STUDIES ON THE ACID DEGRADATION OF CELLULOSIC FIBERS. II: CHANGES OF LOW-ALPHA BAGASSE PULP CHARACTERISTICS

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الخلاصـة :

يُعنى هذا البحث بدراسة التحلل المائي في وسط حمضي وتحت ظروف مختلفة لِلُبِّ مصاصة القصب المحتوي على نسبة منخفضة من ألفا سليلوز، وذلك بتتبع التغيرات في الحصيلة والخواص الكيميائية والفيزيائية للهيدروسليلوزات الناتجة والتركيب الجزيئي الدقيق لأليافها ممثلاً في القابلية للماء والقلوية ودرجة التَّبلُّر. وقد تمت دراسة العلاقة بين هذه الخواص ودرجة النشاط الكيميائي نحو تكوين الزانثات وقابلية الفسكوز للترشيح.

وتتلخص النتائج فيما يلي:

١- عند تعريض لُبُّ مصاصة القصب المحتوي على نسبة ألفا سليلوز منخفضة للتحلل المائي وذلك باستخدام محلول (٦) عياري من حمض الأيدروكلوريك عند درجتي (٣٠) و(٥٠ْ م) - نَجِدُ أن الحرارة العالية تسِّرع من تحلل كلٍّ من الجزيئات الطويلة والقصيرة مما ينتج عنه نقص في حصيلة اللب.

٢ - لم تؤثر درجة الحرارة على القيمة الثابتة لدرجة البلمرة للهيدروسليلوزات الناتجة إلا أن الفترة اللازمة للوصول إليها اختلفت حيث كانت أطول عند درجة حرارة (٥٠ْ م) وذلك لشيوع إعادة تبلر الجزيئات عند درجة الحرارة المنخفضة (٣٠ْ م) بالرغم من أن القيمة المقاسة لدرجة التَّبلُّر كانت أقل في حالة درجة الحرارة المنخفضة، ويرجع السبب في ذلك إلى انخفاض معدل التحلل المائي للهيميسليلوزات عند هذه الدرجة وخاصة الجزء الأكثر ثباتاً. لأن درجة التَّبلُّر المقاسة هى في الحقيقة متوسط لدرجة تَبَلُّر مكونات اللب من سليلوز وهيميسليلوز.

٣ - زادت قابلية الهيدروسليلوز الناتج للقوي ثم انخفضت بعد الوصول للقيمة الثابتة لدرجة البلمرة عند كل من (٣٠) و(٥٠ْ م).

٤ - أدى إجراء التحلل المائي عند كل من هاتين الدرجتين إلى تحسن في النشاط نحو تكوين الزانثات وقابلية الفسكوز للترشيح.

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ABSTRACT

Hydrolysis of low-alpha bagasse pulp, with 6*N* HCl at 30 and 50°C showed that a higher temperature accelerated hydrolysis of both the low and high molecular-weight factions of the pulp and increased the loss in material. The value of leveling off degree of polymerization, LODP, was not affected by temperature. However, it was attained after 1.5 hours at 30°C and after 6 hours, at 50°C. Thus, before the LODP, recrystallization was more pronounced at the lower temperature. However, the value of crystallinity was lower at the lower temperature because of the milder hydrolysis at the lower temperature, which resulted in higher hemicellulose content, particularly of those which resist hydrolysis under such milder conditions. At both temperatures the affinity towards alkali increased at first and then decreased after the LODP. In most cases, the higher temperature resulted in better reactivity and filterability. At the LODP period both the reactivity and filterability remained constant.

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INTRODUCTION

The glucosidic linkages of cellulose molecules are readily hydrolyzed by the action of mineral acids, resulting in the disintegration of macromolecules. The rate of reaction of acid solutions with cellulose is not the same in different parts of the fibers and, as a result, a complex mixture of products of incomplete decomposition of cellulose is formed; the composition of this mixture changes during the course of hydrolysis [1]. Bond cleavage by interaction with H_3O^+ (acid hydrolysis) proceeds at random in a homogeneous reaction system, but is selective with respect to the state of crystalline order in a heterophase reaction system [2]. The changes taking place in the physical supermolecular characteristics of cotton cellulose on addition of zinc chloride during mild hydrochloric acid degradation to leveling off of the degree of polymerization (LODP) were studied in our previous investigation [3]. Both the rate and site of hydrolysis, as well as the supermolecular characteristics were strongly affected by zinc chloride addition. Moreover, the role of zinc chloride was greatly dependent upon the acid concentration [3].

In the present work, low-alpha cellulose pulp was subjected to acid hydrolysis using 6N HCl at different temperatures. The resulting changes in the yield, the chemical and physical characteristics were followed up. The fine structure *e.g.*, the degree of swelling in water and alkali, and the crystallinity were also investigated. A correlation between all these characteristics and the chemical reactivity (xanthation) as well as the viscose filterability was studied. Such a complete investigation was not carried out before.

EXPERIMENTAL

Raw Material

The raw material used in this work was paper kraft pulp prepared from Egyptian bagasse. It was kindly supplied by the pulp mill of Egyptian sugar and distilling company at Edfo.

Bleaching of the pulp

The kraft paper pulp (low-alpha pulp) was subjected to multistage bleaching as follows:

Chlorination: the pulp was chlorinated with 2.5% chlorine at 20°C for 1 hour at a consistency of 3%.

Alkaline extraction: after chlorination the pulp was extracted with 2% sodium hydroxide (based on pulp) at 40°C for 1.5 hour at a consistency of 5%.

Hypochlorite treatment: the pulp was then subjected to hypochlorite bleaching. The active chlorine in the hypochlorite corresponded to 50% of the amount of chlorine supplied in the first step.

Acid treatment: the pulp was then treated with 0.5% hydrochloric acid (based on pulp) at room temperature for 20 minutes at a consistency of 3%.

Acid Hydrolysis Technique

An amount of pulp corresponding to 15 gram dry weight was placed in a 1 liter round-bottomed ground joint flask, fitted with a reflux condenser.

It was treated with 750 ml 6N hydrochloric acid at the specified temperature and for different periods. This was followed by filtration through a sintered glass funnel, and thorough washing with distilled water. Finally, the pulp was allowed to dry at room temperature.

Analysis of Hydrolyzed Products

The α-, β-, γ- cellulose and pentosan contents were determined according to American Tappi Standards [4].

Fine Structure, Accessibility, Chemical Reactivity, and Filterability

There are no absolute methods for measuring the fine structure and accessibility of cellulose. However, some of the cellulose properties give a clear comparative indication of these characteristics, *e.g.* the degree of swelling in water or in sodium hydroxide liquor, the ratio of crystalline to amorphous cellulose, and the reactivity of cellulose in a particular chemical reaction.

In this work the degree of swelling in water was estimated by determining the water retention value (W.R.V.). The degree of swelling in sodium hydroxide liquor was measured by determining the liquor retention value (L.R.V.) and the sodium hydroxide retention value (NaOH R.V.). The W.R.V., L.R.V., NaOH R.V., crystallinity, and reactivity towards xanthation as well as filterability of the viscose formed were determined as mentioned before [5]. The degree of polymerization (D.P.) was determined as discussed before [3].

RESULTS AND DISCUSSION

Hydrolysis at 30°C

It is clear from Table 1 that carrying out the hydrolysis at 30°C for 0.75 and 1.5 h decreased the yield to 96.8 and 90.8%, respectively. The α-cellulose increased with the time of hydrolysis until it became 79.17% after 1.5 h; the β- and γ-celluloses as well as the pentosans decreased. The decrease in yield, which was accompanied by an increase in α-cellulose, and decrease in both β-cellulose and γ-cellulose and pentosans indicates that the initial hydrolytic action took place on the more accessible shorter-chain carbohydrate fractions. The D.P. decreased till it reached its leveling-off value of 486 after 1.5 h. Prolonging the time of hydrolysis after the leveling off D.P. (LODP) did not seem to have a great effect on the yield of α-cellulose, and pentosans.

The fine structure of the pulp was affected in a different way. The affinity towards water decreased continuously with the time of hydrolysis. However, the L.R.V. and NaOH R.V. increased, and at the same time the crystallinity decreased. This went on till the LODP was reached. After the LODP, both the L.R.V. and NaOH R.V. decreased with hydrolysis. The reactivity towards xanthation was impaired before the LODP and then improved after the LODP. This could be explained by removal of part of the more hydrophilic and more reactive hemicelluloses before the LODP. The removal of these hemicellulose fractions resulted in great improvement in filterability. After 1.5 h, *i.e.*, at the beginning of the LODP the reactivity was improved in spite of the decrease in the more reactive hemicelluloses. This is most probably due to the decrease in D.P. Lower D.P. means shorter-chain macromolecules and consequently better dissolution during xanthation. Both the reactivity and the filterability did not seem to be affected by prolonging the time of hydrolysis after the LODP.

Table 1. Effect of Temperature on the Hydrolysis of the Low-Alpha Pulp With 6N HCl.

Temperature	(°C)	30					50			
Time	(h)	0	0.75	1.5	6	9	0.33	1.5	6	9
Analysis of Pulp										
Yield	(%)	100	96.8	90.8	90.4	88.2	88.8	85.7	80.3	78.4
α-Cellulose	(%)	72.75	75.12	79.17	79.10	78.4	74.20	72.00	70.08	68.10
β-Cellulose	(%)	11.06	10.00	9.50	10.30	12.00	4.91	4.11	0.99	0.87
γ-Cellulose	(%)	3.00	2.9	1.14	1.14	1.20	5.04	6.82	10.70	8.30
Pentosan	(%)	28.4	27.1	24.8	24.8	22.2	25.8	23.4	19.6	17.7
D.P.		903	709	486	486	486	638	597	480	475
W.R.V.	(%)	179.8	144.1	128.6	123.1	120.8	135.8	120.1	120.2	103.2
L.R.V.	(%)	320.6	330.2	356.4	339.9	332.1	344.0	352.2	354.0	318.1
NaOH R.V.	(%)	56.1	60.3	68.9	64.4	62.3	63.5	64.5	66.3	59.4
Crystallinity	(%)	78	74	61	73	75	69	75	77	79
Reactivity										
(% insol. cellulose)		40.4	48.9	44.4	44.9	44.4	22.4	6.8	2.4	2.4
Filterability		>10:1	2.3:1	1.6:1	1.6:1	1.6:1	1.2:1	1.2:1	1.2:1	1.2:1

Hydrolysis at 50°C

It is clear from Table 1 that at 50°C the yield decreased continuously with the time of hydrolysis. The α-cellulose increased after 20 minutes and then decreased by further hydrolysis. The pentosans decreased continuously with the time of hydrolysis. The D.P. decreased till it reached a constant value of 480 after 6 h. Further hydrolysis after the LODP resulted in further decrease in yield, α-cellulose and pentosans. The initial increase in α-cellulose which was accompanied by a decrease in pentosans indicates that the intial hydrolytic action took place mainly in the hemicellulose fraction. After its initial increase the α-cellulose began to decrease before the LODP was reached. This indicates that the long-chain cellulose macromolecules were hydrolyzed. After this both the long-chain cellulose macromolecules and the lower molecular–weight hemicelluloses were hydrolyzed as indicated by the continuous decrease in α-cellulose and pentosans. The crystallinity decreased at first and then began to increase before the LODP. The increase in crystallinity continued after the LODP was reached. This could be accounted for by digestion of the more resistant and amorphous hemicelluloses. The latter is indicated by the decrease in pentosans. The initial decrease in crystallinity was accompanied by a great increase in L.R.V., NaOH R.V., reactivity, and filterability. The increase in the affinity towards alkali and the improvement in reactivity continued till the LODP was reached. However, the filterability was not affected probably due to the increase in crystallinity. At the beginning of the LODP the affinity towards alkali, the reactivity, and the filterability were improved. Further hydrolysis increased the crystallinity and lowered the affinities towards water and alkali. However, both the reactivity and filterability did not seem to be changed.

Effect of Temperature

It is clear that the higher temperature accelerated hydrolysis and raised the dissolution of material in the acid. The loss in material was 3.2–11.8% at 30°C and 11.2 –21.6% at 50°C. Moreover, the higher temperature resulted in pulps with a lower α-cellulose and lower pentosans. The value of the LODP was the same at both temperatures. This indicates that it is not affected by temperature. However, the LODP was attained after 1.5 h when the hydrolysis was carried out at 30°C, and after 6 h when it was carried out at 50°C. This probably due to the higher degree of swelling at the lower temperature. This also indicates that at the intial stages of hydrolysis, *i.e.*, before the LODP, recrystallization was more pronounced at the lower temperature. However, this does not seem to be compatible with the values of crystallinity, which were lower at the lower temperature. This could be explained by the fact that the lower temperature resulted in higher amount of hemicelluloses, particularly the more resistant ones, which were more difficult to remove under the milder hydrolysis conditions. Apparently, the measured value of crystallinity is a mean value for all pulp components which are mainly cellulose and hemicellulose. Both temperatures resulted at first in a continuous decrease in the W.R.V. with the time of hydrolysis. However, the affinity towards alkali increased at first and then decreased with the time of hydrolysis after the LODP was attained. In most cases, the reactivity towards xanthation was improved by hydrolysis and the higher temperature resulted in better reactivity and better viscose filterability. As the LODP was attained both the reactivity and filterability remained constant.

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