

CONVERSION OF LIGNIN. 2. PRODUCTION OF HIGH-OCTANE FUEL ADDITIVES

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ABSTRACT

Lignin conversion procedures have been developed, allowing for preferential production of specific high-octane fuel additives of two distinct types, i.e., (1) C₇-C₁₀ alkylbenzenes; and (2) aryl methyl ethers, where aryl mostly = phenyl, 2-methylphenyl, 4-methylphenyl, and dimethylphenyl. Process (1) comprises base-catalyzed depolymerization (BCD) and simultaneous partial (~ 50%) deoxygenation of lignin, followed by exhaustive hydrodeoxygenation and attendant mild hydrocracking of the BCD product to yield C₇-C₁₀ alkylbenzenes as main products. Process (2) involves mild BCD with preservation of the lignin oxygen, followed by selective C-C hydrocracking, preferentially yielding a mixture of alkylated phenols, which upon acid-catalyzed etherification with methanol are converted into corresponding aryl methyl ethers (see above) possessing blending octane numbers in the range of 142-166.

INTRODUCTION

It was previously reported that lignin is susceptible to high-yield depolymerization/upgrading leading to reformulated gasoline compositions as final products.¹ Two different processes were developed, i.e., (1) a two-stage process comprising base-catalyzed depolymerization (BCD) of the lignin feed in supercritical methanol as reaction medium, followed by deoxygenative hydroprocessing (HPR) to yield a reformulated hydrocarbon gasoline, consisting of a mixture of C₅-C₁₁ mostly multibranched paraffins, C₆-C₁₁ mono-, di-, tri-, and polyalkylated naphthenes, and C₇-C₁₁ alkylbenzenes,² and (2) another two-stage process comprising mild BCD, followed by non-deoxygenative hydrotreatment/mild hydrocracking (HT), to yield a reformulated, partially oxygenated gasoline, consisting of a mixture of (substituted) phenyl methyl ethers and cycloalkyl methyl ethers, C₇-C₁₀ alkylbenzenes, C₅-C₁₀ mostly multibranched paraffins, and polyalkylated cycloalkanes.³

Alternative procedures based on lignin as feed have been now developed, specifically oriented toward production of valuable, high-octane fuel additives of two types, i.e., (a) C₇-C₁₀ alkylbenzenes; and (b) aromatic ethers, *viz.*, aryl methyl ethers, where aryl mostly = phenyl, methylphenyl, or dimethylphenyl.

C₇-C₁₀ alkylbenzenes, in permissible concentrations of about 25 wt%, are considered as essential components of current gasolines. Therefore, it was an objective of the present work to demonstrate that lignin could provide an abundant renewable source of such compounds as gasoline additives. Aryl methyl ethers, due to their extraordinarily high octane numbers, could likewise be of considerable potential value as lignin-derived fuel additives.

EXPERIMENTAL

Materials. Three different lignin samples were used in the study, i.e. (1) a Kraft Indulin AT sample, pretreated by washing with aqueous KOH and water; (2) an organosolve sample, supplied by REPAP Technologies, Inc.; and (3) a sample obtained as by-product in the NREL ethanol process.⁴ Relatively small differences in chemical reactivity were observed for these samples.

Catalysts. The preferred base catalyst-solvent systems used in BCD runs were methanolic solutions of NaOH with concentrations in the range of 5.0 to 7.5 wt%.

Two hydrodeoxygenation catalysts possessing high C-O hydrogenolysis selectivity and low ring hydrogenation activity,⁵ i.e., CoMo/Al₂O₃ and RuMo/Al₂O₃, were employed. The preparation of these catalysts is described elsewhere.⁵ Mild hydrocracking catalysts used for conversion of residual oligomeric components in the production of C₇-C₁₀ alkylbenzenes (see next section) included CoMo/SiO₂-Al₂O₃ and solid superacids. The preparation of the latter type of catalysts, e.g., sulfated oxides, was described in detail elsewhere.^{6,7}

Selective mild hydrocracking catalysts, *viz.*, catalysts causing selective C-C hydrogenolysis in oligomeric components of BCD products with preservation of O-containing groups (see next section) included various solid superacids, in particular Pt/SO₄²⁻/ZrO₂, Pt/WO₄²⁻/ZrO₂, and Pt/SO₄²⁻/TiO₂.³

Etherification catalysts used included previously described superacids,^{6,7} and some recently reported sulfated oxide systems, e.g., $\text{SO}_4^{2-}/\text{MnO}_2/\text{Al}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{SO}_4^{2-}/\text{WO}_3/\text{Al}_2\text{O}_3$.⁸ **Reactors.** Both 300 cc autoclaves and 50 cc Microclaves (Autoclave Engineers) were used in the BCD runs. Most of the hydroprocessing runs were performed in 50 cc Microclaves.

Experimental Procedures.

Base-catalyzed depolymerization (BCD). The BCD procedure is illustrated by the following example of a typical run. A 15.0 g sample of pretreated Kraft Indulin AT lignin (elemental composition, wt%: C, 66.30; H, 6.03; N, 0.10; S, 1.23; O, 26.34) was introduced in a 300 cc autoclave and 120 g of a 7.5 wt% NaOH solution in methanol was added to it (methanol/lignin wt ratio = 7.4:1). The autoclave was purged with nitrogen and the mixture was brought with constant stirring (100 rpm) to 290°C, left to react at this temperature for 10 min with faster stirring (500 rpm), and then quickly cooled down to room temperature. The product was removed from the autoclave, 100 cc of water was added, and the mixture was acidified to a pH of ~ 2.0, using an aqueous 2N HCl solution. The mixture was kept overnight and the accumulated organic liquid/semi-solid phase was separated from the water-methanol layer, washed with some water, dried under a stream of nitrogen, and subjected to Soxhlet extraction with ether. The extract was dried with anhydrous MgSO_4 , filtered, and then freed from the ether on a Rotavapor to obtain the final BCD product. The water-methanol layer was worked up (including methanol removal and subsequent liquid-liquid extraction) to obtain a small portion of organic material which was added to the main BCD product. The total conversion of the lignin feed was 94.6 wt% as determined by the weight of unreacted solid residue. The distribution of the total product (wt%, calculated on converted lignin) was as follows: liquid/semi-solid depolymerized compounds, 98.4; gaseous products (mainly C_1 - C_4 gases and CO_2), 1.6. GC/MS analysis of the liquid/semi-solid BCD product showed that it is mainly composed of mono-, di-, and trialkylsubstituted phenols and methoxyphenols, accompanied by smaller amounts of C_7 - C_{11} alkylbenzenes and branched paraffins (alkyl = mostly methyl and some ethyl or isopropyl substituents). The product also contained some amounts of oligomeric components, which are convertible to monomers by additional treatment (see below). The elemental composition of the BCD product was as follows (wt%): C, 78.46; H, 8.54; N, 0.08; S, 0.05; and O, 12.87. This composition showed that, under the experimental conditions used in this run, the BCD reaction proceeded with a decrease of ~ 50 wt% in oxygen content and with essentially complete sulfur elimination.

Hydroprocessing (HPR) Procedure. For conversion to C_7 - C_{10} alkylbenzenes, the BCD product was subjected to two sequential hydroprocessing steps in autoclave reactors, i.e., exhaustive hydrodeoxygenation (HDO), followed by mild hydrocracking (HCR). These two steps can be performed as a single operation in a flow reactor system in series. The two-step HPR procedure is illustrated by the following typical run. 10.0 g of BCD product and 2.0 g of a $3\text{Co}8\text{Mo}/\text{Al}_2\text{O}_3$ catalyst were introduced into a 50 cc Microclave reactor and the latter was sequentially purged with nitrogen and hydrogen and then pressurized with hydrogen. The reactor was heated to 360°C with stirring (100 rpm) and then kept at this temperature under a H_2 pressure of ~ 1800 psig for 2 h with increased stirring (500 rpm). At the end of the run the reactor was quickly cooled down to room temperature and the hydrodeoxygenated oil product was separated from the catalyst and water (formed during the HDO reaction) by centrifugation. To eliminate any small amounts of residual oligomeric compounds, 15.0 g of HDO product (accumulated from two HDO runs) was subjected to mild hydrocracking in a 50 cc Microclave as follows: 3.0 g of a $3\text{Co}8\text{Mo}/\text{Al}_2\text{O}_3$ catalyst was added to the feed, the reactor was purged and pressurized with hydrogen, heated up to 375°C, and the feed allowed to react at this temperature with constant stirring for 10 min under a H_2 pressure of 2400 psig. The final HPR product was analyzed by GC/MS and found to predominantly consist of C_7 - C_{10} alkylbenzenes (see Results and Discussion).

Selective Hydrocracking (HT) Procedure. BCD products obtained at lower temperatures (250-270°C) contain significant amounts of incompletely depolymerized, oligomeric components. To complete the depolymerization of such components, with attendant preservation of O-containing functional groups, the BCD products were subjected to supplemental mild hydrocracking as illustrated in the following typical example. 10.0 g of a BCD product obtained under mild conditions (265°C; MeOH: lignin ratio = 5:1; 10.0 wt% of added water) and 2.0 g of $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst were mixed and subjected to reaction in a Microclave at 350°C and an H_2 pressure of 1500 psig, for 2 h. A portion of the dark liquid product accumulated from several identical runs (35.8 g) was vacuum distilled and the monomeric distillate fraction, b.p. up to 105°C/0.1 torr (82.2 wt% of the total starting liquid) was analyzed by GC/MS and found to consist predominantly of alkylated phenols and methoxyphenols (see Results and Discussion).

Etherification Procedure. The procedure used for converting the phenolic products into corresponding aryl methyl ethers is illustrated by the following example. A 5.0 g sample of the above vacuum distillate, 15.0 g of methanol, 2.0 g of $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst, and 1.0 g of a water-absorbing agent were subjected to reaction in a Microclave under the following conditions: temperature, 275°C, autogeneous reaction pressure, ~ 1200 psig, time, 2 h. The yield of etheric products, as determined by GC analysis, was 89.4 wt%.

RESULTS AND DISCUSSION

Figure 1 outlines the scheme of the two-stage (BCD-HPR) procedure for preferential conversion of lignin to C₇-C₁₀ alkylbenzenes. Stage I of the procedure comprises BCD treatment of the wet lignin feed (permissible water/lignin weight ratios in the approximate range of 0.1 to 1.5) using an alcoholic solution of NaOH or KOH in methanol or ethanol as depolymerizing agent. The BCD temperature range is between 260-290°C and preferably around 270°C. At this temperature the methanol or ethanol medium is under supercritical condition, which is an essential requirement for effective hydrolysis of the etheric linkages in the lignin structural network. The preferred range for methanol/lignin or ethanol/lignin weight ratios in the feed solution is from 2:1 to 5:1. In this range of weight ratios, and by proper reduction in reaction time, the total number of alkyl substituents in the depolymerized product components can be regulated not to exceed 1 to 3 substituents per depolymerized molecule. These 1 to 3 substituents (mostly methyl groups in the presence of methanol as reaction medium) include some residual alkyl groups originally present in the monomeric lignin units, but, mainly, methyl groups inserted in these units during the BCD reaction. Under selected processing conditions, the BCD reaction is characterized by a very high lignin conversion rate which is reflected in a high-yield (>95 wt%) performance, both in autoclave and flow reactors. The preferred reaction time is between 5 to 10 min in autoclave reactors, and between 1 to 5 min in a continuous flow reactor. At such short reaction times, and particularly for low methanol/lignin ratios, the extent of ring alkylation in the depolymerized products can be easily controlled to the desirable level. As indicated in Figure 1, the depolymerized lignin product obtained by BCD treatment consists of a mixture of alkylated phenols and alkoxyphenols, accompanied by smaller amounts of hydrocarbons. Description of a typical BCD run is provided in the Experimental section.

In Stage II of the procedure (Figure 1) the depolymerized lignin product is subjected to hydroprocessing (HPR) predominantly yielding C₇-C₁₀ alkylbenzenes accompanied by smaller amounts of C₇-C₁₀ branched paraffins and C₆-C₁₀ alkylated naphthenes. HPR comprises two sequential steps, i.e., exhaustive hydrodeoxygenation (HDO) with a catalyst possessing low ring hydrogenation activity, e.g., CoMo/Al₂O₃ or RuMo/Al₂O₃,³ followed by mild hydrocracking (HCR) with a CoMo/SiO₂-Al₂O₃, or preferably with a solid superacid catalyst. The supplemental HCR step results in the effective conversion of some residual oligomeric (mainly dimeric) hydrodeoxygenated products into alkylbenzenes. Work is continuing on the combination of the HDO and HCR steps into a single hydroprocessing operation. The final HPR product consists predominantly of C₇-C₁₀ alkylbenzenes, accompanied by smaller amounts of C₇-C₁₀ branched paraffins and C₆-C₁₀ alkylated naphthenes.

Figure 2 provides the scheme of the two-stage (BCD-ETR) procedure for preferential conversion of lignin to aromatic ethers. Stage I of the procedure comprises mild BCD at 250-265°C, using low MeOH/lignin ratios, e.g., 3:1 to 5:1, and short reaction time, e.g., 5 to 10 min. Under such conditions, the BCD product retains most (>90 wt%) of the original oxygen content of the lignin feed, which is important for the high-yield production of the final etheric products. On the other hand, the BCD product under the above mild conditions contains significant concentrations (about 25-40 wt%) of incompletely depolymerized components. This necessitates a supplemental depolymerizing treatment of the BCD product, i.e., selective C-C hydrocracking with preservation of the O-containing groups, viz., with minimal concurrent C-O hydrocracking. Such a selective treatment is achieved by the use of platinized solid superacids, i.e., Pt/SO₄²⁻/ZrO₂ or Pt/WO₄²⁻/ZrO₂, at 350-365°C under moderate H₂ pressure, e.g., ~1500 psig. Under such conditions, there is essentially no loss of oxygen and the content of oligomeric components in the phenolic product is reduced to <10 wt%. In Stage II of the procedure the distilled monomeric phenols are subjected to etherification with methanol, at 225-275°C, in the presence of a solid superacid catalyst, e.g., SO₄²⁻/ZrO₂, WO₄²⁻/ZrO₂, SO₄²⁻/MnO₂/Al₂O₃ or SO₄²⁻/WO₄/Al₂O₃. In order to displace the equilibrium between phenols and aryl methyl ethers in the direction of the desired etheric products, water-absorbing agents, including zeolites and specially designed pillared clays, are currently being added to the reacting mixture.

Figure 3 provides an example of GC/MS analysis of a vacuum distilled BCD-HT product from Kraft (Indulin AT) lignin. The BCD conditions used in this early run were: temperature, 270°C; MeOH/lignin wt ratio, 7.5; reaction time, 30 min. The BCD product obtained was used as feed for the subsequent HT step which was performed under the following conditions: temperature, 350°C; catalyst, Pt/SO₄²⁻/ZrO₂; feed/catalyst wt ratio, 5:1, H₂ pressure, 1500 psig; reaction time, 2 h. Under these conditions the final BCD-HT product of this early run contained about 73.5 wt% of C₁-C₃ alkylated phenols and methoxyphenols, where C₁-C₃ indicates the total number of carbons in alkyl substituents, viz., 1, 2 or 3 alkyl (predominantly methyl) groups per molecule. In recent optimization of the BCD-HT procedure, the BCD step was performed at 265°C, using a lower MeOH/lignin ratio, e.g., 5:1, and a shorter reaction time, i.e., 5 min. Further, the HT step was performed at a higher H₂ pressure, i.e., 1800 psig. Under these modified conditions a highly desirable BCD-HT product, containing 79.1 wt% of C₁-C₂ alkylated phenols and 2-methoxyphenols (where C₁-C₂ indicates mostly methyl and dimethyl substitution), was obtained. The product contained 12.9 wt% of hydrocarbons and only ~8 wt% of higher phenols. Etherification of the vacuum distilled product with methanol (see Experimental) produced a mixture of the corresponding aryl methyl ethers, which are characterized

by blending octane numbers in the approximate range of 142-166.

Figure 4 provides an example of GC/MS analysis of a BCD-HPR product from NREL lignin as feed, i.e., a lignin sample obtained as by-product in the NREL ethanol process.⁴ The selectivity for production of C₇-C₁₀ alkylbenzenes in this early run is only moderate due to the use of an extended reaction time (1 h) and a high MeOH/lignin wt ratio (7.5:1) in the BCD step, and the use of an extended reaction time (2 h) in the HT step. In order to increase the selectivity of the BCD/HT procedure, the extent of ring alkylation and, in particular, the extent of undesirable ring hydrogenation of the C₇-C₁₀ alkylbenzene products to corresponding alkylated cyclohexanes and cyclopentanes is subjected to sharp decrease in current work by using shorter reaction times and lower MeOH/lignin ratios in the BCD step, and a combination of shorter reaction times and catalysts of lower ring hydrogenation activity, e.g., RuMo/SiO₂-Al₂O₃ or a solid superacid, in the HT step. Under such modified conditions the BCD-HT product predominantly consists of C₇-C₉ alkylbenzenes (approximately 80-85 wt%) accompanied by desirable C₆-C₁₀ multibranching paraffins, 12-19 wt%, and < 4 wt% of alkylated naphthenes.

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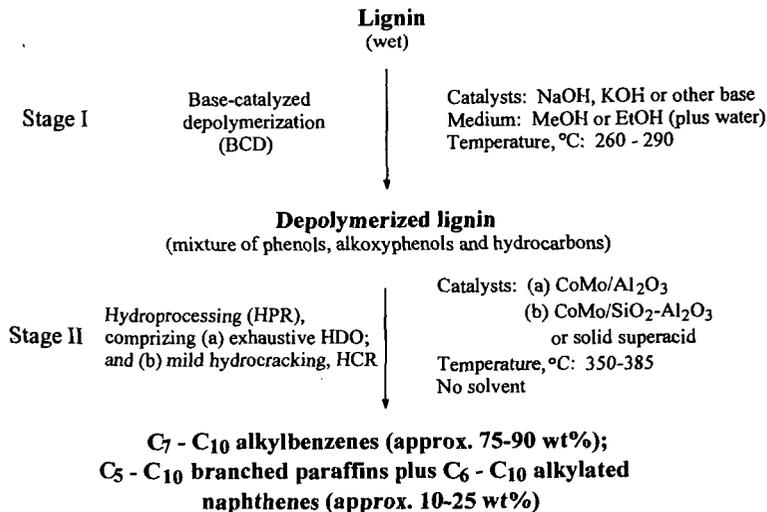


Figure 1. Scheme of two-stage (BCD-HPR) procedure for preferential conversion of lignin to C₇ - C₁₀ alkylbenzenes as fuel additives

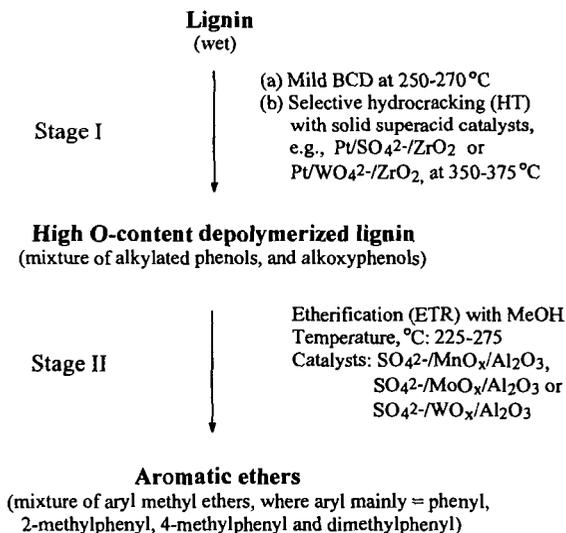


Figure 2. Scheme of two-stage (BCD-ETR) procedure for preferential conversion of lignin to aromatic ethers as fuel additives

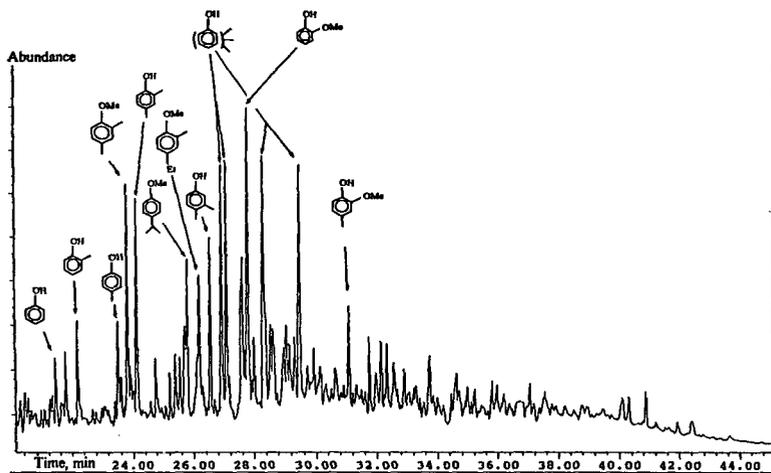


Figure 3. Example of GC/MS analysis of vacuum distilled BCD-HT product from Kraft lignin

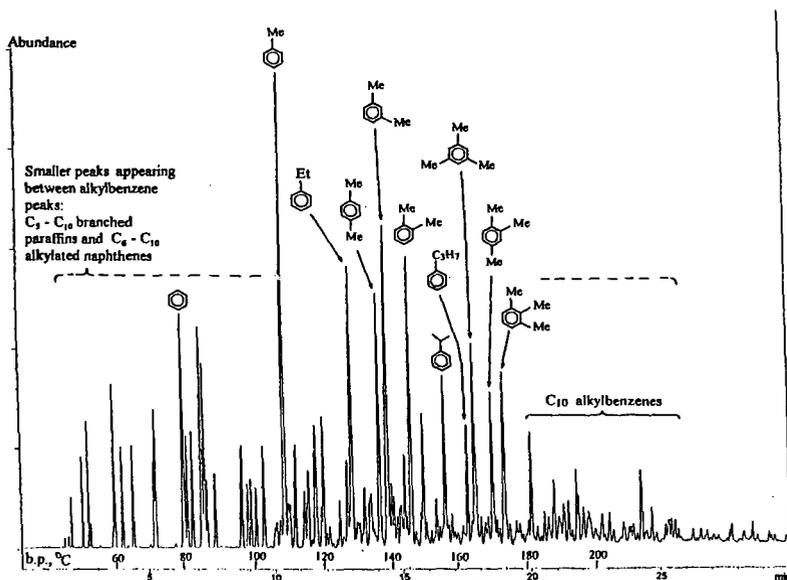


Figure 4. GC/MS analysis of BCD-HPR product from NREL lignin (lignin obtained as by product in the NREL ethanol process)