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Anthraquinone - A Review of the Rise and Fall of a Pulping Catalyst

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Abstract

The application of anthraquinone (AQ) as a pulping catalyst has been well documented in scientific studies and mill applications. AQ is known to increase the rate of delignification, enabling a reduction in pulping time, temperature, or chemical charge and an increase in pulp yield. Specific details of AQ use are not extensively reviewed in this work. The review focusses instead on the critical milestones in the AQ process life cycle including its initial introduction, investigation of the reaction mechanism and evaluation of best use by the pulping industry. The importance and difficulty of an economic justification for use of AQ is discussed. This is complicated by the modest improvement in yield obtained using AQ, and low cost of the displaced chemicals. In many mills, the ability to document increased net mill revenue due to the use of AQ has been impossible. Recent health and safety findings and regulatory decisions have put the continuing use of AQ by the industry in jeopardy. Given the unknown health risks, international regulatory environment, modest improvements available using AQ, and the difficulty in economically accounting for the benefits, this likely represents the final chapter in the AQ life cycle.

Introduction

One of the first reported applications of anthraquinone (AQ) or AQ-derivatives was made in 1972 by Bach and Fiehn [1]. In this work, 25 different compounds were refluxed with hydrocellulose and 2N NaOH for 2 hours. Weight loss was recorded for each reaction. Anthraquinonesulfonates and hydroxylamine were the only two compounds found to stabilize cellulose towards caustic under these reaction conditions. Sodium 2-anthraquinonesulfonate (AMS) was then used as an additive for kraft and soda laboratory pulping of pine. An increase in yield, reduced rejects and lower kappa numbers were obtained in kraft pulping upon addition of 1.0% AMS. Pulp strength properties were only slightly affected. A moderate amount of research work was conducted over the next several years but the use of AMS in kraft pulping was not sufficiently effective from a cost/performance perspective [2,3]. The initial work of Bach and Fiehn suggested that AQ itself was not an effective yield preserving pulp catalyst under the conditions they employed.

The use of AQ itself as an effective pulping catalyst was first reported by H.H. Holton in 1976 [4-6]. Holton reported that AQ could be used to reduce the kappa number under

otherwise identical cooking conditions. During the early 1980's, a significant amount of laboratory pulping work was performed to identify and quantify the potential of low kappa pulping with AQ [7-11]. When the AQ charge was increased to 0.2-0.3% on OD wood, reasonable strength softwood pulps with kappa numbers as low as 15-17 could be obtained. Other researchers obtained similar results using AQ charges of 0.1-0.8% on OD wood [12].

An interesting byproduct of low kappa kraft-AQ cooking is that the low kappa pulps have similar yields to conventional kappa number kraft cooks. When AQ is employed in conventional kappa kraft-AQ cooking, the resulting pulps have been documented to retain a greater percentage of carbohydrate material than conventional kraft pulp at similar kappa numbers, i.e. the pulp yield is higher at a given kappa number [13]. Thus, AQ not only accelerated the kraft pulping reaction, it also stabilized or preserved pulp yield.

Over the next 15 years, researchers worked diligently to evaluate potential applications for AQ in industrial practice. It was determined that AQ could be used for incremental pulp production [14-19], environmental improvement [7,11,20,21], cost reduction [17,22-24], and for non-conventional alkaline pulping processes [14,24-27]. AQ was also found to be beneficial in the pulping of multiple non-wood species [28-33].

During the late 1980's into the 1990's, the desire to pulp to extremely low kappa numbers for environmental reasons led to a resurgence in mill interest in AQ [34]. AQ was well documented to provide an almost zero capital solution to the demand for lower impact bleach plant operations with minimal effect on recovery. Additionally, the development of dispersed AQ made mill application easier [35] resulting in several successful mill trials followed by rapid adoption of AQ in mill kraft pulping processes [36,37]. Mills rapidly shifted from using AQ to pulp to lower kappa numbers to employing the chemical to aid in bottleneck elimination and, to a lesser extent, cost reduction [34]. Recovery, alkali or digester limited mills frequently employed AQ as a method of increasing pulp production. A major cost reduction application was avoiding a limitation in mill recovery capacity [38,39].

AQ was an exciting addition to chemical pulping. Although the net impact was modest, AQ is one of a very limited number of pulping chemistry advances in decades [14]. The nature of the engineering process also magnified the potential financial benefit of that relatively modest improvement from AQ. Mills are intentionally designed so that all major capital areas have about the same production capacity. Relieving a production bottleneck often allowed the entire mill to operate at higher net production improving capital efficiency and labor productivity. The financial benefits to a mill could be much larger than the modest yield increase and/or chemical savings seem, because the incremental costs for the production increase were so low.

The future of AQ, when it was first introduced, was dependent upon approval by the US Food and Drug Administration (FDA) for use as an indirect food additive [40]. FDA approval was required since most paper products eventually find their way into food

contact applications through recycling. Once AQ was approved as a pulp additive in 1987 [41], it was rapidly accepted by the industry with more than 100 mills world wide employing AQ in 1992 [42]. Most of these mills were using AQ as a method to increase production [42].

Concurrent with the effort to determine how AQ could be employed as an enhancement additive for kraft and soda pulping, considerable research was devoted to understanding the reaction mechanism. The obvious rational for this effort was the possibility that understanding the reaction mechanism would lead to a significantly more effective catalyst. That unfortunately was not achieved.

AQ Reaction Mechanism

Redox Reaction Cycle

Initial concerns around the impact of AQ upon kraft pulping systems focused on the transport of AQ to the lignin reaction sites. Because of these concerns, some of the initial laboratory experiments were based upon soluble AQ derivatives instead of AQ [1-3]. AQ is insoluble in water, and only slightly soluble in alkali [43] and most organic solvents [44].

The insolubility of AQ in alkaline liquor is misleading in the context of alkaline pulping, and probably delayed the discovery of the effectiveness of AQ [4]. In the presence of reducing sugars and alkali, AQ is rapidly reduced to anthrahydroquinone (AHQ). The reduction is believed to occur through a two electron transfer [45-48], reducing the AQ to AHQ, and oxidizing glucose to gluconic acid. When AQ is reduced by one electron, anthrahydrosemiquinone (AHSQ) is formed. When two electrons are transferred, AHQ is formed [45-47]. These reduced forms of AQ are water and alkali soluble resulting in the reduced form of AQ being readily available for reaction with the wood. In kraft pulping, HS^- reduces AQ to AHQ when the cooking temperature exceeds 135 °C [49,50].

Chemical components from wood supply the reducing power. The carbohydrate reducing end groups and reducing sugars peeled from the ends of carbohydrate chains supply the electrons required to form the AHQ [51]. In the process, reducing end groups are oxidized to the corresponding aldonic acids stabilizing the carbohydrate chain from further peeling reactions [51-53]. The increase in yield is due to both this stabilization of the end groups that reduces the mass losses to the peeling reaction, and the milder cooking conditions that reduce the kinetic-time-opportunity for peeling and the random cleavage reactions that set up new reducing end groups and establish new peeling sites. Vourinen has estimated that end groups account for less than 1% of AHQ produced in pulping, with reactions of peeled sugars providing the bulk of the reductive chemistry that takes place. This is consistent with the low solubility of anthraquinone in water [54]. Much of the yield increase is not cellulose, it is from the more alkali sensitive hemicellulose [55].

The reduced forms of AQ (particularly the AHQ) react with quinine methides (QM) resulting in ß-aryl ether fragmentation [45, 56-60] and in the improved rate of

delignification associated with AQ pulping [61,62]. The usual mechanism proposes that C-10 carbon of the anthrahydroquinone forms a bond to the C-a carbon of the ß-aryl ether dimer. The ß-aryl ether and AHQ separate producing a C-α/C-β olefin. Forming the double bond on the styrene-like fragment requires two electrons, oxidizing AHQ back to the AQ starting material. Evidence supporting this mechanism is the C-10 to C-a adduct was isolated in model compound studies and when heated in alkali provides similar reaction products to a direct reaction of the ß-aryl-ether model with AHQ [45,60]. The weakness of the adduct mechanism is that reactions carried out with hindered anthraquinones did not change the yield or distribution of products [47] as would be expected if the adduct formation was part of the normal reaction path.

An alternative mechanism proposes an outer sphere single electron reduction [48]. Where this mechanism could explain the lack of sensitivity to bulky substituents on the AQ, there is otherwise little supporting evidence. In electrochemical testing of an anthraquinone and AQ-quinone methide mixtures, the first single electron reduction of AQ was observed as expected, but the mixture did not show the one-electron reduction of the quinone methide or the second reduction of AQ, both normally found at more negative potentials [63]. This was interpreted by the authors as indication the quinone methides were being reduced by the AHQ or AQ semiquinone.

Unfortunately, the details of the experiment effectively excluded the outer sphere electron transfer mechanism; the QM reduction at -1.15 V is too negative to be reduced efficiently in an outer sphere electron transfer. The changes in cyclic voltammetry of the AQ/QM mixture parallel that observed by Landucci for AQ in the presence of water [45] and suggest the semiquinone dimer mechanism common with quinones. This requires the AHQ and QM to form a dimer sharing the protons of the anthrahydroquinone OH groups. The electrons are transferred along with the shared protons providing for reduction at lower potential. This reaction is rapid enough that for cyclic voltametery carried out with some water or alkali present in the solvent, the second reductive wave of anthraquinone at -1.7 V disappears, just as the quiniome methide wave at -1.15 V disappeared. When two protons are transferred, this mechanism produces a ß-aryl ether dimer with the OH group on C-a replaced by hydrogen – effectively a two electron reduction.

In later work by Smith and Dimmel looking for evidence of the single electron mechanism, 80% of the reaction product involved the replacement of the a-OH group of the model, and just 12% formed the 5-carbon ring expected for a single electron process. The outer sphere reduction mechanism also requires that alternative reducing chemicals would also accelerate delignification and extensive evaluations of alternative reducing chemicals have not shown efficacy approaching that of anthraquinones. Unfortunately, the 2-electron hydride transfer that the electrochemical and single electron transfer experiments carried out by Dimmel *et al.* suggest as a possible mechanism, does not appear to be consistent with the reaction products of the model compound studies and might not be part of the reaction mechanism under pulping conditions. At this point, none of the proposed mechanisms is consistent with all the experimental results and the mechanism has to be regarded as uncertain. What is not disputed is that electrons are

supplied to the redox cycle by carbohydrates and the resulting reduced AQ then supplies electrons to oxidizing groups in lignin. [64].

The very nature of the AQ redox cycle severely limits its effectiveness as a pulping catalyst. The cellulose end groups required to reduce the AQ to AHQ (the active form of AQ from a delignification perspective) are very limited. Assuming an AQ charge set at the maximum amount allowed by the FDA for food contact paper, 0.1 %, only 6% of the AQ can be reduced and activated by the end groups present in the native cellulose. There are enough reducing groups present in the wood chips to allow AQ to treat just 0.04% of the lignin ß-aryl ether bonds. The bulk of the reducing groups needed to make AQ effective are provided by alkaline peeling and cellulose chain cleavage reactions. These reactions are the very ones that reduce the pulp yield and pulp viscosity. A yield loss of 11% of the starting wood material is required to produce sufficient reducing sugars to generate the AHQ needed to react with every ß-aryl ether bond. Thus, AQ performance is significantly limited by its reliance on reducing sugars. It might be possible to drive this reaction with a stoichiometric reducing chemical, but efforts to accomplish this have not had notable success [65].

Reaction Rate Studies

Once the initial redox reaction cycle was established, several studies were performed to determine the impact of AQ addition on the rate of delignification. Some of these studies also examined the impact of sulfidity upon AQ performance and whether AQ and sulfide delignification reactions followed the same reaction pathways.

The impact of sulfidity upon the ability of AQ to accelerate delignification was extensively studied on both northern and southern softwoods and northern hardwoods [34]. Care must be taken to optimize the process at each sulfidity level studied. AQ accelerated delignification significantly at sulfidities between 15% and 35%. The effect of AQ on pulping rate was noticeable even at 40% sulfidity. Yield increases were documented over the entire range of sulfidites evaluated. Brogdon and Dimmel [66] used a unique lignin model compound to show that AHQ is a considerably more powerful catalyst than sulfide ion. Other researchers have determined that AQ and sulfide ion have different reaction pathways [67] although as stated above, the reaction mechanism for AQ is not very well understood. It has also been determined that the use of AQ substantially increases the rate of both bulk and residual delignification [68].

Impact of Diffusion in AQ Reactions

There appear to be unexplained differences between AQ trials performed at various mills and laboratories [69]. The discrepancies between different experiments with AQ indicate that something other than the redox reaction chemistry is affecting outcomes. Although we are not sure that these differences are due to pulping conditions, one potentially good hypothesis is that mass transfer is the source of the differences [70]. Experiments differ considerably: type of AQ (AQ, AHQ or 1,4-dihydro-9,10-dihydroxy anthracene), form of AQ (aqueous suspension or bulk solid) and process (batch or continuous). In a study that does not seem to have received much attention, Falk et a1 showed that there is almost

no penetration of chips by insoluble AQ, and very little penetration of chips in the radial and tangential directions after in situ reduction to AHQ [71]. AHQ was shown to diffuse almost exclusively from the axial direction. Resulting chips had a very uneven distribution of AQ relative to the faster diffusing sodium and hydroxide ions. The very slow penetration increased the difference in residual lignin content between the chip surface and chip core. These results suggest that pulping conditions with short heat up times and shorter cooking times would benefit less from addition of AQ than longer resident time cooks. Differences of this type between commercial digesters are common, particularly between batch and continuous processing and older digesters of both types that are often operated well over design capacity.

Chai et al. propose that AQ must be reduced at the surface of the wood chip to exceed the anion exclusion barrier and penetrate cell walls [72]. Although the data they report does support this conclusion, the use of Nafion membranes as a model of the wood cell wall is problematic. The sulfonic acid content of Nafion is four times the concentration of anionic groups in wood. Where the ionic strength of pulping solutions exceeds the bound anion concentration of wood and suppresses anion exclusion, as evidenced by the reasonably uniform penetration of hydroxide and sulfide ions into the wood chips, this is not the case for the Nafion membrane which was designed to pass sodium and reject hydroxide ions in chloralkali cells. It has been demonstrated that increasing surface coverage through AQ particle size reduction improves the rate of AQ reactions. It has also been shown that the addition of surfactants increases the pulping efficiency using AQ. These methods probably work by improving the distribution of the insoluble AQ in the pulping liquor and on the chips surfaces, and increasing the AQ surface area exposed for reaction with sugars.

Blending AQ with Surfactants

Since the early 1990's, research efforts have focused on potential methods to reduce the cost of AQ by either combining it with less expensive materials or with materials which help improve the transport of AQ to the reaction sites. As cost control has become more and more important for mills, the use of AQ in conjunction with various penetrating aids/surfactants has increased. It is believed that the combination of AQ with penetrants improves the transport of AQ and cooking liquor into the wood thus requiring less of the expensive AQ additive reducing the overall cost of the digester cooking aid [73,74]. The use of penetrants also aids in the deresination of wood pores thus opening more area to cooking liquor diffusion into the chip [75]. It has been well established that surfactant based digester additives can be used in combination with AQ [76-81]. Although it is claimed that the surfactants can reduce the required AQ charge, often the effects of the chemicals are additive suggesting that the surface active chemicals are having more of an independent effect on delignification and not significantly enhancing the performance of the AQ. This is not surprising since the surfactants work by a physical effect of assisting the penetration of cooking liquor into wood chips while AQ undergoes a reactive cycle that moves it back and forth between a soluble and insoluble state. After a few of these cycles, much of the AQ is actually consumed in the process via the formation of lignin adducts or condensation products. Even though the use of a penetrant may also assist AQ

transport into the chips, it is more likely that the total charge of AQ is more important than the rate at which AQ gets into the chip.

Several mill scale trials of AQ/penetrant additives have been performed. Outcomes varied considerably with some reporting reductions in white liquor and lower screen rejects, others no observable effects and some mills obtaining only short-lived benefits that could not be reproduced or maintained. Some evidence suggests the sporadic results may have resulted from seasonal wood effects and simply been based upon the time of year the trial was performed [81].

Mill Scale Justification (or Lack Thereof) for Anthraquinone

Economics and Yield

Yield enhancing technologies are typically difficult to document within the pulp and paper industry [82]. A problem with determining any pulp yield increase in a mill environment is the continuous variability of incoming raw materials [83,84]. Pulp mills have difficulties detecting small yield increases on the order of 1-4% [85]. Mill accountants, on the other hand, have no difficulty determining the monthly cost of a digester additive. Therefore, mills using AQ simply as a pulping additive for yield improvement struggle to justify the cost of the application.

Integrated mills that are not process limited and using AQ simply for a yield increase have trouble showing a cost savings. The yield increase is typically lost within the noise of the general mill operation. Employing AQ for yield increase in market pulp mills is more easily documented.

The economics are altered when a mill employs AQ to ameliorate a production limiting condition [22]. Mill trials preformed in digester feed/chip screening limited mills did report production increases but often insufficient to justify the cost of the AQ. Mills with, recovery and liquor processing limitations generally observed the savings in white liquor, lime requirements and or BTUs to the recovery boiler. In these cases, the incremental production is added on to the yield gain and the impact is easier to document. But even in these cases, mills often were unable to implement the savings because the benefits accrued to a different cost center than the cost of the AQ.

Potential Operational Problems Resulting from AQ

Reported operational problems arising from the use of AQ in pulping are the formation of AQ deposits in evaporators and increases in concentrated black liquor viscosity (ropy liquor). Formation of a soluble scale in the first to third evaporator effects has also been reported [86] as has deposition of soluble burkeite scale. These later cases are not directly attributable to AQ but rather to the changes in cooking conditions made possible by the AQ. These lead to a decrease in the critical solids level for burkeite solubility. Only mill evaporators, close to the critical solids level are likely to be affected when adding AQ. High heavy liquor viscosity occurs if reduction in the white liquor charge result in low residual alkali levels. There are unexplained exceptions. Most problems associated with high viscosity of the concentrated black liquor were in mills with black liquor oxidation

and direct contact evaporators. Heat treatment for reduction of black liquor viscosity is effective and is reported to be accelerated by the addition of AQ to the kraft cook [87].

Another operational problem with AQ is that the residual AQ concentrates in tall oil and can lead to problems in tall oil processing equipment [88,89]. Because of this plugging potential, chemical byproduct companies do not value tall oil from mills using AQ as highly as they do from mills which do not use AQ. Thus, the revenue from by product sales may be negatively impacted when using AQ. Blain reports on two Japanese studies which suggest that the use of AQ does not impact turpentine and tall oil yields or quality negatively [68]. Given a reason to discount the value of tall oil from mills using AQ, the by product companies will do so and it becomes the task of the mill to somehow demonstrate that the discount is not justified.

Regulatory Issues Associated with AQ

When AQ was first being employed as a pulping catalyst, it was prepared from coal tar and often was contaminated with carcinogenic compounds, such as benzopyrene [90]. Later results using purified samples, and anthraquinone prepared synthetically from pure compounds did not induce cancer or show mutations. Anthraquinone was not considered to be a particularly toxic chemical. It was reported to have a slight allergenic effect. However, because it was usually handled as a very fine powder, it was difficult to prevent AQ from becoming suspended in the air. This exacerbated allergic reactions and in worst case conditions, it could even become an explosion hazard. Because of this, adequate ventilation and protective clothing, including rubber gloves and a dust mask, are recommended when handling large amounts of AQ powder.

When AQ was introduced to the pulp and paper industry, it was on a government list of suspected carcinogens [91,92]. However, an Environmental Protection Agency list from 1977 [93] includes a section on 9,10-anthraquinones, which states "In general, anthraquinone per se is a relatively inert compound." Most of the carcinogenic and mutagenic activity described in this section of the document involves hydroxy, amino, and nitro derivatives of anthraquinone, and nothing more is said about such activity in the parent compound.

Several papers on AQ have stated that residual AQ was not present in bleached fiber or was not a toxic chemical [6,18,22,94-96]. Nonetheless, a literature review conducted by the Institute of Paper Science in 1978 suggested that the future for anthraquinone hinged on a decision by the Food and Drug Administration (FDA) [40] for the presence of AQ in food packaging. The FDA completed their study of AQ use in pulping in 1987 and listed AQ as safe at additions levels of less than 0.10% on OD wood [41,97]: “9,10-Anthraquinone (Chemical Abstracts Service Registry No. 84-65-1) which has a purity of not less than 98 percent. For use only as a pulping aid in the alkaline pulping of lignocellulosic material at levels not to exceed 0.1 percent by weight of the raw lignocellulosic material.”
Several papers have been published on the AQ concentration measurements in pulps, bleach plant effluents, and alkaline liquors [99-104]. These studies found small amounts

(from non-detectable at 0.1ppm to as high as 5ppm) of AQ present in paper related products. Acute toxicity bioassay of effluent liquors from AQ and non-AQ containing processes [105] determined that no statistical difference in the LC_{50} of *Daphnia magna* existed as a result of AQ addition to the process. At one time, AQ was thought to be safe enough that the US EPA approved it to be spread around municipal airports for bird control [106].

Proposition 65 Listing of AQ as a Potential Carcinogen

Recent challenges to the use of AQ in the paper industry have come from the California Environmental Protection Agency, Office of Environmental Health Hazard Assessment. This state agency issued an intent to list AQ as a chemical known to cause cancer or reproductive toxicity [107]. This action was taken under the auspices of the Safe Drinking Water and Toxic Enforcement act of 1986 (better known as Proposition 65) codified at Health and Safety Code section 25249.5 et seq. The published justification statement for listing AQ (specifically stating its use in pulp and paper among other applications) as a "Prop 65" banned chemical [108] relied on a study performed by the National Toxicology Program [109]. This study concluded that:

> "Anthraquinone (CAS No. 84-65-1) has been shown to cause increased incidence of malignant and combined malignant and benign tumors in male and female mice and increased incidence of combined malignant and benign tumors in female rats. The National Toxicology Program (NTP, 2005) has concluded that there is clear evidence of the carcinogenic activity of anthraquinone in male and female B6C3F1 mice and in female F344/N rats."

Effective September 28, 2007, AQ was listed as a chemical known to the State of California as a carcinogenic chemical [110].

Potential Challenges to the Prop 65 Listing

Since the NTP studies on the carcinogenicity of AQ were undertaken, there have been questions about the veracity of the studies [90]. It is often stated that toxicology and carcinogenic responses are due to chemical impurities in the AQ samples tested rather than due to AQ itself [111,112]. Several studies have been performed on the genotoxicity of AQ. These studies produced conflicting results with regard to the in-vitro mutagenic potential of AQ [113-115]. In particular, both positive and negative results have been reported for AQ in Salmonella mutation assays. Early studies reported that neither AQ nor its metabolites were genotoxic in the Salmonella bacterial mutagenicity assays [113-115]. These studies did not report the purity of the AQ used in their work. In later studies, AQ was found to be mutagenic in the Salmonella mutagenicity assay in the absence of metabolic activation [116,117].

The contradictory results for AQ may be attributable to variable amounts of contaminants resulting from the different production methods or testing methods. It has been suggested that the carcinogenicity of anthraquinone might be due solely to the presence of 9-nitroanthracene, which was present as a contaminant at a concentration known to exhibit mutagenic activity in samples of the AQ employed in some of the positive test cases [111,112]. The 9-nitroanthracene contaminant was also reported in the NTP work [109].

Even though there have been challenges to the listing of AQ as a Prop 65 listed chemical, the decision to keep it on the list has been maintained by the State of California. Part of the rational for keeping AQ as a listed chemical is the routine level of contamination found in AQ samples. If the scientific studies were obtaining samples with trace levels of mutagenic activity, it would be reasonable to assume that industrial grade samples would suffer from similar levels of contamination.

BfR Delisting of AQ

More recently, the German Federal Institute for Risk Assessment (BfR) has announced the removal of anthraquinone from its list of acceptable chemicals in food packaging [118,119]. Previously, BfR had listed AQ as acceptable in direct food contact board up to a maximum concentration of 30 mgKg [120].

BfR chose to reevaluate the recommended uses of AQ after the European Food Safety Authority (EFSA) issued a revised opinion of the maximum acceptable residual levels (MRLs) of AQ on March 2012 [121]. EFSA was not able to reach a determination regarding whether the European Union's maximum AQ residue level of 0.01 mg/kg of food was adequate to protect consumers. BfR also noted that the International Association for Research and Cancer (IARC) concluded in 2012 that while there is inadequate evidence to link the use of anthraquinone with carcinogenicity in humans, there is sufficient evidence in experimental animal studies and, thus, classified AQ as "possibly carcinogenic to humans" [90]. BfR also determined that its internal estimations indicate that AQ residual contamination in paper and paperboard products do at times exceed the permitted limit of 0.01 mg/kg of food. Specifically, it noted that BfR has information where the residue limit for AQ was exceeded in tea and was attributed to the anthraquinone levels contained in the paper and cardboard used as packaging materials [118].

Based on these findings, BfR stated that it is withdrawing its recommendation of approval for the use of anthraquinone in the manufacture of food-contact paper, and will remove it from the lists of approved substances in Recommendations XXXVI and XXXVI /2. BfR also intends to lobby the European Union to categorize the health hazard posed by AQ under Regulation (EC) No 1907/2006, the European Union legislation governing chemical use (REACH).

Notably, while BfR no longer recommends to the EU that use of anthraquinone in the manufacture of paper intended for food contact is acceptable, its use may still be permitted under Regulation (EC) No. 396/2005, on maximum residue levels of pesticides in or on food or feed of plant and animal origin, if its use is "indispensable" in the manufacture of fibers and the use level does not exceed 0.01 mg/kg, regardless of whether the residue is from pesticides or another source.

In general, several pulp and paper companies who certify their products as generally recognized as safe (GRAS) for direct food contact, require that raw materials employed in their process meet or exceed the standards put forth by the US FDA under the Code of Federal Regulations 21CFR 176.170 Subsection B, BfR, EFSA, and California

Proposition 65. As a result, the recent rulings by BfR and the EFSA have substantially reduced the number of paper companies willing to employ AQ as a pulping additive. Additionally, the fact that several health studies have shown mutagenic activity for anthraquinone, even if it is caused by contamination, suggests that there is risk in continued use of the pulping additive by the industry

Summary

The announcement that anthraquinone catalyzed pulping with an acceleration of the process and improvement in yield, was received with enthusiasm by the industry in 1976. As a result, scientists began investigating the chemistry and multiple mills performed trials evaluating the use of AQ in their process. In 1987, AQ received FDA approval to be used as a pulping additive at addition levels of no more than 0.1% applied on OD wood. For recovery-limited mills, and for market pulp mills, AQ proved to be an economical method for incremental pulp production.

Ultimately, AQ utilization was not as extensive as predicted. The ability to prove yield and process value was difficult within typical mill operations. The relatively small impacts of AQ, routine process variability and lack of precision in accounting for the dry mass of wood and fiber losses, all contribute to this accounting challenge. The ability of the accountants to measure the cost of the AQ was extremely easy. The ultimate chemical limitation of AQ in pulping is the redox cycle mechanism. AQ is limited in its overall performance because it needs reducing sugars to activate the catalyst for the lignin fragmentation reactions. By oxidizing carbohydrate end groups, AQ stops the peeling reaction and reduces the amount of dissolved sugars thus self-limiting the reduction of AQ to the active form.

Recent studies have again detected carcinogenic potential in AQ. As before, some of these studies may have used impure samples, but contaminants found in research grades of anthraquinone are common in technical grades as well. Several regulatory agencies have now decided to either ban or to remove their support of AQ as an acceptable pulping additive. The State of California, BfR in Germany, and the European Food Safety Authority have all published opinion notices effectively banning or extremely limiting AQ application in the production of paper or paperboard used in food contact products. In light of the relatively low value of anthraquinone as a pulping catalyst, and the liability risk of its continued use, whether real or not, the use of anthraquinone in the paper industry is declining and appears to be headed to the historical methods category.

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