

ORGANOSOLV PULPING OF COTTON LINTERS

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Compared to prehydrolysis soda pulping, prehydrolysis soda ethanol pulping of cotton linters stabilizes the long-chain cellulose macromolecules against alkaline degradation. The presence of ethanol also results in a more open and accessible fine structure, higher chemical reactivity (in xanthation), and better viscose filterability. Prehydrolysis soda ethanol anthraquinone pulping results in a still higher stabilization of cellulose in cotton, a more open and accessible fine structure, higher chemical reactivity and a better viscose filterability. In this respect, the hydrochloric acid (HCl) is superior to the sulphuric acid (H₂SO₄). The prehydrolysis soda ethanol anthraquinone pulping method gives cotton linters with better chemical reactivity than that of commercial softwood pulp.

Keywords: anthraquinone (AQ), cotton linters, chemical reactivity (xanthation), ethanol, fine structure, filterability, prehydrolysis soda pulping, prehydrolysis soda ethanol pulping, prehydrolysis soda ethanol anthraquinone pulping

INTRODUCTION

Chemical cotton is used in the manufacture of numerous products, from explosives to man-made fibers. Compared to the wood cellulose and cellulose obtained from other sources, chemical cotton is characterized by an exceptionally high degree of purity. For this reason, it has achieved outstanding success in the preparation of derivatives that require high transparency and freedom from color, as well as strength and fibre properties are essential for the final product. However, the ability of cotton cellulose to form viscose is lower than that of technical wood cellulose.¹ Also, the viscose obtained from cotton cellulose has a lower filterability than that prepared from technical wood pulp and pulps from Egyptian reeds.² Cotton cellulose is characterized by a more compact and less accessible fine structure and lower reactivity towards xanthation than bagasse cellulose.³ Xanthation of bagasse viscose pulp results in higher solubility and a lower γ -number for dissolved xanthate than in the case of cotton cellulose.⁴ Other researchers⁵ found out that the degree of crystallinity and crystallite size were higher in organosolv pulps than in soda and sulphate pulps. At the same time, not only the chemical agents, but also the temperature and pressure in the cooking di-

gester had major effects on the cellulose crystalline structure of the cotton linters during cooking.

The aim of the present investigation was to obtain highly reactive cotton linter cellulose with good viscose filterability. In the experiments, ethanol was used in pulping of the cotton linter after a prehydrolysis step. The effects of ethanol on the pulp yield, the chemical pulp properties, the fine structure of cellulose and its chemical reactivity towards xanthation and viscose filterability were investigated, as well as the effects of the anthraquinone added.

EXPERIMENTAL**Raw material**

The Egyptian cotton linters here studied are characterized by a longer fibre length and higher amounts of impurities, compared to other linter types. The linters were cut into approximately 10-mm long pieces placed on a perforated plate with 2-mm in diameter holes, then the material was mechanically purified by letting compressed air through it, which removed considerable amounts of inorganic matter, broken seeds and hull particles still remaining after its ginning.⁶

Prehydrolysis, pulping and bleaching

The prehydrolysis, pulping and bleaching operations were carried out by the procedure described in a previous paper.⁶

Chemical analysis

The ash and α -cellulose contents were determined according to the American Tappi standard methods T 211 os-58 and T 203 os-61, respectively.⁷

Physical properties

The average degree of polymerization (DP) and the degree of whiteness were determined according to earlier applied procedures,^{3,8} while hot alkali solubility – according to the method of Rapson.⁹

Fine structure

There are no absolute methods to measure the fine structure of the pulp. However, some properties of cellulose provide acceptable comparative indication as to its fine structure. Good examples are the degree of cellulose swelling in water and in a sodium hydroxide solution. The fine structure is also indicated by the ratio of the crystalline and amorphous cellulose fractions. In this work, the water retention value (WRV) was estimated according to Jayme's procedures.¹⁰ The liquor retention (LRV) and sodium hydroxide retention values (NaOH-RV) were determined by allowing the pulp to swell in a sodium hydroxide solution of mercerizing strength at 20 °C, followed by centrifugation to remove the excess alkali. The centrifuged pulp was weighed, washed with distilled water to neutrality, dried to constant weight and weighed again. The washings were titrated against standard acid. Finally, the degree of crystallinity was determined according to the method of Hessler and Power.¹¹

Reactivity assessment by xanthation

For estimating its reactivity, the pulp has to be xanthated under conditions that lead to viscose with a still high content of undissolved cellulose, further viewed as indicating the reactivity of cellulose. In this work, the reactivity test was carried out with 0.5 g of pulp, 50 mL of 8% sodium hydroxide and 1 mL of carbon disulphide. The dissolved cellulose was determined volumetrically and deduced from the original amount of cellulose, according to the method of Fock.¹²

Viscose preparation and assessment of its filterability

Filterability was determined by the modified method of Centola and Pancetoli.¹³ Viscose solutions were obtained from 2-g pulp samples, by emulsion xanthation, using 100 mL of a 10% sodium hydroxide solution and 4 mL of carbon disulphide. After xanthation, they were diluted with distilled water until weighing exactly 200 g, and then vigorously shaken.

Filterability was finally measured as the time of filtration by forcing 25 mL of viscose to pass through a sintered glass funnel (G_1) by suction. Another 25 mL of viscose were forced to pass through the same funnel and the time of filtration was again recorded. The ratio between the second and first recorded times provides the filter clogging index (>1), if the filter has been clogged during the first filtration.

RESULTS AND DISCUSSION

Effect of prehydrolysis

The effect of prehydrolysis is illustrated by experiments 1, 2 and 8, as shown in Table 1 (Figs. 1-7). It is evident that prehydrolysis decreased the pulp yield, increased considerably the hot alkali solubility, decreased the DP and, in the case of sulphuric acid prehydrolysis, the degree of whiteness. However, prehydrolysis resulted in higher WRV, LRV and slightly higher NaOH-RV, better reactivity towards xanthation and considerably better viscose filterability. Compared to sulphuric acid, the hydrochloric acid was more effective in depolymerizing the cellulose, yet resulted in lower reactivity to xanthation and lower viscose filterability.

Prehydrolysis soda ethanol pulping

Experiments 2 and 3 illustrate the effects of ethanol in sulphuric acid prehydrolysis soda ethanol pulping. An ethanol:water ratio of 0.5:1 during pulping significantly raised both pulp yield and DP, while decreasing hot alkali solubility, which indicates a stabilizing effect of ethanol on the cellulose macromolecules. The fine structure was also favourably affected by ethanol, as the affinity to water and alkali increased, and chemical reactivity as well as viscose filterability improved. It seems that ethanol penetrates between the cellulose macromolecules and forms hydrogen bonds, thus increasing the intramolecular distances. This is reflected in a higher degree of swelling in water and aqueous alkali, higher chemical reactivity and better viscose filterability. The same general effects were observed in the case of hydrochloric acid prehydrolysis soda ethanol pulping (experiments 8 and 9).

Prehydrolysis soda ethanol anthraquinone pulping

The presence of different amounts of anthraquinone in pulping, following a

prehydrolysis stage with hydrochloric acid, raised the pulp yield and the α -cellulose content at high AQ charges, and increased the hot alkali solubility. It also maintained the affinity to water and alkali, even improving them, especially for the hydrochloric acid prehydrolysis, followed by a high AQ-soda-ethanol cooking. Also, chemical reactivity and viscose filterability were significantly improved, particularly at high AQ levels. The most accessible cellulose fine structure, in terms of high cellulose reactivity and good viscose

filterability, was obtained at the highest anthraquinone charge (0.15%) applied.

A comparison between the sulphuric acid prehydrolysis soda ethanol anthraquinone pulping and the corresponding hydrochloric acid pulping method reveals only a slight difference between yield and α -cellulose content, if any. However, as a rule, the AQ charge provides a much better WRV for the sulphuric acid prehydrolysis process but, accordingly, lower reactivity, as shown in Table 1 (Figs. 8-16).

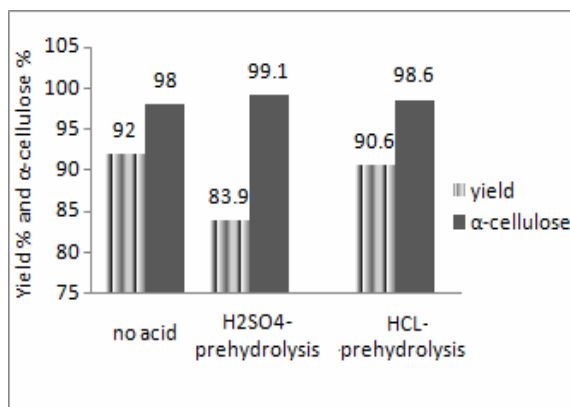


Figure 1: Effect of prehydrolysis on yield and α -cellulose

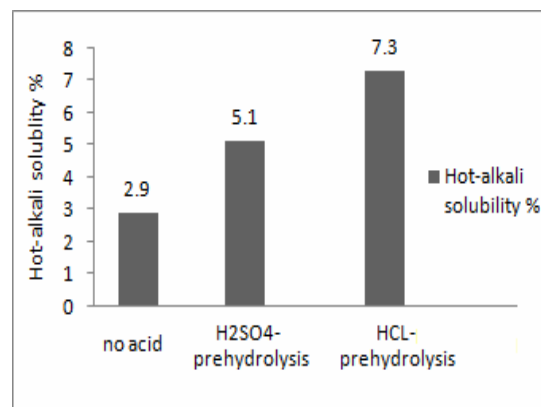


Figure 2: Effect of prehydrolysis on hot alkali solubility

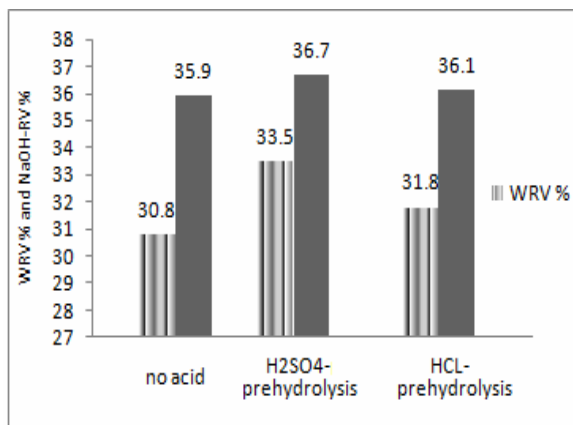


Figure 3: Effect of prehydrolysis on WRV and NaOH-RV

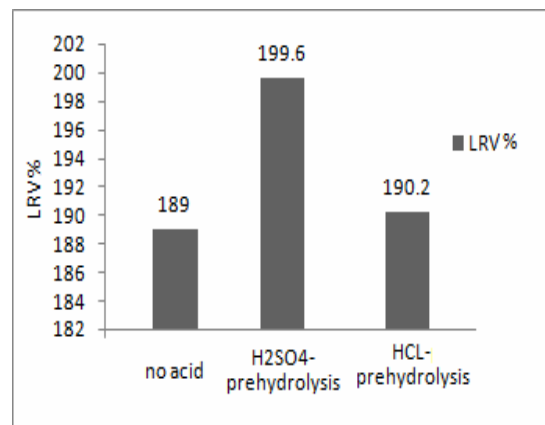


Figure 4: Effect of prehydrolysis on LRV

Table 1
Prehydrolysis soda pulping

Experiment №	1	2	3	4	5	6	7	8	9	10	11	12	13	
Parameters														
Acid used	-	H ₂ SO ₄							HCL					
Concentration of acid used, %	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Maximum temperature, °C	-	100	100	100	100	100	100	100	100	100	100	100	100	
Time at max. temp., h	-	4	4	4	4	4	4	1	1	1	1	1	1	
Concentration of NaOH solution, %	1	1	1	1	1	1	1	1	1	1	1	1	1	
Ratio of ethanol:water	-	-	0.5:1	0.5:1	0.5:1	0.5:1	0.5:1	-	0.5:1	0.5:1	0.5:1	0.5:1	0.5:1	
Concentration of AQ/100 g linters	-	-	-	0.025	0.05	0.1	0.15	-	-	0.025	0.05	0.1	0.15	
Maximum temperature, °C	100	100	100	100	100	100	100	100	100	100	100	100	100	
Time at max. temp., h	2	2	2	2	2	2	2	1	1	1	1	1	1	
Yield, %	92.0	83.9	94.0	92.4	93.4	94.3	94.5	90.6	93.3	93.9	93.5	94.5	94.7	
α-cellulose, %	98.0	99.1	99.3	98.6	99.0	99.2	99.4	98.6	98.9	99.1	98.8	99.3	99.6	
Ash, %	0.02	0.04	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.04	
Hot alkali solubility, %	2.9	5.1	4.1	4.3	4.4	4.5	4.8	7.3	4.8	5.3	5.1	5.8	6.0	
DP	1590	745	975	955	877	860	850	660	730	800	860	890	750	
Degree of whiteness, %	89	85	87	86	87	87	86	89	87	86	87	87	87	
WRV, %	30.8	33.5	39.0	37.9	38.9	45.0	38.5	31.8	32.5	33.0	33.5	35.0	39.0	
LRV, %	189.0	199.6	215.0	216.0	210.5	215.7	229.5	190.2	222.1	223.1	213.0	227.0	231.0	
NaOH RV, %	35.9	36.7	40.2	48.8	41.1	42.0	42.0	36.1	42.6	44.5	38.5	44.5	48.0	
Crystallinity, %	96	94	96	94	94	95	95	96	96	95	95	96	95	
Reactivity (% insoluble cellulose), %	70.9	63.3	46.2	45.0	43.7	40.0	36.5	68.0	53	50.0	38.0	35.5	33.0	
Filterability	3.7:1	1.5:1	1.4:1	2.4:1	2.8:1	1.8:1	1.3:1	2.3:1	2.0:1	2.3:1	2.8:1	1.9:1	1.0:1	

*The liquor ratio in all experiments was of 20:1

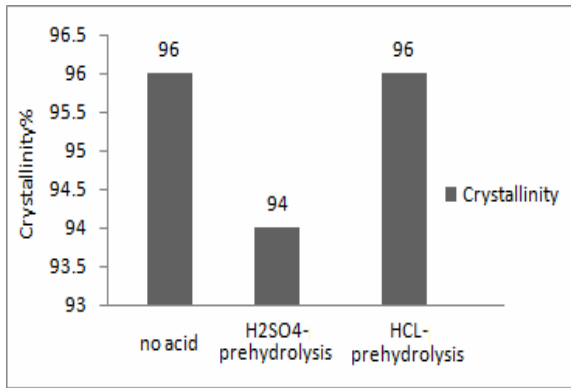


Figure 5: Effect of prehydrolysis on crystallinity

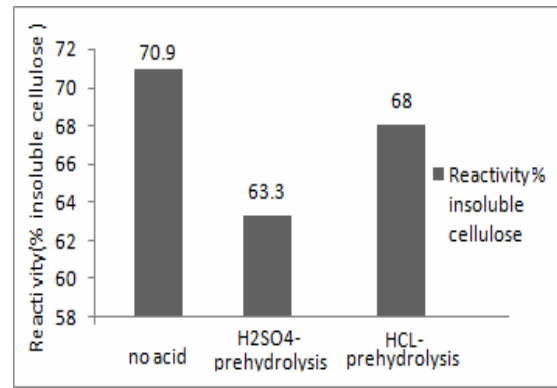


Figure 6: Effect of prehydrolysis on reactivity

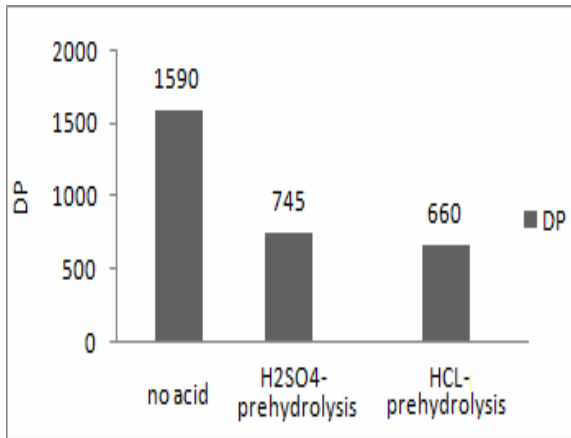


Figure 7: Effect of prehydrolysis on DP

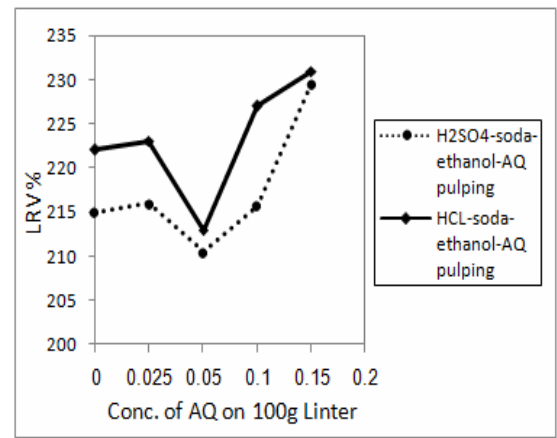


Figure 8: Change in LRV with increase of AQ concentration

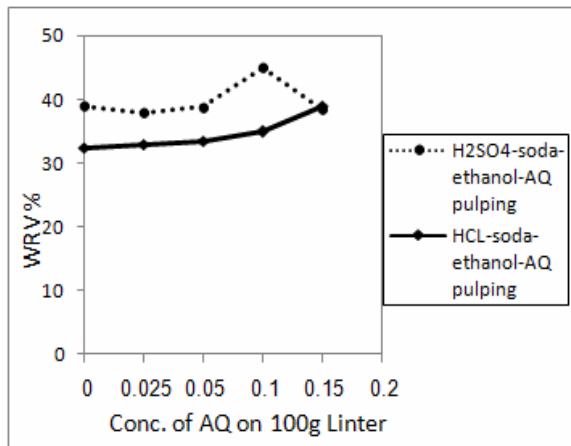


Figure 9: Change in WRV with increase of AQ concentration

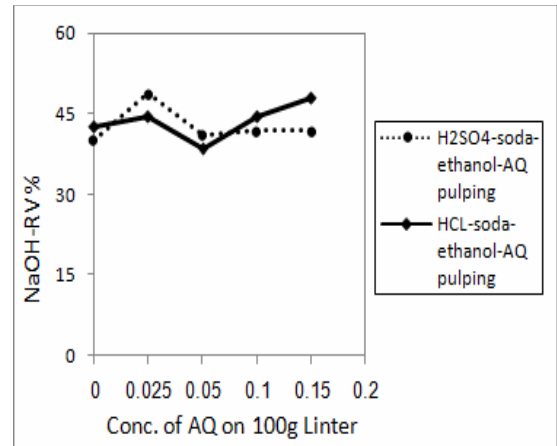


Figure 10: Change in NaOH-RV with increase of AQ concentration

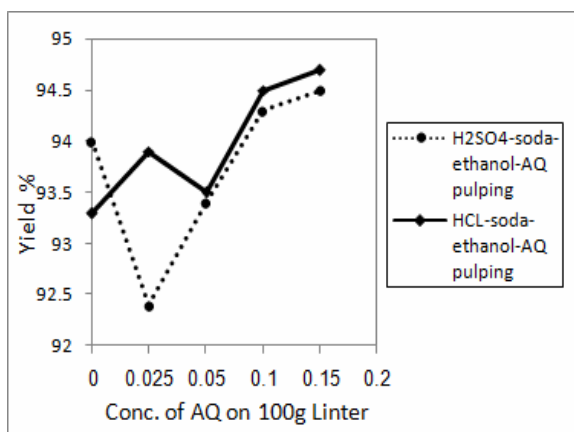


Figure 11: Change in yield with increase of AQ concentration

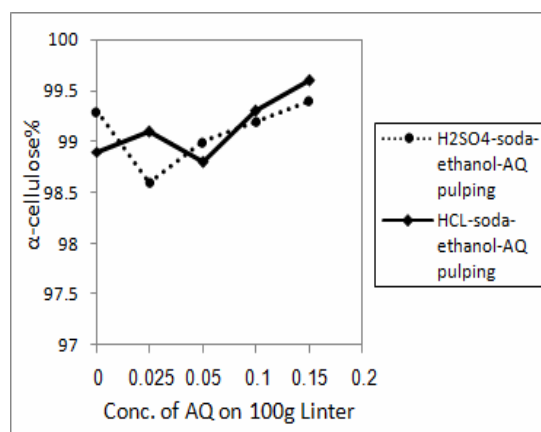


Figure 12: Change in α-cellulose with increase of AQ concentration

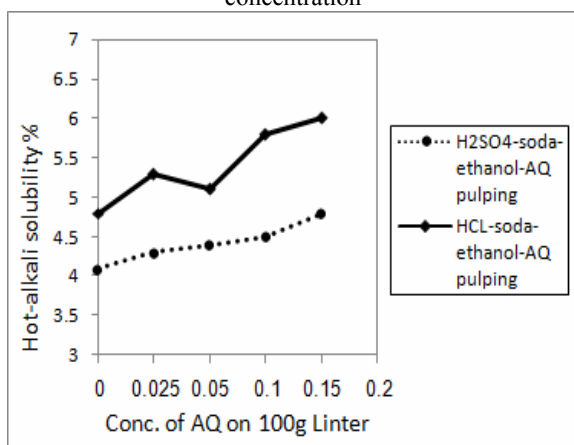


Figure 13: Change in hot alkali solubility with increase of AQ concentration

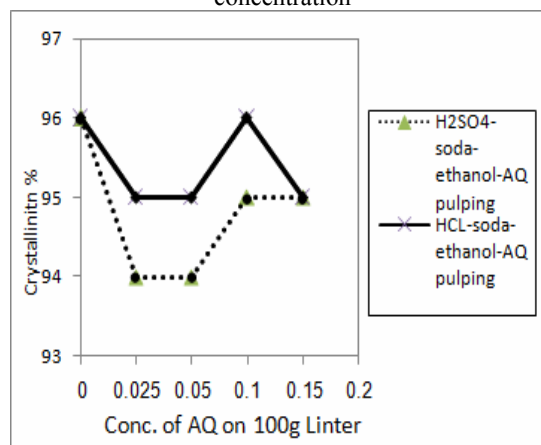


Figure 14: Change in crystallinity with increase of AQ concentration

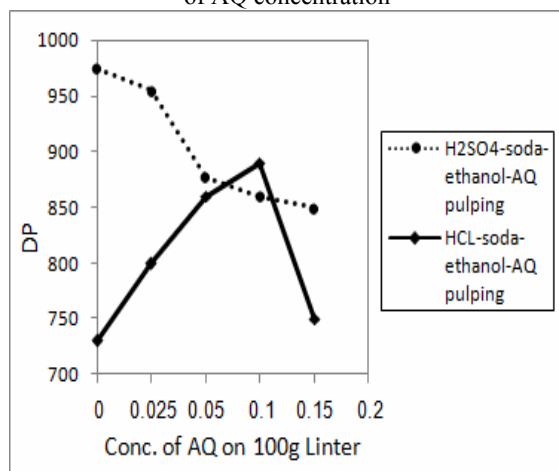


Figure 15: Change in DP with increase of AQ concentration

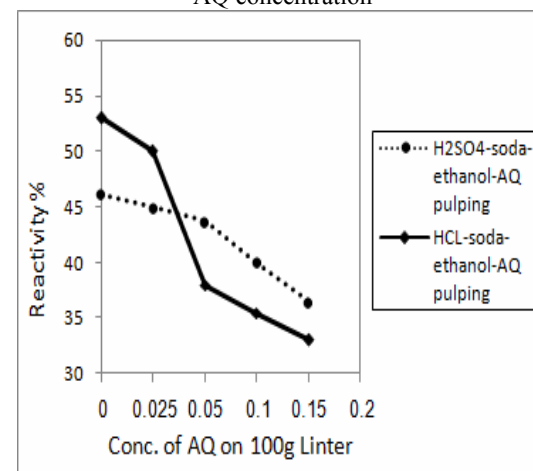


Figure 16: Change in reactivity with increase of AQ concentration

Comparison between the most reactive pulps and commercial softwood pulp

Table 2 and Figs. 17-18 list the most reactive pulps obtained by sulphuric acid and hydrochloric acid prehydrolysis-soda-ethanol-anthraquinone pulping methods, comparatively to a commercial soft wood pulp. It is evident that prehydrolysed cotton linter pulps had a

much higher α-cellulose content, lower hot alkali solubility and a much higher crystallinity than the commercial softwood pulp. Their less accessible fine structure was due to lower WRV, LRV and NaOH-RV values, but a higher reactivity *versus* commercial pulp, as viscose filterability was of the same order.

A comparison between sulphuric acid and hydrochloric acid prehydrolysis pulps shows practically no differences in pulp yield and α -cellulose content, but a clearly higher hot alkali

solubility and lower DP for hydrochloric acid prehydrolysis. It also led to a higher NaOH-RV, higher chemical reactivity and better filterability.

Table 2
Comparison between the most reactive pulps and commercial softwood pulp

Parameters	Experiment №	Softwood pulp	7	13
Acid used	-	-	H ₂ SO ₄	HCL
Concentration of acid solution, %	-	-	0.1	0.1
Maximum temperature, °C	-	-	100	100
Time at max. temperature, h	-	-	4	1
Concentration of NaOH solution, %	-	-	1	1
Ethanol:water ratio	-	-	0.5 : 1	0.5:1
Charge of AQ on 100 g of linters	-	-	0.15	0.15
Maximum temperature, °C	-	-	100	100
Time at max. temperature, h	-	-	2	1
Yield, %	-	-	94.5	94.7
α -cellulose content, %	-	92.0	99.4	99.6
Ash content, %	-	0.02	0.03	0.04
Hot alkali solubility, %	-	9.0	4.8	6.0
DP	-	612	850	750
Degree of whiteness, %	-	90	86	87
WRV, %	-	57.9	38.5	39.0
LRV, %	-	254.4	229.5	231.0
NaOH-RV, %	-	51.9	42.0	48.0
Crystallinity, %	-	87	95	95
Reactivity (% insoluble cellulose), %	-	40.2	36.5	33.0
Filterability	-	1.1:1	1.3:1	1.0:1

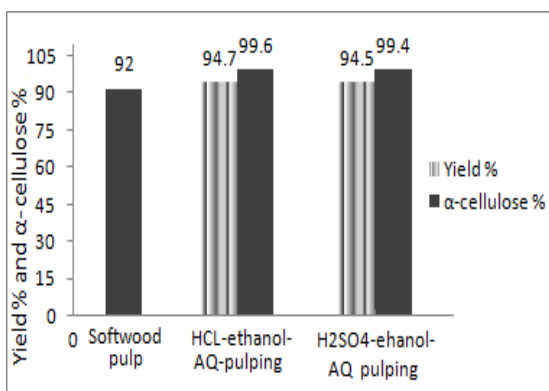


Figure 17: Effect of 0.15% AQ on yield and α -cellulose of prehydrolysed pulp

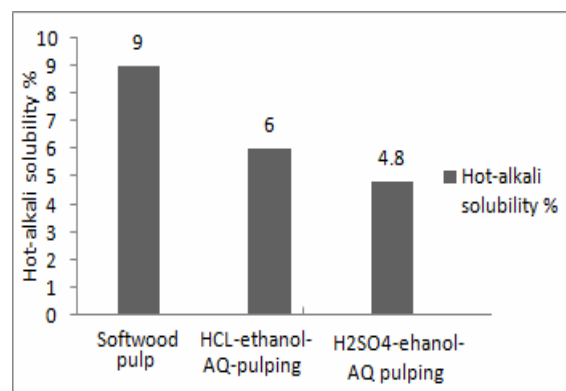


Figure 18: Effect of 0.15% AQ on hot alkali solubility of prehydrolysed pulp

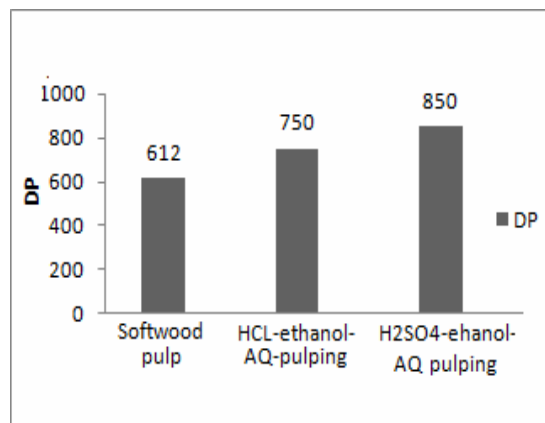


Figure 19: Effect of 0.15% AQ on DP of prehydrolysed pulp

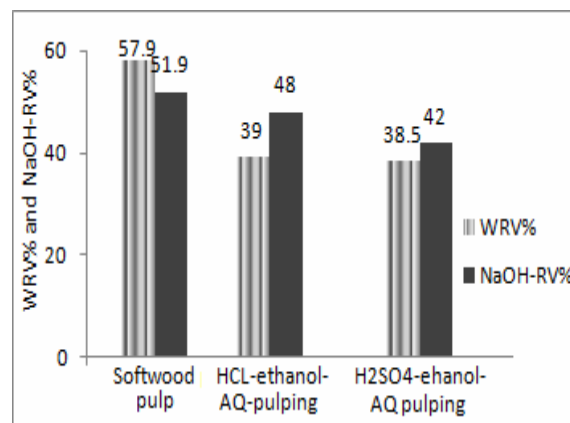


Figure 20: Effect of 0.15% AQ on WRV and NaOH-RV of prehydrolysed pulp

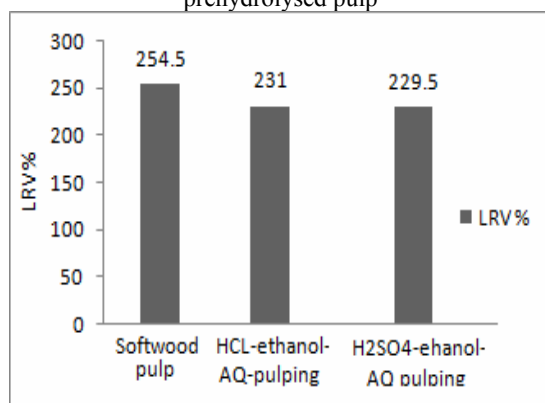


Figure 21: Effect of 0.15% AQ on LRV of prehydrolysed pulp

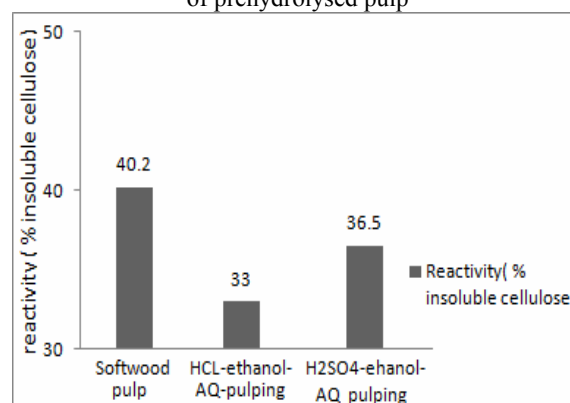


Figure 22: Effect of 0.15 % AQ on reactivity of prehydrolysed pulp

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