

Preparation of a Lignin-Derived Pasting Oil

Scientific Note

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INTRODUCTION

In a fully integrated system for the conversion of lignocellulosics to liquid fuels, conversion of the lignin fraction into a liquid fuel should also be included. The carbohydrate fraction is most efficiently converted to a liquid fuel by biochemical means; however, the lignin, an irregular polyphenolic, is not amenable to such a conversion. Catalytic hydrotreating of lignins to a mixture of phenols and hydrocarbons (primarily aromatic), followed by methylation of the phenols to methyl aryl ethers (MAE), would result in a high octane fuel additive. Singerman (1) has shown that MAE are fully compatible with gasoline.

The most successful process designed to date for hydrotreating lignin to phenols, is that of the Hydrocarbon Research Institute (HRI, Lawrenceville, NJ), which was based on coal and petroleum hydrotreating technology (2). In the HRI Lignol process, kraft lignin was hydrotreated at about 440°C and 1000 psi in an ebullated reactor. Lignin was fed to the reactor slurried in a pasting oil obtained from a recycle slip stream from the reactor. The best catalyst was considered to be MoS₂ on γ -alumina. The goal of the Lignol process was to convert lignin to phenol and benzene for sale as commodity chemicals, so hydrotreating was followed by a thermal dealkylation step and then a complex separation to obtain the desired products. A process to produce a high octane gasoline additive can utilize

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a mixture of phenols and hydrocarbons with much lower associated separation costs. However, the MAE produced must be within the normal gasoline boiling range (38–200°C). About 50% of the phenols produced in the Lignol process prior to dealkylation were ethyl and propyl phenols whose methyl ethers would have boiling points close to or above the normal gasoline boiling range (e.g., 4-propyl anisole, b. pt. 210°C). Part of our research, therefore, is directed at developing catalysts that have hydrodealkylation, as well as hydrodeoxygenation, activity. The effectiveness of the catalysts is initially tested using lignin model compounds in a continuous flow packed bed reactor. The most promising catalysts then must be tested with lignin.

Lignins have been hydrotreated under a variety of conditions using many different solvents or pasting oils, as detailed in a recent review (3). Lignins are quite soluble in aqueous alkali and so much research (4–8) has been performed using this solvent and with added phenol. Aqueous suspensions (9,10) and solutions with organic cosolvents (11) have also been used. However, the high activity alumina- and silica-supported metal and metal sulfide catalysts developed for the petrochemicals industry are able to tolerate only low levels of water. In addition, operation at or above the critical temperature of water (375°C) would involve excessively high pressures (>3200 psi). Many organic solvents have been used in lignin hydrotreating, such as alcohols, benzene, phenolics, anthracene and cresylic oils, and hydrogen donor solvents, such as tetralin and cyclohexane (see the many citations in (3)). Under hydrotreating conditions, all of these materials are likely to be hydrogenated and may also react with lignin and its products, making accurate analysis of catalyst influence on product distribution difficult if not impossible. Many early studies lacked the facilities available today for analysis of the complex mixtures generated on hydrotreating lignins. Often, solvent degradation products are not reported although they must certainly be produced. When using phenol, Goheen (12) reported that excessively high monophenol yields were observed because of incorporation of alkylated solvent products. Davoudzadeh et al. (13) and Anzick (10) observed various solvent-derived products when using tetralin, and similar problems have been seen with 1-methyl naphthalene (14) as the solvent (or suspension vehicle) when hydrotreating lignin.

A considerable amount of work was performed by Crown Zellerbach Corp., following the initial work at the Noguchi Institute, to develop the optimal pasting oil for hydrotreating lignin (12). A "stabilized" lignin tar was used for much of their research, which was produced by hydrogenating the high boiling (>240°C) fraction of a liquified lignin successively until it no longer yielded monophenols. The "stabilized" lignin tar was then recovered by distillation. Later recycle of the product after removal of the monophenolics by vacuum distillation was used as a simplification. The HRI process was developed after this, and even in their earliest papers

(15), they used a recycled heavy oil for slurring the kraft lignin and lignosulfonates being hydrotreated. A more recent study (16) has also used a high boiling ($>285^{\circ}\text{C}$) recycled oil in the hydroliquefaction of spruce sawdust.

To obtain a high boiling lignin-derived pasting oil for use in tests of catalyst activity with lignins, a sample of steam-exploded aspen lignin from Reotek Corp. (Jacksonville, FL) has been catalytically hydrotreated in *m*-cresol. A solvent was necessary to produce the initial sample of pasting oil, and *m*-cresol was found to dissolve the lignin used at moderate temperatures ($\sim 50^{\circ}\text{C}$). Based on a recent study (17,18) of cresol hydrotreating, it was anticipated that *m*-cresol would be converted to only low boiling products, such as toluene and methylcyclohexane. Distillation could then be used to remove the cresol and its products, resulting in a high boiling lignin-derived pasting oil. However, it has been found that undesirable higher boiling point products are formed from cresol, necessitating investigation of the hydrotreating of cresol, and lignin dissolved in cresol, to determine the conditions under which it is possible to produce a lignin-derived pasting oil that is not highly contaminated with solvent-derived products.

EXPERIMENTAL

Lignin

A lignin sample (Reotek Corp.) produced by steam explosion of aspen wood (*Populus tremuloides*) was used. The lignin was isolated from the carbohydrate by dissolution in alkali, removal of insoluble carbohydrate, and then reprecipitation with acid to about pH 4. The lignin was purified by centrifugation and washing with deionized water and then dried in a vacuum oven at 40°C . The ash content of the lignin was determined to be 4.4%. Elemental analysis of the lignin gave 61.13% C, 5.60% H, 32.67% O, and 0.37% N. Prior to hydrotreating, less than 1% of the lignin could be solubilized in acetone by soxhlet extraction.

Catalyst

A nickel-molybdenum (NiO 3.5 wt%, MoO_3 15.5 wt%) impregnated γ -alumina (200 m^2/g specific surface area) catalyst (Harshaw Chemical Co., Beachwood, OH, HT-500, E1/8) was used after crushing and sieving (-170 to $+250$ mesh). Sulfiding was performed on batches of catalyst (~ 40 g) in a tubular reactor after drying at 400°C for 2 h under flowing N_2 , using H_2S (10%) in H_2 (15 psig) at 400°C for 4 h. To ensure uniform sulfiding of the catalyst, it was removed from the reactor, mixed, repacked, and then resulfided using the same conditions. The catalyst was stored in a stoppered flask under N_2 in a desiccator.

Chemicals

The *m*-cresol (97%, Aldrich Chemical Co., Milwaukee, WI) was used as received. The H₂S-containing gases were specially prepared by Air Products and Chemicals, Inc., Allentown, PA.

Tubing Bomb Procedure

Batch hydrotreating experiments were performed in an 18 mL shaking bomb reactor constructed of one inch stainless steel tubing. Two stainless steel balls were included in the reactor to augment mixing. After addition of the feed (5 mL *m*-cresol, 0.3 g catalyst, and 1.5 g lignin if used) the reactor was pressurized with H₂ (1000 psig). Heating was supplied by a preheated fluidized sand bath. Both heat-up and cool-down were very rapid, permitting study of reaction times from 5 to 120 min at temperatures of 350–425°C. After the reactor had cooled down, it was depressurized and a gas sample was taken. The reactor was then washed with acetone to give acetone soluble and insoluble products (separated by filtration) that were evaporated and dried.

Stirred Autoclave Procedure

An Autoclave Engineers 300 mL stirred autoclave was used for larger scale batch hydrotreating experiments. These were performed in the temperature range of 375–425°C and at initial pressures of about 1000 psig of 2% H₂S in H₂. The autoclave was preheated to above the desired temperature so that upon introduction of the feed into the autoclave via an injection system, the desired temperature was rapidly attained (within about 5 min). Samples were removed from the autoclave via a dip-tube, permitting examination of product change with time. Rapid cooling of the product at the end of experiments was achieved by its withdrawal via the dip-tube into a sample cylinder. The feed consisted of the lignin (60 g, when used) dissolved in *m*-cresol (200 mL). Approximately 150 mL of this was injected into the autoclave, where it was hydrotreated in the presence of 12 g of the sulfided catalyst. The uninjected feed was recovered, as well as all product fractions, line, and reactor washings. The gas volume and composition was also measured, so that a mass closure for each experiment could be made.

Analyses

Elemental analyses were performed at Huffman Laboratories, Golden, CO. Separate carbon analyses were obtained for some of the acetone insoluble product fractions using a Coulometrics Total Carbon Analyzer. Gas samples were subjected to a refinery gas analysis on a Carle Gas Chromatograph 111H. The system is capable of analyzing up to 21 different hydrocarbons and other gases with a multicolumn, multivalve automated analysis, as described in the application note No. 156-A of the Carle

Series-S, cat. no. 0156 AGC. Based on the carbon content of the lignin in the feed and the carbon content of the gas and acetone insoluble product fractions, and assuming all the gas and acetone insoluble material was lignin derived, the conversion of lignin to acetone soluble product was estimated as follows

$$\text{Lignin Conversion to Acetone Soluble Product (\%)} = \frac{C_{\text{feed}} - C_{\text{gas}} - C_{\text{insolubles}}}{C_{\text{feed}}} \times 100$$

Liquid chromatography was carried out using a Hewlett-Packard HP1090 liquid chromatograph containing an ultraviolet diode-array detector (HP 1040). Changes in the apparent molecular weight of the products was monitored by high performance size exclusion chromatography (HPSEC) using a PL Gel 50 Å 5 µm column and tetrahydrofuran solvent (flow rate 1 mL/min). Some of the products of cresol hydrotreating were identified by reverse phase liquid chromatography using a HP Hypersil ODS column (5 µm, 100 × 2.1 mm) and a solvent elution program (initially 50:50 water:acetonitrile going to 100% acetonitrile after 5 min where it was held for a further 5 min). Identifications were confirmed by comparisons of retention times and spectra of pure compounds.

RESULTS AND DISCUSSION

Hydrotreating lignin in *m*-cresol at a relatively high temperature (425°C) for up to 5 h did not result in the expected "stabilized" lignin tar. Upon distillation of the hydrotreating product, a crystalline material was obtained that was isolated and identified as anthracene. A peak eluting after cresol in the HPSEC analysis of the products of hydrotreating cresol and lignin-cresol mixtures was identified with the formation of anthracene and alkyl-substituted anthracenes by their distinct UV spectra (a sharp λ_{max} at 250–260 nm). According to Philip and Anthony (19), the elution of anthracenes is retarded because of their adsorption, a nonsize exclusion interaction, with the chromatographic packing. The anthracenes are presumably formed through condensation reactions of cresol and are undesirable because they complicate the separation of lignin- and solvent-derived products. The formation of these condensation products has not been previously reported, probably because most cresol hydrotreating studies have involved the use of diluents and have not been performed with pure cresol.

Using the small tubing bomb reactor and HPSEC analysis of the products, the effect of reaction temperature and time on the formation of cresol-derived products and the depolymerization of lignin was studied. In addition, by carbon analysis of the acetone insoluble products, it was possible to estimate the conversion of lignin to acetone-soluble products. From the results in Table 1, it can be seen that 60 min hydrotreating at higher reac-

Table 1
Effect of Temperature on the Yields of Components in the Acetone Soluble
Product Fraction after 60 Minutes Hydrotreating (Area %)

T, °C	> 1000 ^a	1000–200 ^a	200 ^a	Cresol	Anthracenes
Tubing Bomb Reactor— <i>m</i> -Cresol Alone					
350	0.0	0.0	12.6	87.4	0.0
375	0.0	0.0	13.0	84.3	2.7
400	0.0	0.0	11.5	81.0	7.4
425	0.0	0.0	14.8	66.8	18.4
Tubing Bomb Reactor— <i>m</i> -Cresol + Lignin					
350	3.5	44.5	0.0	49.5	2.5
375	2.1	40.5	0.0	54.6	2.8
400	0.0	40.5	0.0	54.8	4.7
425	0.0	38.9	0.0	51.6	9.5
Stirred Autoclave— <i>m</i> -Cresol Alone					
375	0.0	0.0	11.0	87.2	1.7
400	0.0	0.0	9.6	87.6	2.8
425	0.0	0.0	17.4	70.0	12.6
Stirred Autoclave— <i>m</i> -Cresol + Lignin					
375	0.0	51.6	0.0	44.4	4.0
400	0.0	47.8	0.0	45.8	6.4
400 ^b	3.1	45.0	0.0	46.4	5.5
400 ^c	2.4	49.1	0.0	39.1	9.4

^a Apparent molecular weights in daltons, as measured by HPSEC analysis.

^b Unsampld experiments.

^c Uncatalyzed experiments.

Table 2
Conversions (%) of Lignin into Acetone Soluble Fractions
by Hydrotreating in a Small Tubing Bomb Reactor

T, °C	Reaction time, min				
	5	15	30	60	120
350				87	84
375				85	
400	77	83	85	80	
425				72	

tion temperatures (>400°C) resulted in increased solvent degradation with formation of anthracenes and material that eluted in a peak with an apparent molecular weight (mw) of about 200 daltons.

Prior to hydrotreating, the acetone solubility of the lignin was <1%. Hydrotreating even under the least severe conditions gave a product with greatly increased solubility (Table 2). HPSEC analysis of the acetone solu-

ble products was used to monitor the degree of lignin depolymerization. In HPSEC analysis, a peak at the exclusion volume in a chromatogram is owing to material that is larger in molecular size than the pores of the chromatographic packing material which, for the column used, was equivalent to a mw approximately > 1000 daltons. To produce a good pasting oil lignin, depolymerization should be maximized so that an oil of low viscosity is produced. HPSEC analysis of the tetrahydrofuran soluble fraction of the feed indicated that virtually all of the lignin had mw components > 1000 daltons. Hydrotreating even under the mildest conditions substantially depolymerized the lignin so that its mw was mostly in the range of 1000 to 200 daltons (Table 1). As reaction temperature and time were increased, lignin depolymerization increased, as observed in HPSEC analysis by the disappearance of a distinct peak for lignin with mw > 1000 daltons and a shift in distribution to lower mw of the lignin with mw 1000–200 daltons. However, as with cresol alone, hydrotreating at the most severe conditions resulted in increased formation of anthracenes. The optimal conditions for production of a lignin-derived pasting oil, therefore, are at intermediate reaction times and temperatures. The maximum yields of acetone solubles also occurred at intermediate severity conditions. Low yields at 400°C and short reaction times were probably owing to incomplete lignin conversion, whereas decreasing yields at the highest temperature and longest reaction times was probably owing to increased conversion of lignin to char. From the tubing bomb study, temperatures of 375–400°C with reaction times of 30–60 min appeared to be optimal for production of a lignin-derived pasting oil with minimal formation of cresol degradation products. Consequently, these conditions were further examined using the stirred autoclave reactor.

Experiments in the stirred autoclave were conducted at 375–425°C and sampled at various times to allow examination of their effects. Results from the hydrotreating of *m*-cresol were very similar to those seen with tubing bomb reactor. Cresol degradation at 375 and 400°C appeared to take place at very similar rates, with formation of anthracenes and the 200 mw product. At 425°C, substantial cresol degradation took place, so that this was clearly too high a temperature for batch hydrotreating of lignin with cresol. On hydrotreating lignin at 375 and 400°C, 20 min was sufficient to depolymerize the lignin so that no distinct peak for material with mw > 1000 daltons was apparent. Hydrotreating was continued up to 60 min, resulting in a shift to lower mw of the distribution of the 1000–200 daltons mw lignin-derived material. Only low levels of anthracenes were formed at reaction times up to 60 min. As in the tubing bomb experiments, greater lignin depolymerization and greater anthracene formation occurred at 400 than at 375°C, so that the optimal conditions for producing a pasting oil appeared to be 30–60 min hydrotreating at these temperatures. In the absence of catalyst, hydrotreating lignin in cresol at 400°C resulted in higher yields of anthracenes, gas, and acetone insolubles, with less lignin depolymerization.

Having identified conditions suitable for pasting oil production, larger batches of hydrotreated product were produced by not sampling the experiments. Two experiments at 400°C gave relatively low average yields of acetone insolubles and gases (6 and 1%, respectively, based on the whole feed). Most of the feed (89%) was converted to acetone soluble material so that mass closure on the experiments was very high (96%). Very little (1.3%) acetone insoluble material was produced when hydrotreating cresol alone, so it appears that significant conversion of lignin to acetone insolubles and gases (21 and 5%, respectively) occurred.

To obtain a purely lignin-derived pasting oil, separation of cresol and cresol-derived products from the acetone soluble product was necessary. Only simple methods of separation, such as vacuum distillation and solvent extraction, were studied. Only hexane has been tested so far as the extracting solvent although chlorinated organic solvents might also be useful in achieving the desired separation. Vacuum distillation (at 1 torr up to 50°C) removed 80% of the cresol from the acetone soluble fractions. By comparison, hexane extraction (20 g extracted with 20 mL aliquots) removed only about 20% in two extractions and 37% after four extractions. HPSEC analysis revealed that distillation was also much more selective, the distillate being about 98% cresol. The hexane extracts contained only 68% cresol with about 14% anthracenes and 18% of material with an apparent mw >200 daltons that could be lignin-derived. From these results, distillation appears to be the method of choice in separating the lignin-derived pasting oil from the acetone soluble product. Even with distillation the pasting oil contained a substantial amount of cresol (~45%) and a small amount of the cresol degradation products. Overall, about 31% of the feed was converted to an initial sample of pasting oil, including 75% of the lignin that was in the feed. Hydrotreating this initial sample of pasting oil with additional lignin should increase the lignin content of the pasting oil so that at some point the content of the initial solvent and its products is expected to be negligible. Larger batches of product from hydrotreating lignin and cresol at 375°C must also be prepared so that the pasting oils produced at the two temperatures can be compared and optimal conditions for making larger amounts of pasting oil can be selected.

CONCLUSIONS

By studying the effects of time and temperature on the hydrotreating of cresol, alone and with lignin added, in a tubing bomb reactor and a stirred autoclave, conditions have been found under which a lignin-derived pasting oil can be produced. The unanticipated formation of high boiling cresol degradation products, mostly anthracenes, made production of the pasting oil more difficult than expected; however, using conditions of intermediate severity, anthracenes formation was minimized and sufficient

lignin depolymerization was obtained. Vacuum distillation appeared to be the best method for separating cresol from the acetone soluble product, being more efficient and more selective than extraction with hexane. The initial samples of pasting oil still contained cresol and cresol-derived products; however, repeated hydrotreating of this material with more lignin, followed by removal of low boiling products by distillation, should result in a pasting oil that is almost wholly lignin-derived. Once catalyst testing begins, recycle of the high boiling product will be used to provide pasting oil for subsequent experiments.

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