IMPROVING THE PULP YIELD BY USING PS/AQ AND/OR TWO STAGE OXYGEN DELIGNIFICATION

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ABSTRACT

The effect of polysulfide (PS) and anthraquinone (AQ) addition on kraft cooking is investigated together with oxygen delignification of the high-yield PS/AQ kraft pulps. Addition of polysulfide and AQ increases pulp yield. The yield benefit is considerably lowered when cooking to kappa numbers below 27-28. Oxygen delignification to about 55% delignification preserves the yield increase attained by PS/AQ addition. For two-stage extended oxygen delignification beyond 55% kappa decrease , the yield increase is lowered. Peroxyacetic acid "activation" of the pulp followed by a second oxygen stage also lowered the yield significantly. From the data presented, optimal yield for bleached pulp would be reached when cooking with PS/AQ addition to kappa numbers between 40 and 45, followed by oxygen delignification to kappa numbers around 22. This could then be followed by bleaching with more selective bleaching chemicals like ozone and/or chlorine dioxide.

INTRODUCTION

The main reason for applying polysulfide in kraft mills is to increase the pulp yield through stabilization of the carbohydrates in wood against alkaline degradation (peeling) [1,2]. Addition of AQ in alkaline pulping enhances both the delignification rate and increases pulp yield [3]. The yield increasing effect of polysulfide and AQ is additive or even synergistic [4]. The yield increase by polysulfide pulping is mainly dependent on the concentration of polysulfide in the impregnation and cooking liquor, the impregnation, pulping conditions and wood species [5]. Reduction in chip size, improved impregnation of the chips and reduction in cooking temperature increases the yield effect. The yield gain decreases as the lignin content in the pulp diminishes. Hardwoods give somewhat lower yield gains than softwoods. Addition of 0.5 to 1 kg AQ per ton of pulp in kraft and polysulfide pulping results in a yield gain of about 1% (on wood), 2-5% saving of alkali and 2-3°C reduction in the cooking temperature [4].

At the Peterson Linerboard mill in Moss, Norway, polysulfide and anthraquinone is used to improve pulp yield in the kraft cook. Polysulfide concentration of the cooking liquor is about 5-6 grams sulfur per liter, which occurs when about 50% of the sulfide in the white liquor is oxidized by the Moxy process [6]. The results of polysulfide-AQ pulping at the Moss mill is that when charging ~0.8% polysulfide (as S_0) and 0.03% AQ on wood, a yield increase of about 2.3% on wood is reached at kappa 60.

Further improvements in polysulfide pulping can be made:

- increasing the efficiency of converting the sulfide present in the chemical recovery system to polysulfide, and/or
- improving the yield increase for a given polysulfide charge to the digester system.

The properties of polysulfide pulps are comparable to the properties of kraft pulps. Polysulfide pulps may however be easier to beat than kraft pulps due to the higher content of hemicelluloses.

Oxygen delignification is more selective than alkaline cooking itself. At the same kappa number, a higher yield can be obtained when combining cooking and oxygen delignification [7-10]. The main reasons for introducing oxygen delignification were the beneficial effects on the environment, process economy and energy savings [11]. The main driving force behind oxygen delignification has been reduction in water pollution due to the possibility of replacing the elemental chlorine bleaching stage. Oxygen is cheap compared to other bleaching chemicals, and effluents from an oxygen stage contain no chlorinated compounds that may induce corrosion in the recovery boiler. The burning of effluents from the oxygen stage in the chemical recovery reduces the bleach plant effluent load and increases energy recovery. In most cases, the content of organic matter in the effluent from the bleach plant, as well as the consumption of bleaching chemicals, is reduced by more than 50% by oxygen/alkali delignification before bleaching.

Since the commercialization of oxygen bleaching in South Africa in 1970, studies have been conducted to optimize the process. Kinetic studies using model compounds [12-15] and kraft pulps [16-21] have been carried out in efforts to develop means of selectively removing lignin from the pulp without

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causing a detrimental degradation to carbohydrate structure. In order to maximize the delignification potential of oxygen, two-stage systems have been developed [22-24]. Two-stage oxygen bleaching may be important with TCF bleaching where extra low kappa numbers are required.

EXPERIMENTAL

Pulping

All the pulps that were used in this study were made from Norwegian softwood spruce chips. The pulps were made in our CRS flow-through reactor as described earlier [25]. The pulps include conventional kraft and kraft-PS/AQ pulps that were made by charging all the cooking liquor once, and isothermal kraft and kraft-PS/AQ where a split alkali charge was used. For the ITC polysulfide pulp, the total of 2% polysulfide (as S_0) on wood was charged during the impregnation stage.

Simulation of an extended cook

Two pulps were chosen for simulation of an extended delignification through cooking. The two pulps were the ITC-cooked kraft pulp with a kappa number of 32.6 and the ITC-cooked PS/AQ pulp cooked with 2% polysulfide charge and a kappa number of 30.1. Simulation of an extended cook was performed at 159°C, at a high liquor to pulp ratio of 20:1 in a solution of 13 g/l NaOH.

Oxygen Delignification

The oxygen delignification was performed at 10% consistency in autoclaves. The parameters employed were:

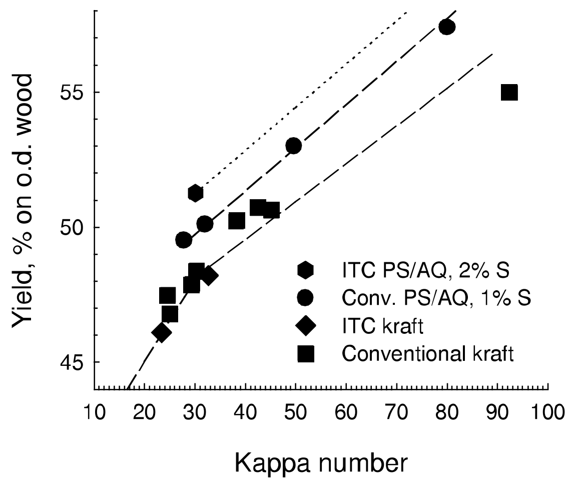
consistency	10 %
NaOH charge	2 - 5%
Temperature	101 °C
Time	90 minutes
$MgSO_4$	0.5 %
Oxygen pressure	6 bars

Peracetic Acid Treatment

Peroxyacetic acid (peracetic acid, Paa) treatment was performed at 10% consistency in plastic bags under the following conditions:

Paa charge	3%
NaOH charge	about 2% to adjust pH to 5-6
Temperature	80°C
Time	60 minutes
MgSO4	0.25%
DTPA	0.2%

Fig. 1: Effect of polysulfide



RESULTS AND DISCUSSION

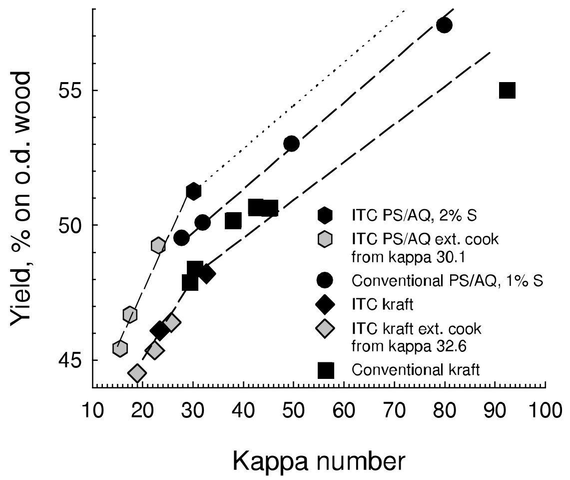
Effect of PS/AQ and Extended Digester Delignification

Figure 1 shows the kappa-yield relationship obtained by addition of different charges of polysulfide. The pulps include conventional PS/AQ and conventional kraft pulps obtained by charging all the cooking liquor at the beginning of the cook. Other pulps were made by simulating isothermal cooking (ITC™) by split alkali addition. Charging 2% polysulfide (as S_0) during the impregnation stage in an ITC-type cook gave the highest yield at kappa number 30. The yield for isothermal kraft pulps was similar to the conventional kraft pulps within experimental errors. The linear regression lines for the kraft and PS/AQ (1% S_0) show good correlation with previously reported slopes of 0.16 (% Yield/kappa) for polysulfide pulping [26] and 0.14 for conventional kraft [5,27]. A similar line with a slope of 0.16 (% Yield/kappa) has been tentatively drawn through the single point for the high-PS ITC cook.

It appears that the lower limit of linearity for kraft pulping is located below kappa number 30, which corresponds with previous authors [8]. From the data presented in this study, one would estimate the limit of linearity to be between kappa numbers 27 and 28. This is further supported by the extended cook simulation shown in Figure 2.

To study in detail the later phase of the kraft cook, two pulps were subjected to extended delignification by NaOH. It has been shown that in this phase of the cook, the sulfide ion plays an insignificant role in delignification [28]. An extended delignification by NaOH at the cooking temperature was therefore assumed an adequate simulation of the final phase of the cook. This assumption is supported by the good

Fig. 2: Simulating an extended cook



correspondence between the yield-kappa relationship for the simulated extended cook and a normal cook to low kappa numbers for the ITC kraft pulps (Figure 2). The effect of extended delignification by NaOH solution on yield and kappa number of two of the isothermal cooking kraft and PS/AQ-kraft pulps cooked to kappa numbers around 30 is shown in Figure 2. The reduction of yield when extending the cook significantly below kappa number 30 was about 0.3 and 0.4 % units (on o.d. wood) per kappa number unit for the kraft and PS/AQ pulps respectively. The yield benefit obtained by the addition of polysulfide and anthraquinone is thus drastically reduced when extending the cook below kappa 27-28.

Figure 3 shows the results of oxygen delignification of various PS/AQ pulps. Only the pulp of kappa number 80 was oxygen delignified in two stages. The yield loss per kappa number

Fig. 3: Oxygen delignification

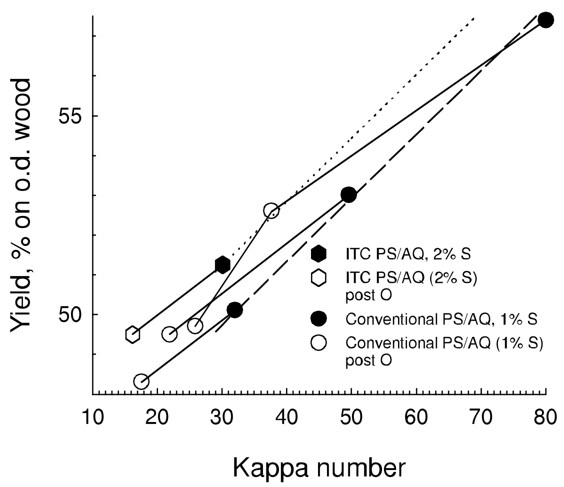
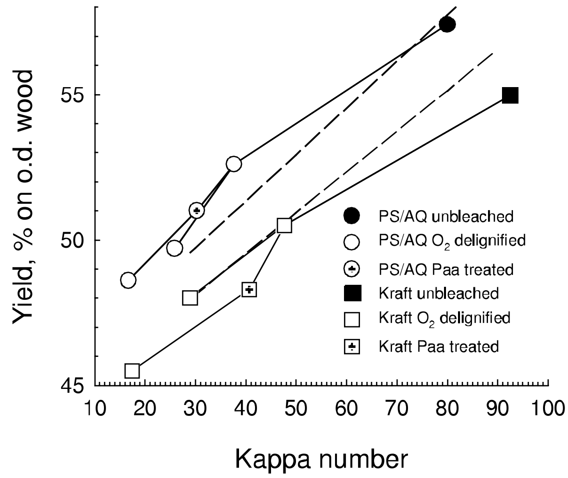


Fig. 4: Extending oxygen delignification



reduction in the first oxygen stage was 0.1 % units. Extending the oxygen delignification beyond 55% by a second oxygen stage resulted in a yield loss per kappa number that was significantly higher than when limiting the oxygen delignification to below 55%. There was a slight improvement in yield when peracetic acid was used as interstage treatment, but for all PS/AQ pulps there was a significant yield loss in the peracetic acid stage (Figure 4). For the kraft pulp, the selectivity of a second oxygen stage could compare favorably with that of the kraft cook, but was inferior to the first oxygen stage. Previous authors have also reported on larger yield losses in a second oxygen stage beyond 50% delignification when bleaching polysulfide pulps of kappa 40 and 49 [26].

In Figure 5, removal of approximately 50% of the lignin by extended cooking is compared to oxygen delignification. By

Fig. 5: Oxygen vs. extended cooking

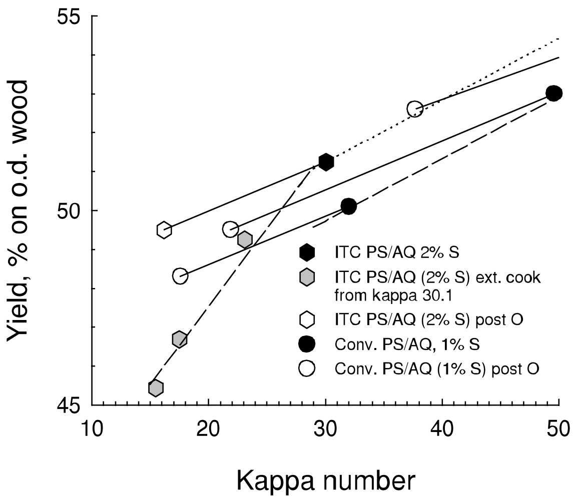
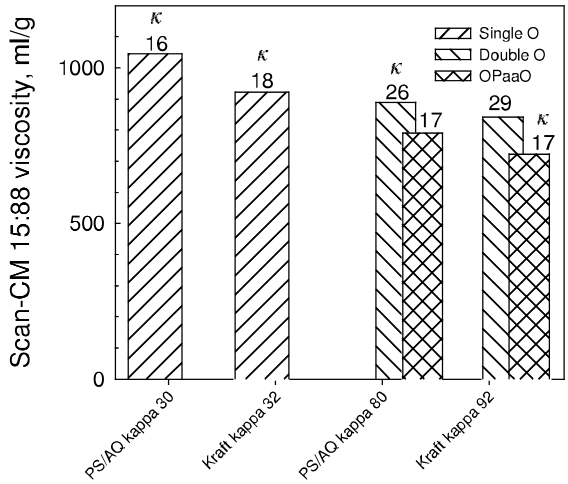


Fig. 6: Pulp viscosities and kappa numbers



extending the delignification of PS/AQ pulp using NaOH, there is a yield loss of 0.4 % units per kappa number decrease, *i.e.* four times the yield loss by oxygen delignification. The results clearly show the good selectivity of oxygen delignification as compared to extended delignification by alkaline pulping to low kappa numbers. Still, multistage oxygen delignification of high-kappa kraft or PS/AQ pulps does not seem like the optimal process for maximizing the yield. If maximum yield is to be obtained, the cook should be stopped at or before kappa number 30. Kappa numbers in the range of 40-45 followed by oxygen delignification to kappa numbers around 22 seem to be the ideal case for maximizing the yield. Other, more selective, delignifying bleaching chemicals like ozone and/or chlorine dioxide should then be considered for final delignification in the bleach plant.

The pulp viscosities after oxygen delignification are higher for polysulfide pulps than for kraft pulps. Comparing different methods for delignification to comparable kappa numbers, the pulp viscosity after extended, two-stage oxygen delignification is lower compared to the pulp viscosity of single-stage oxygen delignified pulps (Figure 6). Similar results were obtained by Varhimo et al [26] when they compared extended two-stage oxygen delignification to normal single-stage oxygen delignification.

CONCLUSIONS

Addition of polysulfide and anthraquinone to the kraft cook increases the pulp yield significantly. An addition of 1 % elemental sulfur and 0.05% anthraquinone increased the yield by approximately 2% on o.d. wood at kappa numbers around 30. Increasing the polysulfide concentration to 2% (as S_0) in a two-stage ITC cook gave a yield benefit around 3.5% on o.d. wood at kappa numbers around 30. ITC kraft pulping did not give any yield benefits above conventional kraft pulping.

Extending the cook below kappa 27 results in a considerable yield loss of about 0.3 % units per kappa for kraft and 0.4 % units per kappa for PS/AQ cooking. The yield benefit obtained by the addition of PS and AQ to the kraft cook is thus considerably reduced when cooking to low kappa numbers.

Oxygen delignification to about 55% decrease in kappa number preserves the yield increase obtained by PS/AQ addition. For PS/AQ and kraft pulps alike, the yield loss is 0.1 % units per kappa number when limiting the oxygen delignification to about 55%. Extending oxygen delignification beyond 55% lowers the yield. From the data presented, optimal yield for bleached pulp seems to be reached using a PS/AQ kraft cook to kappa numbers between 40 and 45, followed by oxygen delignification to kappa numbers around 22. Final bleaching should be performed using a more selective bleaching chemical like ozone or chlorine dioxide.

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