TECHNOLOGY FOR ADVANCED LIQUEFACTION PROCESSES: COPROCESSING STUDIES

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PROJECT OVERVIEW:

The efforts in this project are directed toward four areas: (1) pressure reduction, (2) coal/oil coprocessing, (3) dispersed catalysts, and (4) coal waste coprocessing.

The effect of reducing pressure in coal liquefaction has been part of the effort at the Pittsburgh Energy Technology Center (PETC) for the past two years. The objective of this effort is to reduce pressure without sacrificing product quality or overall conversion and yields. The results to date indicate that a combination of catalyst and solvent quality could be used to effectively reduce pressure.

Past efforts in coal/oil coprocessing had indicated that two significant benefits could be obtained from this approach: (1) demetalation of heavy oils by coal, and (2) higher distillate yields at low coal concentrations. The current effort is aimed at evaluating the relative effects of pressure, dispersed catalysts, and coal concentration in coal/oil coprocessing.

Dispersed catalysts have been the focus of several studies at PETC. One of these studies involved testing a series of dispersed catalysts in batch and continuous tests. Based on these tests, a database was produced which has been used to select catalysts for tests at larger-scale operation. The current effort is directed toward expanding the database to other catalysts. Also, better methods to feed and activate dispersed catalysts in continuous systems are being investigated.

Studies of coal/waste coprocessing in continuous units aimed at investigating the operability, yields and conversions are underway. These studies are coordinated with the technical coordination plan developed by the Advanced Waste Coprocessing Team to develop approaches to waste coprocessing.

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. [3] 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 MoS_2 catalyst prepared at PETC[2] was also used in the microautoclave tests. Aqueous ammonium heptamolybdate (AHM) was used as the precursor for MoS_2 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. Continuous tests were conducted in PETC's 1-L continuous hydrotreating unit. Unit operations, sample work-up and coal conversions for the microautoclave, 1-L batch autoclave, and continuous tests were 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

Model Solvent Hydrogenation. 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 equilibrium[9] 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

	Percentage of Product					
Microautoclave Sample	0-H	2-H	4-H	6-H	other	% Hydrog.
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 H_2 (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%

Coal-Oil Coprocessing. 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.

Coprocessing tests were also conducted in the continuous unit. The results of these tests are shown in Figure 3. A similar trend with respect to coal conversion was observed in the continuous unit as was observed in the batch. Both the 850°F^{+} and heptane insoluble conversions increased from 0% to 5% coal concentration and decreased from 5% to 30%. The effects of pressure and catalyst concentration are also being studied in the continuous unit.

Advanced Waste Coprocessing. A PETC single-stage continuous unit was used to investigate the effect of temperature, waste concentration, and pressure in Advanced Waste Coprocessing. From previous microautoclave (reported in the status report) and semi-batch (above) studies, higher temperatures were required in coprocessing to increase the conversion of HDPE. Figure 4 shows the effect of increasing temperature from 430 to 460°C. Also shown is the effect of replacing coal with plastic (at 430°C). Consistent with the earlier studies, increasing temperature increases the overall conversion. At 430°C, replacing about one third of the coal with plastic enhances the conversion to distillable products. Increasing the amount of coal replaced to approximately 50% of the coal results in no benefit in conversion.

The potential to reduce pressure in coprocessing is one of the appealing facets of coprocessing. Figure 5 presents the effect of pressure and waste concentration with no coal. The solvent used in this series was a coal-derived recycle solvent (L-814) obtained from HTI. This solvent contains approximately 20% material boiling above 850°F. The plastics used in this series was the mixed plastic (50% HDPE, 35% PS, and 15% PP). Also shown on the figure was an actual waste material obtained from Monmouth Recycling Facility (described above). Decreasing the pressure from 1,500 psig to 500 psig resulted in decreased conversion. However, it is not clear whether the decreased conversion can be attributed to loss of waste conversion or decreased conversion of the 850°F+ material in the L-814. It appears that the conversion drop may be attributable to the L-814 material because when the plastics concentration was increased (essentially displacing L-814 material) at 500 psig conversion increased.

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 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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