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ORGANIC CHEMICAL ACCELERATORS FOR ALKALINE PULPING

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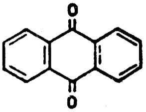
Abstract

The need to make the best use of wood supplies, conserve energy, and reduce the costs of pollution abatement has stimulated research to improve the yield, accelerate the rate, and reduce the odoriferous nature of kraft pulping. Because the structure of lignin is imperfectly understood, the quest for reagents which can accelerate delignification has been handicapped. In contrast, because the structure and reactions of cellulose and other wood polysaccharides are known, deductive methods have been applied in the search for reagents which can protect these polymers from alkaline degradation and thus improve pulp yields. The discovery of the dramatic accelerating effect of anthraquinone on alkaline delignification can, in fact, be traced back to a series of investigations which began with a search for reagents capable of inhibiting the alkaline degradation of cellulose. Against this background, research on pulping additives is reviewed, with particular reference to the current status and potential of catalytic accelerators in alkaline pulping.

Introduction

The search for a reagent to replace sodium sulphide in kraft pulping has been motivated by the desire to develop an alkaline process which would produce a chemical pulp fibre with the same high qualities as those of kraft pulps, without requiring the presence of a sulphur compound. Significant progress was made in 1977, when, as first announced by Holton(1), it was found that the addition of as little as 0.2% (based on o.d. wood) of anthraquinone (AQ, Figure 1) could accelerate the rate of delignification in soda pulping to that of kraft$^{(2-6)}$.

In the four years since the action of anthraquinone in alkaline pulping became widely known, the range of its commercial application has been extensively explored$^{(7-11)}$. It is now apparent that, at its current price, the applications of AQ are not as far-reaching as was initially hoped. Nevertheless, the anthraquinone discovery marks the most significant modification in the chemistry of alkaline pulping since the conversion from soda to kraft pulping about a century ago$^{(12)}$.



Anthraquinone
(AQ)

Fig 1

In soda pulping (aqueous sodium hydroxide, 1-1.3M, 170°C), the brown pulps which are produced from softwood have rather poor physical properties because the cellulose is degraded by lengthy exposure to hot alkali. In the kraft process the alkaline liquor contains sodium sulphide (molar proportions about 0.2 Na_2S:NaOH), which accelerates the delignification. In about two hours at cooking temperature, strong, brown pulps are produced (Table 1), which can be bleached to high brightness without loss of strength$^{(13)}$. The process is effective with all species of wood

	KRAFT	SODA
Pulping Chemicals	$NaOH+Na_2S$	NaOH
Time to/at 170°C, min	90/100	90/170
Total Yield, %	48	44
Tear Index ($mN.m^2/g$) at 11 km breaking length	17	12

Table 1
Comparison of properties of bleachable-grade pulps from spruce, at Kappa number 30

and is very tolerant towards substandard raw materials containing bark and dirt. World production of kraft pulps, bleached and unbleached, reached about 70 million tonnes by 1978. The disadvantages of the process, well documented elsewhere(14,15), include its high capital cost per daily tonne of capacity, the large scale now necessary for its economic operation, its odoriferous nature, and its comparatively low yields, of the order of 45%. In an era of sharply rising costs, diminishing supplies of raw materials and energy, and increasingly high standards of pollution abatement, the kraft process faces both economic and social problems.

Research aimed at improving the economics of kraft pulping draws upon many scientific and engineering disciplines and bears upon every unit process in the mill. However, the reactions in the digester have received a great deal of attention because they lead to poor yields compared to those of sulphite pulps at similar lignin contents. Attempts to improve the process by chemical means have aimed at modifying the response of the wood constituents to the pulping liquor, with the ultimate goal of using sulphide-free liquor to produce kraft-like pulps at an economic rate and yield.

Systematic research along these lines must clearly depend upon an understanding of the mechanism of degradation of the wood components, which, in turn, can stem only from a knowledge of their structure. The structure of cellulose was essentially established by 1923(16), and the mechanism of its alkaline degradation was elucidated in the mid-forties. Therefore, much research has been done on methods for preventing losses of cellulose during alkaline pulping. In fact, it was earlier work aimed at cellulose stabilisation that led to the discovery of the effect of AQ. On the other hand, the structure of lignin still eludes precise description, and the mechanism of delignification is not fully understood; consequently, little research was done on new delignification accelerators until the effect of AQ was discovered.

Alkaline Peeling of Wood Polysaccharides

In the kraft pulping of softwoods to bleachable grades (Kappa No. 30-35), about 95% of the lignin is removed and 35-40% of the wood polysaccharide is dissolved (Figure 2)(17) and degraded to acidic products. Much of this loss of polysaccharides is due to the stepwise removal of their terminal sugar units by the peeling reaction, whose mechanism was elucidated more than thirty years ago(18).

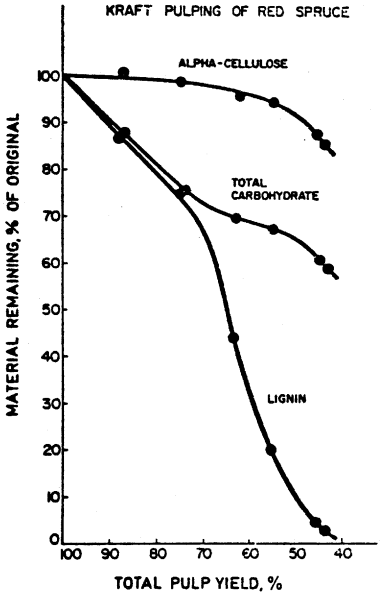


Fig 2—Removal of wood components during kraft pulping

In cellulose and other wood polysaccharides, the 1-4 glycosidic linkages are comparatively stable to alkaline hydrolysis. The terminal sugar moieties, however, are readily removed by alkali because they rearrange from the aldose to the ketose form, which is rapidly split from the chain, exposing another aldose group which can undergo the same reaction. This 'peeling' continues until a second mechanism, the 'stopping reaction', converts the end groups into a metasaccharinic acid unit, which is stable to alklai. The detailed chemistry of these reactions has been thoroughly reviewed elsewhere(18,19). Nevertheless, in the context of this conference, it is worth noting that the fundamental work which underlies the concept of the peeling reaction was done by H.S. Isbell in 1944(20). Isbell proposed a mechanism to explain the conversion, in aqueous alkali, of glucose and other reducing sugars into saccharinic acids. This idea was extended to the polysaccharide field and was soon shown to apply to all 1-4 -linked polysaccharides with reducing end groups. Although alkaline hydrolysis of glycosidic bonds at points remote from the end of the polymer chains is not rapid, some cleavage does take place at the temperatures of alkaline pulping(21). This exposes new terminal aldose groups where peeling can begin, thus increasing the loss in weight.

Since the loss of material by peeling is initiated because the terminal aldose unit, the `reducing end-group´, is alkali-labile, it can be prevented by blocking or modifying the end group. Appreciation of this simple, but fundamental, point led to the identification of a number of possibilities for increasing pulp yield, all based on the addition to the pulping liquor of a reagent to reduce, oxidise, or otherwise alter the structure of the terminal aldose units in the wood polysaccharides. Except for polysulphide, none of these reagents has been applied commercially(22). Nevertheless, in tracing the pathways which led ultimately to the discovery of the action of AQ in alkaline pulping, it is pertinent to review the strategies which were used in the search for reagents capable of blocking alkaline peeling.

Research Strategies

Whereas there was no basis for designing a reagent to accelerate delignification, the rationale for preventing alkaline peeling rested on solid fundamental proof. Therefore, at PPRIC, as in a number of other laboratories, efforts were concentrated on blocking alkaline peeling. We devised a simple, rapid, screening test(19) to determine whether a given reagent would inhibit peeling. A hydrocellulose (obtained by partial acid hydrolysis of cellulose) was used as a substrate. When this hydrocellulose was boiled in aqueous alkali for 2.5 hours it lost some 50% of its weight. Reagents were screened by adding them to this system and determining the weight loss which then occurred. Hydrocellulose was chosen in preference to cellulose itself, which is only slowly attacked by alkali at 100°C although at 170°C,, losses of 10-25% are encountered(23-24). This test was satisfactory for its specific purpose, but as Holton has since pointed out(1), it is possible to miss an important finding by using a model system.

Of two dozen reagents initially examined in our laboratory(19), hydroxylamine was the most efficient, reducing the weight loss of the hydrocellulose in boiling aqueous alkali to only 10%. Thus, it was almost as effective as sodium borohydride, addition of which resulted in a weight loss of about 7%: sodium borohydride, which reduces aldose end groups to alditols, is too expensive to be applied commerically in alkaline pulping, but was used as a bench-mark because of its known high efficiency as a peeling inhibitor(25). In pulping trials with spruce and birch, the carbohydrate yield at a given lignin content was increased when hydroxylamine was present. This effect was partly related to an increase in delignification rate, which was also observed by Chirkin and Tishchenko(26) in their experiments on the action of reducing agents upon lignin. The mechanism of the reaction between hydroxylamine and wood polysaccharides in alkali was oxime formation at the terminal aldose group followed by conversion via the nitrile into the corresponding carboxylic acid(27). It was found that the amount of hydroxylamine required for maximum protection of the end groups was approximately 300 times the theoretical amount required for the stochiometric formation of the oxime, because a competing reaction, alkaline degradation of the hydroxylamine, was comparatively rapid at pulping temperatures. The addition of about 5% of hydroxylamine (based on o.d. wood) led to yield increases ranging from 3 to 8 percent, depending upon wood species and process conditions. Although its use in pulping has been patented(28), the reagent is not quite cost-effective at the levels required.

In the early 1970's, Bach and Fiehn(22), using a hydrocellulose in a screening procedure similar to that developed earlier in our laboratory(19), investigated the effect of a number of redox reagents on polysaccharide stability in hot alkali. They confirmed the action of hydroxylamine but noted the need to find a peeling inhibitor which would not be degraded by hot alkali. This criterion led them to try anthraquinone and a number of its water-soluble derivatives. The most efficient of these was anthraquinone-2-sulphonate (AMS), which equalled the effect of hydroxylamine in the standard test (Table 2). In both kraft and soda pulping, however, the influence of AMS was much more striking than that of hydroxylamine, in that the addition of considerably less than 1% of AMS (based on o.d. wood) increased the pulping rate and the yield at a given lignin content. An addition of only 0.01% of AMS reduced the Kappa number by nearly 10 units, under constant conditions.

Test Substance*	Hydrocellulose Yield, %
Nil (Control)	71.5
Hydroxylamine	94.5
AMS	94.3
AQ	75.8

* Applied at 50% (based on hydrocellulose) and refluxed for 2 hours in 2N NaOH solution

Table 2
The effect of selected additives on the Alkaline Degradation of a Hydrocellulose(22)

Discovery of the Action of AQ in Alkaline Pulping

Bach and Fiehn's report on pulping with AMS stimulated research which led to the independent discovery in Australia, Canada, and Japan of the ability of anthraquinone (AQ) to catalyse alkaline delignification. Holton(1) found that AQ and alkyl anthraquinones accelerated delignification and stabilised carbohydrates far better than did AMS. Significantly, Bach and Fiehn had already screened AQ in their model (hydrocellulose) system, and had found it to be a very poor stabiliser compared to AMS (see Table 2). Bach and Fiehn had overlooked AQ primarily because they were using a model system for evaluating additives. They did not investigate the effect of AQ on wood pulping because of its small effect on the hydrocellulose yield. Had they done so, they would have been the first to discover the powerful catalytic action of AQ, and, to quote Fossum et al.(8), would not have `missed the golden egg'.

The lesson seems to be that serendipitous discoveries are more likely to occur when scientists are working with real systems. In a model system, the complexities which have been removed may be exactly those which are crucial to success.

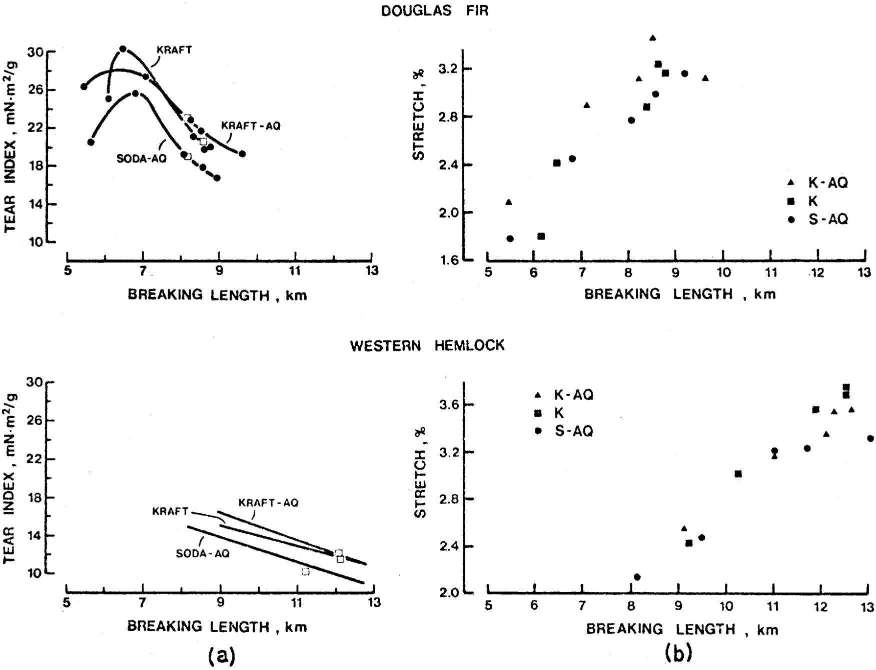


Fig 3—Unbleached soda-AQ, kraft-AQ and kraft pulps from Douglas fir and Western hemlock. Breaking length vs (a) tear index and (b) stretch-to-break. The open squares are 500 ml CSF data (32)

Commercial Applications of Anthraquinone

Anthraquinone received rapid acceptance as a pulping additive, with a North American mill trial being reported(29) in the same year as Holton's first publication. One pulp mill in Japan apparently used AQ, or a hydrogenated form, as early as 1975(3). The number of Japanese mills employing AQ on a continuous basis may well be greater than the 2 recently reported(30), because the use of AQ is especially appealing in Japan, where wood costs are high. In the rest of the world, there are at least 8 mills using AQ on a regular basis(30). The majority were soda mills, which had everything to gain: as laboratory studies(1) had indicated, small doses of AQ (0.05 to 0.2% AQ on oven-dry wood) accelerated soda cooking and increased both pulp strength and yield. One soda hardwood mill obtained an additional benefit: since it began using AQ, it has been able to add long-fibred softwoods to its chip furnish, thereby further improving the pulp strength(31). The soda pulping of bagasse is also greatly accelerated by AQ(32).

Although the soda-AQ process represents a major advance in sulphur-free pulping(9), it will not displace the kraft process in the near future. Bleachable soda-AQ softwood pulps are weaker than kraft pulps(5,9,32,33), as illustrated, for example, by Figure 3(32). Moreover, soda-AQ pulps from some softwood species are harder to bleach, in that they require more chlorine and caustic than their kraft equivalents(34). Some modifications of soda-AQ pulping have recently been announced(35-37) which aim to overcome the strength and bleachability problems.

Laboratory results had also shown that AQ brings benefits to kraft pulping, and once again, the findings were soon confirmed at mill scale(38-39). The mechanical properties of kraft-AQ pulps, except those from black spruce, are generally the same as those of kraft, as exemplified in Figure 4(40). The effects of AQ in kraft pulping are the same as in soda pulping, namely an acceleration of the delignification rate and an increase in pulp yield of 1-2 percentage points. These effects can be used (i) to increase the mill production rate, or (ii) to decrease the

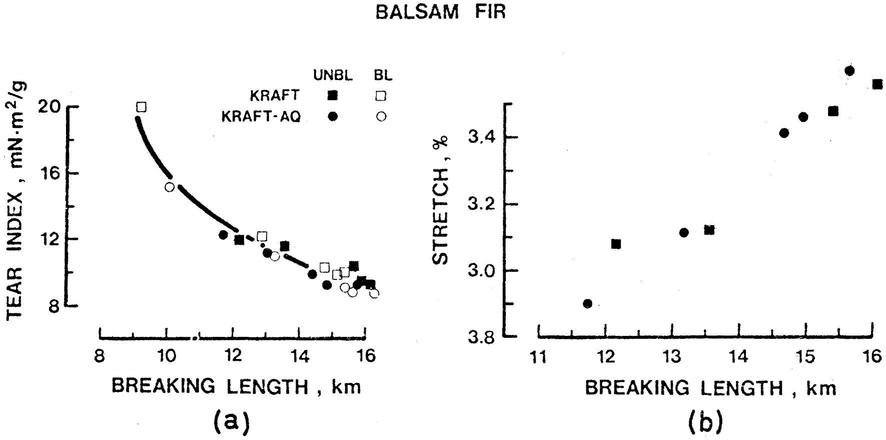


Fig 4—Kraft and kraft-AQ pulps from balsam fir, unbleached and C_DEDED bleached. Breaking length vs (a) tear index and (b) stretch-to-break (40)

alkali, steam, sulphide, or wood charge, while maintaining the production rate. Many possibilities between the extremes of (i) and (ii) can be envisaged, and the best way to use AQ in a given mill depends entirely on the specific situation. In North America and Scandinavia, the price and required dose (0.05 to 0.1% on wood) of AQ are slightly too high for it to be universally attractive for use in kraft mills. AQ may be a useful option, however, for overcoming process bottlenecks and hence boosting the output of a kraft mill in times of strong demand(7,10,11) or for extending the lifetimes of older mills that face large investments for odour control. These limited scenarios imply a rather intermittent use of AQ by the kraft industry.

A new pulping process based on AQ is in the developmental stage: neutral sulphite-anthraquinone (NS-AQ) pulping. It produces a pulp at high yield which nonetheless is reported to be easier to beat than kraft and to have equally good light-scattering properties(41-43). On the negative side, NS-AQ pulps from some species are weaker than kraft pulps, and delignification in NS-AQ liquor is much slower than in kraft liquor at the same alkali charge. NS-AQ pulp is promising as a chemical pulp furnish for newsprint, especially if it can be adequately bleached with only a single hypochlorite bleaching stage(43). The product is stronger than bisulphite pulp at yields well above those of bleached kraft pulp. In a mill trial, newsprint prepared from NS-AQ pulp (17%) and groundwood was found to be comparable with a control sample containing the same proportion of kraft pulp. All strength parameters were equivalent except for wet-web strength, a problem which might be overcome by adjusting the cooking, bleaching, and beating process(43). The NS-AQ process may also be useful for sack paper and liner-board base stock, with substantial yield increases over kraft at the same lignin content. Unfortunately, NS-AQ pulping loses much of its yield advantage over kraft if delignification is extended to Kappa number 30. For fully bleached NS-AQ pulp, it would therefore seem best to stop pulping at 40-50 Kappa and to delignify further with an O_2-alkali stage.

Rapid Acceptance of AQ

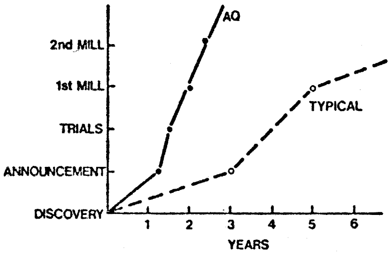


Fig 5—The commercial acceptance of AQ in pulp mills was more rapid than that of most innovations

As previously mentioned, commercial application of AQ followed very soon after the laboratory work: the reasons are that (i) the effects of AQ were easily confirmed in laboratories around the world, (ii) the process was easy to apply to a kraft or soda mill with a minimum of extra equipment, and (iii) the potential benefits were signficant; there was a strong incentive to try AQ.

The action of AQ is, indeed, so striking that it was originally half-suspected of having magical properties(45), but it soon gained the respectable status of `catalyst' as the mechanism of its action was pieced together(46,47). The progress made in elucidating the mechanism may also have contributed to the industry's interest in evaluating AQ.

Modus Delignificandi Anthraquinona

There is now widespread agreement(46-49) that AQ operates as a redox catalyst, as shown in Figure 6, by promoting an efficient transfer of electrons from a source (carbohydrates) to a sink (lignin). Thus, the degradation and solubilisation of lignin are accelerated (faster pulping), and, by end-group oxidation, the carbohydrates are stabilised against attack by alkali (higher yield). The details of the electron-transfer mechanism are still under investigation, but the general form of the redox cycle is

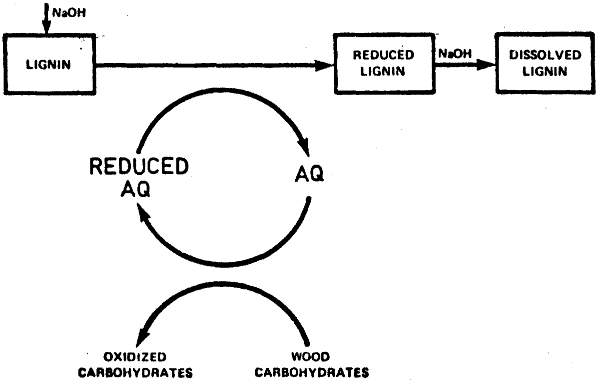


Fig 6—Wood carbohydrates degrading in alkali convert AQ into it's soluble reduced forms; these reduce lignin moieties and promote faster delignification. The AQ functions as a redox catalyst by transferring electrons from carbohydrates to lignin (47)

well established. The oxidation of carbohydrates by AQ has been confirmed by the observation of increased aldonic acid production during pulping$^{(46,50,51)}$. On the lignin side of the cycle, it was shown$^{(47)}$ that a soda-AQ cook of an isolated lignin preparation was accelerated by the introduction of glucose (which reduces AQ), indicating that the reduced form of AQ is at work on the lignin. (Research on reductive delignification has recently been reviewed$^{(52)}$). Evidence for the whole redox cycle was obtained when it was shown that the introduction of small amounts of oxygen into a soda-AQ cook inhibited delignification$^{(53,54)}$ but simultaneously improved the carbohydrate yield (at a given lignin content)$^{(54)}$.

Pulping Additives Other than Anthraquinones

Although no accelerator more cost-effective than AQ has been found, a large number of additives are now known to catalyse alkaline delignification via a redox cycle. They can be divided into 2 categories: (i) those which are known to (or could conceivably) be converted into anthraquinones in the strongly alkaline, oxido-reductive pulping liquor, and (ii) those which, while unrelated to AQ, are alkali-stable and undergo reversible redox reactions. In the first category are found, for example, anthrahydroquinones$^{(6,55,57)}$, oxanthrone$^{(58)}$, dihydroanthraquinones$^{(6)}$, tetrahydroanthraquinones$^{(6,56,59)}$, hexahydroanthraquinone$^{(60)}$, and anthrone$^{(6)}$. Compounds in category (ii) which accelerate delignification somewhat are listed in Table 3.

Phenazine (Table 3) was the first non-carbonyl catalyst to be identified, and, as in the case of AQ, the discovery was made independently in several laboratories. Phenazine was not discovered by chance, but was found as a result of a deliberate search guided by the new awareness of the mechanism of catalysis by AQ. At PPRIC we were screening organic compounds which were known to undergo reversible oxidation-reduction reactions and which were stable in alkaline solution. Our first success was with safranin (Table 3), a soluble orange dyestuff related to

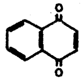
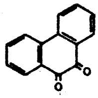
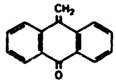
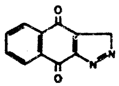
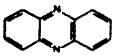
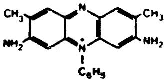
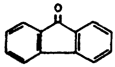
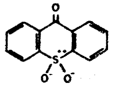
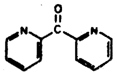
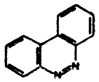
NAME	STRUCTURE	YEAR	REF.
Naphthoquinone(s)		1977	2
Phenanthrenequinone(s)		1977	2
10–Methylene anthrone		1977	2
Benzindazoledione		1979	63
Phenazine		1979	61, 62
Safranin		1979	61
Fluorenone and relatives		1980	64
Thioxanthenone – 5,5'–dioxide		1980	65
Di-2-pyridylketone		1980	65
Benzocinnoline		1980	66

Table 3 – Pulping catalysts other than AQ and its relatives

phenazine, so from safranin we worked backwards to the relatively insoluble, but more effective, parent heterocycle. Unfortunately, phenazine is only a moderately active catalyst; three to five times as much phenazine as AQ is needed to achieve a given delignification rate. Benzidiazoledione is more effective than phenazine, but is still inferior to AQ. The remaining compounds in Table 3 are all weak catalysts, but serve to indicate the generality of the redox cycle mechanism.

Design of New Catalysts

Since the screening of likely redox catalysts over the past 4 years has not revealed any structures which match the performance of the anthraquinones, further advances can perhaps best be made by a more fundamental approach. Some factors affecting catalyst performance were quickly identified e.g. alkaline stability, steric hindrance, and electrochemical reversibility. But why is 2-methylanthraquinone (MAQ) a considerably better accelerator than AQ on a molar basis? Most of the factors are practically equal for the two compounds.

It was first thought that the more negative potential of the MAQ quinone-hydroquinone redox system was the reason for its superior performance. It is more likely, however, that the key factor, as suggested by Werthemann's recent work(67), is the greater tendency of the MAQ to concentrate in the wood. Except for safranin, all the substances listed in Table 3 are relatively insoluble in their oxidised forms. All become soluble when reduced (by carbohydrates) to their dianion (or radical-anion) forms. In these reduced forms the catalysts can penetrate the wood chips during the early stages of cooking. When oxidation reactions take place in the wood, the oxidised form of the catalyst partitions itself between the wood and the liquor. Effective catalysts have hydrophobic oxidised forms which tend to remain in the wood, they are, in this context, `xylophilic'(67). Thus, catalysts with rather insoluble oxidised forms concentrate themselves in the wood, where they can be most effective(68).

Werthemann has found that the efficiency of such catalysts is almost independent of the liquor-to-wood ratio employed for cooking, presumably because after the initial transfer step (Figure 7), the catalyst remains mostly in the wood chip. Conversely, the addition of a solubilising group (e.g. $-SO_3Na$) to the anthraquinone nucleus decreases the efficacy of the compound, because the delignification rate becomes sensitive to the liquor-to-wood ratio.

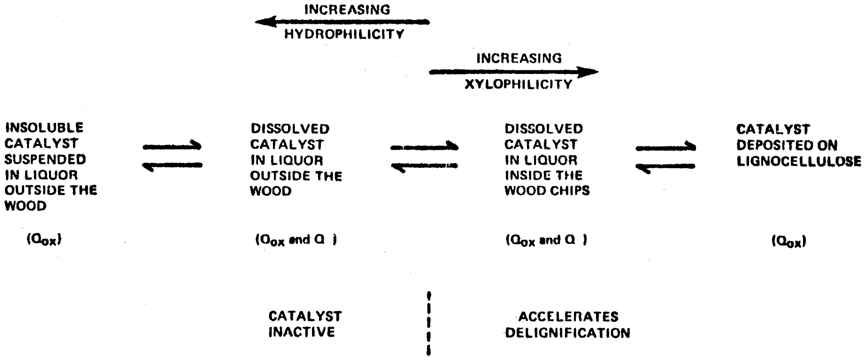


Fig 7—Werthemann's concept of xylophilicity (67) can be illustrated by the above scheme

One can, however, go too far in increasing the xylophilicity of an additive, because if hydrophobic groups are added to a structure to raise its xylophilicity, the solubility of the compound in pulping liquor is decreased. For example, although many polycyclic aromatics such as dibenzophenazines(69) and benzoanthraquinones(2) appear to have adequate redox properties, they are not effective catalysts. The problem lies in their low solubility in pulping liquor. One consequence is that they take excessively long to react with reducing agents and are therefore very slow to enter solution in the reduced form. Thus, a kind of scissors applies to the design of pulping catalysts: the additive should be hydrophobic enough to concentrate itself in the wood, but not so hydrophobic that it loses all solubility in pulping liquor.

AQ as a Research Tool

Despite much elegant work with model compounds(70), research on chemical pulping continues to be hampered by our poor understanding of its chemistry. Therefore, in addition to having commercial significance, AQ has become a new tool for probing lignin reactions in alkaline media. Details of AQ-lignin interactions are also likely to shed light on kraft pulping. Indeed, there has already been proposed a scheme which views sodium sulphide as a reducing agent analogous to reduced AQ(71). The following aspects of AQ-lignin reactions are under active study:

(i) Stable side-products formed by the reaction of AQ with lignin degradation products yield information on how AQ is consumed by side-reactions during pulping(72,73), and also provide clues to the structure of the lignin fragments.

(ii) The nature of the adducts formed between AQ and lignin is under investigation(74) and coupling products between lignin model compounds and AQ have been isolated(75,76). These studies aim to achieve a detailed understanding of the electron transfer which occurs between reduced AQ and lignin.

(iii) AQ radicals ($AQ^{\cdot -}$) can be detected in kraft - AQ and in soda - AQ cooks(77). It is not known whether they form an integral part of the redox cycle, or whether they are only incidental.

(iv) The results of kinetic studies(58) have shown that when the AQ charge is varied under constant alkaline pulping conditions, the reciprocal of the lignin content of the pulp is proportional to the square root of the AQ charge:

$$\frac{1}{\text{Lignin Content}} \propto \sqrt{\text{AQ charge}}$$

All redox catalysts so far tested obey this square-root relationship, and the chemistry behind it remains to be explained.

Concluding Remarks

Anthraquinone is the first commercially significant accelerator for alkaline pulping to be discovered since sodium sulphide was introduced almost a century ago. If it be accepted that its action was discovered because Bach and Fiehn, searching for alkali-stable reagents to inhibit the alkaline degradation of cellulose, observed the effects of AMS, and thus provided a significant lead, then the fundamental steps leading to the discovery of the action of AQ in alkaline pulping can be traced back for over 30 years, to original work done by Isbell in 1944 on the conversion of sugars into saccharinic acids.

Fundamental studies of the reactions of AQ in pulping may well lay the groundwork for further advances, but for the present, it appears that AQ is still the most cost-effective sulphur-free accelerator for alkaline pulping, albeit of limited application. Increased use would result if its cost were reduced relative to that of pulpwood, or if methods could be devised to decrease the amount required to produce a given effect. Alternatively, current research may lead the way to reagents which undergo fewer side reactions during pulping and would thus be more efficient than AQ because they would preserve their catalytic integrity to a greater degree. Perhaps such a catalyst will provide a topic in the next symposium in this series.

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Transcription of Discussion

Discussion

Discussion following papers presented by Dr. D.W. Clayton and Mr.A. de Ruvo

Mr. A.de Ruvo, STFI, Sweden

I want to ask Dr. Clayton about the mechanical properties. What is known about what it is that is really happening in the cell wall that gives rise to the different mechanical properties of pulps? You indicated that there are now methods of improving the properties of soda-AQ pulps to the level of those of kraft pulps. This I find very interesting.

Dr. D.W. Clayton, Paprican

I would like to give you a complete answer, but am afraid I can't. Some of the early work, as you may know, was done with rather large proportions of ethylene diamine (EDA) mixed with the wood because we were trying to develop a method of accelerating delignification. With up to 40% EDA added to the wood we obtained a delignification rate in soda pulping equal to that in kraft. This was an interesting technical result, but was not commercially viable. However, the tear factor at a given tensile value for soda pulp made with this proportion of EDA was extremely high, ranging up to 130, which is very high indeed. We were intrigued by this result, but I am afraid failed to discover a reason for it.

Mr. A. de Ruvo

Unfortunately, I can see our ending up in the usual situation. We notice various changes, but understand so very little of what is happening in the cell wall that we cannot relate them to the quantities we know to be associated with the mechanical properties of paper.

Dr. D.W. Clayton

I don´t agree with you. We need to know the answers to these observations. Above all, we need to know just why it is that AQ, while being chemically equivalent to sulphite in its lignin removal, nevertheless reduces strength and gives us lower tear values at given tensile. Presumably there is some degrading action on the polysaccharide caused by the oxidative power of the AQ, but in that case how is it prevented by the presence of sulphite in kraft pulping? The strengths of kraft and kraft-AQ pulps are identical.

Prof. H.W. Giertz, University of Trondheim, Norway

I would like to make a historical remark. You showed how Isbell´s work is the basis for our understanding of peeling. But I must point out that the first studies of peeling were not designed to increase the yields of kraft pulping, rather the aim was to decrease the yield when producing acetate, high alpha pulps. The whole business of peeling has been explained by a group at Billerud.

A recent Ph.D thesis presented to the University of Trondheim deals with the question of AQ treated kraft pulps. The author was surprised at the very high tear to tensile ratios, and on investigating the fibres found them to be curled by the AQ process. We believe this curling could account for the very high tear strengths found in these pulps. This work was published some months ago in Norsk Skogindustri(1). (The only paper I have found that might be referred to deals with soda-oxygen pulps: this is the reference given - ed.)

Dr. D.Abson, Weyerhaeuser Technology Center, USA

I wonder just how relevant it is to rely so heavily on handsheet properties, such as tear index, when evaluating a new pulping process like soda-anthraquinone. The paper-maker, after all, will be much more interested in its process-related properties, dewatering behaviour or wet strength, which will affect its performance on the paper machine.

A point that should influence our evaluation of soda-AQ pulps, and which may even outweigh the disadvantages of reduced tear strength, is the possibility of simplifying the conversion of sodium carbonate to sodium hydroxide in a sulphur free system. This gives significant benefits in capital and operating costs, and I would be interested to hear your comments.

Dr. D.W. Clayton

Yes, the use of soda-AQ does allow the possibility of direct causticisation, which may considerably reduce costs. It all comes down to a question of economics, whether the product being made needs the better mechanical and optical properties. For some mills strength may be the dominant issue.

On the question of comparing strengths, I quite agree with you. The only reason for my using the tear tensile ratio is its being a very quick and simple method of indicating differences. A detailed comparison would, of course, involve the determination of full beating curves, and measurement of optical properties. My intention was to obtain quick comparisons between different pulps.

Mr. D.G.N. Stirling, Wiggins Teape, UK

Mr. de Ruvo mentioned the effects of temperature and constraint during drying on pulp strength, but I am not certain whether market pulp at 10% air dry would count in your terminology as once-dried or not. Do pulp mills take any steps to limit the damage caused by drying? Are the figures you showed for the differences between sheeted and flash-dried pulps representative of normal flash-dried pulps, where some over-drying can be expected, or are they representative of pulps for which special care has been taken?

Mr. A. de Ruvo

In answer to your second question, we simply sampled a flash-dried pulp while simultaneously making sheets from it. Thus my figures should be representative of normal flash-dried pulp, though they are only a check on the first part of the curve.

They refer only to slushing, which gives of course, very low strength values. A little beating would greatly improve these values, possibly increasing the tensile index to 6 or 7. It is known that the effects of beating on a commercial sample are very small, and this is borne out by the results here. Over-drying can indeed be a problem, and while we were carrying out these experiments we had the idea that it is the free fibres that are most likely to over-dry, and so by rejecting them from the first cycle we could avoid the problem. This concept is patented and in use in two Swedish mills.

In answer to your first question, the critical moisture content is around 30%, so that a 10% moisture content pulp would, in my view, be over-dry. We would like to devise a way of maintaining the full strength in market pulps, but it is a matter of economics.

Mr. P. Howarth, UMIST, UK

Mr. de Ruvo's figure 6 shows how the onset of permanent drying induced fibre damage varies with solids content. We reported at the last symposium on some similar work using the enzyme technique. We entirely agree that when the fibre to water ratio reaches 1:1 damage begins, and we believe this to be a very important result for practical paper-making. If the sheet breaks on the machine and the broke can be removed at a high enough moisture content then the fibre will not be degraded.

We find that air-drying is about the most severe treatment that fibres can be given: an air-dried handsheet is subject to more permanent fibre degradation than paper made on a machine and dried to similar moisture content. The rapid, high temperature drying to which paper is subjected on the machine is far less damaging than slow air-drying.

Mr. de Ruvo

You are suggesting that there is a significant effect of the time-scale of the drying, so that fibres don't notice the rapid changes introduced by the paper machine.

Our studies didn't cover this, but I could well understand how the paper machine might introduce transients, particularly in moisture gradients. It is well known, for example, that Yankee dried board is initially much drier on one side than on the other.

A more profound description of the drying process would need to take into account time dependent phenomena. Since there is a locking phenomenon involved, it is likely that both plastic flow and creep are significant.

Prof. H.W. Giertz

I want to remark on our understanding of the influence of drying on the fibre. Firstly, it must be kept in mind that, as has been pointed out, a fibre always exhibits restricted swelling. Secondly, as was discussed at the 1965 symposium, high molecular weight polymers which can undergo swelling and then go into solution exhibit reduced solubility when subjected to stress. This result I think is very relevant to understanding the mechanisms occurring during drying.

As the fibres dry they shrink and the hemicellulose between the microfibrils comes under stress. This gives rise to the well-documented dried-in stresses. Your results show how paper dried under tension is more difficult to re-slush, and I wonder if it is the presence of the gel system with all the dried-in stresses which is responsible for this. Such secondary fibres would swell less than new ones, and require more mechanical action to achieve the same degree of swelling.

Mr. A. de Ruvo

While I agree with what you say, I am afraid we didn't investigate this. What we wanted to show was that fibres remember the stress histories they experienced during drying. You are referring to a slightly different phenomenon which I can't comment on at this time.

Prof. K.I.Ebeling, Helsinki University of Technology, Finland

In your figure 10 you showed that `sheet dried´ bleached kraft has a higher tensile strength at failure than `flash dried´ kraft pulp. You mentioned that this was due to the differences in drying tensions. Could it also be an effect of `high consistency refining´? The screw press which is always used in conjunction with the flash-drying process, is actually performing some mild high consistency refining.

Mr. A. de Ruvo

In our experimental rig we had only a normal cylinder press before the flash drier. I would not expect this to produce the same sort of refining action that you suggest may occur in a screw press.

Dr. M.B.Lyne, Paprican

Your paper dealt primarily with the strength aspects of recycled fibres, although your title referred to more general practical considerations. Have you therefore considered the behaviour of other parameters, for example the dynamic wetting? This is of course of great important in coating and litho printing.

Mr. A. de Ruvo

As I have said before, the range of our investigations was limited. To date, we have looked at ways of improving the strength of papers made from recycled fibre. Next, which we have already begun, we shall look at de-inking, and this will include some investigations of the dynamic wetting problem you mentioned.

Dr. M.B. Lyne

In your opinion, is it the presence of impurities or the effects of drying on fibre porosity that is responsible for the reduction in rewettability of recycled fibres?

session 3 discussion

Mr. A. de Ruvo

The ways in which raw material has to be treated in order to remove impurities have a great effect, not only on the rewettability but also on all the mechanical properties.

Mr. P.T. Herdman, Wiggins Teape, UK

Going back for a moment to Mr. Howarth's comment, it occurs to me that if the handsheets were dried on discs or in frames following the normal practice, then they would be subjected to very severe drying restraint. Could it be that it is this restraint rather than the time-dependent phenomena suggested that has the dominant effect? This would agree with the data presented in figure 8 of your paper.

Mr. A. de Ruvo

That is quite possible. I was merely making a suggestion, and what you are saying is of course, quite relevant.

Mr. P. Howarth

In our experiments we used both restrained and unrestrained sheets, and as a result are able to say that time is an important parameter. The whole hour that is takes to air-dry a handsheet clearly causes more permanent damage to the fibres than the rapid drying process on the paper machine. Indeed, we have seen that changing the temperature profile on the machine can also affect the extent of fibre damage.

Dr. D. Wahren, IPC

The density of the sheet is much affected by machine drying. Because the drier felt holds the sheet in constant contact with the cylinder, much larger densities are achieved on the machine than in handsheets. Could this density difference be contributing to the results observed by Mr. Howarth? We have conducted also experiments in which paper has been dried under constant z-direction pressure to different densities, and have found that this way we can obtain considerably improved tensile strengths, similar to those found in press-dried paper.

Dr. B.Jordan, Paprican

Could you elaborate more on the connection between drying and curling? We have seen in our experiments differences in curlation between dried and never-dried pulps, though there is definitely some hysteresis present. Dried fibres can be curled, though not as much as never-dried.

Mr. A. De Ruvo

We have shown very dramatically that once-dried fibres do not curl as much as virgin fibres. I ascribe this difference to the major changes in the cell wall that drying causes. Virgin fibre is very much more flexible because of the laminated construction of its cell walls.

Prof. B. Steenberg, R.I.T., Sweden

(Written comment received after the end of the symposium.)

The authors state (page) that it has been suggested that water is active in swelling by "... the equilibration of the partial free energy of free water and of water interacting with the wood polymers", but also as an alternative that "... water is active because of the existence of holes in the fibers." They state that the latter condition "...is a phenomenon into which the laws of thermodynamics offers no insight." They offer the explanation that "...obviously mechanisms regulated by thermodynamics are reversible".

Thermodynamics certainly deals with irreversible mechanisms, as evidenced by the treatment of the Carnot cycle, and by the Third Law.

Thermodynamics, however, is normally applied to macroscopic systems, where the fluctuating extensive variables can be represented by their mean values. In so called small systems, involving for instance, bubbles, drops, pores, or polydisperse systems the thermodynamic variables have probability distributions which can no longer be represented by single values. Second and higher order moments must be included(1).

As long as only bulk properties are measured it is impossible to distinguish a thermodynamic approach using appropriate distribution functions from a concept based on the distribution of so called `holes´.

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