

THE EFFECT OF H₂ PARTIAL PRESSURE AND COAL CONCENTRATION ON CATALYTIC COAL LIQUEFACTION AND COPROCESSING

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INTRODUCTION

An effort is under way at PETC to study the potential of reducing pressure in coal liquefaction. The objective of this effort is to reduce pressure and maintain overall coal conversions, yields and product quality. Several observations have been made during this study and have been reported.^{1,2,3} The potential for reducing pressure appears to be tied to a combination of solvent quality and catalyst concentration. Other observations were made concerning the hydrogenation of products from reactors containing coal. These include suppression of two-ring aromatic hydrogenation in the presence of coal and the large consumption of hydrogen observed in the earliest stages of coal liquefaction.

Cugini et al.¹ and Rothenberger et al.² reported that catalytic hydrogenation of naphthalenes is suppressed in the presence of coal (using supported or unsupported catalysts). This effect was also observed in several other studies.^{4,5,6} The efforts of Cugini et al.² also indicated the need for a combination of catalyst and donor solvent system to reduce pressure. They found that the donor solvent/low pressure/no catalyst system resulted in consistently lower coal conversions than the non-donor solvent/high pressure/catalyst system. Also, high hydrogen consumption was observed during the early stages of catalytic coal liquefaction. Approximately 50% of the hydrogen consumption during a 30-minute test occurred during the heat-up (~ 2 minutes) and subsequent 2 minutes of the test.

The current effort attempts to provide more information regarding the suppression of catalytic hydrogenation of aromatic compounds by coal and the high initial consumption of hydrogen in catalytic liquefaction. The observation of suppression of catalytic hydrogenation of two-ring aromatic compounds is extended to other multi-ring aromatic compounds. These include phenanthrene and pyrene. Also, short-time liquefaction tests are being studied to determine the differences between donor/non-catalytic and non-donor/catalytic systems.

The remainder of the study was directed toward the investigation of coal/oil coprocessing. The effect of coal concentration, catalyst concentration and pressure were investigated as part of this study. The earlier results from coal liquefaction studies had indicated that pressure and catalyst concentration were interrelated. This phase of the effort attempts to extend the results from the coal liquefaction efforts to coal/oil coprocessing. Essentially, it is hoped that catalyst could (to some extent) be used to compensate for pressure reduction as was observed in coal liquefaction applications. Lower coal concentrations were also investigated because of earlier results that had indicated that a synergism to distillate product was observed at low concentration and that coal could be used to effectively remove the metals from the liquid products even at relatively low coal concentrations.⁷

EXPERIMENTAL

Materials. Purified grade 1-methylnaphthalene (1-MN), phenanthrene, pyrene, and tetralin from Fisher Scientific Company were used in these studies. Hondo residual oil, vacuum tower bottoms obtained from Paramount Petroleum Corporation, was used. Blind Canyon coal, DECS-6, from the U.S. Department of Energy's Coal Sample Program and Illinois No. 6 coal were used. A supported molybdenum catalyst, Akzo AO-60, obtained from HTI, Inc. was used in the microautoclave catalytic tests. An unsupported MoS₂ catalyst prepared at PETC² was also used in the microautoclave tests. Aqueous ammonium heptamolybdate (AHM) was used as the precursor for MoS₂ in the 1-L semi-batch tests.

Reactions. Microautoclave reactions were completed in a stainless steel batch microautoclave reactor system (42 mL) constructed at PETC. Semi-batch 1-L reactions were completed in a stainless steel 1-L autoclave. A 97% H₂ / 3% H₂S gas mixture was used in the 1-L tests to sulfide the catalyst. Sample work-up and coal conversions for both the microautoclave and 1-L autoclave tests were calculated by a procedure described previously.⁸

Gas and Pressure Analyses. At the completion of each run, product gases were collected and analyzed at PETC by a previously published method.³ Hydrogen consumption was determined by a method developed at PETC.⁴

GC-Mass Spectrometry (GC-MS). The THF soluble material from the autoclave runs was analyzed by GC-MS to determine the amount of solvent which had been hydrogenated. The samples were run as 1% solutions (w/w) in methylene chloride on a HP 5890A gas chromatograph equipped with a 50 m capillary column of 50% phenylmethylsilicone and a HP 5970 mass selective detector. The integrated areas of hydrogenated solvent peaks were compared against those of unconverted solvent peaks.

RESULTS

The initial studies were directed toward the effect of solvent type. As indicated, coal was found to suppress the catalytic hydrogenation of 1-MN. Two other aromatic solvents, pyrene and phenanthrene, were tested to evaluate the effect of coal addition on aromatic hydrogenation. The results from testing the two solvents as well as the earlier data with 1-MN are shown in Table 1. The data indicate that catalytic hydrogenation of pyrene and phenanthrene is suppressed by the presence of coal as shown by comparing tests B and C for the two cases. Further, exposure to coal continues to suppress the catalytic hydrogenation of phenanthrene even after coal is removed from the system, as shown by a comparison of tests B and D for phenanthrene. However, the results from the pyrene system are not as straightforward, because the tests using fresh catalyst and catalyst recovered after exposure to coal (tests B and D for pyrene) both appear to reach equilibrium⁹ within the reaction time. Figure 1 shows the pressure as a function of time for the two tests with pyrene, fresh catalyst and catalyst exposed to coal. In the case with fresh catalyst, the pressure drops rapidly to 1,470 psig before the pressure levels off for the remainder of the test. This indicates that equilibrium is rapidly achieved during the test. On the other hand, with the catalyst that had been exposed to coal, the pressure drops continuously over the course of the test. This indicates that equilibrium was achieved only after the full reaction time. The net result is that the rate of catalytic hydrogenation of pyrene was also suppressed by exposure of the catalyst to coal just as in the other two examples.

Table 1. Effect of Blind Canyon Coal Addition on Catalytic Hydrogenation of Aromatic Solvents

Microautoclave Sample	Percentage of Product					% Hydrog.
	0-H	2-H	4-H	6-H	other	
Pyrene:						
(A) pyrene only	96	4	0	0	0	4
(B) with catalyst	68	21	2	8	1	32
(C) with coal + catalyst	85	14	0	0	1	15
(D) with THF insols from (C)	66	23	2	6	2	34
Phenanthrene:						
(A) phenanthrene only	97	2	0	1	0	4
(B) with catalyst	47	12	10	24	7	53
(C) with coal + catalyst	80	13	5	1	1	20
(D) with THF insols from (C)	67	16	13	0	4	33
1-Methylnaphthalene:						
(A) 1-MN only	100	----	0	----	0	0
(B) with catalyst	47	----	52	----	1	53
(C) with coal + catalyst	92	----	7	----	1	8
(D) with THF insols from (C)	86	----	12	----	2	14

425°C, 0.5 h, 1000 psig H₂ (cold), and 1000 ppm Mo

Short-time tests were made to compare the effects of catalyst and tetralin on coal conversion. Fast heat-up rates and 2-minute and 30-minute duration tests were conducted. The results of these tests are shown in Table 2. These results indicate that, in this time interval, coal conversion was enhanced in the catalytic case over the tetralin case. Detailed analyses of the insoluble products are being conducted to determine if more coke or hydrogen-deficient species are observed in the tetralin case.

Table 2

Effect of Solvent Quality, Pressure, and Catalyst on Blind Canyon Coal Conversion

					Coal Conversion
A	Tetralin	400 psig (cold)	No Catalyst	2 minutes	70%
B	Tetralin	1000 psig (cold)	No Catalyst	2 minutes	73%
C	Tetralin	400 psig (cold)	No Catalyst	30 minutes	85%
D	Tetralin	1000 psig (cold)	No Catalyst	30 minutes	86%
E	1-MN	1000 psig (cold)	AO-60	2 minutes	79%
F	1-MN	1000 psig (cold)	AO-60	30 minutes	89%
G	1-MN	1000 psig (cold)	MoS ₂	30 minutes	93%

The effects of pressure and coal concentration in coal/oil coprocessing were studied in batch autoclave tests. The results are shown in Figure 2. The results indicate that there does appear to be an area at low coal concentration (between 0 and 10% coal) where the distillate conversion is higher than with no coal. Above 10% coal, the distillate conversion falls with increasing coal concentration. This trend was observed at two pressures, 1,000 and 2,500 psig. As catalyst concentration was increased from 100 ppm Mo to 300 ppm Mo, conversion increased. It appeared that, like in the coal liquefaction system, catalyst concentration could be used to compensate for the effect of pressure reduction.

SUMMARY

The results obtained indicate that the catalytic hydrogenation of two-ring aromatic compounds and several types of multi-ring compounds are suppressed in the presence of coal. It appears that the suppression is the result of a combination of competition and poisoning of specific catalytic sites. This is due to the fact that catalytic hydrogenation of aromatics remains suppressed even after coal is removed from the system.

In the case of tetralin as a donor solvent for coal liquefaction, it seems that there is insufficient hydrogen donated during the early stages of coal liquefaction to prevent the formation of hydrogen deficient species. This results in lower coal conversion compared to catalytic cases. This may contribute to the consistently lower conversions observed in tetralin tests compared to catalytic tests.

Coal/oil coprocessing may be most effective at lower coal concentrations. The distillate yields are higher at coal concentrations between 0 and 10%. At higher coal concentrations the distillate conversion drops with increasing coal concentration. The potential for reducing pressure in coal/oil coprocessing is enhanced by increasing catalyst concentration. At lower pressures, increasing catalyst concentration increases conversions and distillate yield.

DISCLAIMER

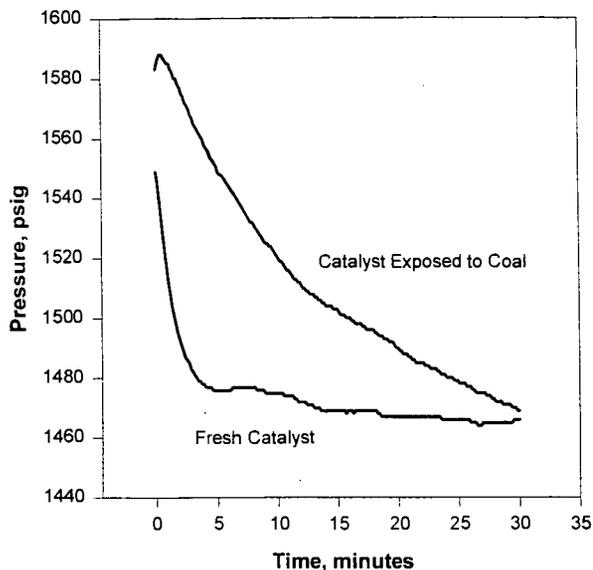
Reference in this manuscript to any specific commercial product or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Figure 1

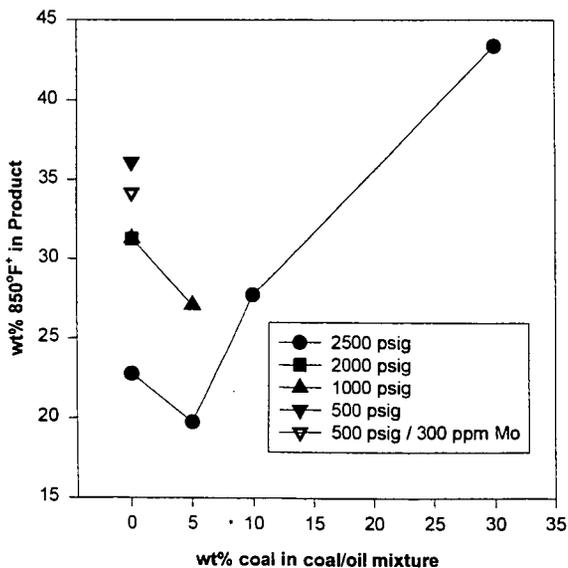
Effect of AO-60 Exposure to Coal on Pyrene Hydrogenation



Microautoclave 425°C, 30 minutes, and 1000 psig H₂ (cold)

Figure 2

Effect of Coal Concentration and Pressure in Coprocessing



Semi-Batch 1-L Autoclave 425°C, 1 h, 100 ppm Mo (added as AHM), 2:1 Hondo Resid to Illinois No. 6 Coal