Anthraquinone polymer catalysts for alkaline delignification of lignocellulosic matter. Part 2. Action in soda pulping conditions on softwood and phenolic β-O-4 lignin models

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Abstract

Two hydrophobic and one hydrophilic anthraquinone (AQ) polystyrene catalysts were tested under soda pulping conditions on thermomechanical fibers, and the results were evaluated based on commercial AQ. Hydrophobic and hydrophilic polymers had efficiency gains of 23%–28% and 57%, respectively, compared to AQ (100% efficiency). Hydrosolubility of AQ polymers played a major role in delignification efficiency, a property that allows a better contact with lignocellulosic fibers. Hydrophobic copolymers were stable under pulping conditions and preserved their catalytic effect entirely by contrast to the hydrophilic AQ, as demonstrated by recovery yields after pulping and catalytic action of the recovered copolymers. Studies on lignin models confirmed that the hydrophilic AQ polystyrene is a better catalyst under soda pulping conditions than the hydrophobic ones. It was demonstrated that AQ polystyrene polymers react with lignin models by electron transfer mechanisms.

Keywords: anthraquinone; catalysts; electron transfer; lignin models; polymers; polystyrene copolymers; soda pulping.

Introduction

A caustic soda pulping was developed many years ago in combination with anthraquinone (AQ) catalysis (Holton 1977). Addition of AQ in amounts <0.1% (based on wood) to alkaline pulping liquor leads to carbohydrate stabilization and increase of pulp yield at about 2% (Blain 1993). However, the industrial application was limited by high AQ cost and by bleaching difficulties of the pulps when compared to kraft pulps (Lachenal and Chirat 2005). Several approaches of the syntheses of AQ derivatives were described based on lignin or quinonoid compounds in order to reduce cost of the pulping catalyst (Wozniak et al. 1989; Dimmel and Bozell 1991; Dimmel et al. 1999, 2002; Francis et al. 2006). Efforts were also described concerning the recovery of AQ in soda pulping by distillation of tall oil (Evans 1980) or in Kraft process by using appropriate digester setup and ultrafiltration (Marcoccia 2001). However, to the best of our knowledge, no industrial recovery of AQ was yet developed. Nevertheless, the interest is unbroken on alkaline pulping processes, which are non-sulfur catalyzed by AQ-type catalysts like impregnation, delignification, extraction (IDE) (Benattar et al. 2004) also in the context of biorefinery processes (Sixta and Schild 2009).

In the first paper of this series (Cazeils et al. 2012), syntheses and characterizations of three linear polystyrenes bearing AQ units were reported (Figure 1). The compounds were designed as possible renewable catalysts for alkaline pulping. In the present paper, the new AQ copolymers will be studied as catalysts for soda pulping by comparison to the traditional AQ. The study will focus on softwood lignocellulosic fibers (thermomechanical pulp), and the catalytic efficiency and the recyclability of the new catalysts will be evaluated. The reaction mechanism will be elucidated based on two phenolic β-O-4 lignin models 1 and 2 (Figure 1).

Materials and methods

All chemicals were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France) and used without further purification. In particular, AQ was employed as powder with 97% purity. Synthesized compounds were chromatographed on Merck 60 silica gel (0.04–0.063). Melting points were measured on a heating microscope Electrothermal 9100 Reichert (Fisher Bioblock Scientific, Illkirch, France).

¹ H and ¹³ C NMR spectra were recorded on a Bruker Avance 300 FT NMR spectrometer (Bruker, Wissembourg, France). Chemical shifts are referenced to solvent residual peak (CHCl₃ at δ 7.26 ppm and CDCl₃ at δ 7.76 ppm). FTIR was obtained with a Paragon 1000 PC Perkin-Elmer spectrometer (Perkin Elmer, Courtaboeuf, France).

Gas apparatus (line transfer temperature: 250 °C) equipped with a Finnigan Trace (Thermo Fisher Scientific, Courtaboeuf, France) GC Ultra Gas apparatus (line transfer temperature: 250°C) interfaced with a Finnigan Trace Ultra Gas mass spectrometer (70 eV) interfaced with a Finnigan Trace Ultra Gas apparatus (line transfer temperature: 250°C) equipped with a PTV injector (splitless mode) with He as carrier gas. GC column: fused silica capillary RTX-5MS column, 15 m, 0.25 mm i.d., film thickness 0.25 μm. Temperature program: 40°C (initial hold time of
HPLC Thermo Separation Product (Thermo Fisher Scientific, Courtaboeuf, France) including SP 1000 pump, Have-2000 automatic injector, and Have-2000 UV detector. Columns: (1) Hyperclone ODS (250 mm×4.6 mm; 120 Å; 5 μm) column for the analyses of lignin model 1 and (2) a Synergy Polar-RP (250 mm×4.6 mm; 80 Å; 4 μm) for the analyses of lignin model 2. The elution profile was identical for the two columns: H₂O/MeOH (80/20 v/v) at 0 min, H₂O/MeOH (85/15 v/v) at 10 min, and MeOH (100%) at 30 min. The flow rate was fixed at 0.6 ml min⁻¹ and the injection volume at 20 μl. The detection wavelength was set at 280 nm and total analysis duration at 40 min.

Syntheses of CP-A, CP-B, and CP-C were described by Cazeils et al. (2012). 1-(4-hydroxy-3-methoxyphenyl)-2-((2-methoxyphenoxy)propane-1,3-diol (model 1) and 1-(4-hydroxy-3-methoxyphenyl)-2-((2-methoxyphenoxy)pentane-1,5-diol (model 2) were synthesized according to literature procedures (Ralph and Young 1981; Apfeld and Dimmel 1988).

Soda pulping reactions were carried out on softwood thermomechanical pulp (TMP) fibers (Pinus pinaster) kindly provided by Steico-Casteljaloux (Casteljaloux, France) in 15-ml stainless steel pressure vessels. The fibers (1 g) were introduced into the reactors, then the white liquor (4.5 ml, water/soda with 25% active alkali and a dilution factor 4.5:1) and the AQ catalysts (1 %, w/w, AQ unit/dry fibers) were added. The reactors were sealed and placed on a rotating wheel (for homogenization) immersed in an oil bath and heated at 100 °C for 35 min, then to 172 °C in 25 min, and maintained for 45 min at the same temperature. The reactors were rapidly cooled with ice. The pulp was filtered, washed with water to pH 7, and dried at 40 °C in an oven for determination of the kappa-number (KN) according to NF ISO 302 standard. For each catalyst, the experiments were triplicated.

The reactivity of the models was studied in the same apparatus as for pulping reactions. Reaction mixture: lignin models (3.7×10⁻³ mol), glucose (7.4×10⁻³ mol), AQ catalyst (2 M equivalents), and aqueous NaOH solution (8 ml, 0.147 mol l⁻¹). The reaction temperature was maintained constant at 150 °C for the selected time period. The reactors were cooled quickly in an ice bath; the content was then transferred into conical flasks and neutralized with dilute HCl aqueous solution. Then, 0.4 ml of the mixture was removed with a pipette and filtered through an HPLC Acrodisc syringe filter (13 mm diameter, 0.45 μm pore size) into a vial, followed by addition of 2 ml of a MeOH solution of 2,5-dimethylphenol (0.86×10⁻³ mol l⁻¹) as internal standard. The vial was sealed, shaken, and a small aliquot withdrawn for HPLC analysis; the experiments were triplicated.

Isolation of compounds from reactivity tests 2-Methoxy-4-[2-(2-methoxyphenoxy)ethyl]phenol (vinyl ethers) from lignin model 1. The reaction was conducted in four 15-ml stainless steel pressure reactors charged with lignin model 1 (80 mg) and NaOH aqueous solution (8 ml, 1 mol l⁻¹). After heating at 135 °C for 3 h, the reactors were cooled with ice. The reaction mixtures were acidified with diluted HCl solution until neutrality, extracted thrice with dichloromethane/ethyl acetate (95/5 v/v). Vinyl ethers were obtained as an orange yellow solid (yield 20%). Both Z, E isomers were identified by GC-MS, but it was not possible to distinguish them because the mass spectra are practically identical. GC/MS (m/z %): 272 (100%), 243 (16%), 211 (84%), 183 (26%), 149 (18%), 137 (48%), 133 (35%), 121 (22%), 89 (23%), 77 (31%).

2-Methoxy-4-[3-(2-methoxyphenoxy)oxan-2-yl]phenol (cyclic product) from lignin model 2. With the same procedure as for lignin model 1, the cyclic product was obtained as a yellow oil (152 mg, yield 50%) after silica gel column chromatography (chloroform, then
chloroform/MeOH 96/4 v/v). $^1$H NMR (CDCl$_3$) δ (ppm): 6.52–7.10 (m, 7H, ArH), 5.52 (s, 1H, OH), 4.38 (d, 1H, COH), 4.11 (m, 2H, CH$_2$), 3.75–3.83 (s, 6H, ArOCH$_3$), 3.55–3.84 (m, 1H, CβH), 2.4 (m, 1H, CyH), 1.84 (m, 3H, CH$_2$ and CyH); GC/MS (m/z%): 330 (26%), 207 (100%), 151 (56%), 137 (86%), 124 (11%), 77 (18%).

Results and discussion

Soda pulping of TMP fibers

Concentration of catalysts with 1% of AQ unit (w/w b.o. wood) was essentially higher than the industrially usual (0.1%) to allow a better recovery and an easier characterization of the catalyst after pulping. The TMP of maritime pine was already defibrated to limit the influence of copolymer diffusion in the lignocellulosic material. TMP fibers (1 g) were placed in mini reactors with NaOH (25%) (see Experimental part). Owing to the low amounts of pulp input, the pulp yields were not reproducible and were not taken into account. Catalyst efficiency was estimated by measuring the KN, which was targeted to ca. 35 for the pulp treated with commercial AQ and at about KN 100 for the pulp without catalyst. The 65 KN difference was enough to estimate the catalytic action of copolymers. An efficiency gain (EG) scale was defined between 100 (with AQ) and 0 (without AQ). The pulping efficiency of the copolymers, defined as EG, was linearly interpolated between these two values (see Table 1).

Pulping in the presence of CP-A and CP-B gave pulps with KN of 18 and 15 points less, respectively, than the pulping without catalyst. Despite their hydrophobicity caused by the polystyrene framework, these polymers still have some efficiency (EG: 28% and 23%, respectively). The slightly higher efficiency of the former could be ascribed to a better accessibility of AQ end groups to lignocellulosic fibers due to the presence of an ether-oxide oxygen atom allowing higher flexibility than the rigid carbon-carbon double bond in CP-B.

Pulping carried out with CP-C gave a KN decrease of 37 points corresponding to an EG of 57%. Obviously, the incorporation of a carboxylic acid function increased the solubility of AQ copolymers in alkaline medium, which led to a better catalytic activity under the selected experimental conditions. This observation may be well explained by a better penetration of the hydrophilic CP-C in the lignocellulosic network. Quite different observations were reported by Wethermann (1981) and Eckert and Amos (1982) concerning the efficiency of AQs substituted by hydrophilic functions: the hydrophilic catalysts were much less efficient than those substituted by hydrophobic functions. The explanation of the authors was a greater affinity of water-soluble AQ derivatives with the aqueous phase than with the solid phase of wood. Moreover, it was supposed that interactions between hydroxyl group of the AQ substituent and quinone carbonyls (chelating effect by hydrogen bonds) prevented reaction of AQ derivatives with lignin. By contrast, alkyl-substituted AQs allowed better catalytic activity in soda pulping than AQ, due to a selective adsorption of the catalyst on lignin (Samp 2004). The discrepancies between polymer and monomer AQ catalysts were likely have to be related to their size and their various conformations experienced in the reacting medium.

AQ copolymers have been isolated after reaction in order to evaluate their behavior and the possibilities for their utilization after recovery. The copolymers became embedded in the lignocellulosic fibers during pulping. They were recovered by selective solubilization in dichloromethane for CP-A and CP-B and tetrahydrofuran for CP-C. The recovery yields of the hydrophobic copolymers CP-A and CP-B were about 95%. $^1$H NMR and SEC analyses before and after pulping did not reveal any degradation. Another pulping with recovered CP-A and CP-B showed no decrease in catalytic efficiency. By contrast, the CP-C behavior was very different. Its recovery after pulping with only 30% yield was low. The $^1$H NMR spectra recorded before and after pulping indicate that the polymer was partially degraded after alkaline reactions. A 30% less catalytic efficiency was found for pulping with recovered CP-C. The incorporation of carboxylic benzoic acid groups could be responsible for the degradation of this catalyst. TG analysis already showed thermal sensitivity of CP-C (Cazeils et al. 2012).

Reactivity of lignin models 1 and 2 in soda pulping

Lignin models are often useful to clarify possible pulping reaction mechanisms. Fragmentation of phenolic lignin models, including β-aryl-ether bonds such as model 1, is considered to be especially well suited to study pulping reactions. The most important mechanistic results on AQ action in alkaline pulping were reported by Dimmel (1985, 1986), Dimmel et al. (1985), and Dimmel and Schuller (1986). These papers reveal the importance of electron transfer between anthrahydroquinone anion (AHQ$^-$) and quinone-methide (QM) in lignin generated by dehydration of phenolic C$_9$ units, bearing a β-O-4 ether bond. The reactions are summarized for lignin model 1 in Figure 2.

The reaction begins by the formation of a QM followed by an electron transfer between AHQ and QM, which leads to an unstable radical anion. A β-O-4 bond cleavage followed by a second electron transfer leads either to coniferyl alcohol or guaiacol, as phenolate anions. Undesirable reactions may also occur during soda pulping. For example, formation of vinyl ethers by a retro-aldol reaction belongs to this type of reactions.
Dimmel and Dimmel et al. found that reactions of QM could also be studied by means of lignin model 2, which displays a kind of built-in “clock” reaction (Dimmel et al. 1985; Dimmel and Schuller 1986; Brogdon and Dimmel 1996a,b). The long alcohol side chain in this model is atypical in lignin, but it is critical and useful for mechanistic studies. The terminal hydroxyl group, ionized at high pH, is able to undergo intramolecular nucleophilic reactions with QM intermediate to give a cyclic product (Figure 3). The rates of QM reactions could be determined relatively to the cyclization by observation of the different product yields. The increase of guaiacol formation vs. cyclization in the presence of AHQ\(^2^\) is a proof for the electron transfer reaction occurring between AHQ and QM.

Similar studies were performed with copolymers CP-B and CP-C by reference to AQ on both lignin models 1 and 2. Experimental conditions were set to observe significant differences between fragmentation reactions. The models were introduced in sealed reaction vessels at 150\(^\circ\)C for various time periods, with NaOH (25 molar equivalents) and glucose (2 equivalents), in order to mimic carbohydrates and generate AHQ\(^2^\) from the AQ catalysts (2 equivalents). The amounts of each product were quantitatively analyzed by reverse-phase HPLC for 5, 10, and 15 min reaction times.

**Lignin model 1** The chromatogram of the reaction mixture after soda pulping of model 1 is presented in Figure 4. In addition to the lignin model and guaiacol, coniferyl alcohol and vinyl ether (Z and E isomers) have been detected. Peak (a) is assigned to a glucose degradation product because it was also present in control experiments without model and catalyst.

The rates of disappearance of model 1 were the same for soda and soda-catalyzed pulpings (Figure 5a). These results indicate and confirm that the common QM formation is the rate-determining slow step for the alkaline reactions in the presence or absence of catalyst.

The catalytic efficiencies, determined by measuring the amount of guaiacol formed, are in the following order: AQ > CP-C > CP-B > control (no-catalyst) (Figure 5b). EGs at 15 min reaction times are for CP-B and CP-C, 52% and 84%, respectively.

Rates of coniferyl alcohol formation are in the following order: AQ > CP-C > CP-B > control (no-catalyst) (Figure 5c). By contrast, rates of vinyl-ether formation are control (no-catalyst) > CP-B > CP-C > AQ (Figure 5d).

Relative proportions of vinyl ethers and coniferyl alcohol liberated from lignin model 1 are in accordance with catalytic efficiencies of copolymers. In general, more guaiacol entails the generation of more coniferyl alcohol and less vinyl ethers. At 15 min reaction time, CP-C enhances the formation of coniferyl alcohol by 62%, whereas CP-B increases its formation only by 13%. Results about the formation of vinyl ether products are in accordance with Dimmel’s mechanisms.
CP-B enhances the formation of vinyl ethers by 89%, whereas CP-C increases their formation by 32% (15 min reaction time). Accordingly, in the latter case, the electron transfer was less efficient, and more retro-aldol reaction was occurring. These data can be interpreted that the electron transfer between the AQ supported on polystyrene and QM is more efficient in the case of CP-C than for CP-B.

Lignin model 2 The HPLC chromatogram of the reaction mixture after soda pulping of model 2 (Figure not shown) displayed in addition to the lignin model and guaiacol the cyclized product; coniferyl alcohol analog could not be found in the chromatogram.

The disappearance rates of model 2 were the same for soda and soda-catalysts pulpings (Figure 5a'). The catalytic efficiencies, measured by the amount of produced guaiacol, (Figure 5b') confirmed previous results on model 1: AQ (100%)>CP-C (52%)>CP-B (23%)>control (no catalyst) (0%) (15 min reaction time). The cyclic product (Figure 5d') was formed in high yields with concomitant important conversion of model 2; the relative efficiencies are control (no-catalyst) (100%)>CP-B (89%)>CP-C (41%)>AQ (0%).

Results of lignin model 2 also confirm Dimmel’s hypotheses about the involvement of an electron transfer mechanism (ETM), even in presence of polymeric catalysts. ETM occurs at higher distances than regular bimolecular reactions such as nucleophilic additions or substitution reactions. The model 2 compound discloses the nature of reactions between AHO2- and QM. Competing reactions occur: (1) nucleophilic mechanism with ionization of terminal hydroxyl function, which react internally on the Cα of QM leading to cyclization; (2) ETM characterized by β-aryl ether cleavage leads to liberation of guaiacol and coniferyl alcohol-like compound (see Figure 3).

Comparative catalyst efficiencies on TMP fibers and lignin models 1 and 2

The catalytic action of AQ derivatives under soda pulping conditions was evaluated in first approximation based on pulp by KNs and for models based on rates of guaiacol formation after 15 min. From these data, EGs were calculated (Table 2).
EGs calculated for TMP fibers and lignin model 2 were similar. So, the presence of a Cγ-alkyl chain in lignin model 2 mimics quite well the polymer character of lignin.

Table 2 Comparative EG (%) during soda pulping catalysts of TMP fibers (see Table 1) and lignin models after 15 min reaction time.

<table>
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<tr>
<th>Catalyst</th>
<th>EG (%) after 15 min</th>
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<tbody>
<tr>
<td></td>
<td>TMP fibers</td>
</tr>
<tr>
<td>Without catalyst</td>
<td>0</td>
</tr>
<tr>
<td>CP-B (hydrophob.)</td>
<td>23</td>
</tr>
<tr>
<td>CP-C (hydrophil.)</td>
<td>57</td>
</tr>
<tr>
<td>AQ</td>
<td>100</td>
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</table>

Lignin model 1 appeared to be more representative of the reactivity of phenolic β-O-4 units in the presence of AQ catalysts. Nevertheless, for soda pulping, the hydrophilic nature of AQ polymer, which favors its solubility in the liquor, appears to be the most important parameter for a good catalytic efficiency. It enhances the first reaction with carbohydrates to reduce AQ into AHQ2- species, which are the reactive entities with lignin. By contrast, the hydrophobic polymers (CP-A or CP-B) were insoluble in the pulping liquors, except the AHQ2- units formed by reaction with carbohydrate fragments with low molecular weight. This low solubility decreases to a large extent electron transfer between AHQ2- and QM.

Despite its hydrophobic nature, CP-B was able to enhance delignification: it is likely that some lignin fragments play the role of electron mediators in a similar fashion as it was observed in biological systems.
Conclusions

New polystyrenes bearing AQ units were tested as soda pulping catalysts in order to evaluate their respective delignification efficiency. The first results revealed that the hydrophilic polymer CP-C due to the presence of carboxylic functions was twice more efficient than the hydrophobic polymers CP-A and CP-B. It appeared that the hydrosolubility of AQ polymers plays a major role in the delignification efficiency allowing a better contact with the lignocellulosic fibers. On the other hand, recovery yields and tests of catalytic efficiency of recovered copolymers show that hydrophobic copolymers are not changed chemically and have the best potential of recyclability. Not unexpectedly, the effective hydrophilic catalyst is “consumed” during pulping, i.e., it is degraded and offers a rather low rate of recovery and loses its catalytic activity after recycling.

The studies on lignin models 1 and 2, by measuring the guaiacol yields formed, confirm that the hydrophilic AQ polystyrene CP-C is a better catalyst in soda pulping than the hydrophobic AQ polystyrenes. The formation rates of other compounds such as coniferyl alcohol, vinyl ethers, and cyclic compound are in agreement with the electron transfer mechanisms of AQ-catalyzed pulping.

Acknowledgements

The authors acknowledge Agence Nationale pour la Recherche (France) for financial support and Les Dérivés Résiniques et Terpéniques (DRT, Dax France), Smurfit Kappa Cellulose du Pin (Facture, France), Fibre Excellence (Saint Gaudens, France), and Gascogne Paper (Mimizan, France) companies for their collaboration in the research program Pulpecat.

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Received December 14, 2011. Accepted May 2, 2012. Previously published online June 16, 2012.