

Hydrodeoxygenation of Lignins and Model Compounds

Scientific Note

M. A. RATCLIFF, D. K. JOHNSON, F. L. POSEY,
AND H. L. CHUM*

*Chemical Conversion Research Branch, Solar Energy Research
Institute, 1617 Cole Blvd., Golden, CO 80401*

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INTRODUCTION

In the production of liquid fuels from lignocellulosic materials, the carbohydrate components can be converted into ethanol fuels by fermentation processes. However, the lignin fraction, an irregular polymer of phenylpropane units, is not amenable to such a conversion, but can be transformed into phenolic compounds and hydrocarbons by hydrotreating. The phenolic fraction, when converted into methyl aryl ethers, can be blended with gasoline, together with the hydrocarbon (primarily the aromatics) fraction. Singerman (1) demonstrated that methyl aryl ethers produced from coal liquids were fully compatible with gasoline to replace or supplement the aromatic components (e.g., benzene, toluene, xylenes). The most desirable phenols for conversion into methyl aryl ethers are phenol, cresols, and xylenols, because the resultant ethers have high octane numbers and their boiling points fall within the range of gasoline. We are investigating the conversion of lignins into phenols and hydrocarbons (2) by mild hydrodeoxygenation (HDO) routes.

Lignins are the most abundant renewable resource of aromatic compounds that could be used as gasoline octane improvers and extenders. Since this application does not require extensive separation of phenolic

*Author to whom all correspondence and reprint requests should be addressed.

compounds, but, in fact, utilizes a mixture of phenolic compounds converted into their corresponding methyl ethers and the aromatic hydrocarbons, the usually high separation expenses are avoided. Methanol, another inexpensive resource, which can be manufactured from renewable resources or from fossil fuels, is utilized to synthesize the ethers from the mixed phenols. The problems that can arise from incompatibilities between methanol and gasoline fuels, such as excessive vapor pressure, which leads to increased evaporative emissions and vapor lock are thus avoided. The corrosivity problems are also circumvented because of the ether formation. Water miscibility decreases substantially, and thus the common problem of phase separation is not present.

The approach taken here is based on coal and petroleum hydrotreating processes as well as early work in the field of hydrodeoxygenation (HDO) of lignins (3–7), that has recently been reviewed (8). MoS_2 on γ -alumina catalyst was considered the best for the hydrocracking stage of the Hydrocarbon Research Institute's (HRI) Lignol Process (9), in which hydrotreating was to be followed by thermal dealkylation for the production of phenol and benzene. An optimal catalyst for the conversion of lignins into phenols would possess the following characteristics: high conversion at modest temperatures to minimize char formation from lignin, high selectivity to phenols to prevent higher hydrogen consumption that accompanies hydrocarbon formation, dealkylation capability for side chain removal or rearrangement, tolerance to water formation, durability, and low cost.

The most successful process designed to date is that of HRI. The important features of their ebullated design were the very good mixing between catalyst, lignin, and hydrogen; a narrow temperature distribution throughout the reactor; and the rapid separation of volatile reaction products from the reactants in the reactor, thus avoiding secondary reactions. A batch reactor is, however, simpler to operate and would allow a more rapid screening of catalysts/supports and operating conditions and for that reason is the most commonly employed research reactor. The features we tried to include in our reactor design were good mixing, the ability to process small quantities of lignin, easy removal of vapor products, and also easy conversion to batch operation. 1-Methylnaphthalene, a solvent often used in coal hydrotreating studies, was selected for the lignin experiments because of its supposed stability at high temperatures in hydrogen atmospheres. Hexane was chosen as solvent for the model compound studies.

While studying the effect of catalyst/support material on the hydrotreating of the lignins themselves, it was decided to also study the effect of catalyst/support on a small number of relevant model compounds. The use of model compounds has the advantage that the chemistry should be more easily understood. The first model compound studied was 4-propylguaiaicol (4PG) so that comparisons could be made with other model compound studies (10,11), and extended to include a higher

temperature range. The HRI work has suggested it is important to go to at least 400°C.

METHODS AND MATERIALS

Lignin Hydrotreatment Setup

Lignin hydrotreating was carried out in a small (10 mL) stainless steel pipe bomb reactor. In addition to the lignin and solvent, the reactor was loaded with two steel balls and connected to a mechanical shaker to improve mixing. The reactor was rapidly heated (~ 1 min to 350°C) by raising a preheated fluidized sand bath up to cover the bottom half of the reactor. The gas inlet was at the bottom of the reactor and outlet at the top. In the flow experiments, the flow of gas out of the reactor was controlled by a letdown valve and the pressure by a back-pressure regulator. The gas flow rate out of the reactor (~ 35 mL min⁻¹) was monitored using a rotameter and the gas composition was determined by analyzing the contents of a gas sample bottle by GC. The product vapors were condensed out in a cold finger trap ($\sim -10^\circ\text{C}$). The letdown valve and the stainless steel line to the trap were heated (250°C) to maintain the products in the vapor phase. The trap was packed with glass wool to help knock down any aerosols that might be formed. A thermocouple was used to monitor the reactor temperature during the experiments.

In the batch experiments, the equipment was modified such that the reactor was capped at the outlet before the letdown valve. The reactor was pressurized (to 69 atm or 1000 psig) at the start of the experiment prior to heating and then the hydrogen shutoff valve was closed. On heating, the pressure was allowed to rise unchecked (to about 164 atm, or 2400 psig). At the end of the batch experiments, the reactor pressure was letdown into a large gas reservoir (2 L) from which gas samples were taken for analysis.

In all experiments, the reactor was loaded with a 1:2 ratio of lignin (~ 1.9 g) to solvent (~ 3.8 g). The lignin used was obtained from an organosolv (methanol:water = 70:30 v/v) pulping of aspen wood (4:1 liquid:wood) with phosphoric acid (.05 M) as catalyst at 165°C for 2.5 h. The characterization of this sample is given by Chum et al. (12,13). 1-Methylnaphthalene (used as supplied by Aldrich Chemical Co.) was used as the solvent, although its role was more likely that of a vehicle for the lignin. Most of the work was carried out using a Co/Mo catalyst supported on γ -alumina (Harshaw Catalyst Co., Co/Mo-0601; 3% CoO, 15% MoO₃, 230 m²g⁻¹). Some early experiments were run using a Ni/Mo catalyst (Ketjen Catalyst Co., 153-1.5E) supported on alumina. Both catalysts were ground to a fine powder (>80 mesh) and then presulfided in batches (~ 50 g) with hydrogen sulfide gas (10% in hydrogen) at atmospheric pressure and 400°C for 4 h. The treated catalysts were then stored in a dry box under an inert atmosphere of nitrogen or carbon dioxide.

After the reactor was loaded with lignin and solvent, the catalyst (.2–.3 g) was added to the reactor in the dry box.

At the end of experiments three fractions were collected for analysis. The material found in the trap was washed out and made up to a known volume and called the condensate. The material in the reactor was washed out with tetrahydrofuran (THF) and then filtered. This produced two fractions; the THF-soluble residue and the THF-insoluble residue. The condensate and THF-soluble residue were analyzed by a Hewlett-Packard HP 1090 Liquid Chromatograph equipped with a UV-visible diode-array detector and an Alltech C18 reverse phase column (10 μ particle size, 25 cm \times 4.6 mm). Gel permeation chromatography was performed using a Polymer Laboratories PL-Gel 50 Å column 5 μ particle size, 30 cm \times 7.5 mm). Gas chromatography (Varian 3700) and GC-MS (HP 5985) were also used to identify and quantitate phenolic and hydrocarbon products using a 30 m \times .32 mm DB capillary column. The details of these analyses have been previously published (8).

Model Compounds Hydrotreatment Setup

The model compound experiments were performed in a trickle-bed reactor constructed from 1/2-in. 316 stainless steel tubing. The reactor was suspended vertically in a tube furnace. The liquid feed was injected at the top by an ISCO LC 5000 syringe pump. Hydrogen was introduced from a high-pressure cylinder at 500 psig. Liquid products were collected in a high-pressure condenser and sampled through a 1/4-in. stainless steel tube isolated by ball and regulating valves. A more detailed description is published elsewhere (14).

The catalysts used include $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ supplied by Strem Chemicals (#42-1500). The MoO_2 content was 10–12%, and the surface area was 64 m²/g in the form of 3/16 in. \times 1/8 in. pellets. The pellets were ground with a mortar and pestle and sieved to 20-14 mesh before loading into the reactor. NiO/MoO_2 on phosphoric acid coprecipitated γ -alumina was supplied by M. Maholland and S. Cowley of the Colorado School of Mines. The detailed preparation and properties of the catalyst are described elsewhere (15). The Ni and Mo contents of the catalyst were 3% and 11.7%, respectively. The P:Al atomic ratio was .5, surface area was 88.2 m²/g, and the average pore diameter was 210 Å. The catalysts were presulfided *in situ* by injecting a solution of 5 vol % methyldisulfide in hexane in the presence of hydrogen at 100 psig. The liquid and gas flow rates were calibrated to maintain approximately 10 vol % H_2S in hydrogen. The presulfiding was performed at 200°C for two h then 400°C for an additional two h.

Research grade hydrogen (99.999%) was used as supplied. 4-Propylguaiaicol (4 PG) was used without further purification as supplied by Frinton Laboratories (#1035). The feed mixture was 75 vol % 4PG in research grade hexanes with .25 vol % methyldisulfide (Aldrich #15,031-2)

to maintain catalyst sulfidation. Burdick and Jackson UV-grade acetonitrile was used as supplied to dilute the liquid samples prior to analysis.

The phenolic and hydrocarbon products were analyzed by gas chromatography (Varian 3700) using a Supelco SPB5 wide bore capillary column and by GC-MS (HP 5985). Water was determined by GC (Varian 3700) using a Poropak QS glass column. Gas analysis was performed on a Carle Model 111H GC (14).

RESULTS AND DISCUSSION

Lignin Hydrotreating

Experiments were performed to establish whether catalyst screening could be carried out in the pipe bomb reactor operated in true batch mode as this would be the easiest mode of operation. In all experiments a certain amount of THF-insoluble residue was obtained in the form of a black, free-flowing powder. In the batch experiments the yield of this residue increased with the severity of the hydrotreating conditions (Table 1). With increasing temperature and reaction time the yield of the THF-insoluble residue increased up to about 50% of the lignin charged. The presence of the Co/Mo catalyst decreased the amount of residue formed except at the higher temperature. The importance of sweeping volatile products from the reactor was also clearly demonstrated. When the Co/Mo catalyst was used the yield of THF-insoluble residue in the flow configuration was a third of that when the reactor was operated in true batch mode at the same temperature. The yield of phenols, although low overall, was much higher when they were swept from the reactor. With continuous removal of products from the reactor the possibility of recondensation of the phenols with the remaining lignin is minimized. With a catalyst present less THF-insoluble residue was produced because the reactive intermediate products from the hydrogenolysis of the lignin were quenched more quickly with hydrogen, also limiting their ability to recondense with the lignin.

The nature of these THF-insoluble residues has not yet been fully determined although from elemental analyses of selected examples (Table 1) they do appear char like. At 400°C, about 31% char is formed in biomass carbonization experiments; this char has 82.7% carbon, 3.8% hydrogen, and 13.5% oxygen (16). These elemental analyses compare well with most of the THF-insoluble residue elemental analyses of Table 1. There is as yet no explanation of the two examples with much lower carbon contents. All the samples subjected to elemental analysis were also subjected to flash volatilization (very rapid heating at 535°C under a stream of helium). In each case very little of the material was volatilized (<20%), and molecular beam mass spectroscopic analysis indicated that the volatiles were dominated by the reaction solvent 1-methylnaphthalene.

Table 1
Comparison of THF-Insoluble Residue Yields from Lignin
Hydroprocessing Experiments, 1.9 g Organosolv Aspen Lignin,
3.8 g 1-Methylnaphthalene, 1000 psig

T, °C	Duration, min	Catalyst	THF insoluble residue, wt % of lignin charged	Combined phenols yield, wt % of lignin charged	THF insoluble residue elemental analysis, %		
					C	H	O
Batch experiments							
404	5	—	11	<1			
399	5	Co/Mo	.5	<1			
406	20	—	36	<1			
410	20	Co/Mo	29	<1	79.92	3.77	16.31
407	60	—	49	1.9	64.96	3.64	31.40
404	60	Co/Mo	30	2.2	83.17	4.01	12.82
453	5	—	41	<1	83.76	4.03	12.21
451	5	Co/Mo	39	<1			
Flow experiments							
418	60	—	48	3.5	81.78	3.85	14.37
406	60	Co/Mo	10	8.2			
428	60	Co/Mo	14	10.0	68.77	3.83	27.40
415	60	Ni/Mo	19	7.6			

The reason for the low overall yields of phenols is not clear at this time. It is possible, despite the fact that the trap was packed with glass wool, that some of the phenolic products escaped as aerosols which can be very difficult to knock down. Agitation may have been another factor. The main phenolic products were phenol (~30%) and cresols (~40%). There were a very large number of products formed in small amounts including xylenols, ethyl phenol, and propyl phenols, plus some hydrocarbons, the largest of which was toluene.

Our preliminary studies designed to test the batch versus continuous product removal, temperature, and pressure range on well-characterized catalysts, and to test our analytical capabilities were performed using 1-methylnaphthalene as solvent. This compound was chosen because of the desire to use a well-defined inert solvent (if such a solvent existed) that would simplify the analytical procedure, and because it has been used extensively in the coal hydrocracking studies and in some lignin hydrotreating investigations. We find that this solvent is *very* reactive to lignin fragments (presumably free radicals) and acts as a trap for them. In both batch and flow experiments naphthalene (~6% yield of 1-methylnaphthalene charged) and a number of dimethylnaphthalenes (~8% yield of 1-methylnaphthalene charged) were formed, further complicating the already complex analytical problem. The premise that 1-methylnaphthalene is an inert solvent, used throughout coal and coal/lignin studies, has been shown to be wrong. In order to continue our experimentation with a more realistic solvent, we are going to generate a lignin pasting oil (the solvent of an operating process) from hydrotreating experiments and use the oil as solvent. We have, however, been able to achieve the objective of the experimentation of showing how important volatile product removal is. The pasting oil production and future experimentation including testing catalysts is being carried out in a stirred autoclave reactor, modified to allow batch experiments with continuous removal of products using 20–100 g lignin per experiment.

Model Compound Hydrotreating

4-Propylguaiaicol can be hydrotreated to three main classes of products. The low-temperature ($\leq 300^\circ\text{C}$) products are primarily catechols. As the temperature increases, mild hydrodeoxygenation products such as phenols result. Complete hydrodeoxygenation, forming saturated and aromatic hydrocarbons, predominates at high temperatures ($>400^\circ\text{C}$) and low space velocities. 4-Propylguaiaicol has been hydrotreated under a variety of conditions using $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{NiS-MoS}_2/\text{P}:\gamma\text{-Al}_2\text{O}_3$ catalysts in the temperature range of $250\text{--}450^\circ\text{C}$, at two molar hourly space velocities ($\text{MHSV } .007 \text{ and } .017 \text{ mol 4PG (g cat.)}^{-1}(\text{h})^{-1}$, which correspond to $\text{WHSV} = 1.17 \text{ and } 2.82 \text{ g 4PG (g cat.)}^{-1}(\text{h})^{-1}$, respectively). Based on early experiments to determine the effect of hydrogen pressure on the reaction, we found that decreasing the pressure from 1000 psig to 500 psig increased the selectivity of propylphenol formation 89%, with

no significant effect on the overall conversion using the MoS_2 catalyst. Therefore, all experiments reported here were performed at 500 psig.

The major phenolic product from the $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was 4-propylphenol, having a maximum selectivity of 48% at 350°C and $\text{MHSV} = 0.007$ (see Table 2). At higher temperatures, hydrocarbon products such as propylbenzene, methylpropylbenzenes, and propylcyclohexane were predominant. No reaction conditions studied so far with this catalyst have given significant yields of dealkylated products. This result is not surprising given that $\gamma\text{-Al}_2\text{O}_3$ is not a very acidic support.

The product slate obtained from 4PG on the $\text{NiS-MoS}_2/\text{P}:\gamma\text{-Al}_2\text{O}_3$ catalyst was notably different from that of the $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst. 4-Propylphenol remained the major product up to 350°C; however, significant dealkylation to phenol, cresols, and ethylphenols occurred (see Table 3). The more acidic catalyst support had higher selectivity toward dealkylated phenols at 300°C than the neutral support did at 450°C (6% vs 3.5%, compare experiments 5 and 6). This selectivity toward dealkylated phenols increased by a factor of 5 at 350°C (compare experiments 6 and 7). Interestingly, GC/MS data suggests that the major cresols formed were meta- and para-cresol having a selectivity as high as 15.7% at $T = 400\text{--}450^\circ\text{C}$ and $\text{MHSV} = 0.017 \text{ mol 4PG (g cat.)}^{-1}(\text{h})^{-1}$. Again, at higher temperatures and the lowest space velocity, the yields of hydrocarbons increase at the expense of phenols production. This product shift could be offset by increasing the space velocity. At 450°C and $\text{MHSV} = .017$, the selectivity to phenols was about 4 times the selectivity at $\text{MHSV} = .007$ (48% vs 12%; compare experiments 9 and 11; not all phenols are reported in the table). Any possible effect of the nickel sulfide on dealkylation has yet to be determined. An identical catalyst without nickel has been prepared and is being subject to testing. However, it is generally accepted that the main effect of nickel in these types of catalyst is to promote hydrogenation, and the acidity of the support is the major factor in dealkylation.

The gas analyses from the NiS/MoS_2 on phosphated γ -alumina catalyzed reactions support the evidence from the liquid analyses that the

Table 2
Selectivities of Major Products on $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3^a$

Expt. no.	Temp., °C	Conversion, %	Propyl-phenols, %	Propyl-benzenes, %	Propyl-cyclohexane, %	Dealky. products, %
1	250	38	7.3	2.9	0	0
2	300	36	35.7	8.7	0	0
3	350	82	48.5	8.5	1.3	.8
4	400	95	11.1	14.6	4.0	3.4
5	450	99	5.9	25.5	5.5	3.5

^aAll reactions run at 500 psig, $\text{MHSV} = .007 \text{ mol 4PG (g cat.)}^{-1}(\text{h})^{-1}$. Conversion = $(\text{mol 4PG}_{\text{in}} - \text{mol 4PG}_{\text{out}})/\text{mol 4PG}_{\text{in}} \times 100$. Selectivity = $\text{mol product/mol 4PG converted} \times 100$.

Table 3
Selectivities of Major Products on NiS-MoS₂/P:γ-Al₂O₃^a

Expt. no.	Temp., °C	Conversion, %	Propylphenols, %	Ethylphenols, %	Cresols, %	Phenol, %
6	300 ^b	53	32.2	1.8	4.0	0
7	350 ^b	63	48.1	9.8	16.2	4.4
8	400 ^b	96	4.4	5.6	13.3	7.0
9	450 ^b	100	0.7	1.7	4.4	4.4
10	400 ^c	98	7.0	8.6	15.7	7.5
11	450 ^c	97	7.1	6.9	15.7	10.4

^aAll reactions run at 500 psig. Conversion and selectivity as defined in Table 2.

^bMHSV = .007 mol 4 PG (g cat.)⁻¹ (h)⁻¹

^cMHSV = .017 mol 4 PG (g cat.)⁻¹ (h)⁻¹

more acidic catalyst increases side chain cracking. At 400°C only .2 mol % of propane was detected in the gas from the Mo/γ-Al₂O₃ catalyst, whereas using the more acidic catalyst support, .5 mol % of propane was formed plus from .1 to .5 mol % propene depending on the reaction temperature and space velocity. Water formation increased with increasing reaction temperature and followed the decrease in phenols selectivity above 350°C because of hydrocarbon formation.

The results reported here, while preliminary, demonstrate the direction of our research efforts to systematically test well characterized catalysts and develop, with researchers at the Colorado School of Mines, bifunctional catalysts for lignin hydrotreating. The data show that increasing the acidity of the catalyst support significantly increases the selectivity to dealkylated products. Additional catalysts with controlled acidity are under investigation to confirm the product trends described above. Complementing the model compound study, lignin investigations using a 300 mL stirred Autoclave Engineers high-pressure reaction vessel, operated in the semicontinuous mode (continuous product removal) are underway.

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