Cold alkali refining of cellulosic pulps derived from Egyptian cotton and bagasse

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A cotton linter pulp, a bagasse dissolving pulp and a bagasse paper pulp were subjected to cold sodium hydroxide refining and the resulting changes in their chemical, physical and submicroscopic characteristics were investigated. In the case of cotton linters the main change took place in the physical and submicroscopic properties and the refining resulted in better reactivity towards xanthation. The α-cellulose content of the paper and viscose pulps increased with alkali concentration until it reached a constant value which depends on the type of pulp and the concentration of alkali. The refining of the paper and viscose pulps impaired their reactivity towards xanthation. The presence of the more hydrophilic hemicellulose increased the swelling ability of the fibres and made them more reactive towards xanthation. The undesirable effects of drying after refining with high alkali concentration could be overcome if the *DP* is sufficiently lowered. In this case the resulting shorter chain macromolecules dissolve more readily during xanthation.

INTRODUCTION

Previous studies about the effect of alkaline treatments were carried out on wood or cotton celluloses. A pulp from agricultural residues differs in its chemical and physical characteristics from wood pulp or cotton linters. However, no work seems to have been carried out on the alkali refining of such pulps. In this work the effects of cold sodium hydroxide refining on a paper and a viscose grade pulp, both prepared from bagasse, were investigated. The work was mainly concerned with the cold alkali refining of celluloses with different supermolecular structure. Three pulps were chosen for this purpose, namely, a cotton linter pulp, a viscose grade pulp and a paper pulp. They were treated in the cold (20°C) with sodium hydroxide solutions of different concentrations and the resulting changes in the chemical, physical and submicroscopic characteristics were investigated. It was also among the aims of this work to correlate between these changes and the changes in the reactivity of the pulps towards emulsion xanthation.

EXPERIMENTAL

The cotton linter pulp was prepared from Egyptian cotton linters, the dissolving pulp was prepared from Egyptian begasse and the paper pulp, which was kindly supplied in an unbleached form by the pulp mill of the Egyptian Sugar and Distilling Company at Edfo, was also prepared from Egyptian bagasse.

Purification of cotton linters

The raw linters were purified by pulping for 2 h under atmospheric pressure with a 1% sodium hydroxide solution at a liquor ratio of 1:20 and a temperature of 100°C. This was followed by hypochlorite bleaching with 1% active chlorine (based on linters). The hypochlorite treatment was carried out for 1 h at 40°C and a consistency of 3%. Finally, the linters were acidified with 0.5% H_2SO_3 for 20 min at 20°C.

Dissolving pulp

Depithed bagasse was subjected to prehydrolysis alkali treatment. Both treatments were carried out under atmospheric pressure for 6 h at 100°C and a liquor ratio of 1:10. The prehydrolysis was carried out with 6% H_2SO_4 (based on depithed bagasse), and the pulping was performed with 28% sodium hydroxide (based on prehydrolysed bagasse).

The natural chlorine requirement of the unbleached pulp was estimated according to Jayme and Rothamel[1]. The estimated amount of chlorine was added to the pulp in the form of chlorine water at 20°C for 1 h at a concentration of 3%. In previous studies about the production of dissolving pulps from Egyptian bagasse [2,3] the best results were obtained when the refining during bleaching was carried out with 16% NaOH (based on pulp) at 80°C for 2 h at a concentration of 7%. These conditions were applied in this work. In the third bleaching stage a buffered alkaline solution of sodium hypochlorite was used. This treatment was carried out at 40°C for 2 h at a consistency of 3%. The active chlorine in the hypochlorite corresponded to 30% of the amount of chlorine used in the first step. Finally, the bleached pulp was acidified with 0.5% H_2SO_3 for 20 min at 20°C.

Bleaching of the paper pulp

The paper pulp was kindly supplied by the pulp mill of the Egyptian Sugar and Distilling Company at Edfo in an unbleached form. It was subjected to a multistage bleaching treatment as before[4]

Table 1 Chemical, physical and submicroscopic characteristics of bleached pulps

		Type of pulp		
		Cotton linters	Viscose pulp	Paper pulp
α-Cellulose	(%)	99.10	91.89	75.79
β-Cellulose	(%)	0.57	5.79	7.37
γ-Cellulose	(%)	0.42	1.74	1.25
Pentosan	(%)	–	7.81	22.42
Ash	(%)	0.08	0.08	0.27
DP		2340	975	695
WRV	(%)	73.9	122.4	205.6
LRV	(%)	247.9	316.5	373.3
NaOH *RV*	(%)	50.7	66.8	71.0
Crystallinity	(%)	91.7	70.1	64.3
Reactivity (% insoluble cellulose)		95.3	68.0	44.1

Alkaline treatment of pulps

An amount of pulp corresponding to 40 g dry weight was treated for 1 h with a sodium hydroxide solution of the required concentration at 20°C and a liquor ratio of 1:20. This was followed by filtration, washing with distilled water and treatment on the filter with 1 litre 10% acetic acid solution. The acid was allowed to drain slowly through the pulp fibres. Finally, the pulp was washed thoroughly with distilled water and allowed to dry at room temperature.

Analysis of pulps

The chemical, physical and submicroscopic characteristics of pulps as well as their reactivity towards xanthation were estimated as before [3,5,6].

RESULTS AND DISCUSSION

Chemical, physical and submicroscopic characteristics of pulps

Table 1 lists the chemical, physical and submicroscopic characteristics of the cotton linters, the viscose pulp and the paper pulp used in this work. It is clear that the cotton linters possessed the highest degree of chemical purity, as indicated by the highest α-cellulose content, followed by the viscose pulp and finally the paper pulp. The latter was characterized by the most open and accessible fine structure, as revealed by the highest affinities towards water and alkali and the best reactivity, followed by the viscose pulp and finally the cotton linters.

It is of interest to mention that although the paper pulp did not meet the chemical requirements of viscose grade pulps, yet it was much more reactive towards emulsion xanthation than the viscose pulp. This might be explained by the higher hemicellulose content of the paper pulp. The more hydrophilic hemicelluloses increase the swelling ability of the fibres and consequently the cellulose hydroxyls become more accessible to reactant molecules. This finds support from the fact that the paper pulp was characterized by higher *WRV*, *LRV* and NaOH *RV*.

Behaviour of the cotton linters, the viscose pulp and the paper pulp towards cold sodium hydroxide refining

Chemical characteristics. The chemical characteristics of cotton linters were practically unaffected by cold sodium hydroxide refining. This is in contrast to the paper and viscose pulps, where the refining was accompanied by changes in the chemical characteristics due to the dissolution of the short chain celluloses and part of the pentosans. The α-cellulose content reached a constant value after refining with 5% NaOH in case of the viscose pulp, and 10% NaOH in case of the paper pulp. This is due to the presence of larger amounts of the short chain celluloses and pentosans in the paper pulp. The attained constant value of α-cellulose was 96.5% in case of the paper pulp, compared to a value of around 97.0% in case of the viscose pulp. The α-cellulose of cotton linters was around 99.3% in the treated and untreated samples. It is also clear from *Table 2* that while the ash content of the cotton linters and the viscose pulp was not affected by refining, the ash content of the paper pulp showed a continuous slight decrease with alkali concentration. This is probably due to the higher ash content of the paper pulp which resulted in a more clear picture of the effect of alkali on its dissolution.

Physical and submicroscopic properties

Depolymerization. The three pulps behaved differently according to differences in their supermolecular structures. Thus, while the cotton linters showed a continuous decrease in the degree of polymerization with increase in the alkali concentration, the *DP* passed through a maximum value before its decrease in the case of the viscose and the paper pulps. The fact that refining with lower alkali concentrations resulted in an increase in the *DP* in the case of the viscose and paper pulps does not mean that it was not accompanied by depolymerization. The latter pulps contained greater amounts of the short chain celluloses and pentosans than the cotton linters. These were attacked and depolymerized more easily than cellulose and the resulting degradation products dissolved readily in the alkaline liquor used in refining. For this reason the average degree of polymerization was increased. The paper pulp contained a higher fraction of the short chain hemicelluloses and consequently attained a maximum *DP* after refining with a higher alkali concentration. After the dissolution of the short chain fractions both the viscose and paper pulps behaved like the cotton linters, which were mainly composed

Table 2 Effect of sodium hydroxide refining on the chemical characteristics

Concentration of NaOH soln (vol %)		–	5	10	15	20
Cotton linters:						
Yield	(%)	–	99.0	95.7	95.4	95.0
α-Cellulose	(%)	99.10	99.30	99.50	99.42	99.43
β-Cellulose	(%)	0.57	0.50	0.45	0.31	0.42
γ-Cellulose	(%)	0.42	0.21	0.13	0.11	0.16
Ash	(%)	0.08	0.07	0.07	0.08	0.07
Viscose pulp:						
Yield	(%)	–	92.8	90.7	90.1	89.9
α-Cellulose	(%)	91.89	96.90	97.07	97.21	97.13
β-Cellulose	(%)	5.79	2.37	1.47	0.95	1.06
γ-Cellulose	(%)	1.74	0.50	0.42	0.29	0.38
Pentosan	(%)	7.81	6.41	2.92	2.63	2.70
Ash	(%)	0.08	0.07	0.09	0.08	0.07
Paper pulp:						
Yield	(%)	–	83.6	76.4	73.7	70.2
α-Cellulose	(%)	75.79	89.40	96.51	96.45	96.50
β-Cellulose	(%)	7.37	3.59	1.08	0.80	0.85
γ-Cellulose	(%)	1.25	0.65	0.53	0.34	0.43
Pentosan	(%)	22.42	9.80	3.38	3.05	2.80
Ash	(%)	0.27	0.26	0.24	0.21	0.18

Table 3 Effect of sodium hydroxide refining on the physical and submicroscopic characteristics

Concentration of NaOH soln (vol %)		–	5	10	15	20
Cotton linters:						
DP		2340	2272	2201	2000	1818
WRV	(%)	73.9	81.4	85.3	65.5	56.0
LRV	(%)	247.9	255.6	258.0	260.0	259.1
NaOH *RV*	(%)	50.7	53.4	56.7	58.4	57.9
Crystallinity	(%)	91.7	87.6	85.1	60.0	62.3
Reactivity (% insoluble cellulose)		95.3	91.0	73.5	69.4	68.4
Viscose pulp:						
DP		975	1270	1253	1240	1230
WRV	(%)	122.4	121.8	105.6	90.7	87.2
LRV	(%)	316.5	300.5	305.1	302.0	302.1
NaOH *RV*	(%)	66.8	60.2	61.3	57.1	57.2
Crystallinity	(%)	70	65	45	38	46
Reactivity (% insoluble cellulose)		68.0	78.9	87.1	76.2	77.6
Paper pulp:						
DP		695	915	1050	1030	965
WRV	(%)	205.6	201.0	159.0	129.2	101.0
LRV	(%)	373.3	360.2	335.2	319.5	317.0
NaOH *RV*	(%)	71.0	66.1	64.8	63.7	62.6
Crystallinity	(%)	64	60	46	39	49
Reactivity (% insoluble cellulose)		44.1	50.4	55.8	58.5	56.5

of homogeneous long chain cellulose macromolecules, and the *DP* decreased with alkali concentration.

Accessibility and fine structure

In case of cotton linters the affinity towards water increased with alkali concentration and was at its maximum after refining with 10% sodium hydroxide, then the *WRV* decreased by further increase in the alkali concentration. The *LRV* and NaOH *RV* increased steadily with alkali concentration up to 15% sodium hydroxide and then remained practically unaffected. This means that the newly formed inaccessible regions, which resulted from drying after refining with 15 and 20% sodium hydroxide, were not affected by water. However, the sodium hydroxide solution used in the determination of *LRV* and NaOH *RV*, being of mercerizing strength, was capable of swelling these regions. The decrease in the affinity towards water and alkali of the viscose and paper pulps could be attributed to the removal of the more accessible fractions by refining with low alkali concentrations, and the increase in the inaccessibility which resulted from drying after refining with high alkali concentrations.

The alkali refining resulted in decrystallization. The higher the alkali concentration, the greater the decrystallization. This was the general behaviour of the three pulps up to 15% alkali concentration. Higher concentrations resulted in a slight increase in crystallinity in case of cotton linters and a more pronounced increase in case of the viscose and paper pulps.

Pulp characteristics and its reactivity towards xanthation

The refining of cotton linters with 5, 10 and 15% sodium hydroxide lowered the *DP*, increased the affinities towards water and alkali, and resulted in better reactivity towards xanthation. Further increase in the alkali concentration to 20% increased the crystallinity, lowered the affinity towards water and had practically no effect on the affinity towards alkali. However, it resulted in a slight improvement, instead of deterioration, in the reactivity. This is due to another factor which tends to improve the reactivity, and thus overcomes the undesirable effects of drying after treatment with high alkali concentration. This factor is the reduction in the *DP* which results in shorter chain molecules and consequently better dissolution during xanthation.

The effect of depolymerization of cellulose is also illustrated from the refining of the paper pulp with 10, 15 and 20% sodium hydroxide, that is after the removal of the short chain fractions by refining with 5% sodium hydroxide. In this case the refining was accompanied by depolymerization of cellulose and resulted in better dissolution during xanthation despite the reduction in the affinities towards water and alkali.

By comparing the reactivities of the paper and viscose pulps it could be seen that the removal of the more hydrophilic hemicellulose, as a result of refining with lower concentrations, deteriorates the reactivity. The effect of the more hydrophilic fractions of the pulp is also illustrated by comparing the reactivities of the untreated cotton linters, viscose pulp and paper pulp (*Table 1*). The best reactivity was exhibited by the paper pulp, followed by the viscose pulp and finally the cotton linters.

CONCLUSIONS

The changes in the chemical, physical and submicroscopic characteristics of pulps produced by cold alkali refining depend on their supermolecular structures. In the case of cotton linters the refining has practically no effect on the chemical characteristics. The physical and submicroscopic properties are mainly affected. The *DP* decreases with alkali concentration and the refining results in a more open and accessible inner structure as indicated by better reactivity towards xanthation. The refining of the viscose and paper pulps is accompanied by changes in their chemical characteristics due to the dissolution of the short chain celluloses and part of the pentosans. The α-cellulose content increases with alkali concentration till it reaches a constant value which depends on the type of pulp and the concentration of alkali. The α-cellulose content of the paper pulp, which contains a greater amount of the short chain celluloses and pentosans, becomes constant after refining with a higher alkali concentration than the viscose pulp. This constant value is slightly higher in case of the viscose pulp.

The ash content of the paper pulp shows a continuous slight decrease with alkali concentration. This behaviour must, however, not be taken as a general behaviour of paper pulps towards cold sodium hydroxide refining. It is most probably due to the higher ash content of the paper pulp used in this work which resulted in a clearer picture of the effect of alkali on its dissolution.

In the case of viscose and paper pulps the refining results first in an increase in the *DP* and after the dissolution of the short chain fractions both pulps behave like the cotton pulp, which is mainly composed of homogeneous long chain macromolecules, and the *DP* decreases with alkali concentration.

In contrast to cotton linters, whereby the refining improves the reactivity towards xanthation, the refining of the paper and viscose pulps impairs their reactivity. This is due to the removal of the more accessible fractions after refining with low alkali concentrations, and the transformation of cellulose I to cellulose II, which is more difficult to bring into solution, after refining with high alkali concentrations.

The changes in the reactivity towards emulsion xanthation, which results from cold alkali refining, are not the result of a single factor. They depend on the chemical as well as the physical and submicroscopic characteristics of the pulp. The presence of the more hydrophilic hemicellulose fraction increases the swelling ability of the fibres and makes them more reactive towards emulsion xanthation. Pulps with higher affinities towards water and alkali are generally characterized by better reactivity. The undesirable effects which result from drying after refining with high alkali concentration may be overcome if the degree of polymerization is sufficiently lowered. In this case the resulting shorter chain molecules dissolve more readily in the alkaline liquor during xanthation.

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