

Catalytic Hydrodeoxygenation and Dealkylation of a Lignin Model Compound

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ABSTRACT

A comparison is presented of the hydrotreatment of 4-propylguaiacol (4PG) exploring two catalysts: MoS₂ on γ -alumina and the dual functionality MoS₂/NiS on phosphated γ -alumina at 250°-450°C and 500 psig of hydrogen. The catalyst with acidic support was found to promote substantial dealkylation of 4PG into a number of alkylated phenols such as methyl- (predominantly meta- and para-), ethyl-, and methylpropylphenols. The main reaction product on the less acidic catalyst was 4-propylphenol. At 350°C, mild deoxygenation to phenols can be maximized, whereas higher temperatures favor the formation of hydrocarbons, aromatic and saturated. Higher space velocities also favor mild deoxygenation to phenols. These studies are relevant to the conversion of lignins into phenolic compounds. Transformation of phenols into methyl aryl ethers produces a suitable gasoline octane enhancer and extender.

INTRODUCTION

In the production of liquid fuels from lignocellulosic materials, the carbohydrate components can be converted into ethanol fuels in fermentation processes. However, the lignin fraction, composed of phenylpropane units, is not amenable to such a conversion, but can be transformed into phenolic compounds and hydrocarbons. 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 are 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.

The approach taken is based on coal and petroleum hydrotreating processes as well as early work in the field of hydrodeoxygenation (HDO) of lignins (refs. 3-7), that has recently been reviewed (8). MoS₂ on γ -alumina catalyst was considered the best for the hydrocracking stage of the Hydrocarbon Research Institute's Lignol Process (9), in which hydrotreating was 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 reasonable cost.

In order to select the best catalysts, well-defined lignin model compounds (e.g., 4-propylguaiacol, or 2-methoxy,4-propylphenol) containing representative functionalities have been employed. The aim is two-fold: mild deoxygenation into 4-propylphenol and partial dealkylation into methyl-, and ethyl-phenols. A commercial

catalyst and a custom-synthesized heterogeneous catalyst (10) have been screened for their HDO and dealkylation activities. The results reported here are preliminary but illustrate the utility of bi-functional HDO catalysts in lignin-model compound hydrodeoxygenation.

EXPERIMENTAL

Equipment. A trickle-bed reactor was constructed from 1/2-in. OD 316 stainless steel (SS) tubing with a 0.035-in. wall thickness and Swagelok tube fittings. The catalyst bed was supported by a 90 micron SS frit which in turn was supported by a 1/16-in. K type thermocouple. The thermocouple entered the reactor from the bottom through a Tee fitting (see Fig. 1). The reactor was suspended vertically in a Lindberg oven (Model 55035). The outlet lines were heat taped and nominally maintained at 160°C between the reactor and the high-pressure condenser. The condenser was constructed from a Whitey 150 mL SS sample cylinder to which copper tubing was silver soldered. During operation, the condenser was maintained at -5°C. The pressure letdown valve was a Whitey SS-22RS-4. A second condenser made from a 3-oz Fisher-Porter bottle was installed downstream of the letdown valve and was immersed in a Dewar filled with isopropanol/dry ice. The rest of the gas handling train consisted of a gas sampling port, Matheson rotameters for flow measurement, and a heavy walled flask containing saturated KOH for scrubbing H₂S before venting to the exhaust system. The parallel gas train which splits at the three-way ball valve, upstream of the letdown valve, allowed continuous operation during liquid sampling from the condenser (Fig. 1). The feed mixture was injected into the reactor by a calibrated Isco model LC-5000 high-pressure syringe pump. Hydrogen was supplied from a high-pressure cylinder with a regulator.

The trickle-bed reactor currently in use has been modified to improve mass balance and ensured adequate catalyst particle wetting and minimized liquid channeling. Thicker wall tubing has been employed in the reactor, and VCR glands were welded to both ends, adapted to a pipe threaded Conax fitting at the top and a 1/2 in. to 1/4 in. Swagelok reducer at the bottom. Directly below the reactor is a high-pressure condenser constructed from a Whitey SS sample cylinder of 150 mL volume. During operation the condenser is maintained at -5°C.

Materials. The catalysts used include MoO₃/γ-Al₂O₃ supplied by Strem Chemicals (#42-1500). The MoO₃ content was 10%-12%, and the surface area was 64 m²/g in the form of 3/16 in. x 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/MoO₃ on phosphoric acid co-precipitated γ-alumina was supplied by M. Maholland and S. Cowley at the Colorado School of Mines. Their detailed preparation and properties are described elsewhere (10). The Ni and Mo contents of the catalyst were 3% and 11.7%, respectively. The P:Al atomic ratio was 0.5, surface area was 8.2 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 % H₂S in hydrogen. The presulfiding was performed at 200°C for two hours then 400°C for an additional two hours.

Research grade hydrogen (99.999%) was used as supplied. 4PG was used without further purification as supplied by Frinton Laboratories (#1035). The feed mixture was 75 vol % 4PG in research grade hexanes with 0.25 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.

Analysis. The liquid samples (generally 0.75-1 g) were diluted to 100 mL in acetonitrile.

Water Determination:

The diluted samples were mixed 1:1 with an internal standard solution of absolute methanol in acetonitrile. The separation and quantitation of water was performed on a Varian 3700 gas chromatograph equipped with an autosampler, integrator, and a glass column 6 ft x 0.2 mm ID packed with Porapak QS. The carrier gas was high-purity helium.

Hydrocarbons and Phenolics Determination:

The individual reaction products were identified on a Hewlett Packard Model 5985 GC/MS. Each identification was checked by search and comparison with computer library spectra and by comparison with mass spectra generated from known standards for most of the compounds. The components were also identified by their retention times and were quantified on the Varian 3700 using a Supelco SPB5 wide bore capillary column, 30 m x 0.75 mm ID, 1- μ film. The column temperature was programmed starting at 40°C, held for two minutes then increased at a rate of 3 degrees/minute to 280°C. The injector and flame ionization detector temperatures were 220°C and 280°C, respectively. Helium carrier gas was used at 12 mL/min.

Gas Analysis:

Gas samples were analyzed on a Carle Model 111H gas chromatograph equipped with two thermal conductivity detectors, one for H₂ and the other for light hydrocarbons. After sample injection, hydrogen was separated by a Pd diffusion tube at 600°C and then a 5 ft x 1/8 in. Porapak Q (80/100) column using N₂ as the carrier gas. The remaining gases were separated on a series of three columns: (1) 6 ft x 1/8 in. Molecular Sieves, (2) 2.5 ft x 1/8 in. Squalane, and (3) 12 ft x 1/8 in. n-octane Poracil C using He as the carrier gas. The columns were accessed sequentially by automatic valves which are controlled by a Hewlett Packard 3388A integrator.

Operating Procedure. The reactor was operated in the integral mode for catalyst screening. The reactor was loaded with 1-1.5 g of catalyst which was presulfided as described above. A typical experiment was performed as follows. The chilled water circulator, oven, and heating tape were switched on and set to the desired temperatures. The hydrogen pressure regulator was used to pressurize the system to 500 psig. The syringe pump was loaded with the feed mixture and calibrated to the desired flow rate. Once all the temperatures had stabilized, the syringe pump was switched to inject the feed into the reactor and the hydrogen flow rate adjusted with the letdown valve to give the desired rate of 900 mL H₂/mL 4PG (equivalent to a typical petroleum hydrotreating rate of 5000 SCF/bbl). The system was allowed to equilibrate for one hour before sampling began. Liquid samples were obtained by switching to the parallel gas train, thereby isolating the condenser which was then depressurized. Samples were removed with a syringe through a septum at the bottom of the condenser. One gas sample was obtained toward the end of each run by switching to the parallel gas train, attaching an evacuated SS sample cylinder to the sampling port, and opening the letdown valve slightly to fill the cylinder.

Results and Discussion

4-Propylguaiaicol has been hydrotreated under a variety of conditions using MoS₂/ γ -Al₂O₃ and NiS-MoS₂/P: γ -Al₂O₃ catalysts in the temperature range of 250-450°C, at two molar hourly space velocities (MHSV 0.007 and 0.017 moles 4PG/g cat.*h which correspond to WHSV = 1.17 and 2.82 g 4PG/g cat.*h, 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 MoS₂ catalyst. Therefore, all experiments reported here were performed at 500 psig.

The major phenolic product from the MoS₂/γ-Al₂O₃ catalyst was 4-propylphenol having a maximum selectivity of 47% at 350°C and MHSV = 0.007 (see Table 1). At higher temperatures, hydrocarbon products such as propylbenzene, methylpropylbenzenes and propylcyclohexane are predominant. No reaction conditions studied so far with this catalyst have given significant yields of dealkylated products. This result is not surprising given that γ-Al₂O₃ is not a very acidic support.

Table 1. Selectivities of Major Products on MoS₂/γ-Al₂O₃

Temp. (°C)	Conversion (%)	Propylphenols (%)	Propylbenzenes (%)	Propylcyclohexane (%)
250	38	7.3	2.9	0
300	36	35.7	8.7	0
350	82	48.5	8.5	1.3
400	95	11.1	14.6	4.0
450	99	5.9	25.5	5.5

All reactions run at 500 psig, MHSV = 0.007 moles 4PG/g cat.*h. Conversion = (moles 4PG_{in} - moles 4PG_{out})/moles 4PG_{in} * 100. Selectivity = moles product/moles 4PG converted * 100.

The product slate obtained from 4PG on the NiS-MoS₂/P:γ-Al₂O₃ catalyst is notably different from that of the MoS₂/γ-Al₂O₃ catalyst. 4-Propylphenol remained the major product up to 350°C; however, significant dealkylation to phenol, cresols, and ethylphenols occurred (see Table 2). Figures 2 and 3 compare the selectivities of dealkylated phenolics from the two catalysts used. The more acidic catalyst support gave higher yields of dealkylated phenols at 300°C than the neutral support did at 450°C (6% vs. 3.5%, compare experiments 11 and 16 in Figures 3 and 2, respectively). This selectivity toward dealkylated phenols increased by a factor of 5 at 350°C (compare experiments 15 and 16). Interestingly, GC/MS data suggests that the major cresols formed are meta- and para-cresol having a selectivity as high as 15.5% at T = 400°-450°C and MHSV = 0.017 moles 4PG/g cat.*h. Again, at higher temperatures the yields of phenols decrease at the expense of hydrocarbon production. This product shift can be offset by increasing the space velocity as demonstrated in Figure 4. At 450°C and MHSV = 0.017, the selectivity to phenols is about 4 times the selectivity at MHSV = 0.007 (compare experiments 19 and 20 in Figure 4).

The gas analyses from the NiS/MoS₂ on phosphated γ-alumina catalyzed reactions support the evidence from the liquid analyses that the more acidic catalyst increases side chain cracking. At 400°C only 0.2 mole % of propane was detected in the gas from the Mo/γ-Al₂O₃ catalyst, whereas using the more acidic catalyst support, 0.5 mole % of propane was formed plus from 0.1 to 0.5 mole % 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.

Table 2. Selectivities of Major Products on NiS-MoS₂/P:γ-Al₂O₃

Temp. (°C)	Conversion (%)	Propylphenols (%)	Ethylphenols (%)	Cresols (%)	Phenol (%)
300	53	32.2	1.8	4.0	0
350	63	48.1	9.8	16.2	4.4
400	96	4.4	5.6	13.3	7.0
450	100	0.7	1.7	4.4	4.4

All reactions run at 500 psig, MHSV = 0.007-moles 4PG/g cat.*h. Conversion and selectivity as defined in Table 1.

The results reported here, while preliminary, demonstrate the direction of our research efforts to test systematically, well characterized catalysts and develop, with researchers at the Colorado School of Mines, bi-functional 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 are underway (11).

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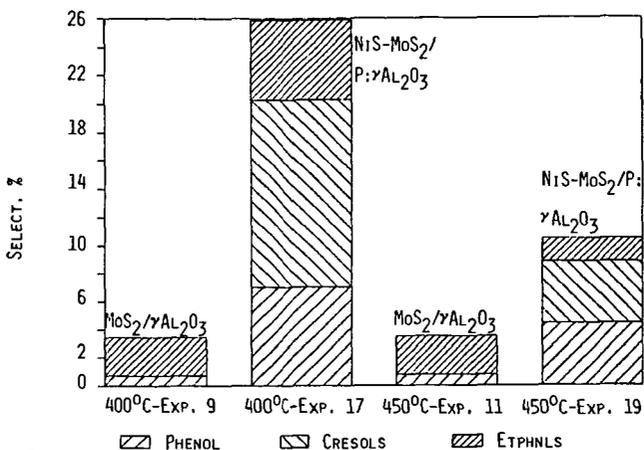


FIGURE 3. COMPARISON OF DEALKYLATED PHENOLS FROM 4-PROPYLGUIAIACOL HYDRO-TREATED ON $\text{MoS}_2/\gamma\text{Al}_2\text{O}_3$ AND $\text{NiS-MoS}_2/\text{PHOSPHATED-}\gamma\text{Al}_2\text{O}_3$, $\text{MHSV} = 0.007$ MOLES $4\text{PG}/\text{G CAT.}\cdot\text{H}$.

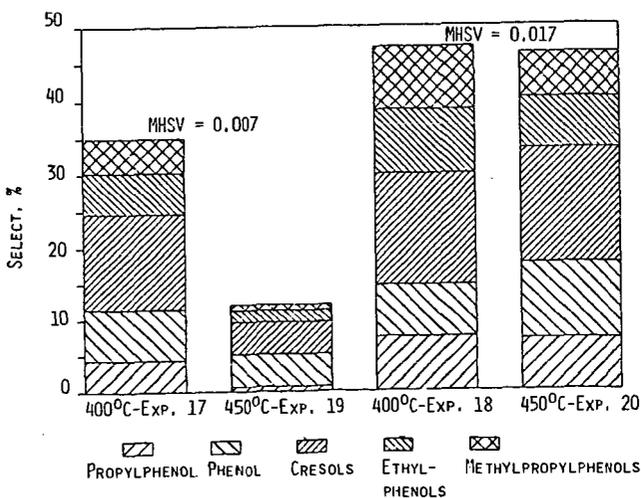


FIGURE 4. EFFECT OF SPACE VELOCITY AND TEMPERATURE ON THE SELECTIVITY OF PHENOLS FROM 4-PROPYLGUIAIACOL HYDROTREATED ON $\text{NiS-MoS}_2/\text{PHOSPHATED-}\gamma\text{Al}_2\text{O}_3$, $\text{MHSV} = \text{MOLES } 4\text{PG}/\text{G CAT.}\cdot\text{H}$.