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New 2-methyl Anthraquinone Synthesis Approach and Application in Soda-anthraquinone (AQ) Pulping

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ABSTRACT

We tried to synthesize the 2-methyl anthraquinone (2-MAQ) with reaction between phthalic anhydride and toluene instead of using 2-methyl phthalic anhydride and benzene. This process didn't generate significant of amount of 1-methyl anthraquinone (1-MAQ) as byproduct. The other advantage of this pathway is using less toxic toluene instead of benzene known as carcinogen. 2-MAQ synthesized this pathway was as effective as reagent grade from commercial available based on soda-anthraquinone(AQ) pulping results.

Keywords : 2-methyl anthraquinone (2-MAQ), soda-anthraquinone(AQ) pulping, 2-methyl phthalic anhydride, phthalic anhydride

1. Introduction

Chloroform, dioxins, and polychlorinated compounds are main pollutants generated during the bleaching process when chlorine, hypochlorite or chlorine dioxide is used. The chloroform problem can be solved when hypochlorite is eliminated from the bleaching process, even though hypochlorite is the excellent bleaching chemicals for kraft pulp and easy to handle. Single bleaching process is not enough to get target brightness pulp. So, several different bleachingsteps are used to reach target brightness known as bleaching sequences. The amounts and types of generated pollutants depend on the combination of bleaching chemicals in sequence.

Elemental-Chlorine Free (ECF) and Totally Chlorine Free (TCF) bleaching sequences have been adapted as more environmentally friendly bleaching process. Some mills have tried to close-out the water usage cycle as Totally Effluent Free (TEF) process with adapting of either ECF or TCF bleaching sequence. Chlorine dioxide has been used for ECF bleaching sequence and oxygen-based bleaching chemicals for TCF bleaching sequences. Oxygen-based bleaching chemicals are not as much as effective in brightening and

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delignification as chlorine-based chemiat a given costs. For an adapting ECF or TCF bleaching sequences at reasonable bleaching chemical costs, incoming pulp to bleaching tower should be low enough lignin content which needs extended delignification.

Extended delignification means more lignin removal in pre-bleaching stage. In conventional kraft pulping, softwood kraft pulp were produced at kappa number ~30 and hardwood pulp at 15~20. Based on kraft pulping kinetics study, liquor profiling during pulping process could improve the pulping efficiency (1). Lower hydroxide ion and high sulfide concentration and initial phase delignification and level-out hydroxide ion concentration in bulk and residual phase delignification is the key points. This concept hasbeen adapted as commercial pulping process for continuous cooking digester [MCC (Modified Continuous Cooking), EMCC (Enhanced Modified Continuous Cooking), ITC (Iso-Thermal Cooking)], and batch cooking digesters [RDH (Rapid Displacement Heating), Super batch].

Oxygen is more selectively removing the residual lignin in pulp than pulping process. Limitation of oxygen delignification is the poor solubility of oxygen in water, which requires good mixing to allow enough contact between oxygen and pulp. Medium consistency mixing technology affords good contact between oxygen gas and pulp. Oxygen delignification process can reduce thirty to forty five percent of the residual lignin in pulp.

Additives as anthraquinone (2) or polysulfides (3) were proven for improving pulp yield. These chemicals oxidize the reducing end of carbohydrate to aldonic acid, which retard the peeling reaction. Reduced these can accelerate the delignification process.

Other approach to application AQ in alkaline pulping is replacing the sodium sulfide with AQ. Black liquor gasification (BLG) process offers the potential for a more efficient utilization of the fuel value than conventional recovery furnace in kraft pulping (4,5). BLG processallows a mill to generate more electricity or use some of hydrogen and carbon monoxide gas in the flue gas for chemical synthesis. However, the regeneration of sodium sulfide is tedious process. With efficient catalyst for soda pulping can afford only small amount of sulfur entering the system with wood, chemicals and fuels could be adsorbed on gas adsorbing tower.

As better pulping additives, 2-methyl anthraquinone (2-MAQ)was reported than anthraquinone for pulp yield increase or lower kappa number of pulp (6, 7). 2-MAQ has been synthesized by the reaction between 2-methyl phthalic anhydride and benzene (8). In this work, we propose the possibility of 2-MAQsynthesis between phthalic anhydride and toluene which process is cheaper and using less toxic chemicals. We also investigated the pulping properties of synthetic product with application in soda-anthraquinone (AQ) pulping.

2. Experimental

2.1 Synthesis of 2-methyl anthraquinone

We synthesized the 2-methyl anthraquinone based on the Danielsen (8)with some modifications. Phthalic anhydride (1.50 g), toluene (7.5 mL) and aluminum chloride (3.0 g) in a 100 mL Erlenmeyer flask were carefully heated to 65℃ in a heating mantle, until evolution of HC1 gas practically ceased. After being cooled to room temperature, the products were mixed with 10 g of crushed ice and 1 mL

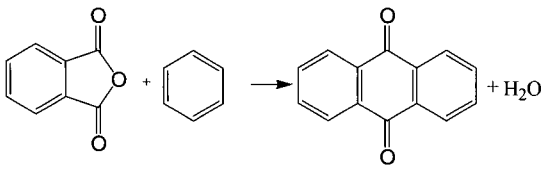


Fig. 1. Condensation Reaction between phthalic anhydride and benzene to produce anthraquinone.

of conc. HCl. The products were extracted with diethyl ether (20 mL x 2) and the organic layer was collected, dried over sodium sulfate, and concentrated to ~ 5 mL. Petroleum ether (2 mL, b.p. 60-80℃) was then added and the products allowed to precipitate.

Two benzoylbenzoic acid intermediates, 2-(4-methylbenzoyl)-benzoic acid (MBBA) and 2-(5-methylbenzoyl)-benzoic acid, were expected and were detected by mass spectroscopy (MS). The yields of the two intermediates were quantified by gas chromatography (GC) after esterification with ethereal diazomethane. It was assumed that the response factor of these intermediates relative to 2,6-dimethoxyphenol were similar to that of 2-benzoylbenzoic acid obtained from Aldrich (2-benzoylbenzoic acid is the intermediate in Fig. 1).

A capillary column of DB-XLT (0.25 mm I.D., 0.25 m film thickness, 15 m) from J&W Scientific was used. The yield and purity of intermediates and products will be discussed in the body of the paper. The ring closure of the benzoylbenzoic acid intermediates (Fig. 1) was performed with conc. sulfuric acid (20 mL) at 100℃ for 30 minutes. After cooling, the reaction products were poured onto crushed ice and stirred. The precipitate was filtered, washed with water and dried. Recrystallization from ethanol gave a product that was rich in 2-MAQ. The purity of the recrystallized product was analyzed by GC using the same column as above.

2.2 Soda-AQ pulping

Soda-AQ pulping was processed with sugar maple (*Acer saccharum* Marsh) wood chips in an M & K digester. The cooks used an effective alkali charge of 14%, 2-methyl AS of 0.116% and liquor-to-wood of 5. Pulping temperature was maintained two hours isothermally at 165 ℃(T_{max}) including 90 minute of the heating up period. Sodium sulfite (1.0% on chips) was added as an oxygen scavenger to all soda cooks that were catalyzed by an anthraquinone.

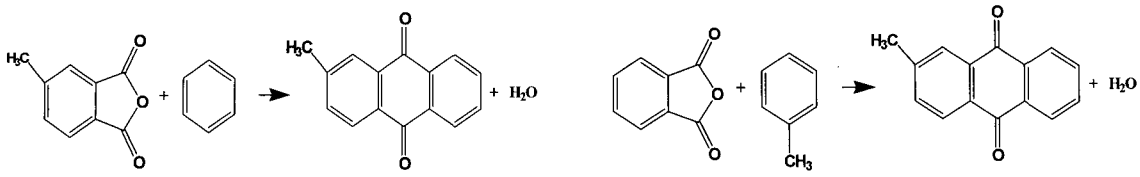
3. Results and Discussion

3.1 Comparison between two different 2-methyl anthraquinone synthesis methods

The dominant route for commercial production of AQ involves the condensation reaction between phthalic anhydride and benzene (Fig. 1). This reaction can be conducted in the liquid phase as described in the Experimental Section or by adsorbing gas molecules of the two chemicals above onto the surface of a supported catalyst that catalyzes condensation (9).

As shown in Fig. 2, position of methyl group in methyl AQ can be directed by the two different reaction reagents from phthalic acid or benzene. Benzene and 4-methyl phthalic anhydride reaction can lock the methyl group position in products as 2-MAQ. In toluene and phthalic anhydride reaction, methyl group position can be determined by the intermediate formation step or ring closing step.

The logical approach for the production of 2-MAQ would be to replace benzene with



(A) Reaction between 2-methyl phthalic anhydride and benzen

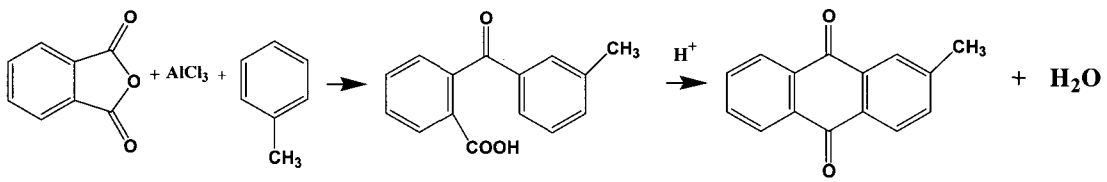
(B) Reaction between phthalic anhydride and toluen

Fig. 2. Two different approaches for 2-methyl AQ synthesis condensation reactions between 2-methyl phthalic anhydride and benzene (A) and between phthalic anhydride and toluene (B).

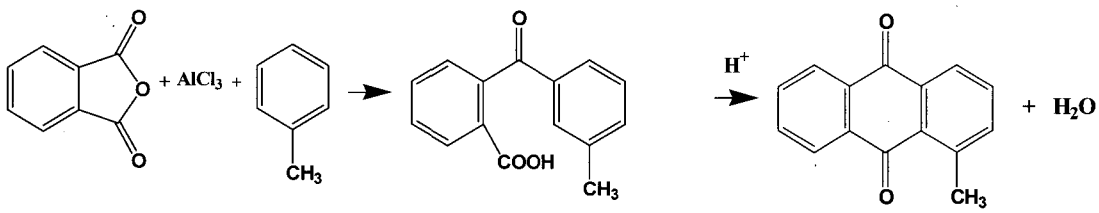
toluene and obtain a mixture of 1- and 2-MAQ. Toluene is generally less expensive than benzene on a mass basis. The Chemical Marketing Reporter listed $0.40/kg for benzene and $0.36/kg for toluene in January 2003 (10). More recently (March 2005), the reported prices were $1.13/kg and $0.70/kg, respectively (11).

Formation of 2-methyl anthraquinone or 1-methyl anthraquinone in this synthesis depends on the intermediate formation step and following ring closing step (in Fig. 3). New bond formation for intermediate between phthalic anhydride and toluene could be positioned at three different positions, ortho-, meta-, and para-position.

In ortho- intermediate (Fig. 4a), ring closure can occur only one position (* marked) give 1-MAQ. Depending on the ring closing position, this intermediate can give 1-MAQ(ring closing in *B position) or 2-MAQ (ring closing in *A position) for meta-intermediate (in Fig. 4b). Newly formed bond are freely rotate and ring closure can occur both position. Steric repulsion between carboxyl group and methyl group in ring closing transition state is the determining factor for

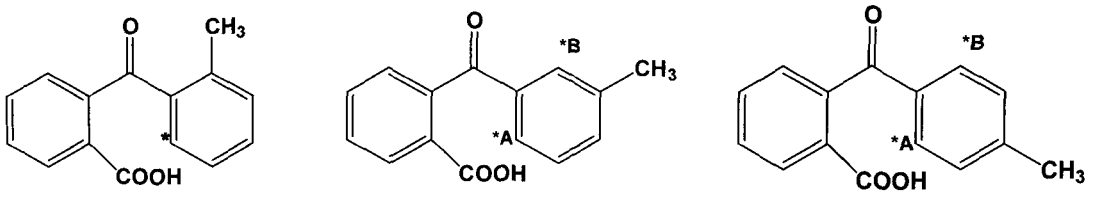


(A) 2-methyl Anthraquinone synthesis pathwa



(B) 1-methyl Anthraquinone synthesis pathway

Fig. 3. 2-Methyl anthraquinone and 1-methyl anthraquinone synthesis mechanisms by the $AlCl_3$-mediated Friedel-Crafts Reaction between phthalic anhydride and toluene.



a b c

Fig. 4. Methyl anthraquinone synthesis intermediates from phthalic anhydride and toluene reaction.

products. In para- intermediates, ring closure can occur both position (*A or *B) give 2-MAQ (in Fig. 4c).

No evidence was found indicating that the formation of 1-MAQ was significant. If small amount of 1-MAQ were formed in this process, it could not hurt the catalytic capability.While 2-MAQ is a superior catalyst to AQ, 1-MAQ is reported to be slightly inferior (6) in pulping catalytic ability. The synthesis was performed in duplicate and the re-crystallized product and detected by thin layer chromatography. The yield of 2-MAQ were more than 75%. Although not quantified, there was a loss of mass when the crude product was washed with water and this would be consistent with the loss of 2-(4-methylbenzoyl)-benzoic acid (MBBA) that contains a carboxylic group.

The mass spectra for methyl esters of the two benzoylbenzoic acid intermediates are shown in Fig. 5. The upper spectrum was assigned to 2-(4-methylbenzoyl)-benzoic acid methyl ester because it was the larger of the two GC-MS peaks and had many similarities to the spectrum of 2-(4-methylbenzoyl)-benzoic acid (MBBA)that was in the computer data base of the GC-MS instrument. The lower spectrum was assigned to 2-(5-methylbenzoyl)-benzoic acid methyl ester.

3.2 Comparison of purchased and synthe sized 2-MAQ as pulping catalysts

A total MAQ dose of 0.15% on chips was selected for the synthesized MAQs (0.116% 2-MAQ and 0.034% 1-MAQ). This higher dose was chosen because we wanted to decrease the pulping time from 2.5 to 2.0h at 165℃. This application of synthesized MAQ (MAQ-Syn.) was compared to 0.116% 2-MAQ and 0.004% 1-MAQ from the purchased MAQs (MAQ-Ald.).

The results are shown in Table 1 and it can be seen that MAQ-Syn. gave superior results and this was most likely due to the higher dose of impurities. Those impurities were not as effective as 2-MAQ for pulping additives but still showed catalytic activity (6) which caused the higher yield and lower kappa number for synthesized 2-MAQ in this study.

4. Conclusions

We synthesized the 2-MAQ with reaction

Table 1. Comparison of purchased and synthesized MAQs as pulping catalysts

Catalyst	2-MAQ/1-MAQ Dose, %	Kappa Number	Pulp Yield, %
MAQ-Ald.	0.116/0.004	20.4	54.7
MAQ-Syn.	0.116/0.034	18.9	54.9

between phthalic anhydride and toluene instead of conventional synthetic pathway using 2-methyl phthalic anhydride and benzene. In this approach, 2-MAQ was a major product. This pathway proved to be less expensive with using cheaper toluene instead of benzene. This other advantage of this pathway is using less harmful toluene instead of benzene known as highly carcinogen.

2-MAQ synthesized this pathway was gave more yield and less lignin content in soda-AQ pulp than the reagent grade from commercial available based on soda-AQ pulping results. Those impuritieswere not as effective as 2-MAQ for pulping additives but still showed catalytic activity in soda-AQ pulping.

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