

ALTERNATIVES TO KRAFT PULPING

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Kraft pulping, in spite of its wide practice, suffers from some serious disadvantages, such as the odour problems, lower pulp yield and high investment requirements. To overcome these difficulties considerable efforts have already been made. In this paper, feasibilities of alternative methods to kraft pulping have been examined and discussed.

A kraft mill, even by utilizing the best available technology, cannot be made completely odour-free. However, there are several sulphide-free and non-sulphur pulping methods. Among these, soda-anthraquinone (AQ) pulping process seems to be promising.

Pulp yield can be increased by using polysulphide, H_2S or AQ in the cook. The first two are used exclusively in kraft cooking, and so the odour problem cannot be overcome. AQ on the other hand, is also suitable in a sulphur-free cook which eliminates the odour problem of the pulp mill. Soda-AQ pulping is more suitable with hardwoods.

There is an ample opportunity of reducing the investment cost in a kraft mill by replacing the conventional recovery furnace with alternative devices now under development or by eliminating some of the steps in the recovery cycle. There are also possibilities of eliminating the causticizing step and the lime kiln in any alkaline pulping process by replacing NaOH with disodium borate in cooking or by introduction of TiO_2 , Fe_2O_3 or ilmenite ($FeO \cdot TiO_2$) in the recovery stage.

INTRODUCTION

The most practised chemical pulping to-day is the kraft process. About 95% of the present production of chemical

pulp is done in kraft mills (1). The reason may be attributed to its superior pulp quality, relatively shorter cooking cycle,

fully developed recovery cycle and high production flexibility (nearly all pulp grades can be produced and any fibrous material can be used). In spite of all these advantages, this process suffers from some serious disadvantages, such as its odour problems, lack of specificity in delignification, i. e., while lignin is dissolved, a significant amount of carbohydrate material is also dissolved resulting in a lower yield of pulp, and high capital investment requirements. Hence to face the stringent pollution regulations and economic crisis, the disadvantages must be eliminated.

Thus, while searching for the alternatives to the kraft process, the approaches should be directed to solving the deficiencies of this universal process and maintaining its inherent advantages. Hence, alternative methods to do away with the disadvantages of the kraft process are discussed in this article.

METHODS OF REDUCING ODOUR PROBLEMS

The kraft process is notoriously famous for the malodorous sulphur compounds consisting of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide originating from Na_2S of the kraft white liquor (2). About 75% of the bad smelling sulphur compounds emitted by a kraft pulp mill originates in the recovery furnace and the direct contact evaporators; some 20% comes from the cook, and the remainder from different sources (3). In the conventional process, the malodorous gases can be reduced by black liquor oxidation (4, 5). In spite of that some odours are emitted. In serious cases, gases may be collected and destroyed to render them odour-free (6). Some of the measures

have been economically feasible, but additional installations tend to increase investment costs. Over and above, the kraft mill cannot be converted in such a way to make it totally odourless.

In view of the problems associated with kraft odour, considerable researches into sulphide-free and non-sulphur chemical pulping methods have been conducted during the last few years. Alkaline sulphite pulping, known for many years, was reassessed and thoroughly investigated by Ingruber and Allard (7). They demonstrated that this process gave both pulp yield and strength properties comparable to those of kraft process. The alkaline sulphite pulps are brighter and have considerably better brightness stability than the kraft pulps. The advantages of the alkaline sulphite spent liquor over the kraft black liquor are its high degree of oxidation, low and inoffensive odour and low toxicity to fish when released to streams. The major disadvantages of the alkaline sulphite process compared to those of the kraft are the high chemical requirements, longer cooking time, higher cooking temperature and the necessity to convert the high sulphidity green liquor to sodium sulphite pulping liquor containing also sodium hydroxide. These constraints strongly disfavour pulping by the alkaline sulphite process.

The use of anthraquinone (AQ) in alkaline sulphite pulping has also been investigated (8). The addition of AQ in the cook reduces the cooking chemical charge to the level of the kraft process, but the cooking time is still longer and cooking temperature higher. Attempts were also made to eliminate the kraft odour problems but retaining the kraft pulp properties by

using AQ-neutral sulphite process (8,9). With this process substantially higher yield of pulp is obtained. Many paper making properties of the pulp are exceptionally good in spite of higher pulp yield. No foul odour is emitted in the system. But the disadvantages of higher cooking temperature and longer cooking time cannot be eliminated. Moreover, the preparation of cooking liquor containing Na_2SO_3 and Na_2CO_3 is rather complicated.

One of the widely studied odour-free pulping processes is soda-oxygen pulping (10-13). The process involves three steps: (i) initial soda cooking by the use of sodium hydroxide to a higher lignin content than the normal, usually to a Kappa number in the order of 50 for hardwoods and 80-100 for softwoods (11), (ii) mechanical fiberization of the softened chips to ensure maximum surface transfer area and finally (iii) subsequent delignification with alkali and oxygen under pressure. The objective of the final oxygen stage is to reduce the lignin content to the level of normal chemical unbleached pulps, which cannot be attained by the soda process alone. Thus, the oxygen stage delignifies the pulp from a much higher lignin content to a lower lignin content without serious degradation of the pulp, to be ready for subsequent bleaching. The degradation of the pulp however becomes serious from Kappa 25 to 15 and below (11).

Both unbleached and bleached pulps obtained by the soda-oxygen process provide yields which are quite comparable with those obtained by the kraft process (3,10) and the same type of raw material can be utilized (3). The strength of the

unbleached pulp, in particular the tearing strength, is not as good as that of kraft pulp (3,10,14). However, if the soda-oxygen pulping method is aimed at attaining a pulp quality similar to that obtainable by the kraft method, the soda stage needs to be continued to the fibre liberation point; but this offsets the yield (10).

As the soda and the oxygen stages together consume more alkali than does the kraft process, the recovery system, in particular the causticizing system, needed is larger than that required for the kraft process. Moreover, an oxygen reactor for high pressures and additional equipment are required for operation of the oxygen stage. As a consequence, the soda-oxygen pulping may not be cheaper than the kraft.

More recently, the discovery of addition of anthraquinone (AQ) to the normal soda cook, to the order of 0.05-0.15% on OD wood basis, promises of being the most dramatic breakthrough in the quest for an odour-free pulping process (15-17). The mechanism of its action during pulping is not completely understood, but in effect it enables to produce pulps in kraft yield and with lower active alkali typical of the kraft process.

From the viewpoint of environmental pollution, AQ itself or the emissions from AQ-soda pulping appears to pose no significant hazards (11). It is indicated as non-carcinogenic and of low toxic potential when encountered in dust form, although it can be a minor irritant to allergic skins. As the AQ applied in pulping is virtually destroyed when the liquors return to the recovery cycle, only traces appear in the waste wash liquors and the final pulp and

paper. These traces range from below detection limits to a few parts per million range. Extensive studies have shown no environmental consequences from AQ in pulping.

There are many other approaches of sulphur-free pulping. Pulping with organic bases, such as soda amines (18-20) is practical and efficient from pulping view point and can offer pulps equivalent to kraft. The problem yet to be seriously investigated lies in recovering and recycling of the bases and/or the utilization of the amine-lignin complexes. At present the use of amines in soda pulping is not economical as they react irreversibly with the pulp and are not fully recoverable (21, 22).

Another sulphur-free process is the "Pollution-free" pulping process (23) which has been tested in a 10 t/d pilot plant in Japan. In this process chlorine chemicals and sodium hydroxide are used as delignification and bleaching agents for the defiberized pulp. The pulp yield ranges from that of normal for the kraft process to more than 60% and the quality is reported to be comparable to that of kraft pulp in many respects. As the wood chips must be initially mechanically fiberized, some doubt exists whether the results achieved with hardwoods will be as satisfactory with softwoods. Moreover, the installation and operating costs of the process exceeds those of the kraft process.

Recently, there has been another approach of obtaining kraft-like pulp. This is by peroxide delignification of soda pulp (24). The process is comprised of initially a soda pulping stage with partial delignification to the point of incipient fibre

liberation and then following a mechanical defiberization step. The pulp is subjected to a secondary delignification treatment with hydrogen peroxide and sodium hydroxide at atmospheric pressure. Peroxide pulp compares favourably with kraft pulp in respect of yield and strength properties (except burst strength). The disadvantages include high sodium hydroxide consumption, added installation cost for fiberizing and peroxide stages, high peroxide dose (1-2% on OD wood), etc.

YIELD INCREASING METHODS

It is well recognised that the yield by the kraft process is lower resulting in higher production cost of pulp than the sulphite process. Moreover, in the future the increase in the production cost of pulpwood is expected to exceed that of the market price of pulp (25). In addition, it is likely that there will be a dearth of pulp wood in years to come (26). These factors together create a large challenge to kraft pulping to achieve more effective utilization of wood.

For the time being, from the point of view of increasing the yield, three possibilities may be considered: polysulphide (27), hydrogen sulphide (25, 28) and anthraquinone (15-17). The first two possibilities include sulphur, and thus can be practiced only in kraft cook. Anthraquinone, on the other hand, is also suitable in a sulphur-free cook, eliminating the odour problems of the kraft mill.

When any yield increasing method is developed, it may be asked whether this increase in yield is still attainable after

bleaching and whether the quality of the pulp is comparable to that of normal kraft pulp.

Kraft pulping with the addition of polysulphide results in an increased yield. The polysulphide cook can be done by using elementary sulphur in a portion of white liquor (27). Alternatively, polysulphides or sulphur can be obtained from white liquor (29), green liquor or black liquor (27). The largest yield increase per unit weight of added sulphur was found to be 1.5 to 4% sulphur based on wood (30). The increased yield is 1.5-2 times the added sulphur. A laboratory study (27) showed that the yield increase was retained after further delignification by oxygen-alkali. The strength properties of the polysulphide pulps are comparable to those of kraft except for tear factor (27, 30, 31). Which is considerably lower. Another limitation of the process is reduced brightness of unbleached pulp (31). Over and above, it retains the odour problems associated with the kraft mill.

The other yield increasing method is the hydrogen sulphide pulping, which is carried out in two-stages, the first stage being a treatment of wood chips with hydrogen sulphide in presence of sodium hydrogen sulphide, followed by delignification in a second stage under approximately normal kraft cooking conditions (25, 28). The authors obtained an increase of unbleached pulp yield of 5-6 percentage points for pine compared with normal kraft. There is no difference in bleaching yield between the H₂S and the kraft pulps (28). Thus, with higher unbleached pulp

yield with the H₂S process, there is a net gain in bleached yield. The H₂S pulp is weaker than the kraft if comparison is made at the same Kappa number of unbleached pulp (28). If compared at the same yield, the difference in the strength properties are either negligible or very small (3); but there is no sense in the production of pulp of equivalent yield by the use of a more complicated method. The odour problem is also a serious disadvantages of the process.

Recently, the catalytic effect of anthraquinone on alkaline pulping (15-17) has been established. Small addition of AQ, in kraft and soda cooking markedly enhances the rate of delignification with improved yield (Fig. 1) AQ addition in the order of 0.05-0.15% on OD wood basis is sufficient to provide the benefits (15, 17, 32). The catalytic effect of AQ is more effective in soda pulping than kraft pulping (Fig. 1). It is not unlikely that soda-AQ pulp can surpass the conventional kraft in respect of rate of delignification and pulp yield (15,21). Thus, it can represent a solution to replace the kraft process.

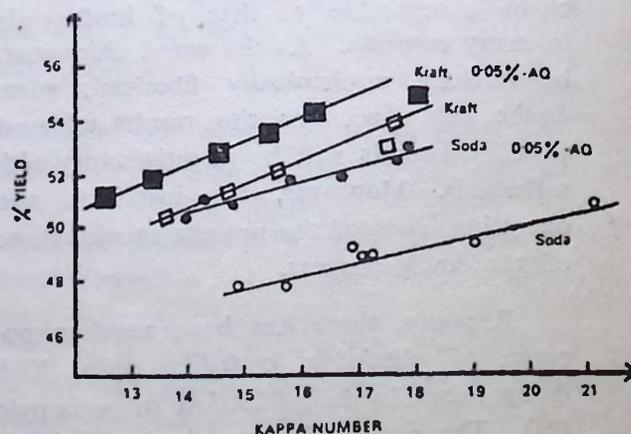


Fig. 1. Increased delignification and yield due to addition of AQ

More economic benefits in soda-AQ pulping are obtained with hardwoods than with softwood (15, 16). As regards the quality of soda-AQ pulps, no generalization can be made. It appears to be dependent on wood species. Soda-AQ pulps from black spruce have about 20% lower tear than kraft pulps (Fig. 2). Douglas fir (Fig. 3) showed a tear reduction of about 10%. Contrary to this, the tear was not impaired in a mixture of spruce, balsam and

pine as shown by Holton, cited by MacLeod *et al* (33) and in *Pinus radiata* (34). Other strength properties compare favourably with the kraft (33). In the case of bagasse and a mixture of hardwoods, the soda-AQ and kraft pulps were quite similar in all strength properties. The quality of kraft-AQ pulps is equivalent to its kraft counterpart (33).

At present, the application of AQ is limited to mills already practicing soda pulping and to those kraft mills which are under environmental pressure to switch to soda (32). In the future, this trend is expected to increase leading to such conversions as the pollution regulations become more stringent.

METHODS OF REDUCING INVESTMENT COST

Chemical pulping is very capital intensive as many sub-processes and functions are essential for a high level of self-sufficiency in energy and expensive chemicals. If the sub-processes can be simplified or the number be diminished without diminution in self-sufficiency, the investment cost can be reduced.

In a kraft mill the machinery costs are about 48% of the total investment, of which about 27.5% is in the chemical recovery plant (35).

Thus, there is a certain potential for simplification of the recovery cycle. This can be achieved by replacing the conventional recovery furnace or by eliminating some of the stops in the recovery cycle. Development of a recovery furnace is in progress around the world and examples may be cited of the wet-combustion, partial

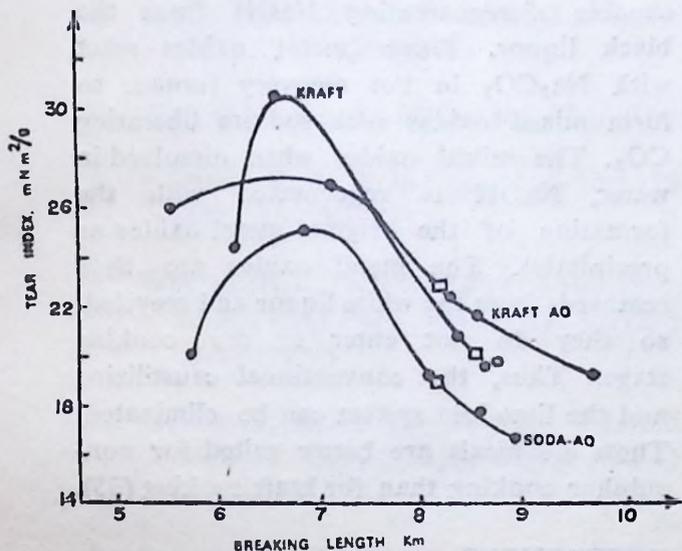


Fig. 2. Tear reduction due to AQ addition

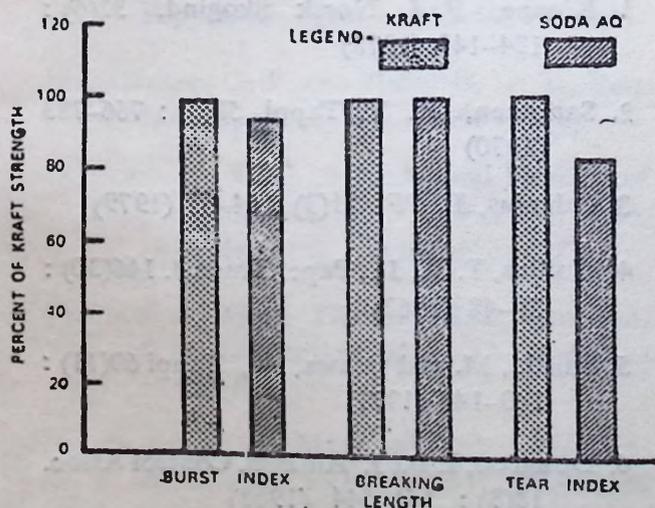


Fig. 3. Tear reduction in Douglas fir

wet combustion, fluidised bed, hydro-pyrolysis, SCA-Billerud methods, etc. There are also possibilities for eliminating some of the steps in the recovery cycle by replacing NaOH by disodium borate (Na_2HBO_3) in kraft and soda pulping (36) and by introduction of titanium dioxide (37), ferric oxide (38) or ilmenite (39) in the recovery furnace or outside it in reaction with the smelt.

The disodium borate works in the cook with the same alkalinity as sodium hydroxide (36). Thus, it is possible to replace NaOH in the soda or kraft cooks (with or without additive). There is very little difference in the pulp yields from the hydroxide and the borate based pulping, nor are there any differences in pulp properties. From the point of delignification, replacement of NaOH by Na_2HBO_3 works better with hardwoods than with softwoods. The special feature of the process is that the smelts obtained in burning black liquors is autocausticized. It regenerates the cooking chemical and no carbonate appears in the green liquor as with the hydroxide based cook. Thus, complete causticizing and lime cycle may be avoided, with consequent elimination of the buildings and equipment concerned. As a result, the investment cost in a pulp mill is significantly reduced: to the order of about 7.5 million USD for a mill of 600 t/d capacity (36). From the energy point of view, the borate based pulping is also advantageous. Elimination of the lime kiln means savings in oil. Part of this oil saved is burnt in the recovery furnace to compensate for the heat losses caused by the extra load of inorganic chemical in the recovery process. However, according

to Janson (36) the net change in energy consumption implies larger savings than losses and the total gain in energy amounts to about 6 USD/tp. The author showed savings in the overall operating costs of 3 USD/tp when the borate replaced the NaOH.

Introduction of titanium dioxide, ferric oxide or ilmenite in the recovery furnace or outside it in reaction with the smelt is capable of regenerating NaOH from the black liquor. These metal oxides react with Na_2CO_3 in the recovery furnace to form mixed oxides with sodium liberating CO_2 . The mixed oxides when dissolved in water, NaOH is regenerated with the formation of the original metal oxides as precipitates. The metal oxides are then removed from the white liquor and recycled, so they do not enter in the cooking stage. Thus, the conventional causticizing and the lime kiln system can be eliminated. These chemicals are better suited for non-sulphur cooking than for kraft cooking (35).

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