

THE EFFECT OF COAL ADDITION
ON SOLVENT HYDROGENATION AND COAL CONVERSION
IN A MODEL ALKYLNAPHTHALENE SOLVENT

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INTRODUCTION

Model compounds are useful because they offer insight into the processes of more complex systems. They allow one to study a controlled system of known structure and relatively well mapped reaction pathways, in the hope that the information obtained therein is transferable to real systems. The problem with the study of model systems is that those very constraints which make the system easy to understand may in turn hinder the application of that understanding to real systems. This is particularly true in the study of coal liquefaction, where the complexity of the coal system often gives rise to unanticipated results.

The current paper discusses how the addition of even small amounts of coal (1:1 coal:catalyst) can dramatically affect the catalytic hydrogenation of model two-ring aromatic solvents. The catalyst, a novel, unsupported molybdenum catalyst preformed during a separate solvent hydrogenation step, appears to be selectively deactivated toward solvent hydrogenation, but not coal conversion. The effect is observed in two model solvent systems, 1-methylnaphthalene and Panasol. Adding coal-derived preasphaltene and asphaltene materials seems to have the same effect.

EXPERIMENTAL SECTION

Materials. Panasol[®], a mixture containing mostly alkyl naphthalenes, was obtained from Crowley Chemical Company and used without further purification. Purified grade 1-methylnaphthalene from Fisher Scientific Company, found to be 99% pure by gas chromatography, was used without further purification. Blind Canyon coal, DECS-6, from the U.S. Dept. of Energy's Coal Sample Program, was used in these studies. A unique, high surface area, preformed molybdenum catalyst was prepared at the U.S. Dept. of Energy's Pittsburgh Energy Technology Center (PETC). The catalyst consisted of the recovered solid from a semi-batch 1-L stirred autoclave reaction of ammonium heptamolybdate, hydrogen sulfide, and Panasol under 17 MPa (2500 psi) hydrogen at 425°C [1]. The catalyst contained 50% C, 30% Mo, and 20% S, and possessed a BET surface area of approximately 250 m²/g. The supported iron catalyst was prepared by precipitation of FeOOH from a solution of ferric nitrate onto Raven[®] carbon black. The supported molybdenum catalyst was prepared in a similar fashion from ammonium heptamolybdate.

Reactions. Reactions were completed in a stainless steel batch microautoclave reactor system constructed at PETC. The cylindrical reactor portion has a volume of 43 mL, and the total internal volume, including all tubing and connections, is 60 mL. The reactor was equipped with an internal thermocouple and a pressure transducer for continuous monitoring of pressure and temperature throughout the run. The reactor was mounted on a rocker arm, which extends into an electrically heated sand bath. In typical experiments, the reactor was charged with various combinations of solvent, coal, catalyst, a sulfur source, and then was pressurized with hydrogen. Unless otherwise stated, a full charge consisted of 6.6 g solvent, 3.3 g coal, 0.1 g catalyst, 0.1 g sulfur, and 7 MPa (1000 psi) ambient temperature hydrogen gas. The reactor was then attached to the rocker arm (180 cycles / minute) and plunged into a preheated sand bath, where it was heated up to 425°C in 2 to 4 minutes. It was held at temperature in the sand bath for 30 minutes, and then removed and allowed to air cool, typically in less than 5 minutes, to room temperature. The reactor was vented and the gas collected for analysis.

Sample Workup Procedure and Coal Conversion Calculation. During workup, the reactor (including tubing) was cleaned and rinsed with tetrahydrofuran (THF). The material collected was combined and filtered through a 0.45 micron filter under 40 psi nitrogen gas pressure, yielding the "THF solubles" and "THF insolubles." Coal conversion was calculated based on the mass of MAF coal from the measured mass of THF insolubles adjusted for catalyst and coal mineral matter. After the THF insolubles were

weighed, the soluble material was stripped of solvent on a rotary evaporator until mass balance was obtained. Although this generally removed most of the THF solvent, some was occasionally observed by H-1 nuclear magnetic resonance (NMR) in the resulting THF soluble fraction. In runs where coal was used in the reactor, the THF solubles were extracted by heptane, and the procedure was repeated to obtain a heptane-soluble fraction. In each case, the soluble portion was derived essentially from the original Panasol or 1-methylnaphthalene solvent and its reaction products, and (when coal was present) a small amount of coal-derived material.

Gas and Pressure Analyses. At the completion of each run, product gases were collected and analyzed at PETC by a previously published method [2]. Total hydrogen consumption for the run was calculated based on the difference between initial and final (cold) gas pressure as adjusted for product gas slate. In some runs, gas composition data were not available, or had to be estimated from a similar experiment. Hydrogen consumption as a function of time was calculated from the total (hot) gas pressure, recorded at 10 s intervals during the run, total hydrogen consumption, and the assumption that product gases were produced in a linear fashion throughout the run. Assumptions were also made concerning the liquid-vapor equilibrium of the solvent, the solubility of hydrogen in the liquid phase, and the fact that part of the reactor tubing does not extend down into the hot sand bath. A more complete description of the hydrogen consumption measurements is found in reference 3.

Gas Chromatography. Gas chromatography was performed either with a Hewlett Packard HP5880A gas chromatograph (GC) equipped with flame ionization detector (FID) or a Hewlett Packard HP5890A GC equipped with an HP5970 mass selective detector (GC/MS).

Low-Voltage, High-Resolution Mass Spectrometry (LVHRMS). LVHRMS data were obtained on a Kratos MS-50 high-resolution mass spectrometer interfaced to a personal-computer-based data system developed at PETC. The sample was introduced into the ion source through the batch inlet system at a temperature of 200°C. The magnet was operated with a static resolving power exceeding one part in 30,000 with an average dynamic resolving power (while scanning) of one part in 26,000. Quantitative calibration of tetralins relative to naphthalenes was accomplished with known mixtures of tetralin and 1-methylnaphthalene. Further details on the LVHRMS technique and data reduction routines are provided in references 4 and 5.

Nuclear Magnetic Resonance. Both H-1 and C-13 NMR of the samples were recorded on CD₂Cl₂ solutions of the samples on a Varian VXR-300 NMR spectrometer equipped with a 5-mm broadband probe. C-13 NMR spectra were the result of 700 time-averaged scans recorded with 90° pulse widths and a recovery time of 60 s, requiring approximately 12 hours of spectrometer time per spectrum. Decoupling was applied only during acquisition.

RESULTS AND DISCUSSION

Verification of Analytical Results: 1-Methylnaphthalene and Panasol Solvents. In order to verify the accuracy and reproducibility of the analytical methods, microautoclave hydrogenations were made using 1-methylnaphthalene solvent, 7 MPa initial (cold) hydrogen pressure, and (if used) catalyst. The series consisted of a thermal (no catalyst) run, the preformed dispersed molybdenum catalyst (Mo), an iron (Fe/C) and a molybdenum (Mo/C) catalyst, the latter two supported on carbon black. 1-Methylnaphthalene, 5- and 1-methyltetralin, naphthalene, and tetralin constitute 97% of the products (by GC) from this simple solvent system. Independent determinations of 1-methylnaphthalene hydrogenation to tetralins were made by each of the analytical methods: gas analysis, GC, LVHRMS, and NMR. The results, their averages and standard deviations are listed in Table 1.

Panasol is a fairly complex hydrocarbon mixture, with some 130 GC peaks above the 0.01% threshold level. It contains about 80% alkylated naphthalenes (2-methylnaphthalene is the largest single constituent at 22%), and 5-10% each of alkylated benzenes, tetralins, and biphenyls. It has a proton aromaticity of 0.48, and a carbon aromaticity of 0.84, corresponding to an "average" structure of dimethylnaphthalene. Since the alkylnaphthalenes in Panasol were expected to hydrogenate similarly to 1-methylnaphthalene, a series of microautoclave reactions with Panasol was completed under the same conditions as those for the samples of Table 1.

The results are given in Table 2. For GC and LVHRMS, the hydrogenation determination was made from direct measurement of naphthalenes and tetralins in the products as compared to the starting Panasol. Hydrogenation was estimated from gas analysis by fitting the hydrogen consumption with that necessary to convert a given amount of dimethylnaphthalene to the corresponding tetralins. Hydrogenation was estimated from NMR data by fitting the aromaticity change to a given conversion of dimethylnaphthalene to the corresponding tetralins. Although the hydrogenation estimates for Panasol do not agree with each other as well as they do in Table 1, the average results are still within the standard deviation of the 1-methylnaphthalene hydrogenations.

Effect of Coal Addition on Solvent Hydrogenation Using Preformed, High Surface Area Mo Catalyst. A series of microautoclave experiments was completed using 6.6 g of either 1-methylnaphthalene or Panasol solvent, 7 MPa initial (cold) hydrogen pressure, and 0.1 g preformed high surface area molybdenum catalyst. The runs contained 0.0, 0.1, 0.2, and 3.3 g of coal, respectively. Figure 1 shows the hydrogen consumption plotted as a function of time over the course of each run. A substantial amount of hydrogen is consumed during the heat-up period (i.e., before time zero in Figure 1); in fact, the "liquefaction" of the 0.1 and 0.2 g coal samples is probably completed by the time the plot starts. The residual, or observed hydrogen consumption is most likely due to hydrogenation of the solvent. In the Figure, it can be seen that the rate of hydrogen consumption consistently follows the order 0.0 g > 0.1 g > 0.2 g. The rate for the 3.3 g coal sample is still trending downward at the end of the run, with hydrogen consumption probably attributable to coal conversion rather than solvent hydrogenation.

Total hydrogen consumption for these runs, including the heat-up periods, is listed in Table 3. Not surprisingly, the greatest hydrogen consumption, 55 mmol, was found with the highest loading of coal, 3.3 g. This can be attributed to the fact that two acceptors were available for the gaseous hydrogen - both the solvent and the coal. Consistent with Figure 1, the addition of small amounts of coal to the solvent does not produce an intermediate result. Rather, the total hydrogen consumption with both 0.1 g (26 mmol H₂) and 0.2 g (22 mmol H₂) of added coal is less than that for either no added coal (29 mmol H₂) or 3.3 g added coal. For comparison, the thermal hydrogenation of 1-methylnaphthalene and Panasol, listed in Tables 1 and 2, consumed only 2 and 3 mmoles hydrogen, respectively. The results are more striking when one examines hydrogenation of naphthalenes in the solvent as analyzed by LVHRMS. The percentage of naphthalenes converted to tetralins is highest in the no coal case, and decreases rapidly with increasing amounts of added coal, from 31% to 12%. Unfortunately, heptane contamination from the workup procedure makes it impossible to obtain a quantitative estimate of solvent hydrogenation from NMR aromaticity measurements. However, the results are qualitatively supported by examination of the NMR spectra.

These results demonstrate that the rate of hydrogenation of these solvents is diminished by the presence of small amounts of coal in the reactor. However, the total hydrogen consumption was still greatest for the maximum loading of coal. That is, hydrogen was still going to the coal though not to the solvent. One explanation for this phenomenon might be that the type of structures present in the coal and initial coal derived products hydrogenate more readily than the solvent. In a popular model of liquefaction, the first products of coal dissolution are the asphaltenes and preasphaltenes. These are generally thought of as large, aromatic systems consisting of three or more condensed rings. This argument is supported by work which has shown that three ring systems hydrogenate faster than two ring systems [6]. However, the argument is difficult to accept in circumstances where only a small amount of coal is present. The results of Figure 2 would seem to indicate that coal dissolution happens very quickly in these cases. Even if the coal-derived products hydrogenate more quickly, there would still be adequate time and hydrogen to hydrogenate the solvent.

Effect of Recycled Catalyst on Subsequent Reactions. The next sequence of experiments helps illustrate what happened to the catalyst on exposure to coal. These experiments begin with the THF insolubles from the reaction which had employed 0.2 g of coal with fresh catalyst, cited in the previous series ("A" in Figure 2). This material, presumably consisting of the recovered catalyst and a very small amount of unreacted coal, was used as the catalyst for a new experiment, hydrogenating 1-methylnaphthalene solvent with no fresh coal ("B" in Figure 2). The THF insolubles from the second run were used as the catalyst in a third run, this time containing 1-methylnaphthalene solvent and 3.3 g coal ("C" in Figure 2). The total hydrogen consumption, solvent hydrogenation as measured by LVHRMS, and coal conversion (in the cases where 3.3 g of coal was

reacted) are summarized in Figure 2. The same data for experiments with 3.3 g coal with fresh catalyst ("D"), and 0.0 g of coal with fresh catalyst ("E"), are included for comparison.

Solvent hydrogenation, as seen in Figure 2, is highest for the case of fresh catalyst, and no added coal. Solvent hydrogenation drops by a factor of over two upon exposure of the catalyst to 0.2 g coal, and does not recover, maintaining its value when the recycled catalyst is used in a subsequent run. Solvent hydrogenation drops further when the catalyst is exposed to more coal. Coal conversion, on the other hand, is uninhibited by the use of recycled catalyst. Hydrogen consumption is highest for the experiments which employed a full charge (3.3 g) of coal, intermediate for the case of fresh catalyst and no coal, and lowest for cases in which the catalyst had been exposed to coal but there was not enough coal present to take up hydrogen itself.

In an effort to pinpoint the origin of the catalyst inhibitor, 0.4 g of the THF-solubles, heptane-insolubles fraction (i.e., asphaltenes and preasphaltenes) was taken from a reaction which had employed 3.3 g coal and fresh catalyst and added to a hydrogenation reaction containing 1-methylnaphthalene and fresh catalyst, but no coal. The result ("E") is displayed with the others in Figure 2. Solvent hydrogenation (at 4%) was almost completely suppressed to levels below those obtained with 3.3 g coal present. Hydrogen consumption was much the same as when fresh catalyst was used with small amounts of coal or recycled catalyst was employed.

Discussion and Conclusion. The results of Figure 2 are not consistent with a simple competition for catalyst sites. The fact that solvent hydrogenation with coal present did not recover to previous levels with the "recycled" catalyst indicates some persistent change in the catalyst, i.e., poisoning. The fact that there was no impairment of coal conversion when coal was added, together with a hydrogen consumption value similar to what it would have been for fresh catalyst, indicates that any deactivation of the catalyst did not affect coal conversion.

Plainly, some deactivation of the catalyst has taken place. Otherwise the diminution in solvent hydrogenation would not have occurred. However, a substantial amount of catalytic activity remains. There is no other explanation for the coal conversion or total hydrogen consumption data with 3.3 g coal.

Supported and unsupported catalysts have been used for first stage coal liquefaction. Exposure to coal has been known to affect the long-term activity of supported catalysts. Unsupported catalysts are normally once-through catalysts and are not exposed to coal for long times. Long term deactivation of unsupported catalysts would not be a problem. Rapid and selective deactivation of specific catalyst sites upon exposure to coal would be a greater concern.

Deactivation of supported catalysts has been the subject of a number of studies [7]. The poisoning effect of nitrogen bases on catalysts, especially for those catalysts which have acidic active sites, has been extensively studied in the areas of petroleum cracking [8], coal liquefaction [9], and coprocessing [10]. The formation of carbonaceous deposits on the catalyst surface has also been implicated in the loss of hydrogenation activity in coal liquefaction catalysts [11]. Studies have shown that carbon supports confer higher resistance to fouling by carbonaceous deposits than do alumina supports [12]. The preformed, high surface area molybdenum catalyst used in the coal addition studies reported here is an unsupported catalyst in the sense that it is being developed for once-through use. However, the catalyst still contains 50% carbon, and probably shares much in common with molybdenum catalysts on carbon supports. The observation of catalyst poisoning is therefore significant.

The fact that solvent hydrogenation (at least that of double-ring aromatic compounds) is inhibited while coal conversion, a process which also requires hydrogen, is not, would support the existence of different types of catalytically active sites. Suppose the catalyst contains different types of active sites, and some of these sites bind substrates more strongly than others. In this representation, the best, i.e., most strongly interacting sites are required for hydrogenation of Panasol. However, other weaker sites exist in greater numbers, and are adequate for providing hydrogen to the decomposing coal matrix. Most catalyst poisons act by adhering to an active site and preventing interaction with any other substrates. If the poisoning agent, whatever its identity, is not a particularly strong catalyst poison, it would only adsorb and adhere to the most strongly interacting

sites. In this manner, the sites needed for solvent hydrogenation would no longer be available. On the other hand, the byproducts of coal conversion can use the less active sites, so conversion remains relatively unchanged. Such a system would exhibit the observed characteristics of both catalyst poisoning and competition for catalyst sites.

At this point, it is not known whether the hydrogen going to the coal is involved with hydrogenating aromatic rings, or simply capping fragments formed from bond scission. However, these preliminary results would appear to serve as a warning that the best catalysts for coal liquefaction may not necessarily be found by hydrogenating model compounds.

Further work is in progress to identify the poisoning agent or agents, and to determine if its effect on the catalyst is reversible.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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**TABLE 1: Comparison of Analytical Results
for 1-Methylnaphthalene Hydrogenation**

<u>Technique</u>	<u>Thermal</u>	<u>Mo</u>	<u>Mo/C</u>	<u>Fe/C</u>
Gas Analysis	2%	37%	58%	33%*
GC	2%	31%	50%	25%
LVHRMS	0%	29%	50%	20%
C-13 NMR	2%	29%	45%	20%
AVERAGE\pmSD	2\pm1%	32\pm4%	51\pm5%	25\pm6%

* gas pressure data estimated due to leak

**TABLE 2: Comparison of Analytical Results
for Panasol Hydrogenation**

<u>Technique</u>	<u>Thermal</u>	<u>Mo</u>	<u>Mo/C</u>	<u>Fe/C</u>
Gas Analysis	4%	34%	55%	27%
GC/MS	NA	NA	46%	17%
LVHRMS	1%	31%	56%	31%
C-13 NMR	5%	25%	36%	27%
AVERAGE	3%	30%	48%	26%

**TABLE 3: Effect of Added Coal on Naphthalene Hydrogenation by
Preformed Dispersed Molybdenum Catalyst**

<u>Solvent</u>	<u>Coal (g)</u>	<u>mmol H₂ Consumed</u>	<u>% Naph to Tet (LVHRMS)</u>
Panasol	0.0	29	31
1-MeNp	0.1	26	22
Panasol	0.2	22	14
Panasol	3.3	55	12

Figure 1: Effect of Added Coal on the Rate of H₂ Consumption.

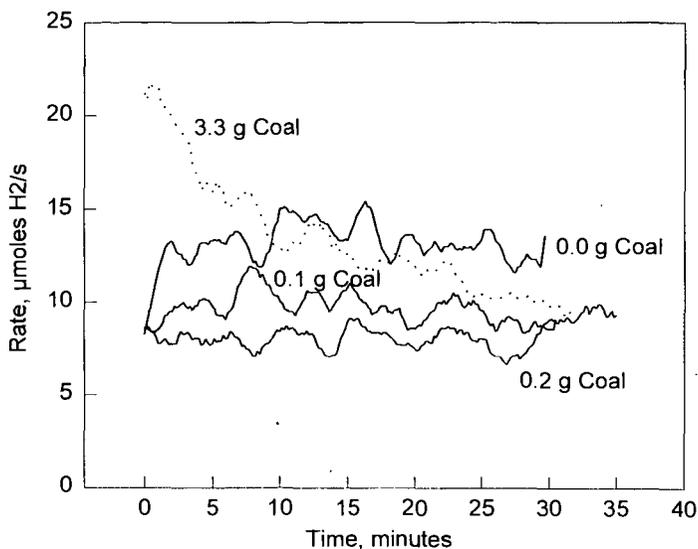
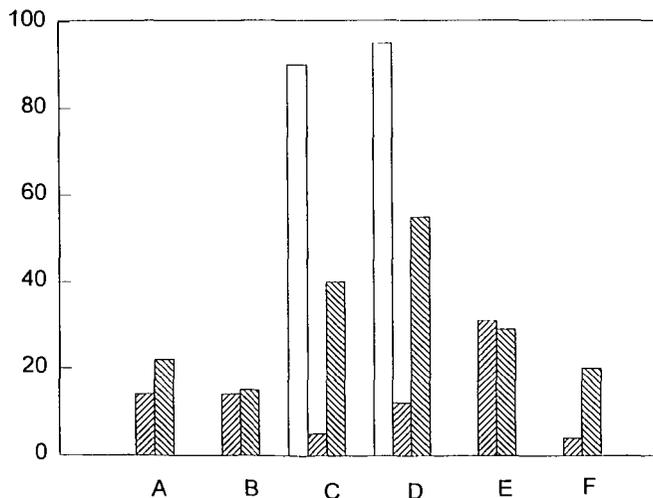
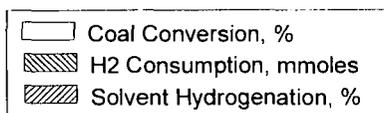


Figure 2: Summary of Coal Conversion, Solvent Hydrogenation and Hydrogen Consumption for Fresh and Recycled Catalyst



A: 0.2 g Coal, Fresh Catalyst
 B: No Coal, Recycled Catalyst from "A"
 C: 3.3 g Coal, Recycled Catalyst from "B"
 D: 3.3 g Coal, Fresh Catalyst
 E: No Coal, Fresh Catalyst
 F: No Coal, 0.4 g THF Solubles, Fresh Catalyst