THE POSSIBILITIES TO APPLY POLYSULPHIDE-AQ PULPING IN KRAFT MILLS

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ABSTRACT

Developments in polysulphide pulping during the last 35 years are reviewed with emphasis on the successful PS-pulping experience at the Peterson kraft mill in Moss, Norway. New and economical PS generation technology not disturbing the Na/S-balance in kraft mills will enhance application of PS-pulping world wide. Multi-stage PS-pulping may improve the yield increase for a given PS-sulphur charge to a digester system. Especially PS-black liquor impregnation followed by kraft cooking with conventional white liquor is interesting.

Drying of fresh wood chips before PS-AQ pulping has a negative effect on obtainable yield increase.

The paper and board making properties of polysulphide-AQ pulps are comparable to kraft pulps from a given wood source. PS-AQ paper grade pulps seem to preserve their paper making properties by recycling better than kraft pulps containing less hemicelluloses.

INTRODUCTION

The use of polysulphide in kraft pulping dates back to a U.S. patent by Fuller and Woodside in 1943 [1]. In 1946 Häglund [2] reported a considerable increase in pulp yield when sulphur was added to kraft cooking liquor. Alfedsson, Samuelson and Sandstig 1963 [3] showed that the yield increase was caused by oxidative stabilization of polysaccharides against the peeling reactions.

Kleppe and Kringstad, 1963 [4] found that the increased yield by PS-pulping of softwoods (spruce) is mainly due to a higher retention of glucomannan and partly of cellulose. By PS-pulping of hardwoods (birch) a higher retention of xylan was shown to be the main yield effect, but an increased yield of glucomannan as well as cellulose has also been reported, 1964 [5].

Extensive research on PS-pulping was done during the 19-sixties by Sanyer and Laundrie, 1964 [6], Venemark 1964 [7], Landmark, Kleppe and Johnsen 1965 [8], Teder 1965, 1969 [9], and Clayton and Sakai 1971 [10]. In spite of promising results from laboratory and mill scale research works the adoption of PS-pulping in kraft mills has been very slow. Major reasons for this have been the fear for reduced tearing strength of pulps and troubles in the chemical recovery cycle. Other reasons were potential corrosion problems, the lack of exact methods for determining mill scale pulp yield and the general reluctance to adopt new technology.

In the 19-sixties and seventies a few pulp mills around the world and among them two Norwegian kraft mills practised PS-pulping by replacing the saltcake make-up by elementary sulphur and a non sulphur containing sodium salt (NaOH or Na_2CO_3). The Norwegian mills applied rather high WL sulphidity of 40 to 45% and a major part of the added sulphur was lost as SO_2. The PS-pulping liquor was prepared by dissolving about 1% sulphur (on o.d. wood) in WL. These mills, which were making bleachable and sack paper grade pulps, obtained about 1.5 -2% yield increase (on o.d. wood), corrosion protection of the batch digester and no significant change in pulp properties except for easier beaten pulp. In the 19-seventies the Norwegian mills abandon PS pulping due to restructuring of the mills.

By the mid seventies it was obvious that governmental restriction on SO_2 loses in the future would prevent PS-pulping based **only** on sulphur make-up. It was therefore clear that the solution for applying PS-pulping in kraft mills was to find economical methods for converting part of the sulphide present in the kraft chemical recovery cycle to elementary sulphur.

POLYSULPHIDE PULPING AT THE MOSS MILL

The Moss mill is today an integrated pulp and paper mill producing linerboard specialities from softwoods (pine and spruce). The pulp mill has a production capacity of 550 ton/day and the pulping take place in a Kamyr dual vessel digester.

PS-pulping started at the mill in June 1973 [11] by dissolving 1.2-1.5% sulphur (on o.d. wood) in the WL. The added sulphur compensate for the sulphur loses, and the WL-sulphidity varied from about 40-45%. The yield increase was estimated to be 2-3% (on o.d. wood). The paper making properties of the pulps at kappa number level of 60-70 were satisfactory for making sack paper and linerboard products. No special operational or corrosion problems were caused by the PS-pulping process.

Since 1976 the polysulphide cooking liquor has been

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prepared by catalytic air oxidation of the sulphide present in the WL through the Moxy process [12]. The flow sheet of the Moxy system is shown in Fig. 1.

It consists of two parallel anthrasite filters and two reactors. The two parallel reactors contain totally 6.5 tons of a special carbon catalyst. The throughput of WL is about 60 m^3/h with only a few minutes retention time in the reactors.

By operating with a clean catalyst about 70% of the oxidized sulphide is converted to PS-sulphur at an oxygen/sulphide molar ratio of 0.35-0.4. The rest of oxidized sulphide forms thiosulphate , which is an inactive cooking chemical. The best pulping results are obtained when 50-60% of WL sulphide is oxidized.

The efficiency of the Moxy system is very much dependent on the cleanliness of the white liquor and an efficient filtration is very important. The suspended $CaCO_3$ from the white liquor absorbed on the catalyst bed has to be removed by acid cleaning. This is normally required every 2-3 weeks. More frequent washing is needed at the end of the catalyst lifetime. The lifetime of the catalyst of **one to three years** is very much dependent on the suspended solid content of the white liquor feed to the Moxy reactors. The efficiency of converting sulphide to polysulphide is sometime reduced to less than 50% before the acid cleaning.

When operating at a white liquor sulphidity of 32-35% the polysulphide concentration in the cooking liquor at the Moss mill is of about 5-6 g. sulphur per litre.

The kappa number of the pulp is around 65. Since 1980 0.35 kg AQ per ton of pulp has been added to the cooking liquor in order to enhance the delignification rate and further increase the pulp yield [13, 14].

The results of the present polysulphide-AQ pulping at Moss mill can be summarized as follows:

- The reduction in wood consumption (per ton of pulp) is about 4.3%.
- The increased pulp capacity of the Kamyr digester is about 4.5%.
- The increased pulping capacity when chemical recovery is a “bottleneck” is about 10%.
- Corrosion protection of the Kamyr digester is achieved and non excessive corrosion of other mill equipment has been experienced.
- Less odour is formed during pulping.
- The paper making properties of the pulp is very suitable to making low weight liner board
- The investment in the Moss PS-AQ system had a very short payback time of less than 8 months.

Improvements in PS-pulping can be made by oxidizing green liquor instead of white liquor. This is demonstrated in Fig.2 which shows results from a pilot Moxy reactor trial.

Increasing the sulphide content in the chemical recovery system, will also, as shown in Fig. 2 and Fig. 3 enhance the PS-content of cooking liquor and thereby the yield increase.

The use of an efficient SO_2 scrubber for the flue gases from the chemical recovery unit and an efficient odour destruction system, will allow kraft mills to operate at a recovery melt sulphidity level of 40% without violating pollution abatement requirements.

SINGLE AND MULTISTAGE POLYSULPHIDE PULPING

At present polysulphide pulping is practised in nine kraft mills world wide. Two of the mills are in Europe and the other seven are in Japan [15]. The total production capacity for PS-pulps is about 2.8 mill tons/year. All the mills are using catalytic air oxidation of the sulphide in the white liquor for generation of polysulphide, either by the Moxy-process (5 mills) or by the Chioda process [16]. The two processes are both using carbon as a catalyst and are requiring efficient WL liquor filtration before the PS-reactors. Other PS-generation technologies now being commercialized is the Paprilox process [17,18] and the Quantum process [19]. Both of these processes are using MnO_2 as an active oxidation catalyst. The first one is in a kraft mill’s caustizisers and the other one is an air feeder reactor for white liquor.

The PS generation technologies used today are based on partial oxidation of the sulphide present in available green or white liquor. In order to obtain maximum yield benefit all of the cooking liquor is charged as impregnation liquor at the start of the cooks in temperature ranges of 90-120 °C. This is considered as a single stage PS-pulping procedure.

By multi-stage PS-pulping the chips are impregnated and/or treated with only a part of the cooking liquor, where most of the charged PS-sulphur is present. The rest of the cooking liquor (pulping chemicals) is added in later stages of the cook. The purpose of multi-stage PS-pulping is to have the polysulphide present in the chips at the highest possible concentration before the peeling reactions take place at any significant rate. The

Table I. A comparison of multi-stage and single stage polysulphide pulping of spruce chips (Landmark, Kleppe and Johnsen, Norwegian Pat. No. 110389, 1966).

Process	Yield increase at kappa no. 36 compared to conv. Kraft pulping (35% WL sulphidity, 17.8% ea. alkali as NaOH)
Single stage PS-pulping with 1.3% PS (on o.d. wood) Impregnation with all cooking liquor (18.5 % ea. as NaOH) at the beginning of the cook, liquor/wood ratio: 3.6, cooking temperature 170 °C	2.2% (on o.d. wood)
Two-stage PS-pulping with 1.3% PS (on o.d. wood) dissolved in part of WL **Stage 1**: Impregnation at 90-100 °C with all of the PS-sulphur addition present in a cooking liquor corresponding to a 10% ea. charge as NaOH, liquor/wood ratio 1.7. **Stage 2**: Addition of WL, corresponding to 8% e a. and performing the cook at a temperature of 170 °C and liquor/wood ratio of 3.6.	3.0% (on o.d. wood)
Two stage PS-pulping with 1,3% PS (on wood) dissolved in black liquid. **Stage 1:** Impregnation with a black liquor containing 8 g. PS/l and 0.3% ea. (on o.d. wood) at 90 – 100 °C. **Stage 2:** Withdrawal of excess PS-black liquor and addition of 17,8% ea. as NaOH and performing the cook at 170 oC at a liquor/wood ratio of 3.6.	3.7% (on o.d. wood)

application of multi-stage PS-pulping require , however, that elementary sulphur be added to the digester system without disturbing the Na/S balance in the mill.

A possible solution for multistage PS-pulping is to separate the sodium and sulphur chemicals in the recovery system like the Chemrec recovery process [20], where H_2S can be converted to sulphur through a Claus process. Another way to make elementary sulphur available for multi-stage PS-pulping may be by purging of electro filter "saltcake" in order to get rid of potassium and chloride build-up in a closed cycled pulp mill.

The yield increasing effect of multistage polysulphide pulping is demonstrated in Table I. The data are taken from Norwegian Pat. No 110387 by Landmark, Kleppe and Johnsen (1966).

As can be seen from Table I, there is a considerable yield benefit by multistage PS-pulping. It is especially interesting to notice the high yield increasing effect of using polysulphide dissolved in black liquor.

Addition of small amount of AQ to the PS-black liquor would surely further improve the pulp yield [13]. The use of black liquor from PS-AQ pulping as impregnation liquor may make it possible to recycle some of the AQ-additive, as it is known from the literature [14], that about 50% of AQ-addition to PS-cooking is still present in the black liquor withdrawn from the cook.

Most of the laboratory investigations on PS-pulping reported in the literature have been made on air dried chips. A recent research work at the Norwegian University of Science and Technology [21] has shown that drying of fresh wood chips before PS – AQ pulping had a very negative effect on the pulp yield increase, even when the chips were properly steamed. Soaking of the air dried chips for 24 h. in water before steaming did not give any significant yield improvement. The pulping results are shown in Table II.

Table II. Single stage PS – AQ pulping of fresh and air dried spruce chips with 1% PS and 0,05% AQ (on o.d. wood)

Pulp grade	Chips	Ea Alkali charge % NaOH on wood	H-Factor	Kappa no	Yield increase over conv. kraft pulping at kappa no. 40 and 80
Bleachable pulp	Air dried (82.6% dryness)	19%	1320	45	2.2
	Air dried and soaked in water, 24 h.. (44.7% dryness)	19%	1324	39	2.4
	Fresh chips (57% dryness)	19%	1320	40	4.2
Liner board pulp	Air dried chips (82,6% dryness)	16,5	900	84	2.8
	Fresh ships (57% dryness)	165	904	76	5.6

Table III. Papermaking properties of handsheet made from undried and recycled (Air dried, heat treated and repulped) 30 Kappa no. spruce pulps with different hemicellulose content.

Pulp	Single stage PS – AQ pulps with 2% yield increase (on wood)		Multistage PS-AQ pulp with 3,5% yield increase (ITC- cooking)		Kraft pulp (ITC-cooking)	
	Undried pulp	Recycled pulp	Undried pulp	Recycled pulp	Undried pulp	Recycled pulps
Rev. in PFI mill	6000	(6000)	6000	(6000)	8000	(8000)
°SR	23	19.5	22	18.5	21	19
Tensile index, KNm/kg	105	84 (-20%)	104	85 (-19%)	103	78 (-24%)
TEA, J/kg	2215	1400 (-37%)	2100	1370 (-41%)	2300	1350 (-45%)
Tensile Stiffness, Nm^2/kg	8945	8450 (-6%)	8700	9030 (+3%)	8955	8310 (-7%)
Tear Index, Nm^2/kg	12.1	16.1 (+33%)	11.8	15.9 (+35%)	14.3	19.2 (+34%)

* The pulps were tested in the H-form after removing of the 100 mesh primary fines.

PAPERMAKING PROPERTIES OF POLYSULPHIDE – AQ PULPS

Based on what is known from the literature the following general statement can be made:

1. Bleachable PS-AQ pulps with yield increases up to about 4% (on wood) have papermaking properties similar to comparable conventional kraft pulps from the same wood source, except for better beatability and somewhat lower Elemendorf tearing strength.

2. High kappa no. PS–AQ pulps (kappa no. 60 – 90) with yield increases up to about 5% - 6% (on wood) have papermaking properties very similar to conventional kraft pulps of equal lignin content and from the same wood source.

An investigation performed at the Norwegian University of Science and Technology [22] has shown that bleachable PS – AQ pulps have less deterioration in papermaking properties after recycling (drying, heating and repulping without beating) than comparable conventional kraft pulps with lower hemicellulose content. Results from the investigation are shown in Table III.

CONCLUSION

1. Polysulphide pulping has been practised at the Peterson kraft mill in Moss/Norway for more than 24 years. The results have been reduced wood consumption per ton of pulp, improved pulp production capacity, reduced odour formation and prevention of digester corrosion. Non excessive corrosion of other mill equipment has been experienced.

2. Polysulphide pulping in Moss has since 1976 been possible through catalytic air oxidation of the sulphide present in the white liquor applying the Moxy process. However, air oxidation of green liquor looks even more promising due to a higher efficient conversion of sulphide to polysulphide sulphur.

3. Addition of small amounts of AQ (0,5 - 1 kg per ton of pulp) improves the yield gain further and enhance the rate of delignification by polysulphide pulping.

4. At present there are 2 kraft mills in Europe an 7 kraft mill in Japan practising PS- pulping. All of these mills are using a carbon catalyst for converting the sulphide in white liquor to polysulphide. The production capacities for PS pulps world wide is estimated to about 2,8 mill tons per year.

5. Multistage polysulphide pulping can improve the yield increasing effect of a given amount of PS-sulphur charged to a digester system. An unexpected high yield increase was obtained by PS - black liquor impregnation followed by kraft cooking with conventional white liquor. Multistage PS-pulping may, however require separation of Na on S in the chemical recovery system, like application of Chemrec recovery technology.

6. Drying of fresh wood chips before PS - AQ pulping seems to have a very negative effect on obtainable yield increases.

7. The papermaking properties of PS - AQ pulps with yield increases in the range of 3 – 6% (on wood) are very similar to comparable conventional kraft pulps from a given wood source.

8. PS - AQ paper grade pulps seem to preserve their papermaking properties by recycling better than comparable kraft pulps containing less hemicelluloses.

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