydrocellulose were determined as described earlier[12].

Some of the oxidations of cellobiose were performed in teflon-lined autoclaves, mainly according to the same procedure as used for the oxidation of hydrocellulose. When the effect of the solvent on the chemical reaction rates of cellobiose was studied, however, the oxidations were carried out in the equipment shown in Fig. 10. The alkaline solution was first heated at the reaction temperature and saturated with oxygen. Cellobiose dissolved in a small amount of water was then injected into the solution. Oxygen was bubbled into the solution throughout the reaction. After 90 min, the reaction mixture was taken off through a cooler, and the sugars and hydroxy acids were analyzed by gas chromatography[12,13].

Pine (*Pinus sylvestris*) mill chips were used in the pulping experiments. The chips (200 g) were pretreated in a rotating digester with 6 autoclaves. The pretreatment conditions are presented in Table 4. The pretreated chips were washed in water, dried at ambient temperature, and delignified further by soda-AQ pulping under following conditions: liquor-to-wood ratio 4; charge of NaOH and AQ, 19 % and 0.3 % on pretreated wood, respectively; time to 170 °C, 120 min. The cooking time was varied. The kappa numbers of the pulps were determined according to SCAN-C 1:77, the corresponding lignin contents were obtained by multiplying the kappa numbers by a factor of 0.152[14], and the

TABLE 4

The Pretreatment Conditions of Pine Chips.

| Pretreatment | AMS-$O_2$ | EtOH-$O_2$ | $NaBH_4$-$N_2$ |
|---|---|---|---|
| Liquor-to-wood ratio, $dm^3/kg$ | 5 | 5 | 5 |
| NaOH, % on wood | 8 | 8 | 4 |
| EtOH, weight-% | - | 40 | - |
| AMS/$NaBH_4$, % on wood | 1 | - | 1 |
| $MgSO_4$, % on wood | 1 | 1 | - |
| $O_2/N_2$-pressure, kPa | 600 | 600 | 600 |
| Time to 80 °C, min | 25 | 25 | 25 |
| Time at 80 °C, min | 40 | 40 | 40 |

lignin-free yields were calculated as the differences between total and lignin yields. The viscosities of the pulps were determined according to SCAN-C15:62.

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