HIGHLY REACTIVE COTTON LINTERS FROM REFINING OF PREHYDROLYSED AQ-SODA PULP

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Prehydrolysed cotton linters were subjected to soda- and soda-AQ pulping, followed by hot and cold refining. The presence of AQ in different concentrations during soda pulping resulted in a more open and accessible fine structure, especially with 0.1% AQ concentration; compared to hot refining, cold refining was more efficient. Further improvement in cotton linter characteristics was observed when AQ was added through the acid prehydrolysis step, preserving soda pulping, especially with cold alkali refining.

Keywords: anthraquinone (AQ), cotton linters, prehydrolysis-soda pulping, cold refining, hot refining

INTRODUCTION

Chemical cotton is used in the manufacture of numerous products, from explosives to man-made fibres. Compared to 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 with good clarity, freedom from colour, as well as strength and fibre properties, which 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 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, as well as lower reactivity towards xanthation than bagasse cellulose.[3] Xanthation of bagasse viscose pulp results in higher solubility and lower γ-number for dissolved xanthate, as compared to cotton cellulose.[4]

Dissolving pulps with a high α-cellulose content were obtained by treating bleached pulp with a concentrated sodium hydroxide solution at room temperature (cold refining), or with a more diluted sodium hydroxide solution, at a higher temperature (hot refining); such treatments raised the alpha cellulose content in the pulp as they dissolved the hemicellulose. Cold refining was a true extraction phenomenon in which the alkali dissolved the hemicelluloses from swelling pulp without degradation and alkali consumption.[5] However, boiling cellulose in a dilute sodium hydroxide solution involved first a complicated degradation reaction, followed by secondary extraction of the degraded products.[6] Previous studies dealt with AQ efficiency on delignification during alkaline pulping.[7] Cold refining helps the swelling of cotton linter, while AQ penetration leads to linter decrystallization, even at low AQ concentration.[8] The present investigation compares the effect of AQ addition to acid prehydrolysis and soda pulping liquors, performed in separate steps, followed by cold and hot refining, and explains the chemical, physical characteristics and also the accessibility of the resulting samples. Such a comparative study has not been carried out before.

EXPERIMENTAL

Raw material

The Egyptian cotton linters here studied are characterized by longer fibres 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, after which 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.[9]

Prehydrolysis, pulping and bleaching

The prehydrolysis, pulping and bleaching operations were carried out as described in an earlier study.[9]

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.[10]

Physical properties

The average degree of polymerization (DP) and the degree of whiteness were determined according to earlier applied procedures,[3,11] while hot alkali solubility – according to Rapson's method.[12]

Fine structure

There are no absolute methods to measure the fine structure of the pulp. However, some properties of cellulose provide acceptable comparative hints on 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.[13] 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 Hessler and Power's method.[14]

Reactivity due to xanthation

For estimating the reactivity of the pulp, it was xanthated under conditions that led to viscose, there still remaining a considerable 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 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 Fock's method.[15]

Viscose preparation and measurement of filterability

Filterability was determined by the modified method of Centola and Pancetolli.[16] 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 to pass through a sintered glass funnel (G_1) by suction. Another 25 mL of viscose was forced to pass through the same funnel and the time of filtration was again recorded. The ratio between the second and the first time values recorded provides the filter clogging index (>1), if the filter had been clogged during the first filtration.

RESULTS AND DISCUSSION

Table 1 and Figures 1-6 show the effect of hot and cold refining on the chemical, physical and submicroscopic characteristics of soda-cotton pulp. It is clear that both hot and cold refining of cotton pulp, with 5% and 15% NaOH, respectively, improved the pulp properties, so that alkali refining resulted in a more open and accessible fine structure than the unrefined pulp, which evidences higher WRV, LRV and NaOH RV values and better reactivity towards xanthation. This effect is due to the mercerizing effect of NaOH on the highly compact cotton fibres, while the increased yield and α-cellulose indicate the degrading effect of alkali refining on short-chain carbohydrates. It seems that the most beneficial effect on the physical and submicroscopic characteristics of the pulp was obtained at a higher alkali concentration (15%) and a lower temperature (20 °C); consequently, alkali treatment at low temperature (20 °C) enhances the expansion and swelling of fibres, which results in a more open and accessible fine structure, as indicated by higher LRV and NaOH RV values, higher reactivity towards xanthation and lower crystallinity.

Table 2 illustrates the role of AQ in soda pulping after prehydrolysis with 0.1% H_2SO_4, followed by hot alkali refining with 5% NaOH based on linters. In experiment 2, sodium hydroxide alone was used in pulping while 0.05, 0.1, 0.15 and 0.2% AQ (based on prehydrolysed material) were used together with sodium hydroxide during pulping, in experiments 4 to 7. It was shown that the presence of AQ in soda pulping, followed by hot refining, increased the yield and α-cellulose at all concentrations, as due to the stabilizing effect of AQ on the carbohydrate chains. Also, AQ has a marked effect on the bleachability and delignification of pulp (as indicated by the degree of whiteness), since the AQ enhances the fragmentation of lignin macromolecules into soluble low-molecular weight fractions. The most significant effect of AQ was visible in the fine structure, as indicated by the increase of WRV, LRV, NaOH RV and higher pulp reactivity, up to a 0.2% AQ concentration, as compared to experiment 2, in which there is no AQ. Hot refining resulted in a slight decrease in DP, which was due to the degrading effect of hot alkali on the carbohydrate chains. The best results were obtained with 0.1% AQ (based on pulp), which resulted in a more open and accessible fine structure than those obtained with other quinone concentrations.

Table 1
Effect of hot and cold refining on chemical, physical and submicroscopic characteristics of soda cotton pulp

Experiment	1	2	3
Concentration of H_2SO_4 solution, %	0.1	0.1	0.1
Maximum temperature, °C	100	100	100
Time at maximum temperature, h	4	4	4
Concentration of NaOH solution, %	1	1	1
Maximum temperature, °C	100	100	100
Time at maximum temperature, h	2	2	2
Refining of bleached pulp		Hot	Cold
Concentration of NaOH/100 g linters, %	-	5	15
Maximum temperature, °C	-	100	20
Time at maximum temperature, h	-	1	1
Analysis of bleached pulp			
Yield, %	88.2	98.1	99.5
α-cellulose, %	98.3	98.6	98.7
Ash, %	0.03	0.03	0.03
Hot alkali solubility, %	3.3	2.71	3.9
DP	850	850	810
Degree of whiteness, %	86	88	87
WRV, %	38.4	42.0	39.0
NaOH RV, %	40.0	43.0	45.0
LRV, %	210.1	227.0	226.0
Crystallinity, %	97	97	96
Reactivity (as % insoluble cellulose)	60.8	56.0	49.1
Filterability	1.9:1	1.5:1	2.1:1

Table 2
Behaviour of soda-AQ pulps during hot refining

Experiment	2	4	5	6	7
Concentration of H_2SO_4 solution, %	0.1	0.1	0.1	0.1	0.1
Maximum temperature, °C	100	100	100	100	100
Time at maximum temperature, h	4	4	4	4	4
Concentration of NaOH solution, %	1	1	1	1	1
Concentration of AQ/100 g linters	-	0.05	0.1	0.15	0.2
Maximum temperature, °C	100	100	100	100	100
Time at maximum temperature, h	2	2	2	2	2
Refining of bleached pulp (hot)					
Concentration of NaOH/100 g	5	5	5	5	5
linters, %	100	100	100	100	100

Maximum temperature, °C	1	1	1	1	1
Time at maximum temperature, h					
Analysis of bleached pulp	98.1	98.5	99.5	99.6	99.8
Yield, %	98.6	98.9	99.1	99.2	99.2
α-cellulose, %	0.03	0.02	0.02	0.03	0.02
Ash, %	2.71	2.21	3.1	3.5	4.2
Hot alkali solubility, %	850	840	825	750	800
DP	88	89	90	91	92
Degree of whiteness, %	42.0	42.7	43.9	42.5	42.3
WRV, %	43.0	43.8	45.3	44.0	43.3
NaOH RV, %	227.0	228.5	237.5	235.5	234.2
LRV, %	97	96	95	96	96
Crystallinity, %	56.0	50.8	43.5	45.0	48.1
Reactivity (as % insoluble cellulose)	1.5:1	2.3:1	1.8:1	2.0:1	2.5:1
Filterability					

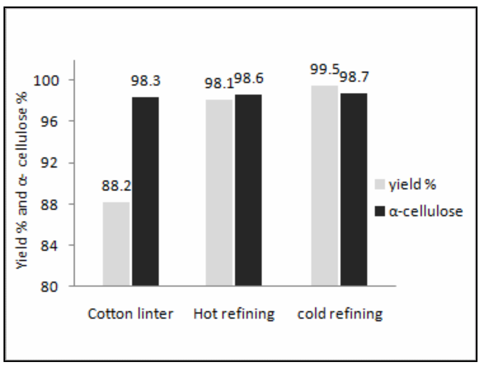

Figure 1: Effect of hot and cold refining on yield, %, and α-cellulose, %

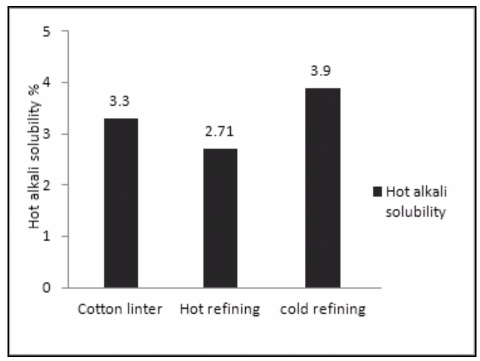

Figure 2: Effect of hot and cold refining on hot alkali solubility, %

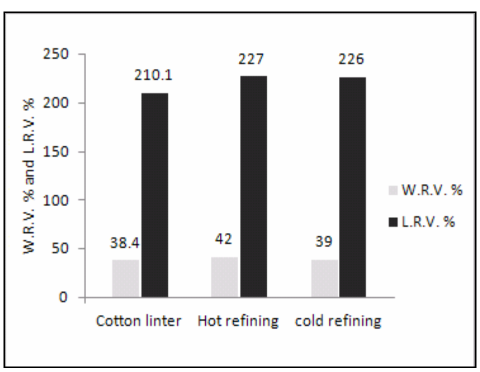

Figure 3: Effect of hot and cold refining on WRV, %, and LRV, %

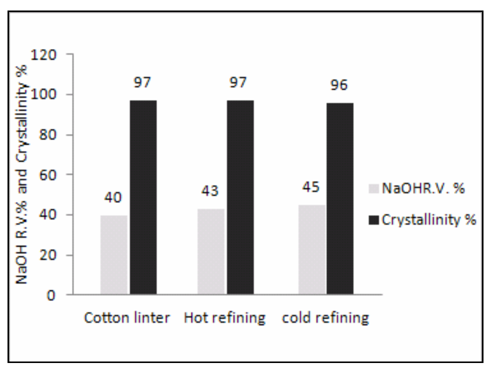

Figure 4: Effect of hot and cold refining on NaOH RV, %, and crystallinity, %

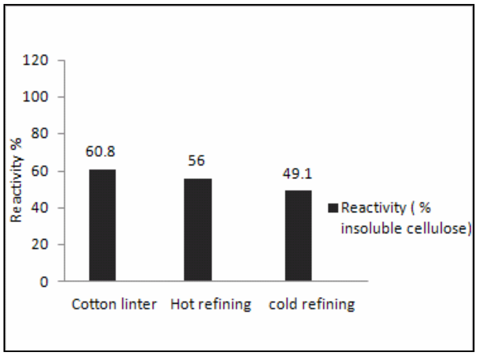

Figure 5: Effect of hot and cold refining on reactivity (% insoluble cellulose)

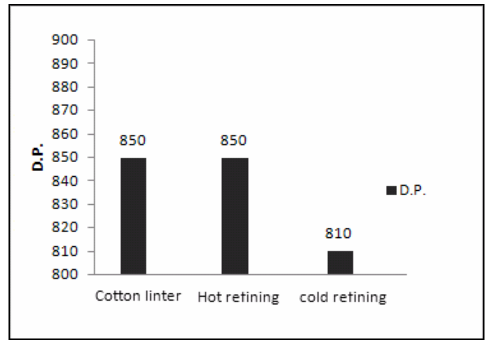

Figure 6: Effect of hot and cold refining on DP

Table 3
Behaviour of soda-AQ pulps during cold refining

Experiment	3	8	9	10
Concentration of H_2SO_4 solution, %	0.1	0.1	0.1	0.1
Maximum temperature, °C	100	100	100	100
Time at maximum temperature, h	4	4	4	4
Concentration of NaOH solution, %	1	1	1	1
Concentration of AQ/100 g linters	-	0.05	0.1	0.15
Maximum temperature, °C	100	100	100	100
Time at maximum temperature, h	2	2	2	2
Refining of bleached pulp (cold)				
Concentration of NaOH/100 glinters, %	15	15	15	15
Maximum temperature, °C	20	20	20	20
Time at maximum temperature, h	1	1	1	1
Analysis of bleached pulp				
Yield, %	99.5	99.7	99.6	99.5
α-cellulose, %	98.7	99.2	99.3	99.0
Ash, %	0.03	0.02	0.02	0.03
Hot alkali solubility, %	3.9	3.8	3.2	3.9
DP	810	800	820	850
Degree of whiteness, %	87	91	92	91
WRV, %	39.0	43.0	44.0	42.0
NaOH RV, %	45.0	45.6	45.7	43.0
LRV, %	226.0	228.0	228.9	227.0
Crystallinity, %	96	96	95	95
Reactivity (as % insoluble cellulose)	49.1	42.0	36.6	43.0
Filterability	2.1:1	1.8:1	1.3:1	2.0:1

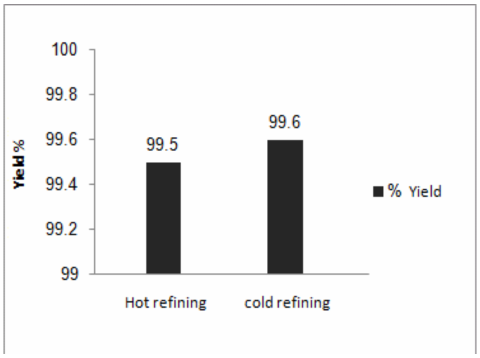

Figure 7: Effect of hot and cold refining on yield, %, of soda-AQ pulp (0.1)

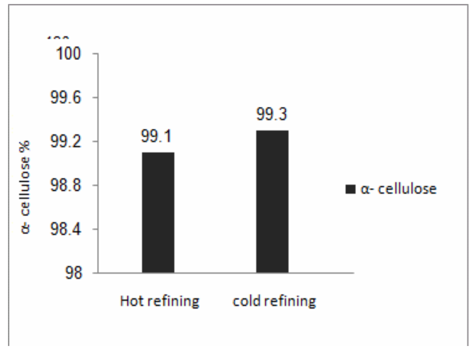

Figure 8: Effect of hot and cold refining on α-cellulose, %, of soda-AQ pulp (0.1)

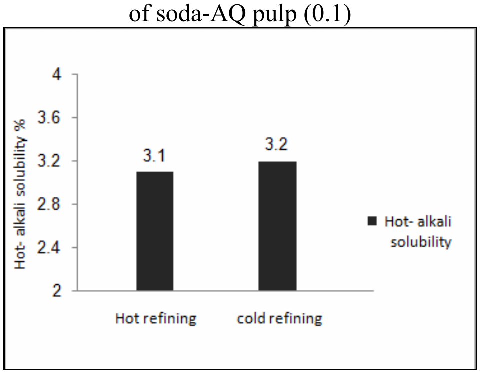

Figure 9: Effect of hot and cold refining on hot alkali solubility, %

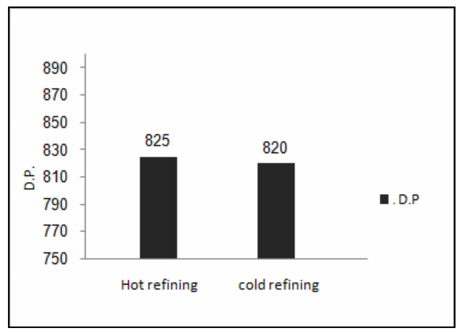

Figure 10: Effect of hot and cold refining on DP of soda-AQ pulp (0.1)

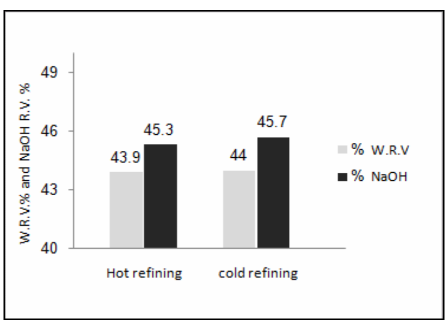

Figure 11: Effect of hot and cold refining on WRV, %, and NaOH RV of soda-AQ pulp (0.1)

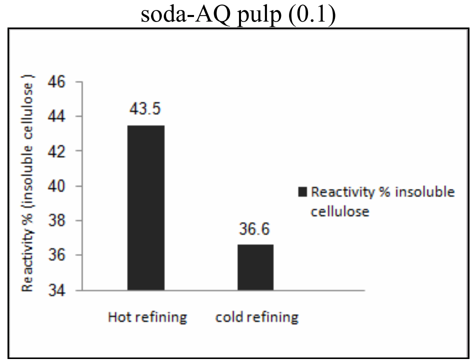

Figure 12: Effect of hot and cold refining on reactivity, %, (insoluble cellulose) of soda-AQ pulp (0.1)

Table 4
Comparison of the results for the most accessible soda-AQ pulps after hot and cold refining

Experiment	5	9
Concentration of H_2SO_4 solution, %	0.1	0.1
Maximum temperature, °C	100	100
Time at maximum temperature, h	4	4
Concentration of NaOH solution, %	1%	1%
Concentration of AQ/100 g linters	0.1	0.1
Maximum temperature, °C	100	100
Time at maximum temperature, h	2	2
Refining of bleached pulp	Hot	Cold
Concentration of NaOH/100 g linters	5%	15%

Maximum temperature, °C	100	20
Time at maximum temperature, h	1	1
Analysis of bleached pulp		
Yield, %	99.5	99.6
α-cellulose, %	99.1	99.3
Ash, %	0.02	0.02
Hot alkali solubility, %	3.1	3.2
DP	825	820
Degree of whiteness, %	90	92
WRV, %	43.9	44.0
NaOH RV, %	45.3	45.7
LRV, %	237.5	228.9
Crystallinity, %	95	95
Reactivity (as % insoluble cellulose)	43.5	36.6
Filterability	1.8:1	1.3:1

The behaviour of soda-AQ pulps during cold refining is shown in Table 3. In experiment 3, sodium hydroxide alone was used in soda pulping, followed by cold refining with 15% NaOH (based on prehydrolysed pulp), while AQ in concentrations of 0.05, 0.1 and 0.15% were used together with NaOH in experiments 8, 9 and 10, respectively, followed by cold refining. It was found out that AQ enhances the stabilization of the carbohydrate molecules, thus increasing the yield and α-cellulose, and improving pulp accessibility, since it gives a more open and accessible fine structure, as indicated by higher WRV, LRV, NaOH RV values, higher reactivity and decreased crystallinity. As compared to experiment 3, in which there was no AQ, filterability also improved. The best results were attained at a 0.1% AQ concentration, when the accessibility of the fine structure markedly increased, and reactivity, together with filterability, were considerably improved, while the further increase in AQ concentration, up to 0.15%, increases the inaccessibility of the pulp. This may be due to the high stabilizing effect of quinone and of its higher concentration, together with the effect of drying after refining at high alkali concentration (0.15%), as indicated by the decrease in LRV, NaOH RV and also by a lower reactivity.

Tables 2 and 3 show that cold refining was more efficient in the extraction and solubilization of the short-chain carbohydrates than hot alkali refining, which, together with the stabilizing effect of AQ on the carbohydrate molecules, resulted in increased yield and α-cellulose. The best results were obtained at 0.1% AQ, since it gives a more open and accessible fine structure, as shown by higher WRV, LRV, reactivity and better viscose filterability, while hot alkali solubility and DP were not significantly affected. A comparison of the results obtained for the most accessible pulps after cold and hot refining is shown in Table 4 and in Figures 7-12 The most significant and pronounced effect of AQ occurred when it was added together with H_2SO_4 (0.1%) in the prehydrolysis step. Hence, the acid aids AQ to penetrate among the chains, thus enhancing the stabilization of the chains, as shown by the higher value of DP, α-cellulose and yield. Also, the presence of AQ helps to separate the fibres, breaks the hydrogen bonds and provides better accessibility of the hydroxyl groups to the reactant molecules, which leads to a pulp with a more open and accessible fine structure, as shown by the higher WRV, LRV, NaOH RV values and also by the higher reactivity in xanthogenation. However, the best results were obtained when using cold refining with 15% NaOH at 20 °C – as in experiment 12. This was due to the mercerization and swelling effects of alkali at 20 °C and 15% concentration, in addition to the solubilization of short-chain molecules, reflected in the higher value of DP and in a high hot alkali solubility, comparatively with hot refining experiment (11); also, cold refining enhances the expansion and swelling of fibres, thus increasing the accessibility of the fine structure, as shown by the higher reactivity and better filterability; however, in hot refining there appeared some short-chain molecules, since hot refining causes a higher degradation, as indicated by the lower DP value, lower hot alkali solubility and lower filterability, comparatively with cold refining.

A comparison between the effect of AQ in acid prehydrolysis and soda pulping on linter properties is shown in Table 5 and Figures 13-20.

Table 5
Comparison between the effect of AQ in acid prehydrolysis and soda pulping on linter properties

Experiment	5	9	11	12
Concentration of H_2SO_4 solution, %	0.1	0.1	0.1	0.1
Concentration of AQ/100 g linters, %	-	-	0.1	0.1
Maximum temperature, °C	100	100	100	100
Time at maximum temperature, h	4	4	4	4
Concentration of NaOH solution, %	1	1	1	1
Concentration of AQ/100 g linters, %	0.1	0.1	-	-
Maximum temperature, °C	100	100	100	100
Time at maximum temperature, h	2	2	2	2
Refining of bleached pulp	Hot	Cold	Hot	Cold
Concentration of NaOH/100 g linters, %	5	15	5	15
Maximum temperature, °C	100	20	100	20
Time at maximum temperature, h	1	1	1	1
Analysis of bleached pulp				
Yield, %	99.5	99.6	99.7	99.6
α-cellulose, %	99.1	99.3	99.9	99.8
Ash, %	0.02	0.02	0.02	0.02
Hot alkali solubility, %	3.1	3.2	1.24	1.6
DP	825	820	923	1137
Degree of whiteness, %	90	92	90	91
WRV, %	43.9	44.0	51.0	47.2
NaOH RV, %	45.3	45.7	53.0	50.4
LRV, %	237.5	228.9	240.0	234.1
Crystallinity, %	95	95	95	95
Reactivity (as % insoluble cellulose)	43.5	36.6	40.0	34.0
Filterability	1.8:1	1.3:1	1.4:1	1.1:1

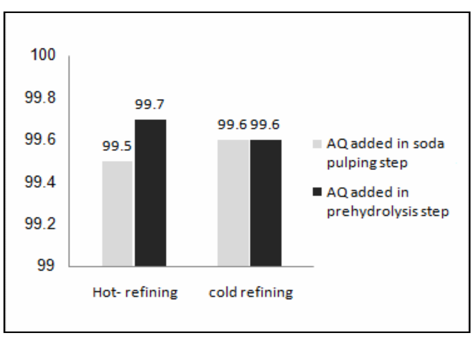

Figure 13: Effect of AQ addition in both prehydrolysis and pulping

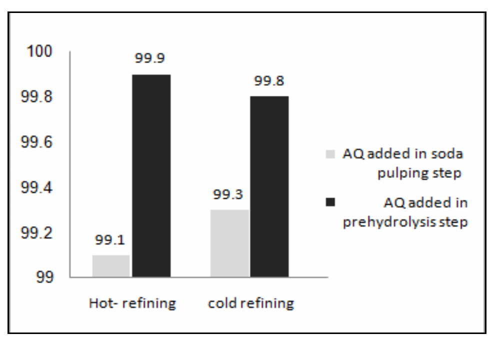

Figure 14: Effect of AQ addition in both prehydrolysis and pulping step on α-cellulose, %

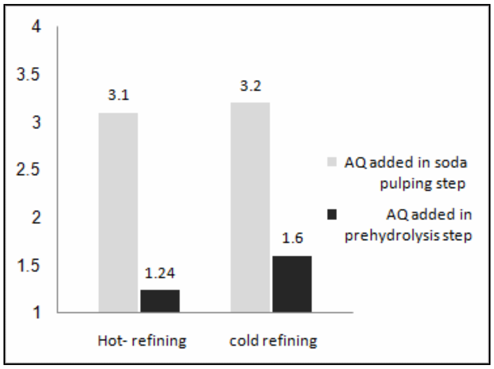

Figure 15: Effect of addition of AQ in both prehydrolysis and pulping step on hot alkali solubility, %

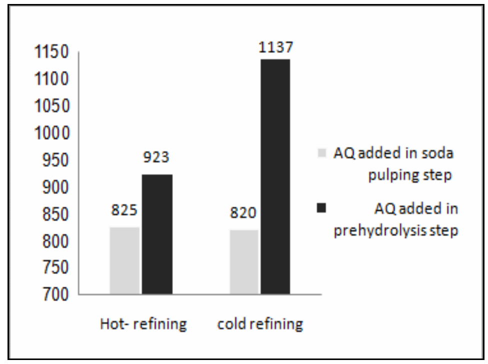

Figure 16: Effect of addition of AQ in both prehydrolysis and pulping step on DP

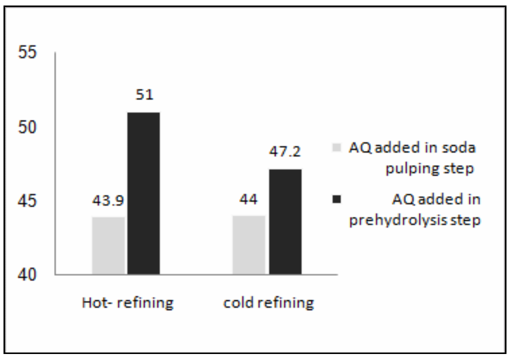

Figure 17: Effect of addition of AQ in both prehydrolysis and pulping step on WRV, %

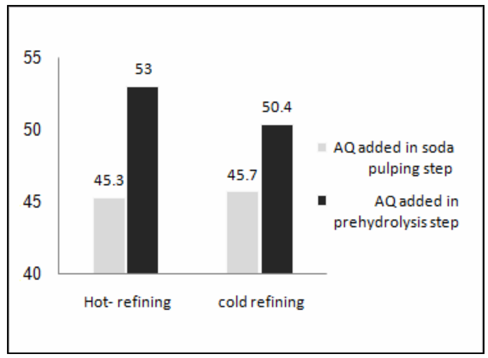

Figure 18: Effect of addition of AQ in both prehydrolysis and pulping step on NaOH RV, %

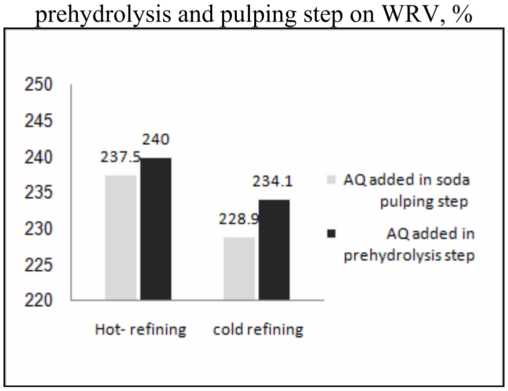

Figure 19: Effect of addition of AQ in both prehydrolysis and pulping step on LRV, %

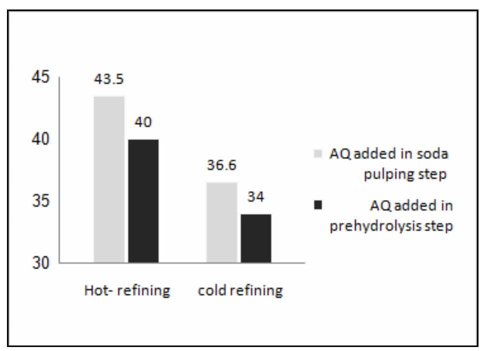

Figure 20: Effect of addition of AQ in both prehydrolysis and pulping step on reactivity, % (%, insoluble cellulose)

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