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Recent Developments in Soda-AQ Cooking

Introduction

The kraft process is the dominant process for the production of chemical pulp. It provides a pulp with high strength properties, but it has some disadvantages, such as the comparatively low pulp yield, a complicated and capital-intensive recovery system and the emission of malodorous substances, mercaptans and dimethyl sulphide. Even small quantities of these substances cause odor problems, and they may not be accepted in the future. Besides the optimization of the odor-abatement systems for the kraft process, sulfur-free options for the production of chemical pulp must be considered.

The possible process alternatives that can potentially reduce and avoid the formation and emission of malodorous and toxic sulfur-containing compounds are the soda-AQ and the organosolv pulping processes. The organosolv processes, however, are not considered to be significant competitors to the soda-AQ process due to the explosion risk and the extremely low pulp quality. The addition of anthraquinone (AQ) to the soda cooking increases both the delignification rate and the pulp yield[1]. However, the industrial implementation of the soda-AQ process for softwood species has been delayed. The major reasons for this low interest from the pulp and paper industry have been the poorer bleachability and lower pulp quality compared to the high-grade softwood kraft pulps[2, 3]. Furthermore, AQ is an expensive chemical and no methods for the recovery of AQ are available. In recent years, there has been renewed interest in soda-AQ pulping as a sulfur-free and odor-free alternative to the kraft process. Besides the elimination of the typical "kraft pulp mill

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Recent Developments in Soda-AQ Cooking

A modified soda-AQ process has been developed for softwood species with a higher chemical concentration and temperature profiling. Compared at a given sheet density, the strength properties of the fully bleached modified soda-AQ pulp are comparable to those of a modern kraft pulp of ITC type. The modified soda-AQ pulp still requires a higher bleaching chemical consumption to reach a given ISO-brightness in an ODEDED sequence. Since sulfur enters the process with the wood and the sulfur-containing chemicals, the soda-AQ process is not totally sulfur-free. The development of new technology to control the S/Na-balance is needed.
The results of these studies clearly show that the modified soda-AQ process is an interesting sulfur-free and odor-free alternative to the kraft process for the production of high quality chemical pulps from softwood.

Jüngste Entwicklungen beim Soda-AQ-Aufschluss

Ein modifiziertes Soda-AQ-Aufschlussverfahren mit fortschrittlicher Chemikalienkonzentration- und Temperatursteuerung wurde für Nadelholz entwickelt. Bei gleicher Papierdichte sind die Festigkeitseigenschaften dieses Zellstoffs vergleichbar mit denen eines modernen Sulfatzellstoffs. Im Vergleich zum Sulfatzellstoff war jedoch ein höherer Bleichchemikalieneinsatz notwendig, um einen bestimmten Weißgrad zu erhalten. Aufgrund des Schwefeleintrags in den Prozess durch das Holz liegt kein absolut schwefelfreier Prozess vor. Es bedarf daher der Entwicklung einer neuen Technologie, um die S/Na-Balance zu steuern.
Die Ergebnisse dieser Untersuchungen zeigen deutlich, dass das modifizierte Soda-AQ-Aufschlussverfahren eine interessante schwefel- und geruchsfreie Alternative zum Sulfatverfahren für die Produktion von Hochqualitätszellstoff aus Nadelholz ist.

Pulp property	Increased [OH$^-$]	Increased [AQ]	Increased Temperature
Pulp yield	Maximum at 0.5 M	+	-
Pulp viscosity	Maximum at 0.5 M	+	-
Fiber strength	Maximum at 0.5 M	+	-
Pulp bleachability	+	-	-

Table 1: The effect of increased [OH$^-$], [AQ] and cooking temperature on pulp yield, viscosity, strength and bleachability

odor", the gasification-based recovery processes are potentially competitive with the conventional recovery processes in a sulfur-free environment. The soda-AQ process, however, is not totally sulfur-free since small quantities of sulfur are present in the wood.

At STFI, within the "The Ecocyclic Pulp Mill" research program, financed by MISTRA, the Swedish "Foundation for Strategic Environmental Research", a significant research effort has been devoted to improving the strength properties and bleachability of softwood soda-AQ pulps. The effects of sulfur in the soda-AQ process have also been evaluated. In this paper, the results of these different studies are presented and discussed.

The influence of process conditions in soda-AQ cooking

The optimum conditions for the modified softwood soda-AQ process have been explored in extensive laboratory studies[4, 5, 6]. The flow-through technique was used in cooking experiments. The influence of [OH$^-$], [AQ] and temperature on the cooking selectivity, pulp yield and pulp viscosity at a given kappa number, and pulp properties, including bleachability and fiber strength, was investigated. The cooking time at the different cooking conditions was adjusted to obtain a kappa number of 26.

The influence of cooking conditions on the softwood soda-AQ pulp properties and bleachability are summarized in **Table 1**, were "+" denotes an improvement and "–" a reduction of the studied pulp property. As seen in Table 1, pulp yield, pulp viscosity and fiber strength pass through a maximum when the [OH$^-$] during the cook is increased. The maximum occurs at a [OH$^-$]=0.5 mole/L. A positive effect of an increased [OH$^-$] is seen in the pulp bleachability. An increase in [AQ] is positive for all pulp properties except for the bleachability. However, an increase in [AQ] also results in a higher production cost, since the AQ is comparatively expensive and cannot be recovered.

The results also show that a reduced cooking temperature increases the selectivity of the cook with regard to both pulp yield and viscosity. However, the cooking time needed to reach a given kappa number is negatively affected by a decrease in temperature. A decrease in cooking temperature should therefore be accompanied by an increase in [OH$^-$] concentration to enable the termination of the cook in the bulk delignification phase.

Modified soda-AQ cooking

The results indicate that it is difficult to produce a soda-AQ pulp with both good fiber strength and good bleachability in a single stage cook. The results suggest that the total alkali charge in the soda-AQ cook should be divided into at least two charges and kept at a relatively high level during the cook. The high residual [OH$^-$] should be recirculated and used in a first cooking stage. The cooking temperature should be kept low, 155–160 °C, and the [AQ] should be as high as is affordable. An [AQ] > 0.2 % on pulp is not however realistic today.

A modified soda-AQ softwood (*Pinus sylvestris*) pulp was produced according to these findings in the laboratory and compared to a modern kraft pulp of the ITC-type with respect to bleachability and the strength properties of fully bleached pulp. It should be pointed out that a kraft process of ITC- type is vastly superior to the conventional kraft process. The initial EA-charge was the same, 14 % on wood, in both processes, as was the [OH$^-$] in the counter-current cooking zone, 15 g/L. The EA-charge in the co-current cooking zone in the soda-AQ cook was increased from 5 % in the reference kraft cook to 9 % on wood. The cooking temperature was 158 °C in the soda-AQ cook and 157 °C in the reference kraft cook. In order to keep the same cooking time, the soda-AQ cook was continued to a kappa number of 35 instead of 25 for the reference kraft cook. The pulp properties and carbohydrate composition are given in **Table 2**.

Bleachability

The pulps were bleached in an ODEDED-sequence to obtain 88 % ISO-brightness. The kappa number after

Table 2: Pulp properties and carbohydrate composition of modified soda-AQ and kraft softwood pulps

Pulp	Kappa number	Total yield % on wood	Viscosity mL/g	Brightness % ISO	Carbohydrate composition % on pulp: Cellulose	Xylan	Gluco-mannan
Modified Soda-AQ	34.9	48.5	1020	30.9	81,2	7,6	11,2
Kraft	25.3	47.1	1230	35.7	82,2	9,1	8,7

the oxygen delignification was approximately 14 for the modified soda-AQ pulps and approximately 12 for the modified kraft pulp. **Figure 1** shows the chlorine dioxide consumption, as OXE/kappa O_2, tonne of pulp*, during each D-stage and also the total OXE to reach 88 % ISO-brightness. The soda-AQ pulp consumed 115 OXE/kappa O_2, tonne of pulp, while the kraft pulp consumed only 86 OXE/kappa O_2, tonne of pulp. As is shown in figure 1, the greatest differences in chlorine dioxide consumption are in the D2-stage. Compared with a "conventional" soda-AQ pulp, the modified soda-AQ pulp consumes approximately 15 % less bleaching chemicals (not shown in the figure). As expected, the high [OH^-] level in a modified soda-AQ process improves the bleachability of the pulp.

* OXE/kappa 0_2, tonne of pulp means oxidation equivalents per kappa number after oxygen stage and per tonne of pulp

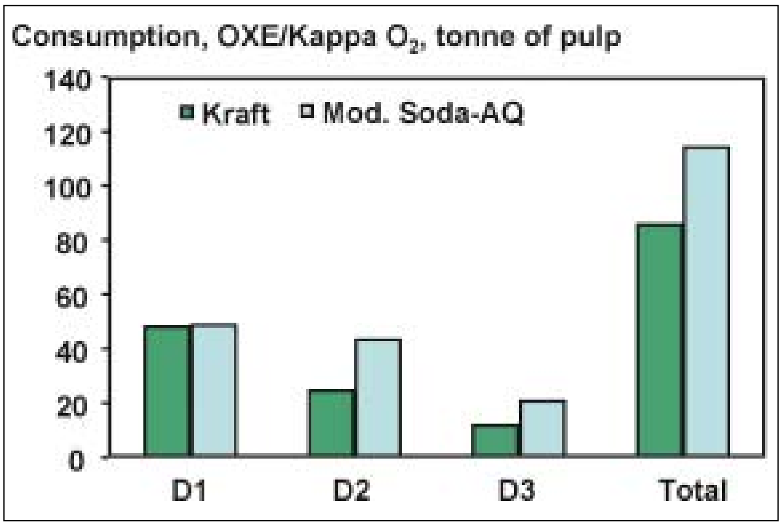

Fig. 1: The bleaching chemical consumption to reach 88 % ISO-brightness, expressed as OXE / kappa O_2, tonne of pulp, for the three D-stages and for the whole bleaching sequence

Strength properties

The unbleached soda-AQ pulp has less short fibers (0.5 - 1.0 mm) and more long fibers (1.5 – 3.0 mm) and the fine particle content (20 – 80 mm) is higher than in a kraft pulp, **figure 2**. Soda-AQ fibers are broader than kraft fibers, as was also shown by Kibbelwhite and Bawden[7]. A light microscope study showed that soda-AQ fibers appear to be more collapsed than kraft fibers. The soda-AQ pulp also includes more fine particles, mainly ray parenchyma cells, than the kraft pulp. The more collapsed soda-AQ fibers may form a tighter fiber network, which is harder for the fine particles to penetrate during washing and thus leaves more particles in the pulp.

The fully bleached (ODEDED) modified soda-AQ and kraft pulps were evaluated with respect to their strength properties after beating in a PFI-mill. The beatability, defined as tensile index at a given number of revolutions in a PFI-mill was, as expected, somewhat higher for the modified soda-AQ pulp than for the reference kraft pulp, **figure 3**. Compared at 1000 revolutions in the PFI-mill, the tensile index is approximately 10 units higher for the modified soda-AQ, i.e. approximately 10 % better than the kraft pulp. This is probably due to a significantly higher glucomannan content, 2.5 %, in the modified soda-AQ pulp.

Fig. 2a: Microscopy picture of soda-AQ fibers in 10 times enlargement

Fig. 2b: Microscopy picture of kraft fibers in 10 times enlargement

The modified fully bleached soda-AQ pulp has a tear index approximately 10 % lower than that of the kraft pulp at tensile index 85 Nm/g, **figure 4**. This cannot be explained by the higher pulp yield of the soda-AQ pulp only[8]. A possible explanation could be the chemical attack on the carbohydrates induced by AQ and by high [OH^-] in modified soda-AQ cook.

In **Table 3** the strength properties, interpolated to a density of 700 kg/m^3, are summarized for modified soda-AQ and kraft pulps. The strength properties of the modified soda-AQ pulp are clearly comparable to those of modern kraft pulp of ITC-type. The differences in strength properties, if any, are approximately 5 %. The modified soda-AQ fibres form dense sheets after beating in PFI-mill and this will slightly affect the different strength properties. When compared at given sheet density, the tensile index is approximately 5 units higher for the kraft pulp. As shown in Table 3, there is no difference in tear index between the modified soda-AQ and kraft pulp. However the fiber strength evaluated as rewetted zero-span tensile index is slightly lower. The results indicate that high quality chemical pulps can be produced from softwood using a modified soda-AQ process. However, pilot-paper machine tests and industrial trials with industrial refining must be carried out to evaluate the full potential of modified softwood soda-AQ fibers.

Sulfur in the soda-AQ process

The handling of sulfur in a reference kraft mill and in a conventional soda-AQ mill has been evaluated using advanced process simulation[9]. The reference kraft mill is a theoretical pulp mill producing bleached softwood kraft market pulp using today's most recent available technology in all process departments. The mills were based on an annual production of 630 000 tons bleached air-dried pulp.

Even though the soda-AQ cooking process is "sulfur-free", sulfur accumulates in the liquor system. The sulfur enters the process not only with wood raw material but also as sulfuric acid used in soap acidification, in the D- and Q-stages and as $MgSO_4$ in the O-stage. Approximately 0.3 kg sulfur/ton enters with wood raw material. The total sulfur intake in the reference kraft mill was approximately 10 kg/ADT, as shown in **fig-**

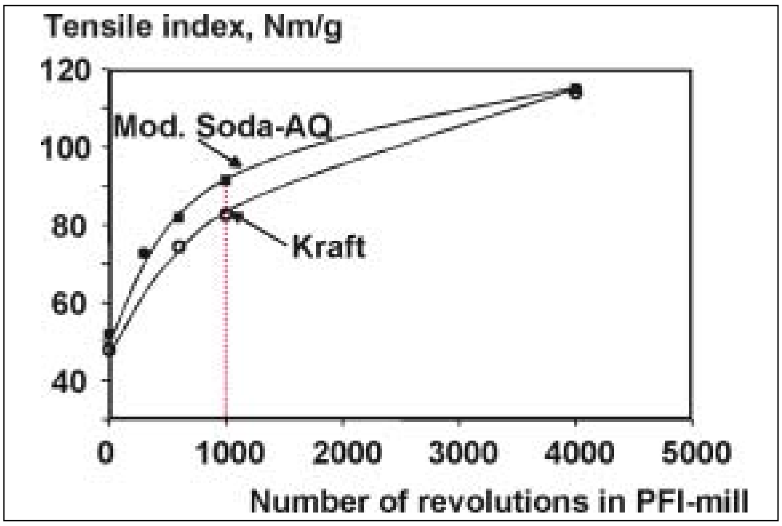

Fig. 3: Tensile index versus number of revolutions in a PFI-mill of fully bleached modified soda-AQ and of kraft pulps

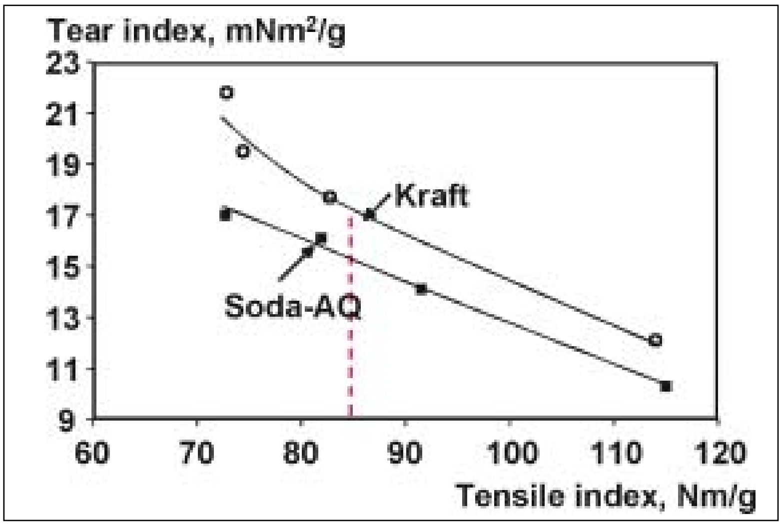

Fig. 4: Tear index versus tensile index of fully bleached modified soda-AQ and of kraft pulps

ure 5. However, the purged bleach plant effluent contains about 5 kg sulfur/AD tonne of pulp. The net intake to the recovery area is therefore about 5 kg sulfur. To balance this intake, precipitator dust from the recovery boiler (about 17 kg/ADT) was purged.

In the soda-AQ process it is necessary to reduce the sulfur intake to the process as far as possible. The sulfidity level will still be considerable, about 10 %, even if the net intake of sulfur to the recovery area in the reference kraft mill could be reduced to 2 kg sulfur/ADT, **figure 6**. This can possibly be achieved by replacing parts of the spent acid used in the soap separation with CO_2, and the $MgSO_4$ used in the oxygen stage by $MgCO_3$. But it also requires that the precipitator dust purge be kept at about 17 kg/ADT. If the dust purge is to be lowered the sulfidity will increase dramatically.

Harder restrictions regarding spillage in the chemical recovery plant will reduce the amount of sulfur that can be taken to the recovery. Purging precipitator ash leads to a high loss of alkali. A more effective alternative for the control of the sulfur balance by a specific "sulfur-kidney", e.g. heat treatment of black liquor[10], is definitely needed in soda-AQ mill with conventional recovery boiler.

Final remarks

One of the advantages with soda-AQ cooking is that odor problems are reduced. The process can easily be applied in existing pulpmills. The process design is somewhat simpler and risk of sulfur-induced corrosion, especially in the recovery boiler, is reduced. The sulfur-free lignin produced as a by-product in a soda-AQ mill is an interesting raw material for fine chemical production. Since some sulfur enters the process with the wood and the use of sulfur-containing chemicals, the soda-AQ process is not totally sulfur-free. The development of new technology to control the S/Na-balance is needed.

The results of these studies clearly show that modified soda-AQ cooking is an interesting sulfur-free and odor-free alternative to kraft cooking for the production of high quality chemical pulps from softwood. The pulp yield of the modified soda-AQ pulp is slightly higher than that of the modern kraft pulp. Compared at a given sheet density, the strength properties of modified soda-AQ pulp are comparable to those of a modern kraft pulp. However, the modified soda-AQ pulp still requires a higher bleaching chemical consumption to reach a given ISO-brightness.

Table 3: The strength properties of fully bleached modified softwood Soda-AQ pulp and kraft pulp. The comparison is made at a density of 700 kg/m³. Zero-span tensile index* was measured as rewetted zero-span tensile index.

Pulp	Tensile index Nm/g	Break elongation %	Tensile energy absorption index mJ/g	Tensile stiffness index kNm/g	Tear index KNm/g	Zero-span tensile index* Nm/g
Modified Soda-AQ	74	3.4	1850	7.3	18.0	144
Kraft	79	3.3	1800	7.6	18.0	153

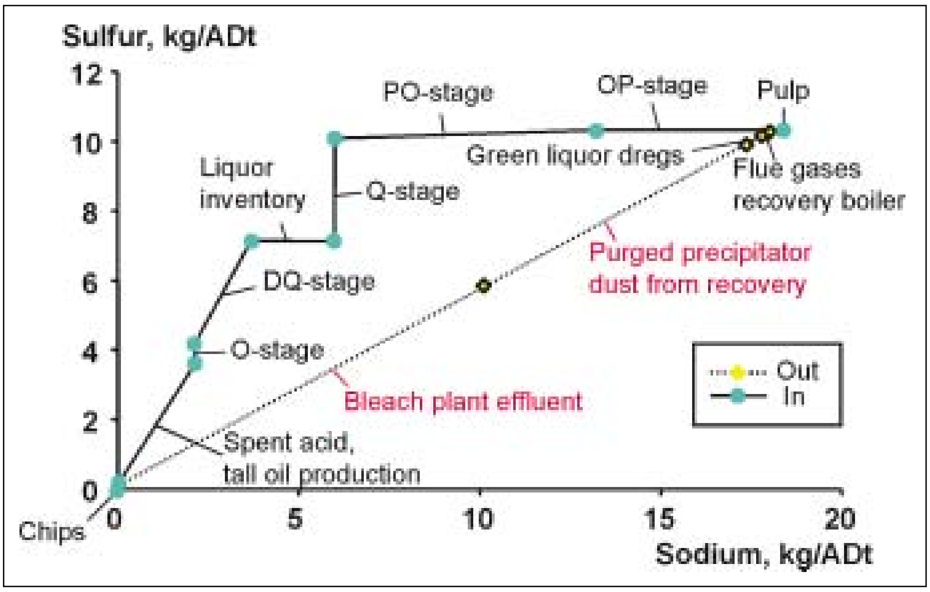

Fig. 5: A vector diagram showing the sulfur-sodium balance for the reference mill with ECF bleaching, OQ(OP)(DQ)(PO)

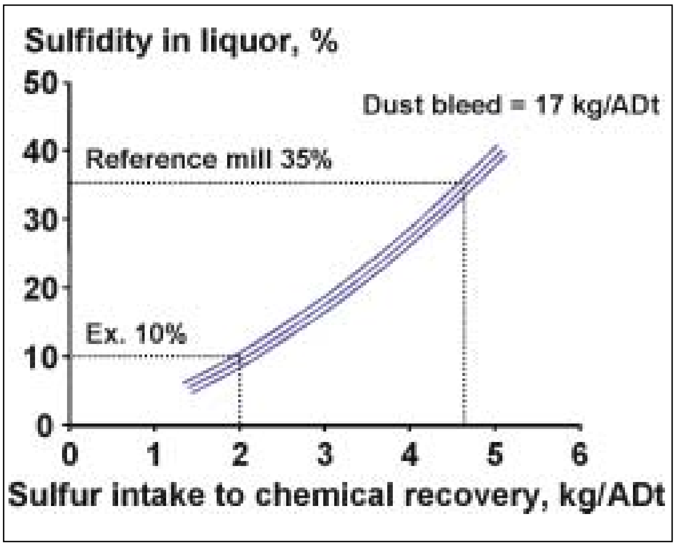

Fig. 6.:
The sulfidity of the white liquor at different levels of recycled sulfur in the recovery system. The amount of precipitator ash purged from the recovery boiler is 17 kg/Adt in this example. In the calculations, losses and spillage in the chemical recovery plant, the digester house and the washer room are proportional to the sulfidity.

We believe that, by a more powerful alkali profiling, the bleachability and strength properties of modified soda-AQ pulp can be further improved and that the new modified soda-AQ process will be seriously considered as a possible minimum impact pulp mill for the production of chemical pulp from softwood.

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