

Anthraquinone pulping: fifteen years later

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ABSTRACT: *The paper reviews the current position of anthraquinone pulping in the light of fifteen years of worldwide experience.*

KEYWORDS: *Anthraquinone, bibliographies, development, history, processes, pulping, reaction mechanisms, review, utilization.*

Introduction

Background

Major advances in wood pulping chemistry are rare. Most of the news on novel technology for pulp mill application concerns advances in engineering and equipment rather than chemical changes.

Anthraquinone (AQ) pulping is therefore a good example of a relative rarity. It is a new pulping chemical process that has succeeded. Its application as a solution to many mill problems or deficiencies is common worldwide. The chemical is now in use in over 100 mills. Future prospects for the continued and even expanded use of the chemical in alkaline pulping are very promising. Interest in AQ applications now encompasses possibilities that were only curiosities until recently.

This paper will review the essential elements of AQ pulping and describe some of the new developments, applications, and aspects of the technology that have evolved over approximately the last 15 years.

A lucky combination of properties

Some key attributes are essential for a technically successful reducing and

oxidizing (redox) pulping catalyst. It must be stable to hot, strong alkali; susceptible to reduction by aldehyde functional polysaccharides to a form that can reduce and degrade active, transient lignin structures; and soluble in the reduced form in hot alkali. A technically successful catalyst must also have zero toxicity, no adverse environmental effects, and cost effectiveness. AQ has become a successful pulping chemical because it possesses all the qualifications listed above.

AQ reaction mechanisms

There are two effects from which all possible applications of AQ derive:

- Acceleration of alkaline pulping
- Carbohydrate stabilization with yield preservation

There are a wide variety of uses from these two basic effects.

AQ catalysis is a chain of events. Initially AQ is insoluble in the cooking liquor. As such it does not possess any catalytic function. To be effective, each molecule of AQ must be free and independent in the pulping liquor. Only then can each molecule interact effectively with active parts of the lignin molecules as they are produced or ex-

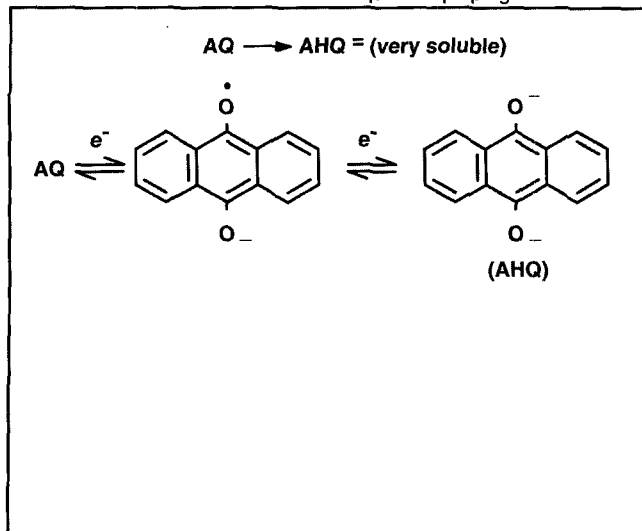
posed by the pulping liquor. How then does AQ become soluble?

AQ solubilization occurs by electrochemical reduction. Electrons from aldehyde groups on the ends of the polysaccharide portion of the fiber transfer to the AQ molecule. The loss of electrons by the aldehyde groups converts them to carboxylic acid groups. This is a transformation which fortunately also stabilizes the polysaccharide molecules to the loss of yield process known as peeling. This is the repeated detachment and degradation of sugar groups from the end of the polysaccharide chains. Since polysaccharides are an important constituent of cellulose and hemicellulose, the suppression of peeling during AQ pulping produces an increase in yield by preserving the chemical integrity of fibers.

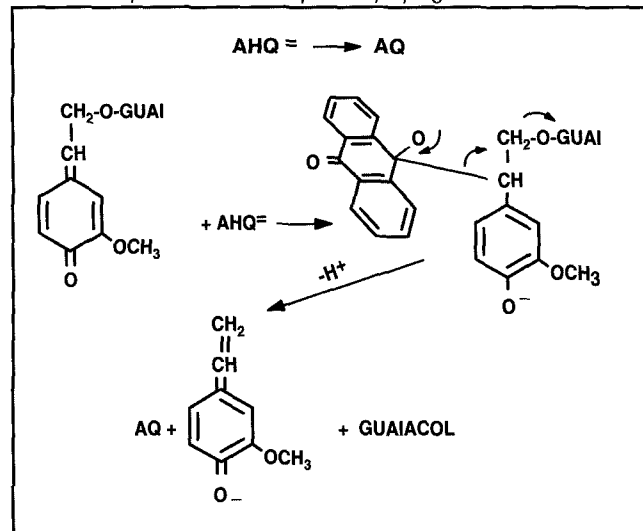
The transfer of electrons to the AQ molecule converts it to a reduced form, probably anthrahydroquinone (AHQ), as shown in Fig. 1. The AQ may be marginally soluble under the severe conditions of pulping, it may be reduced by mobile reducing sugars released by the wood, or both of these conditions may occur. Regardless, the AQ must come into molecular contact with the reducing species allowing it to participate in the redox reaction.

The generally accepted mechanism for AQ pulping acceleration involves the attack of AHQ on transient, reactive lignin structures (1). These form under cooking conditions by the action of alkali on phenolic structures in native lignin. Electrons transfer from AHQ to the lignin structure causing it to cleave. In the process, the original oxidized form of AQ regenerates. Figure 2 illustrates this for model compounds representing a quino-methide, a reactive lignin intermediate struc-

1. Electrochemical reduction in anthraquinone pulping



2. Oxidation process in anthraquinone pulping



ture thought to form during alkaline pulping. Among the undesirable reactions of the quinomethide are its near-irreversible attachment to other parts of the lignin or to sugar groups remaining as part of the fibers. The destruction of the quinomethide also prevents its self-conversion into an entity that only slowly degrades.

Figure 3 gives an overall picture of the function of AQ. The cyclic nature of the process suggests that the same AQ molecules cause both the delignification acceleration and polysaccharide stabilization. This generally accepted theory explains why so little AQ does so much. Recent literature suggests that AQ may also take part in other reactions besides those described above (2). Evidence suggests that AQ may also oxidize some parts of the lignin. The AHQ may reduce part of the polysaccharides.

The above mechanisms indicate that AQ must be present early in the pulping operation to have maximum effect. Polysaccharides degraded before AQ can stabilize them are not repairable. Alternative reactions of the reactive transient lignin structures lead to missed opportunities to break their bonds and promote delignification. There are a limited number of weak points in native lignin.

AQ does not remain in the pulping solution forever. It chemically com-

bines irreversibly with reactive parts of the lignin structure (3). Electrochemically reduced derivatives of AQ which form in the pulping liquors (4) may be the actual species involved in these reactions rather than the AQ or AHQ themselves. **Figure 4** illustrates a possible route to removal of AQ by a reaction that forms a substituted benzanthrone. This AQ-derived chemical structure has been isolated from pulping solutions.

Most of the AQ is in the black liquor at the end of the cook. Almost all of it chemically combines with the lignin in solution. From 10–25% of the originally added AQ remains in uncombined form also in the black liquor. This residual AQ has a catalytic effect when a portion of the weak black liquor is recycled to subsequent batch digester cooks (5). A minor portion remains on the pulp fibers either combined with residual lignin on the fibers or as the original AQ. Chemical pulp bleaching generally removes all the chemical to nondetectable levels (6). Eventually, the recovery boiler burns essentially all the AQ regardless of its form.

Uses of AQ today

Currently, AQ applications in alkaline pulping include four basic categories:

- Nonconventional alkaline processes

- Incremental capacity applications
- Cost reduction considerations
- Environmental uses.

Environmental applications further subdivide into two separate categories. One involves lower air pollution through sulfidity reduction or through the total elimination of sulfur. The other concerns reduced bleach plant effluent pollution of waterways by extended pulping to lower kappa numbers.

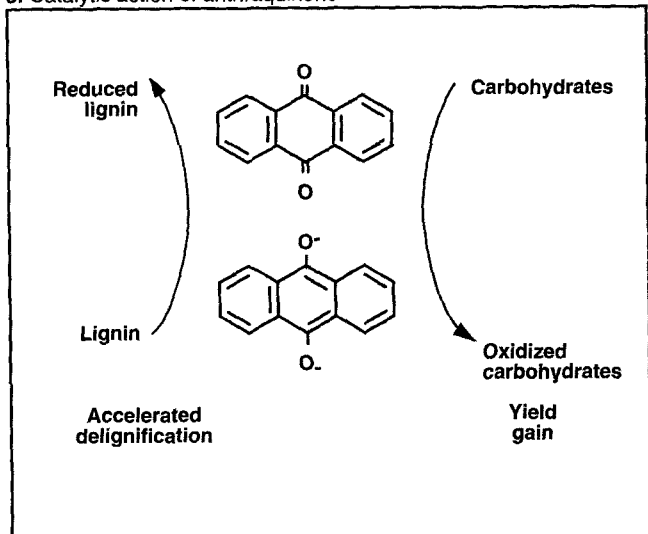
Three nonconventional alkaline processes are currently in use or have achieved pilot status. These are combinations of AQ with sulfite or bisulfite ions, AQ in the polysulfide process, and combinations of AQ and methanol.

AQ combinations with sulfite and bisulfite

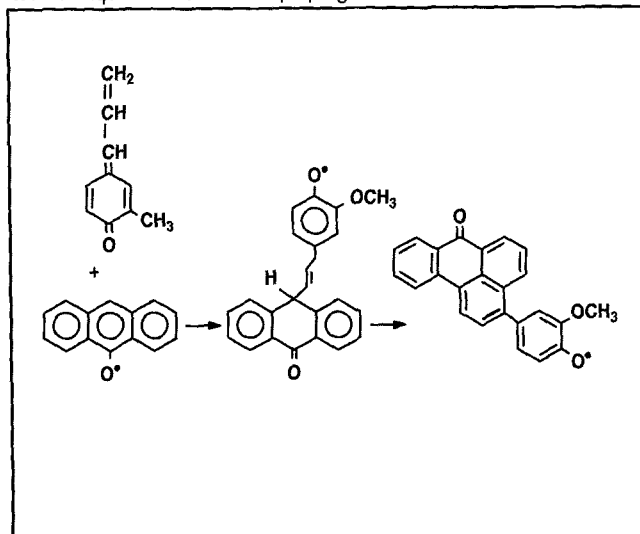
Around 1980, a series of publications suggested there may be a synergy between AQ and sulfite or bisulfite ions (7–11). The processes employing this combination of chemicals are the following, which are listed in increasing order of pH and in decreasing order of yield:

- Neutral sulfite semichemical (NSSC) with AQ for rapidly cooking softwoods to high-strength, high-yield pulp suitable for linerboard grades

3. Catalytic action of anthraquinone



4. Anthraquinone removal in pulping



- Neutral sulfite with AQ (NS-AQ) for high-yield softwood pulps cooked to nearly bleachable lignin contents with kappa no. ca. 40. (These pulps are particularly suitable in combination with a subsequent oxygen delignification stage to prepare for subsequent bleaching from a relatively low lignin content.)
- Alkaline sulfite with AQ (ASAQ) pulping, which is the high pH sulfite equivalent of kraft pulping for producing pulps down to bleachable lignin contents.

A key feature of the AQ and sulfite or bisulfite combination is the much wider pH range over which AQ is effective. All the combinations, however, are essentially alkaline. When Na_2CO_3 gradually replaces part of the NaOH to modify the soda AQ pulping, AQ becomes progressively less effective. In pure carbonate cooking liquors, there is no AQ effect (10). A pH of 12–13 or above is essential for cooks without sulfite or bisulfite ions.

There are dramatically different results if substantial amounts of sulfite or bisulfite are present. AQ remains highly effective down to approximately neutral pH. This allows the effective use of the chemical in the NSSC or NS-AQ processes. The initial pH levels of the cooking liquors are below the minimum for other alkaline

AQ pulping processes and decrease even further during pulping.

The ability to pulp softwoods is another feature of these mildly alkaline processes. NSSC cooking is normally confined to hardwoods. It gives a very high-yield, stiff fiber useful primarily for corrugating applications. In contrast, the NSSC with AQ and NS-AQ processes are useful on softwoods to form high-yield linerboard grade pulp and nearly bleachable grade pulp, respectively.

Much academic interest in pulping processes featuring a combination of AQ and sulfite liquors has resulted in a wealth of publications. None of these processes has been very successful to date, however. No kraft mill has switched to any such process. The problems include slow pulping rates compared to the equivalent kraft cooks, the need for complicated and expensive recovery systems, and a difficulty in reaching sufficiently low kappa numbers for NS-AQ pulping without the addition of an oxygen stage. Nevertheless, a handful of mills in the world do use the NS-AQ or NSSC with AQ processes. Each case has been a conversion from a sulfite or an NSSC mill. Other mills have conducted trials.

The use of sodium sulfite as an additive to other pulping processes is a way of improving fiber tear strengths (12). It is particularly applicable for

soda AQ softwood pulps which have tear strengths which are normally significantly lower than those of equivalent kraft pulps. The tear strengths can increase significantly by sodium sulfite additions of ca. 4% on wood (13). It is obvious, however, that the addition of sulfur compounds would complicate the soda pulping recovery cycle and make the process of doubtful practicality unless run at low sulfidity.

AQ combinations with polysulfide

A unique aspect of AQ as a pulping additive is its activity as a pulping accelerator and a chemical to increase yield. Most other additives offer only one or the other benefit. Generally it is a yield gain.

Polysulfide pulping is a modified kraft pulping technology from which substantial yield gains in both hardwoods and softwoods result. Its distinguishing feature is the presence of substantial quantities of polysulfide formed from high sulfidity kraft liquor by a proprietary chemical process.

The mechanism of pulp yield stabilization with polysulfide is probably similar to that of the AQ process, i.e., oxidation of polysaccharide groups to carboxylic acids. One would therefore suspect that the introduction of AQ to a polysulfide cook might lead to a

greatly reduced AQ augmentation of yield. Published studies show that AQ and polysulfide yield effects are at least additive and often synergistic (14, 15). Using AQ and polysulfide in combination provides a measurable yield increase compared to the kraft process. The increase is often greater than the sum of the effects of either technology alone. The yield effects can be quite dramatic. As much as a 9% increase in pulp production results solely from using 0.08% AQ along with a polysulfide modification of a kraft cook. Bleachability and pulp strengths do not suffer relative to the kraft example except, perhaps, for a slight tear strength loss in bleached softwood. This is not surprising, considering there are many fewer fibers per unit weight of pulp.

The polysulfide and AQ pulping process is currently in use in at least one pulp mill (14). The commercial importance of the combination could increase dramatically, however, if it proved valuable for maintaining conventional kraft-like yields in extended cooking systems.

AQ combinations with methanol

At the time of writing this paper, the wood pulping world awaited news of the startup of a new Organocell mill in Germany. Pulping at this site will employ only sodium hydroxide, methanol, and catalytic amounts (ca. 0.1% on wood) of AQ. Key improvements of the original Organocell process developed in the 1970s have made this approach to pulping sufficiently attractive for use in a full-scale production facility. The process has changed from a complex and difficult two-stage, acid and base pulping system to a single-stage system with two cooking zones; a considerable drop in the methanol content to 30% of the liquor; and a drop in cooking temperature and pressure to values more typical of the kraft process (16). The result is a controlled operation using more conventional equipment to produce hardwood and softwood pulps that are easily bleachable, easily beaten, and

of acceptable tear strength and exceptional breaking length. The new mill recovers and recycles the methanol. The Organocell process typically carries the softwood pulping to kappa no. 30.

The alkaline sulfite with anthraquinone and methanol (ASAM) process is another new process employing AQ as catalyst and methanol as a second additive. The addition of methanol to the originally proposed ASAQ process has apparently resulted in greatly improved technology (17). An interesting aspect of this process is the ability to reach low kappa numbers at very high yields. For softwoods the kappa number is 20, and for hardwoods it is 10. The low unbleached lignin contents, very high strengths, and the easy bleaching properties of the pulps provide an excellent basis for the production of chlorine-free, fully bleached pulps. This is a big advantage on a millwide scale. Kraft-like yield and strength properties are typical. Widespread acceptance will depend on the practicality of the high digestion pressures (ca. 200 psi) and the acceptance of a modern sulfite recovery technology by an industry steeped in kraft traditions.

The technical success of these pulping technologies suggests that a synergy may exist between AQ and methanol. Evidently much potential still exists for AQ pulping research with emphasis on methanol as an AQ penetration aid.

Bottleneck elimination

Overview

Although the prospect for effective sulfur-free alkaline pulping of both softwoods and hardwoods generated the most excitement when AQ pulping first became available in 1977 (18), the primary use of the technology over the following 15 years has been for the elimination of bottlenecks. This involves increasing production above normal equipment capacity limitations. Many mills increased capacity by this technique usually with no significant capital investment. Both the accelera-

tive and increase in yield effects of the chemical are important in this application.

AQ will not alleviate every bottleneck in the pulp and paper mill. It is necessary that a mill can use the extra production for sale to other mills in the case of market pulp mills, for the production of more salable paper or board product in completely integrated mills, or for the elimination of purchased pulp. Thus, paper machine bottlenecks or limited markets for pulp can negate the usefulness of AQ at a particular time and site. For bleached fiber mills a bleach plant limitation can also function as a blockage in the pulp line, preventing the use of any extra brownstock in most cases. Within the pulp mill itself, undersized brownstock washers can be limiting in the same way. In these examples, it is not even possible to handle the extra pulp yield at constant chip processing.

For most parts of the world, the economical use of AQ for incremental pulp production requires more wood processing per day through the entire system to benefit completely from the multiplier effect of the two basic AQ advantages. Application of the technology is usually not justifiable on the basis of extra yield from a constant weight of chips alone. Such would be the case for a continuous digester with a chip feeder bottleneck or an overloaded evaporator train. Although constant throughput reduces wood costs as a result of AQ induced higher yields, this application is only viable in areas of high wood cost. An example would be Japan, where the use of AQ or related compounds is almost universal.

This paper will now examine the most feasible and commonly used applications of AQ for elimination of bottlenecks. The economic analysis of debottlenecking strategies is discussed elsewhere (19).

Recovery furnace

The high cost of kraft recovery furnaces makes their replacement infrequent. Modernization can increase their capacity within limits. Usually

the pulp mill eliminates bottlenecks in other areas until the boiler is running over name plate capacity. It therefore seems that the most common pulp mill bottleneck is the recovery furnace. Another paper on AQ pulping described a successful mill trial of such an application for the production of softwood linerboard (20).

It is not surprising that the most common AQ application for incremental capacity increase involves using the two basic effects of AQ to increase pulp production by alleviating recovery furnace overloads.

AQ dosages within the range of 0.05–0.10% AQ on o.d. wood find common use for this purpose. The lower and upper parts of the range are most applicable to hardwoods and softwoods, respectively.

The basic benefits in terms of acceleration and yield increase depend on the particular mill in question, the wood furnish, and the cooking conditions including effective alkali and sulfidity content. Many publications detail the specifics (19). One can expect 2–4% less organic material removal from the wood and 6–10% less inorganic material in the black liquor. These changes result from a 1–2% yield increase and a 6–10% reduction in applied effective alkali, both resulting from the presence of AQ.

The actual increase in boiler capacity resulting from these changes depends on the character of the bottleneck. If the overall black liquor solids level is the limiting factor, the reductions of both inorganic and organic solids per ton of pulp allows an increase in wood chip throughput. At the same time, there is a greater yield on that wood. This is the basis of the multiplier effect. Throughput increases of at least 10% occur in mills for this type of application.

Somewhat lower capacity increases result if the limitation is in terms of steam generation. This limitation arises when the recovery furnace is at capacity for removal of heat from the furnace by the formation of steam. In other words, the furnace is burning as much of the dissolved organic mate-

rial as possible. Then pulp production will only increase by a reduction in the amount of dissolved organic materials per ton of wood. In this case, the potential capacity increases are smaller but still amount to a substantial 5–7%. This comes from both the increased wood throughput and the higher fiber production per ton of wood. This is one of the few cases in which the yield increase but not the acceleration effect of AQ is used.

In either of the above cases, the percentage reduction in applied white liquor is significantly greater than the percentage reduction in dissolved organic materials. Further, a slightly greater percentage of the dissolved organic materials will come from lignin which is higher in caloric value than polysaccharides. Both effects lead to a black liquor of higher BTU value per ton.

The boiler limited AQ application should also be of increasing interest as mills find ways to delignify to lower and lower pulp lignin contents before the application of chlorine chemicals in the bleach plant. All the extra organic materials removed will be sent back to the recovery furnace. In some cases, this will place a new stress on the operation. The use of AQ to minimize the overall yield loss will both increase fiber production per ton of wood and decrease the extra load on the boiler. This will help the mill to maintain its original production rate.

White liquor shortage

A white liquor shortage may be the result of an undersized lime kiln or an undersized recausticization area. Lime dumping could alleviate the kiln problem. Purchasing expensive cooking chemicals for addition to the white liquor as makeup will partially solve the lack of recausticization capacity.

Capital investment is another approach which may or may not be desirable at the time.

AQ can also help expand production in a kraft mill with this limitation. The chief benefit derives from acceleration in this case, since the effective

alkali applied to the wood will decrease by 8–10% on application of 0.05–0.1% AQ on o.d. wood. The 2–4% greater fiber production per weight of wood, however, will also help.

Overall, this application potentially gives the highest overall AQ-derived increases in production—over 10% higher pulp production through the processing of more wood chips at greater yield. It is also valuable to recall that AQ can help maintain production during a temporary white liquor shortage. In addition, it can reduce or eliminate the excessive alkali consumption and yield loss when cooking decayed wood or a furnish with a high bark content (21).

Digester capacity limitation

Perhaps digester capacity limitations constitute the most direct application of the two basic effects of AQ. Here a mill uses 0.05–0.10% AQ on o.d. wood to give a higher wood throughput and a higher yield from the wood. Use of AQ-induced pulping acceleration reduces the *H*-factor by a reduced cooking time rather than reducing the applied white liquor.

The theoretical increase in mill throughput is as much as 12% for normal responses to AQ. This value may occur in continuous digesters with the capacity to increase chip flow. It is limited to ca. 4% in digesters with a chip feed bottleneck (19, 22). For batch digesters, the benefit will be related to the cooking time reduction compared to the cover-to-cover cycle time for the digesters.

Permanency of bottleneck elimination

For any particular mill site, the AQ approach will continue in use until there is a capital investment to alleviate the bottleneck. After the capital investment, AQ use will continue if the chemical will alleviate the next bottleneck. This happens naturally with replacement of old equipment and systems. In some cases, depreciated capital investments are more economi-

cal than long-term chemical costs. Even then, however, the AQ approach allows the mill to opt for the cost of chemicals and invest available capital elsewhere. This might be in paper machine upgrades or pollution control. For any particular mill, however, there is probably no permanency for bottleneck elimination.

From a worldwide viewpoint, there may be some permanency, however. On a map of the world, individual AQ applications to eliminate bottlenecks could be represented by lights turning on and off over the years. But always there are lights.

Cost reductions

The reduction of costs at constant production rates is one of the applications many mills have initially considered for AQ. This would be interesting to kraft mills that do not have a production bottleneck or environmental problem to which AQ can be applied.

Cost reduction applications have many aspects. Once AQ use occurs in a mill operation and technical changes take advantage of its presence, there will be many cost changes. Economic studies have shown, however, that there are three basic determining factors relevant for assessing the economics of AQ use (19, 22). These are the wood costs, the AQ costs per ton of pulp, and the sum of these balanced against the value of the resultant extra production. Other cost reductions and increases are relevant as trim.

Using AQ for cost reduction at constant production rates, there is no extra pulp produced so the economic analysis reduces to a simple comparison of the cost of the AQ with the savings in wood cost. At this point, a real benefit is only possible in locations with very high wood cost. The previous mentioned example of Japan is applicable here. Wood costs are moving upward in some parts of North America, however. This has recently generated some interest in cost reduction applications.

There are also reports of unusually positive results from AQ applications.

In those cases, the benefits may be sufficient to justify use of the chemical for cost reductions alone. One example is a report of laboratory investigations and mill trials at three Spanish kraft mills (23). The yield increases and pulping acceleration were so much higher than reported by most observers that the use of AQ for cost reduction may be viable in this case. It may be highly significant that the wood in each mill was eucalyptus (*E. globulus*, *E. camaldulensis*, and *E. rostrata*). This is particularly interesting because AQ finds worldwide use in a greater percentage of mills pulping eucalyptus than any other single wood species (24). On the other hand, other publications present much more normal data for the kraft AQ pulping of this species (25). There is obviously a need for more work on the response of AQ to the various species of the eucalyptus genus.

Environmental considerations

Sulfur replacement

In terms of their catalytic effects on the alkaline delignification of wood, AQ and the hydrosulfide ion appear to be equivalent. AQ is hundreds of times more effective, molecule for molecule. It is not surprising, therefore, that the magnitude of accelerative effects of AQ is at a maximum at 0% sulfidity. The effects decrease as the sulfidity increases to very high levels. Thus AQ has little influence on kraft pulping rates at 40-50% sulfidity.

A very different case results with AQ-induced yield increases. Sulfidity has much less effect. This is not surprising since the hydrosulfide ion does not directly affect pulp yield. Although AQ may offset sulfur reductions in the cooking liquor with no net change in pulping rate, the result is a net yield increase over the original kraft value.

The aim of sulfidity reductions is almost exclusively the reduction of sulfur containing gas emissions in either reduced or oxidized form to a level that satisfies local regulations. Each mill will have a particular sulfidity at

which it can meet its requirements. It will depend on the original sulfidity, the type of wood species, and the engineering controls already in place for controlling emissions. In the experience of the author, an older uncontrolled mill would require a reduction to essentially zero sulfidity, but mills with some engineering controls may find that low sulfidity with AQ is an effective final tool to satisfy regulations completely.

Soda AQ pulping

Within a few months of the first public disclosure of AQ pulping in 1977 (20), one organization began using AQ in its soda hardwood mill. Results of this successful application of the chemical appeared in papers a few years later (26, 27). Use of the chemical has continued to the present day.

It is significant that this example was a hardwood mill that was already using the soda process because of its sensitive location. History has shown that the soda AQ process is only really economically viable with hardwoods and nonwood species.

Compared to the uncatalyzed soda case for hardwoods, soda AQ pulping offers so many advantages that there should be no hesitation about adopting AQ. AQ charges of 0.06-0.075%, which are well within the favorable economical range, will give 3.5-4% higher yields on wood, i.e., 7-8% more pulp. These are yields as high or higher than kraft cooks. The strengths of the pulps produced should be as high or nearly as high as the same fiber cooked by the kraft process (13) and higher than the unmodified soda cooks which the soda AQ process would replace. In an existing integrated soda plant, this is likely to mean less use of purchased kraft softwood in fine paper production. A possible exception is 100% bleached eucalyptus integrated paper mills. This leads to cost savings and a superior paper printing surface.

Although there have been few AQ-induced conversions of hardwood kraft wood pulping mills directly to soda pulping, there are at least a dozen or

so soda hardwood mills around the world with at least one in every continent. AQ is used in the production of approximately 2/3 of the pulp from all these mills.

Rather high charges of AQ are necessary for softwoods to coax the soda process along to bleachable grades. Application levels when pulping to a conventional kappa number of 30–35 with spruce or pine are 0.15–0.25% on o.d. wood. This exceeds the 0.1% level which the U.S. Food and Drug Administration mandates for the production of food grade paper. These relatively high AQ levels are not even sufficient to replace the hydrosulfide. Effective alkali charges 10–30% higher than the equivalent kraft or, alternatively, higher *H*-factors are necessary to reach the same kappa number. There is a double effect on lime kiln and recausticization capacity. This is because no free caustic derives from the partial hydrolysis of sodium sulfide when the smelt transfers from the dry liquid salt form to the aqueous green liquor.

Softwood fiber strength has also been an important consideration that has limited kraft to soda AQ conversions to hardwoods. Soda AQ tear strengths for bleachable grade softwood pulps are significantly lower (ca. 15–20%) than those of the equivalent kraft cooks (13). Conversely for soda AQ hardwoods, many studies have shown pulp strengths similar to those of kraft pulps and higher than soda pulps (13).

Softwood soda AQ pulping is effective as the first stage of a two-part, high-yield soda AQ oxygen pulping system. The soda AQ cook carries the process to linerboard lignin contents followed by refining and an oxygen stage to bleachable kappa numbers. In this case, oxygen delignification would reduce air pollution. The product is comparable to kraft pulps. It employs relatively low AQ levels of ca. 0.1% compared to the soda AQ softwood case.

Low sulfidity AQ pulping

As in soda-AQ pulping delignification catalysis of AQ is critical for inducing kraft-like performance in low sulfidity pulping. Adding AQ maintains pulping rates and pulp quality as removal of the sulfur of the original kraft cook occurs. The augmentation of yield is not critical. Unlike the soda case, there is little yield loss at constant kappa number when lowering the sulfidity without a catalyst from 35% to 15% or less. The usual AQ-induced yield increase, however, does occur to give yields at low sulfidity that are higher than those of the conventional kraft cook. The yield increases over kraft are only slightly less than those from AQ in conventional kraft cooks (28, 29).

The magnitude of the yield increase of low sulfidity AQ cooking compared to a kraft reference, when both are cooked with the same *H*-factor and to the same kappa number, depends on the strategy of AQ use. For a constant *H*-factor at the desired sulfidity and pulping to the same kappa number as in the kraft base case, the applied effective alkali and the AQ levels are balanced against each other. For example, as the effective alkali level is decreased at constant kappa number, the AQ charge must be increased correspondingly and the yield advantage over the kraft case becomes greater. Each mill can choose the most advantageous balance between these cooking variables based on technical and economic circumstances.

The AQ pulping option for air pollution applications came at a time when pulp mills worldwide were assessing technologies for curing their sulfur emission problems. There was almost a universal adoption of engineering pollution controls. The future looked dim for the potential for significant applications of low sulfidity AQ pulping. Part of the problem appeared to be that only moderate decreases in sulfur emission resulted from moderate decreases in sulfidity. Sulfidity reductions to 0–3% with the soda AQ process are not practical for softwood

pulping. Although hardwood soda AQ pulping was a highly viable process, this choice had many negative implications for mill operations and capital investments. Accordingly, most mills adopted engineering controls with very rare exceptions.

There has been renewed interest in low sulfidity AQ pulping in recent years. Many kraft operations have found that engineering controls, although extremely effective, have not been totally satisfactory. Sulfur dioxide emissions generated by the burning of collected total reduced sulfur (TRS) gases now pose a problem at some sites. At other mills, TRS gas release from point sources such as washers may still be excessive. This is particularly true in areas in proximity to urban or tourist sites or both. The result is a new interest in low sulfidity AQ pulping. Mill trials are under way or in the planning stage around the world. At some sites, low sulfidity AQ pulping is currently in use on a full-time basis.

A primary concern to a mill considering a change to low sulfidity AQ is the reduction in emissions as a function of sulfidity reductions. There is little or no qualitative information in the literature, although there are a number of unofficial reports. In some mills emission reductions parallel sulfidity reductions with a 50% emission reduction resulting from a 50% sulfidity reduction. In other mills up to an order magnitude decrease in TRS emissions has been reported on cutting sulfidity in half. Perhaps the difference results from the way the mill was run in the original kraft case. An overloaded kraft furnace may respond well in terms of reduced emissions at lower sulfidity.

A kraft boiler may indeed operate more efficiently at low sulfidity. A lower concentration of sulfur compounds in the liquor should reduce fouling in the evaporators and down time due to plugging in the upper sections of the furnace. These phenomena derive from higher inorganic salt solubility (30) and less sticky ash (31), respectively, at lower sulfur content.

A minor degree of bottleneck elimination may also result from the AQ-derived yield increase over the kraft base case for a fully loaded furnace. The weight of solubilized organic materials fed to the furnace will decrease. This would directly benefit the steam-limited boilers. There is a limitation on the magnitude of the increase, however. The soluble inorganic material level cannot decrease as in the kraft AQ case unless the sulfidity reduction is low and the AQ charge is high. In conclusion, low sulfidity AQ pulping is perhaps the only application of the catalyst that can have two major effects. There is reduced air pollution and the potential for elimination of bottlenecks in the mill leading to a higher pulp throughput.

The causticizing and lime kiln areas of the mill will be subject to more stress on conversion to low sulfidity AQ pulping. Although the active alkali charge does reach a minimum on reducing sulfidity with AQ (22), the effective alkali charge will remain constant, or even increase, depending on the amount of AQ charge and the magnitude of sulfidity reduction (28, 32). When changing sulfidity, effective alkali relates more closely to recaustizing capacity demands than does active alkali. Further, less free caustic is produced on dissolving the smelt. This caustic results from the partial hydrolysis of sodium sulfide to sodium hydrosulfide. Therefore, sulfidity reductions at constant or increased pulp output require excess capacity in the liquor regeneration area.

Reduced bleach plant effluent

Environmental pressures to reduce bleach plant discharges of dissolved organic waste have forced bleached kraft mills to search for new solutions to this problem. Particularly in 1992, there was increasing interest in AQ pulping as a way to achieve extended delignification. Many mills around the world are showing interest in this approach with many trials in the planning or completed phases. The goal of these trials is to use the chemical to

reduce the kappa number of the pulp before entering the bleach sequence. For practicality, this requires no reduction of the nonlignin yields or degradation of fiber properties such as would occur with a simple extension of kraft cooking to well below kappa no. 30. Both the pulping acceleration and the increased yields obtained from AQ are important functions in low lignin pulping.

A simple extension of kraft pulping by a suitable adjustment of *H*-factor or effective alkali or both typically degrades fiber strength potential and reduces the nonlignin fiber yield. A suitable optimization of nonadditive pulping conditions, however, can produce low lignin content pulp with acceptable physical properties and bleachability (33, 34). The introduction of AQ provides an additional and powerful tool to lower the unbleached kappa number while maintaining the desired fiber characteristics and yields. It also provides an alternative means of extended pulping where the otherwise necessary changes in nonadditive pulping conditions are not desirable at a particular mill.

It is possible to use more than one strategy for AQ-assisted extended pulping. One study probably took the technology to its limits by using it to effectively replace high-consistency oxygen bleaching (33, 34). In this work, the kappa number was reduced from 40% to greater than 50% on the standard kraft results, i.e., from 35 to as low as 15. Softwood brownstock kappa numbers below 20 were achieved by using fairly extreme conditions. Some of these conditions may not be acceptable to a kraft mill today. AQ levels of 0.1–2%, which are at or above the Food and Drug Administration-mandated maximum, provided the most extreme degrees of delignification. These levels would significantly increase the cost of production.

With more modest goals, normal AQ doses provide a useful result. Adding 0.06–0.08% AQ on o.d. wood to an existing softwood 25–30% sulfidity bleached kraft pulping operation employing either continuous or batch di-

gesters provides a significant drop of 4–6 points in the original kappa no. 30. Kappa number reductions greater than 6 points will result using the maximum dose within Food and Drug Administration regulations (0.1% AQ). With this strategy, the total yields of the unbleached pulp will remain approximately constant at the reduced kappa numbers in most cases. The lignin-free yield will increase as a result of the yield-saving effect of the pulping catalyst. With the maintenance of constant effective alkali levels in this strategy, no significant change in recovery furnace solids per ton of pulp will result. During a subsequent optimization there can be changes to the cooking conditions appropriate for the mill in question.

Another important aspect of the work cited above (33, 34) concerns the pulp properties and bleachability. The authors reported that subsequent bleaching of the low-lignin pulp did not diminish quality compared to the conventional pulp, although the brightness ceiling of the chlorination extraction chlorine dioxide (CED) sequence may have been slightly less at intermediate AQ dosages. AQ helped preserve the zero span tensile strength of fibers cooked to the low kappa numbers with 0.05% or 0.1% AQ and CED bleached.

Engineering methods to achieve extended cooking are in use at many pulp mills around the world. These well developed technologies stem from the observation that superior delignification and an improved product results when the effective alkali concentrations are at a lower, more constant level and when there is minimum dissolved lignin in the cooking liquor during the whole cook. Continuous digesters appear to be particularly easily adapted to modified cooking procedures. Excellent systems are also available for batch digesters.

Engineered systems do not preclude the use of AQ. The chemical may help to augment the degree of delignification and maintain conventional post-bleaching yields. Chemical approaches to maintaining acceptable

yields by polysulfide AQ pulping may be necessary with extended cooking strategies.

Mill experience

Application strategies

No mill should encounter any problem or loss of production when running an AQ trial or when starting its regular use. To the author's knowledge, no mill has ever shut down production when introducing AQ to its kraft or soda pulping operation. Indeed the rapid growth of AQ on a commercial scale is attributable in large part to its ease of application and to the absence of any production downtime or unusable pulp.

A gradual approach minimizes problems, however. A typical strategy involves an addition of AQ to a kraft cook without any changes to the normal cooking conditions, whether using batch or continuous digesters. The kappa number will drop to a degree which depends on the amount of AQ applied, the type of wood, and the pulp product. The total yield generally remains approximately constant, although there will be less lignin and more useful fiber components remaining. There should be no viscosity effect. This can be the first step in virtually all applications of AQ where its use is to protect both the yield and the pulp quality.

The next step depends on the goal set for the introduction of the chemical. For low lignin pulping, the goal has already been achieved. It only remains to optimize the variables including the AQ level to achieve the maximum kappa number reduction at minimum cost with maintenance of fiber quality.

For most other applications, the mill will want to maintain its normal kappa number. Reducing the effective alkali charge to restore the original kappa number will most often accomplish this for recovery boiler and white liquor shortage applications. There will be a higher yield. Note especially that it is necessary to monitor carefully the residual effective alkali to ensure that no organic deposition problems occur as the solids level increases in the evapo-

rators. For mills initially running with low residuals, it is preferable to carry out preliminary laboratory studies.

Where digester bottlenecks are the target, reducing the H -factor through a reduction in cooking time will restore the original kappa number.

It is also possible to combine the first two steps by adding AQ and simultaneously adjusting the conditions to maintain the original kappa number. This is easier with batch digesters and requires extensive laboratory and pilot plant work.

An alternate way to use the acceleration involves reducing the H -factor by a cooking temperature reduction. In kraft pulping, a ca. 3–3.5°C reduction is possible. This is not a common option, but it is available as a steam-saving measure if the mill has sufficient control over this variable. It is not an economical choice in most cases, however, since the adoption of lower pulping temperatures depletes the acceleration effect of AQ and leaves only the yield gain. It is perhaps most applicable in rare instances of soda mill conversions to soda AQ pulping. The acceleration effect is so large in this case that it can be used in a number of ways.

For the conversion of a kraft mill to low sulfidity, the first and second steps can be the same as for the furnace bottleneck case. Add AQ to the normal kraft process and allow the kappa number to drop. A reduction of the effective alkali charge would restore the original kappa number. Then one would eliminate sulfurous chemicals from recovery cycle makeup. The sulfidity would fall over a period of weeks while the effective alkali and AQ levels were adjusted to maintain the target kappa number. The TRS and sulfur dioxide emissions would be monitored until the specified targets are reliably met. The sulfidity at which this can be done would then be the level for regular production.

The general strategy of application of the chemical to either a batch or continuous digester is the same. Introduce it as early as possible in the impregnation stage and distribute it as evenly as possible. The polysaccha-

ride stabilization reaction in particular occurs very early in the cook below 100°C. Any delay in the arrival of AQ at the reaction site is a lost opportunity to save yield. Pulping acceleration effects of the reduced forms of AQ occur as the temperature rises to ca. 130–140°C. Electrochemical studies demonstrate the changes in concentrations of the reduced and oxidized AQ species with temperature increases and show how the concentrations apparently reflect their involvement in the changing chemical processes (35).

Addition mechanics

It is possible to add AQ either in its natural form as a yellow crystalline powder or as an easily pumped, low-viscosity dispersion in water. The best of the aqueous dispersions are very stable over periods of many months and are extremely convenient to use.

Addition of the dispersion to batch digesters is most commonly in the white liquor. It should, however, be added to the white liquor line to the digester (preferably the low pressure side of the white liquor pump) but never to the white liquor storage tank. The high salt concentration of the white liquor would destabilize the dispersion or slurry. This is an irrelevant factor in the agitated conditions during white liquor addition, but it could cause serious plugging of lines and pumps after the AQ settles out as a fine powder in the bottom of the white liquor tank. Ideally, the period of AQ dispersion addition to the white liquor line will coincide with the injection of white liquor. Addition can also be in the black liquor line or the combined white and black liquor lines.

For continuous digesters, the AQ dispersion or slurry has been pumped into the top circulation loop of the digester in single-vessel systems or of the impregnation tower in two-vessel systems. Addition of the AQ formulation is also possible by pumping into the white liquor lines. One must remember when running modified continuous or extended modified continuous cooking that all the AQ

must be applied through the first white liquor addition point to ensure its application early in the cooking process.

For a permanent mill setup using a ca. 50% by weight water dispersion, which is the preferred method in North America, the only significant investments will be a suitable metering device, if one is not already available, and a storage tank sized for ca. two weeks full production. Moyno pumps are the most trouble free and accurate means of adding the dispersion, but diaphragm pumps suitable for slurries of crystalline solids are also suitable. The suction side of the liquor pump or the pump driving the top circulation loop are the most common addition points in batch digesters and continuous digesters, respectively.

Conclusion

It is highly significant that interest in AQ pulping has escalated in the last one or two years, a time of severe recession throughout the world. Most surprisingly, even new applications for bottleneck elimination have occurred during this period of low pulp prices and poor markets. It will be interesting to observe the effects of economic recovery on AQ demand.

Other developing applications for the chemical may be more recession proof by their very nature. This would be especially true for systems which require AQ to be efficient, for example NSAQ, Organocell, and ASAM. The place of AQ in mills using this technology as part of their air and water pollution control should also be reasonably secure.

Perhaps there is truth in the frequent generalization that it takes 10–15 years for a new technology to reach its zenith. In spite of its rapid initial adoption at some mills, AQ may still be in its growth period.

There was a question in 1979 regarding AQ, "Will it take off?" (36). The answer 13 years later seems to be a resounding "Yes!" ■

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Received for review July 24, 1992.

Accepted Oct. 14, 1992.

Presented at the TAPPI 1992 Pulping Conference.