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Role of Ethoxide Ion in Soda-Ethanol Pulping of Egyptian Bagasse

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ABSTRACT. Role of ethoxide ion in alkaline-ethanol pulping was studied by the application of mild soda pulping conditions to prehydrolysed bagasse and monitoring the changes in pulp properties as a function of the concentration of ethanol.

Low concentration levels of ethoxide resulted in the cellulose supramolecular structure to become more amorphous and enhanced dissolution of short-chain carbohydrates by increasing the susceptibility of the pulp towards alkali. Thus, high-alpha pulp with improved accessibility and chemical reactivity to xanthation were obtained. Higher ethoxide concentration levels decreased the degree of pulping (delignification), lowered the alpha-cellulose content and decreased the accessibility of the pulp. These effects are attributed to a combination of: a) degradation of long-chain alpha-cellulose, b) the inability of ethoxide ion, compared to hydroxide ion to penetrate into the original native structure of the fibres thus leading to insufficient degree of pulping and, c) the self-condensation of lignin, catalysed by ethoxide ion. The addition of anthraquinone (AQ) to the alkaline ethanol pulping liquors permitted the retention of different amounts of hemicellulose and lignin.

Introduction

The chemistry of the soda-methanol process has only been incompletely characterised. The reactions probably follow a course similar to that of soda pulping, but with methanol promoting lignin dissolution and decreasing condensation processes[1]. In the soda pulping of spruce chips at high impregnation temperatures, the addition of ethanol to the cooking liquor greatly increased the selectivity of delignification and gave pulps having higher brightness and yield at a given kappa number, than the corresponding soda and kraft pulps[2]. Aqueous ethanolic soda cooking of southern yellow pine mixtures gave pulps at yields and lignin contents similar and lower than ethanolic soda

pulps, respectively[3]. The addition of ethanol of an alkaline-sulfite anthraquinone liquor had only a marginal effect on pulping[4].

From the literature it is clear that no attempts have been made to study the role of ethoxide ion in soda ethanol pulping or the effect of addition of ethanol on the chemical, physical and supramolecular structure (accessibility) of the resulting pulp. The aim of the present investigation was to remedy these deficiencies and to prepare various grades of cellulosic pulps.

Experimental

Materials

The raw material used was a depithed Egyptian sugar cane bagasse kindly supplied by the pulp mill of the Egyptian Sugar and Distilling Company at Edfo, Egypt.

Methods

Prehydrolysis, Pulping and Bleaching

The prehydrolysis was carried out at 100°C for 5 hr. As prehydrolysing agent, 5% H_2SO_4 (g/100g bagasse) were used at a liquor ratio of 10:1.

Soda pulping was carried out at 100°C for 6 hr with 20% active alkali (Na_2O) corresponding to 25.8% NaOH (g/100g prehydrolysed material) at a liquor ratio 10:1. The amounts of alcohol and anthraquinone added to the pulping liquor are shown in the Tables (1-3).

TABLE 1. Alkaline pulping in presence of ethanol.

Experiment number		1	2	3	4	5
Ethanol: water ratio		–	1 : 10	1 : 5	1 : 3	1 : 1
Ml alc./100 ml pulping liquor	%	–	9.1	16.6	25.0	50.0
Analysis of bleached pulp yield	%	33.2	33.5	33.8	34.2	36.5
Permanganate number (of unbleached pulp)		12.9	13.0	13.1	14.0	15.1
α-cellulose content	%	89.8	90.1	91.3	89.5	88.6
Pentosan content	%	7.6	7.4	6.2	7.9	9.3
D.P.[(a)]		980	990	1015	925	945
W.R.V.[(b)]	%	87.1	91.3	92.8	89.6	85.4
L.R.V.[(c)]	%	230.1	240.0	258.1	252.5	251.2
NaOH R.V.[(d)]	%	49.2	51.0	53.3	52.1	51.0
Crystallinity	%	80.2	79.1	76.1	77.2	78.0
Reactivity towards xanthation	%	31.5	39.7	46.2	44.5	40.7

(a) Degree of polymerization.
(b) Water retention value.
(c) Liquor retention value.
(d) Sodium hydroxide retention value.

TABLE 2. Upgrading pulps prepared by ethanol-soda process.

Experiment number		1	2	6	7
Conc. of NaOH (g/100 g of unbleached pulp		8*	8	16	20
Analysis of pulp yield	%	33.2	33.8	30.0	28.0
α-cellulose content	%	89.8	91.3	93.2	94.1
Pentosan content	%	7.6	6.2	4.5	4.2
D.P.		980	1015	965	890
W.R.V.	%	87.1	92.8	98.4	94.1
L.R.V.	%	230.1	258.1	281.8	270.2
NaOH R.V.	%	49.2	53.3	58.3	54.1
Crystallinity	%	80.2	76.1	72.0	75.2
Reactivity	%	31.5	46.2	49.0	52.0

*) This experiment was carried out without alcohol in pulping.

TABLE 3. Effect of addition of anthraquinone during alkaline solvent pulping.

Experiment number		1	3	4	8	9	10	11	12	13
AQ (g/100 g pulp)		–	–	–	0.15	0.15	0.15	0.20	0.20	0.20
Ethanol: water ratio in pulping		–	1 : 5	1 : 3	–	1 : 5	1 : 3	–	1 : 5	1 : 3
Analysis of bleached pulp yield	%	33.2	33.8	34.2	35.4	35.8	36.7	36.5	37.0	38.5
Permanganate number		12.9	13.1	14.0	11.8	12.3	13.6	12.4	13.6	14.6
α-cellulose content	%	89.8	91.3	89.5	87.5	87.2	85.3	83.3	85.2	83.3
Pentosan content	%	7.6	6.2	7.9	9.4	9.4	11.3	12.5	11.8	12.8
D.P.		980.0	1015.0	925.0	850.0	868.0	850.0	805.5	880.0	850.0
W.R.V.	%	87.1	92.8	89.6	81.3	82.5	81.3	100.0	97.6	96.0
L.R.V.	%	230.1	258.1	252.5	268.4	280.0	264.0	273.9	279.5	269.5
NaOH R.V.	%	49.2	53.3	52.1	46.7	64.0	56.9	46.2	44.0	47.3
Crystallinity	%	80.2	76.1	77.2	83.3	84.1	82.0	79.0	76.9	83.2

The following CEH sequence bleaching was applied in this work.

The chlorination (C) involved treatment of the pulp (3% consistency) with chlorine water of 3% concentration (based on pulp) at 20°C for 1 hr.

This was followed by an alkaline extraction step (E) carried out at 80°C and 7% consistency for 2 hr at various concentrations as shown in the Tables.

The hypochlorite treatment (H) of the pulp (3% consistency) was for 2 hr at 40°C used an alkaline sodium hypochlorite solution containing 1.5% (based on pulp) active chlorine.

Analysis of Pulps

American Tappi Standards Methods[5] were employed as specified in our previou study[6].

Results and Discussion

Production of High-Alpha Pulps by Soda-ethanol Process

Soda pulping in the presence of ethanol (Table 1)

In experiment 1, pulping was carried out by the action of aqueous sodium hydroxide, while in experiments 2-5 the pulping was conducted using alcoholic sodium hydroxide solutions.

Different amounts (9.1, 16.6, 25.0 and 50% based on pulping liquor) of ethanol (97%) were used in experiments 2-5, respectively.

The chemical, physical and supramolecular structure characteristics of the resulted pulps are listed in Table 1. It is clear that increasing the ethanol level increased the yield from 33.5 to 36.5% and decreased the rate of delignification as measured by the permanganate number values. Thus, under the pulping conditions applied in this work, the higher ethoxide ion levels during the alkaline pulping seem to slow the delignification rate. This may be attributed to more than one factor. The increase in the ethoxide ion concentration implies a stronger degradative effect on the carbohydrate chains while the steric effect of the ethoxide ion hinders its penetration into the original native structure of the fibre. This is less reactive in nature and resists swelling and consequently leads to insufficient degree of pulping. There is another role which may be played by the ethoxide ion in lowering the degree of pulping, thus, the ethoxide ion may act to create carbanions at the active methylene groups in some of the lignin units. These carbanions may condense with carbonyl groups of other molecules and lead to self-condensation of lignin which will delay its dissolution in the pulping liquor. It was found that the effects of the above factors during pulping become more pronounced at higher ethanol levels. Moreover, it was noticed that pulp 5 still retained uncooked fragment. It is clear from Table 1 that, compared with soda pulping (pulp 1), at the lower concentration levels of alcohol (pulps 2 and 3), the presence of the ethoxide ion helped in dissolution of the short chain hemicelluloses. The presence of the ethoxide ion together with the aqueous alkali seems to penetrate into the cellulose and hemicellulose chains leading to a tendency of the latter to dissolution. The pentosan content of the pulp decreased from 7.6 to 6.2% and consequently the α-cellulose increased from 89.3 to 91.3%. This change caused the D.P. of the long-chain cellulose macromolecules to increase from 980 to 1015.

The most important effect of the alkali-ethanol pulping liquors took place in the supramolecular structure of the produced pulp. The presence of the alcohol helped to increase the swelling effect of the hydroxide on the cellulose chains and the disorder of their arrangement. Consequently the crystallinity decreased while the free accessible hydroxyl groups increased.This was manifested by the increase in the water retention value (W.R.V.), liquor retention value (L.R.V.) and sodium hydroxide retention value

(NaOH R.V.) of the pulp. Also, the tendency of the pulp to xanthate formation increased. However, the presence of alcohol at these concentrations have only minor effects on the degree of pulping.

At higher levels of ethanols (pulps 4 and 5) the ethoxide ion increased degradation of the long chains of the cellulose. This caused a decrease in the α-cellulose content, being 91.3, 89.5 and 88.6% in case of pulps 3-5, respectively. At the same time the D.P. decreased to ≈ 900. The increased pentosan contents of pulps 4 and 5 of 7.9 and 9.3%, respectively, may be attributed to a strong connection of the lignin skeleton. The insufficient degree of pulping achieved resulted in being retained part of the original native structure of the fibres. This structure resists swelling in water and alkali is less reactive and also possesses a low degree of accessibility. Thus, the W.R.V., L.R.V., NaOH R.V. and tendency towards xanthation of pulps 4 and 5 were lower than those of pulps 2 and 3.

High alpha grade pulps from the ethanol-soda process (Table 2).

This section describes an attempt to produce high-alpha grade pulps. From the previous section, the optimum pulp characteristics were obtained in experiment 3. However, the extensive increase in the D.P. value is objectionable specially if the pulp will be used for the production of viscose or acetate rayons. High D.P. values afford highly viscous solutions which are unsuitable for spinning into fibres. Moreover, the increased hemicellulose contents above certain levels retard the filtration of the cellulose solution, the step prior to spinning. This is due to the higher instability and the decomposition of hemicellulose xanthate.

For these reasons, in the following experiments attempts were made to reach the proper D.P. and hemicellulose value in addition to the other pulp properties. This could be attained by increasing the concentration of sodium hydroxide in the second step of bleaching.

It is clear from Table 2 that increasing the alkali concentration from 8 to 16% (based on pulp) increased the α-cellulose content (from 91.3 to 93.2%), decreased the pentosan content (from 6.2 to 4.5%) and reduce the D.P. value (from 1015 to 965). The digestion and removal of short-chain hemicelluloses and appropriate degradation of long-chain cellulose improve the reactivity towards xanthation. Further increase in the alkali concentration to 20% (pulp 7) resulted in a further decrease in the yield and the D.P. The accessibility of the pulp towards water and alkali decreased which is due to the preferential digestion of the more hydrophilic (amorphous) fractions in the higher alkali concentration. However, further improvements to the reactivity were achieved because the proper D.P. enhances the penetration of the reagents through cellulose reaction. Thus, in addition to the accessibility, the degree of cellulose purification and suitable D.P. are necessary to produce high alpha pulp at high level of processability.

2. Production of Low-alpha Pulps by Soda-ethanol Process

Low-alpha pulps have a wide utilization in the manufacture of different paper grades. It is well known that the hemicellulose fraction is of considerable importance in

papermaking. As a general rule, the greater the hemicellulose content, the faster will be the pulp respond to beating, the harder and denser will be the resultant paper, the higher will be its burst strength and tensile strength, and the greater will be its transparency.

A low lignin content is generally also required. However the complete removal of lignin may result in considerable loss and degradation of cellulose.

In the first phase of this investigation it was found that the higher alcohol concentration during soda pulping allowed considerable amounts of lignin to remain in the original native fibres. Moreover, our previous study[6] showed that the addition of anthraquinone (AQ) during soda pulping retained a considerable amounts of short-chain hemicellulose fractions due to the stabilization effect exerted by AQ on these fractions.

Accordingly, the effect of the addition of the AQ during soda-ethanol pulping was investigated in terms of the hemicullose content and accessibility of the produced pulps.

Effect of addition of AQ during soda-ethanol pulping (Table 3)

It is clear from the data in Table 3 that the addition of AQ to the soda pulping liquor (experiments 1,8 and 11) increased the yield and enhanced the delignification. The lowest permanganate number achieved was in experiment 8. AQ stabilized the short-chain hemicellulose fractions. Thus, increasing the AQ concentration decreased the α-cellulose value and increased the pentosan content, also the accessibility of the produced pulps increased with AQ concentration. This was indicated by the decrease in the crystallinity and the avementation of the sodium hydroxide liquor retention value. The addition of ethanol retarded the effect of AQ on delignification. This retardation was indicated by the increased permanganate number in experiments 9, 10, 12 and 13 where the highest value was recorded.

The D.P. decreased when the concentration of AQ and ethanol were increased. This is due to the retention of short chain hemicelluloses and also lignin. Most soda-ethanol-AQ pulps were characterised by improved accessibility. This was indicated by increased W.R.V., L.R.V. and NaOH R.V. as well as the lower degrees of crystallinity which could be attributed to the greater amorphous hemicellulose contents.

References

[1] **Sarkanen, K.V.,** Chemistry of solvent pulping, *Tappi J.*, **73**(10): 215 (1990).

[2] **Marton, R.** and **Granzow, S.,** Ethanol-alkali pulping, *Tappi J.*, **65**(6): 103 (1982).

[3] **McGree, J.K.,** Alkali-alcohol-water delignification of softwoods, *Proc. Pac. Chem. Eng. Confr.* **3**, 209 (1983).

[4] **Wang, D.L.K., Ramirez, F.** and **Patt, R.,** Alkaline sulfite-anthraquinone pulping of bagasse with and without the addition of ethanol, *holzforschung*, **41**(6): 383 (1987).

[5] **Technical Association of the Pulp and Paper Industry,** *Tappi Standards*, **360,** Lexington Avenue, NY, 10017 (1957).

[6] **Helmy, S.A.** and **Abou-State, M.A.,** Viscose pulps from Egyptian bagasse with high chemical reactivity, *Holzforschung*, **45**(6): 433 (1991).

دراسة دور أيون الإيثوكسيد في التلبيب بالصودا-إيثانول لإنتاج أنواع مختلفة من لب السليلوز

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المستخلص . تناول هذا البحث الدور الذي يلعبه أيون الإيثوكسيد إذا ما أضيف الإيثانول إلى الصودا أثناء تلبيب مصاصة القصب ويتلخص هذا الدور في النقاط التالية :

١- أدى استخدام تركيزات مخفضة من الكحول إلى تحسين في الصفات الكيميائية والفيزيائية للب وفي هذه الحالة يساعد أيون الإيثوكسيد محلول الصودا في إبعاد جزيئات الكربوهيدرات سواء السليلوزية والهيميسليلوزية عن بعضها مما يزيد من ذوبان الأخيرة في القلوي وتحسن صفات اللب .

٢- أدى استخدام تركيزات مرتفعة من الكحول إلى انخفاض كل من درجة التلبيب وخواص اللب الكيميائية والفيزيائية . وقد يرجع السبب في ذلك لعدة عوامل :

أ - زيادة تكسير جزيئات السليلوز في كل من القلوي وأيون الإيثوكسيد .

ب - التكاثف الذاتي لجزيئات اللجنين في وجود الإيثوكسيد .

جـ - احتفاظ اللب بجزء كبير من الشكل النباتي للألياف نتيجة لانخفاض درجة التلبيب - هذا الشكل ذات نشاط كيميائي منخفض .

٣- أمكن تحضير لب على درجة عالية من النقاء والنشاط الكيميائي وذلك بزيادة تركيز القلوي في الخطوة الثانية من التبييض .

٤- بإضافة الأنثراكينون مع الإيثانول أثناء التلبيب بالصودا أمكن تحضير أنواع مختلفة من لب الورق المحتفظ بنسبة من الهيميسليلوز واللجنين معًا .