ADVANCED LIQUEFACTION PROCESSES RESEARCH

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Recent activities at PETC have been directed toward three areas: examining the effect of solvent quality/catalyst activity to enable operation at lower pressures, coal/oil coprocessing with dispersed catalysts, and coal/waste coprocessing. Previous microautoclave and batch testing has explored coal liquefaction activity at hydrogen pressures below 2500 psig. Efforts in the current year have extended the work to continuous operations in a 1-liter unit at pressures of 2000 and 1500 psig. Regarding coal/oil coprocessing, the use of FCC decant oil and Hondo Resid will be discussed. Previous coal/oil coprocessing efforts at 30 % coal were expanded to include 5 and 10 % coal cases. Testing of dispersed catalysts was extended to the petroleum resid-only system. Efforts under coal/waste coprocessing now include tests with actual waste plastics. Previous coal/waste coprocessing tests utilized a simulated waste plastic mixture to investigate the effect of composition on slurry rheological properties and reactor temperature on yields.

INTRODUCTION

Current research activities at PETC are examining the potential for reducing pressure and utilizing waste plastics and/or petroleum bottoms material as a vehicle. The objective is to reduce pressure while maintaining overall coal conversions, yields, and product quality. The potential for reducing pressure appears to be tied to a combination of solvent quality and catalyst concentration. Other observations concerned the influence of coal on the hydrogenation of products under liquefaction conditions. These include suppression of 2-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] indicated the need for a combination of catalyst and donor solvent 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. These studies also indicated high hydrogen consumption during the early stages of catalytic coal liquefaction. In micro autoclave studies, 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.

These efforts were directed toward coal/oil coprocessing. The effect of coal concentration, catalyst concentration and pressure were investigated. Earlier results from coal liquefaction studies 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 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 indicated 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: Liquefaction experiments were conducted with minus 200-mesh Illinois No. 6 coal (Burning Star No. 2). Coal/waste coprocessing experiments utilized plastics supplied by Hydrocarbon Technology Inc. (HTI) as 3.2-mm (1/8-in) extrudates. High density polyethylene (PE), melting point 135°C, density 0.96g/mL, was manufactured by Solvay Polymers. Polystyrene (PS), melting point 95°C, was manufactured by BASF. Polypropylene (PP), density 0.94g/mL, was manufactured by AMCO Plastics. Waste plastics from the Monmouth County Recycling Facility (New Jersey) was shredded to 1/4 x 3/4 in. and obtained from HTI. All plastics were mixed with dry ice and ground before use. A fluid catalytic cracking (FCC) decant oil was obtained from Conoco's Ponca City refinery. A mildly hydrogenated FCC decant oil also containing some coal liquids (L-814) obtained from HTI was used as the coal derived solvent. Hondo residual oil, a vacuum tower bottoms fraction, was obtained from Paramount Petroleum Corporation. Aged Akzo AO-60 Ni-Mo/Al_2O_3 catalyst was obtained from run POC-1 at HTI. Aqueous ammonium heptamolybdate (AHM) was used as the precursor for MoS_2 in 1-L semi-batch tests.

Reactions: Semi-batch (batch slurry, flow-through gas) tests were performed in a 1-Liter (1-L) stirred-tank reactor system. The feed charge consisted of 400 g of slurry that consisted of a 2:1 ratio of solvent to added solids (coal or coal + plastics). Catalysts, if any, were activated in situ during heat-up. The experiments were performed for 1.0 h at 4 SCFH H_2/H_2S (3%). Continuous tests were conducted in PETC's 1-L continuous hydrotreating unit. Unit operations, sample work-up and coal conversions for the 1-L batch autoclave and continuous tests have been described previously.[8]

RESULTS AND DISCUSSION

The effects of pressure and coal concentration in coal/oil coprocessing were studied in semi-batch autoclave tests. The results for the three solvents are shown in Figures 1- 4. The results for Hondo resid/coal mixtures at different coal concentrations shown in Figure 1 suggest that there is an area at low concentration (between 0 and 10% coal) where the conversion to 850°F- distillate is higher than with no added coal. Above 10% coal, the distillate conversion falls with increasing coal concentration. The trend was observed at two pressures 1000 psig and 2500 psig. Reduction in pressure from 2500 psig to 1000 psig resulted in an increase in 850°F+ resid content of about 7%.

Experiments were also conducted using FCC decant oil instead of Hondo Resid in coprocessing. The results are shown in Figure 2. Trends were similar in that coal/oil mixtures resulted in higher distillate yields than using the decant oil alone. Reduction in pressure also resulted in approximately a 7 wt% increase in 850°F+ distillate content. The optimal coal concentration appeared to be a slightly higher (~10 %) than with the Hondo resid.

Experiments using the L814 solvent, a hydrotreated decant oil, did not indicate any synergism. The results are shown in Figure 3.

A comparison of the three solvents tested is shown in Figure 4. It is thus apparent that the response of conversion to coal addition is dependant on both the quantity of coal added and the character of the co-processing candidate.

The effect of Mo catalyst loadings on the conversion of Hondo resid without coal is shown in Figure 5. As the added catalyst was increased from 100 ppm to 300 ppm and 500 ppm Mo, conversion was essentially unchanged. A selcted number of batch tests were performed at different Mo catalyst concentrations. Data from these tests of coal plus solvent were tabulated in Table 1. In these tests the effect was more pronounced when conversion was low. It appears increasing catalyst concentration may offset the negative effect of pressure reduction. The results parallel earlier observations in the coal liquefaction system, where catalyst concentration could be used to compensate for the effects of pressure reduction.

The results achieved in the semi-batch unit were confirmed by coprocessing tests conducted in the continuous unit. Preliminary results with Hondo and Illinois 6 coal are shown in Figure 6. More tests are in progress. A similar trend with respect to coal conversion was observed in the continuous unit as was observed in the semi-batch. Both the $850^{o}F^{+}$ and the heptane insoluble conversions increased from 0% to 5% coal and decreased from 5% to 30%. The increase in conversion at 5% coal seems larger in magnitude than observed in the semi-batch experiments. The effects of pressure and catalyst concentration are also being studied in the continuous unit.

Two continuous tests were made to investigate coal/waste coprocessing. The objectives included testing the effect of plastics concentration, solvent type (FCC decant oil vs Hondo resid), pressure, catalyst type, and the use of actual municipal waste plastics. Analysis of results is not yet complete from the continuous tests.

SUMMARY

Based on conversion to $850^{o}F^{-}$ distillate, coal/oil coprocessing may be most effective at lower coal concentrations. A maximum in the distillate yields is observed at coal concentrations between 5 and 10%. At higher coal concentrations the distillate conversion drops with increasing coal concentration. Dispersed catalyst concentration can be used to compensate for small reductions in pressure. 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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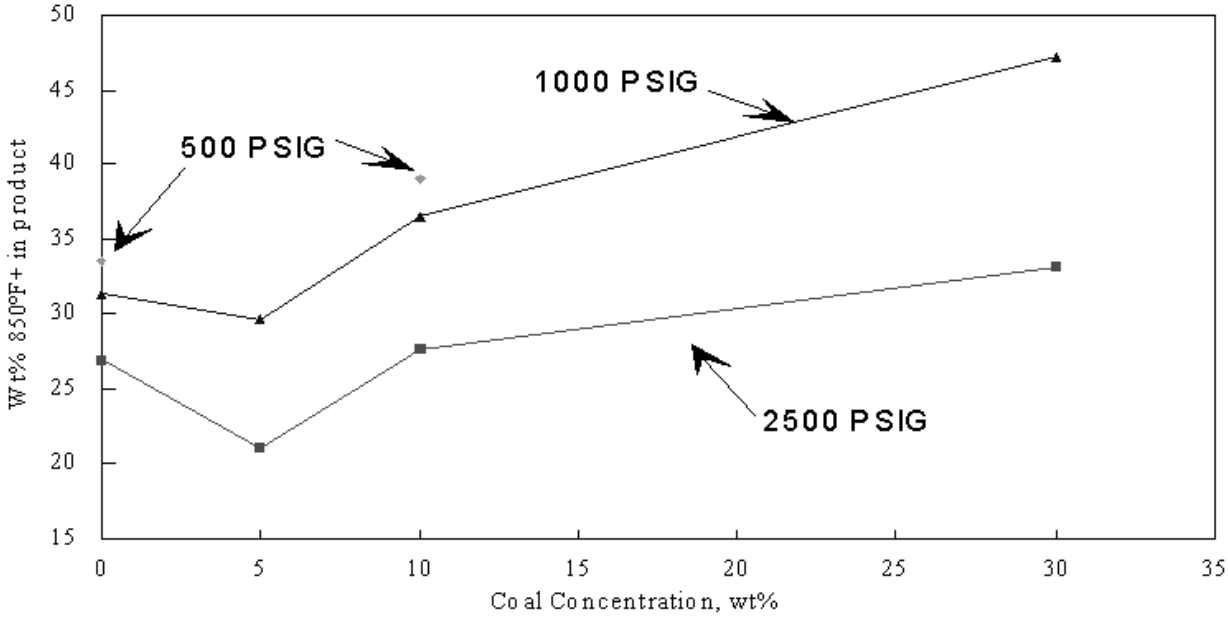
Table 1. Effect of Mo Concentration on Distillate

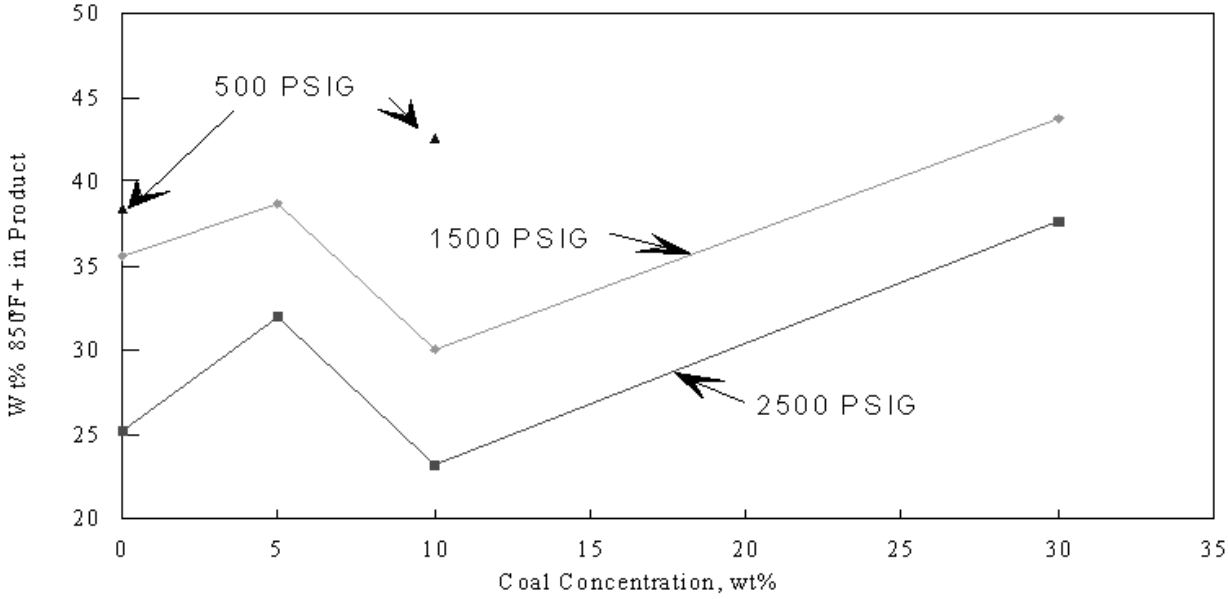
Solvent	Coal Concentration wt%	Pressure (PSIG)	Catalyst Concentration (PPM)	Non-distillate content, wt% 850°F^{+}
L814	0	1,000	300 100	23 28
FCC Decant oil	10	500	500 100 0	40 43 49
Hondo Resid	10	1,500	500 100	34 46

Figure 1. Effect of Coal Concentration and Pressure With Hondo Resid



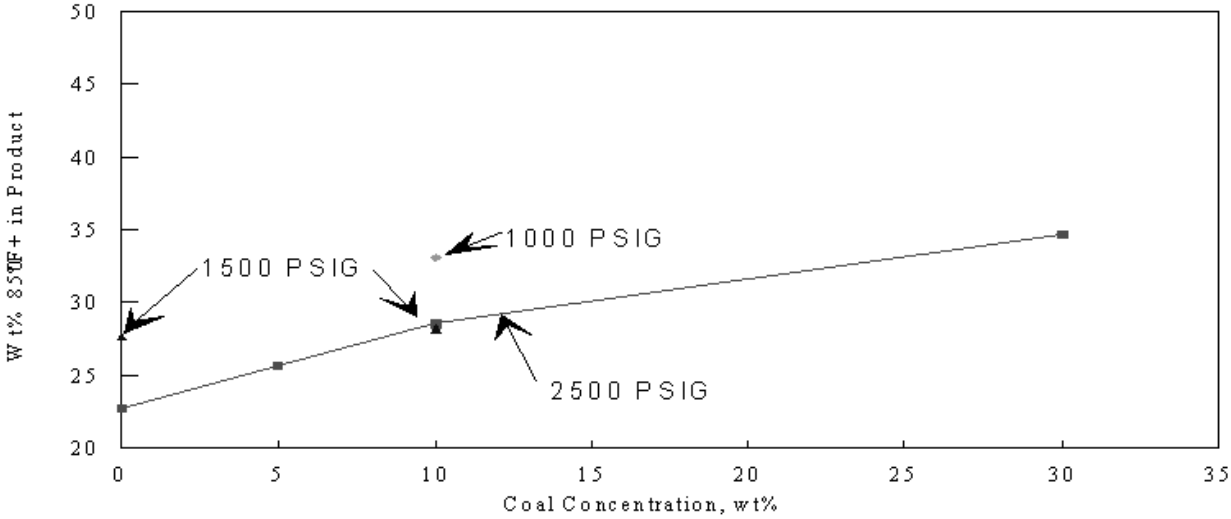
Semi-Batch 1-L Autoclave 425°C, 1h, 100 ppm Mo (added as AHM), Illinois No. 6 Coal

Figure 2. Effect of Coal Concentration and Pressure With FCC Decant Oil



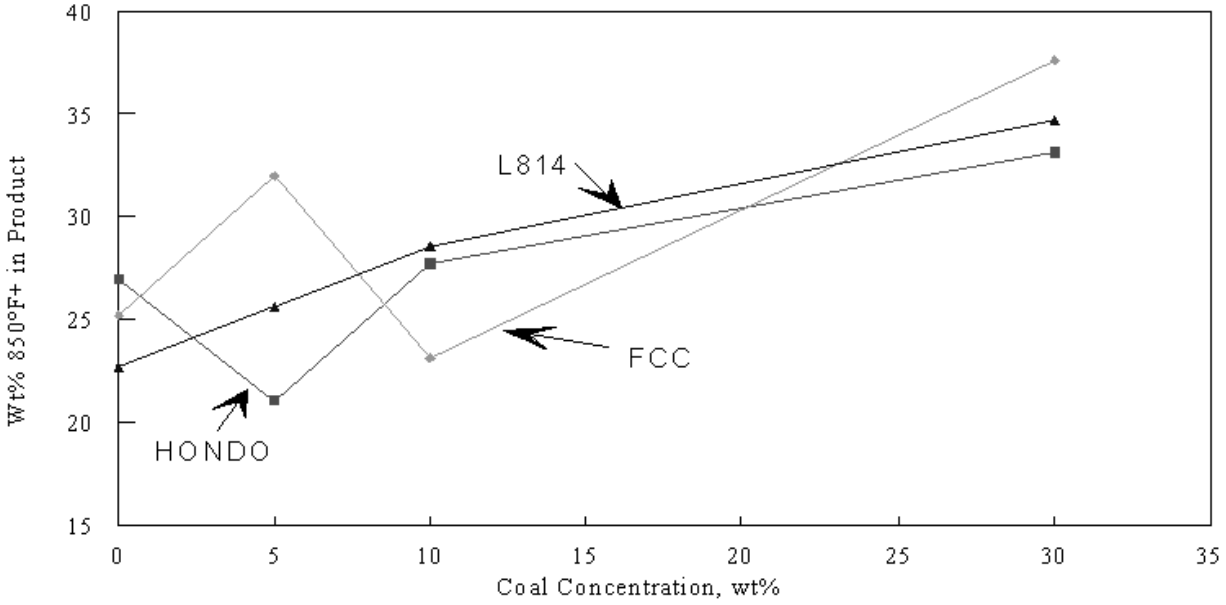
Semi-Batch 1-L Autoclave, 425°C, 1h, 100 ppm Mo (added as AHM), Illinois No. 6 Coal

Figure 3. Effect of Coal Concentration and Pressure with L814



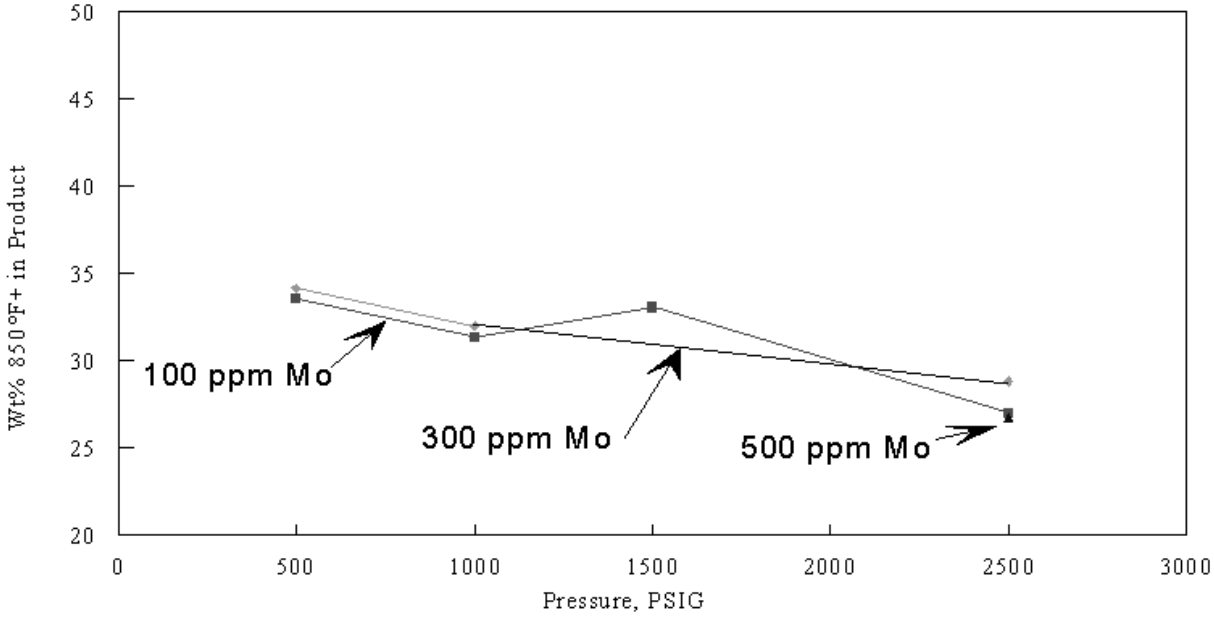
Semi-Batch 1-L Autoclave, 425°C, 1 h, 100 ppm Mo (added as AHM), Illinois No. 6 Coal

Figure 4. Effect of Solvent and Coal Concentration in Coprocessing



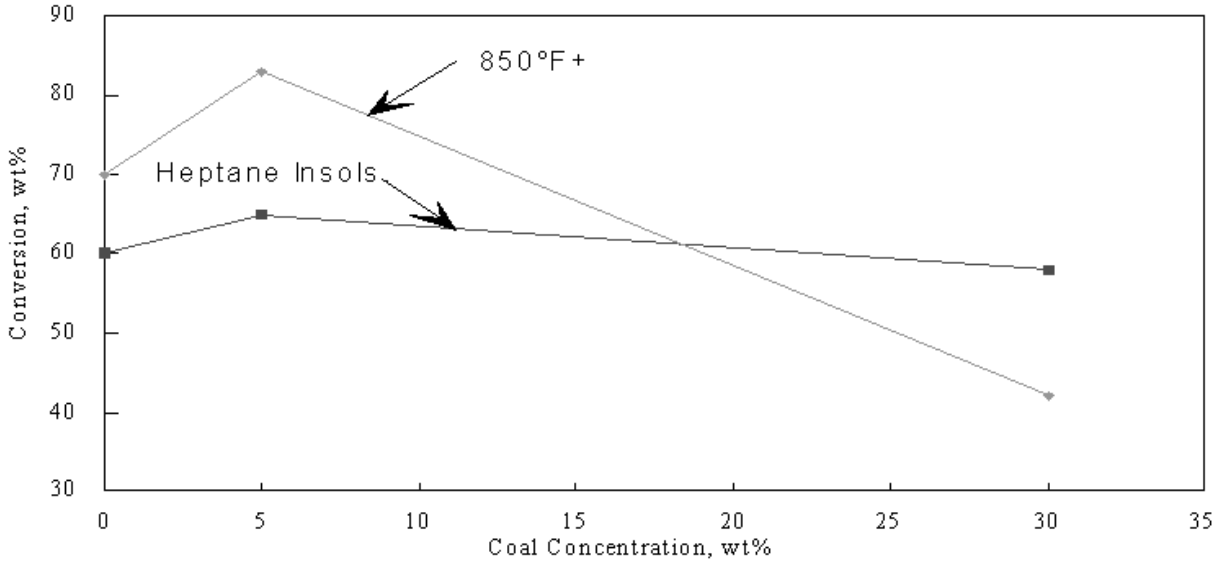
Semi-Batch 1-L Autoclave, 425°C, 100 ppm Mo(added as AHM), 2500 PSIG, Illinois No. 6 Coal

Figure 5. Effect of Mo Concentration and Pressure



Semi-Batch 1-L Autoclave, 425 °C, 1 h, Hondo Resid

Figure 6. Effect of Coal Concentration (Continuous Tests)



435°C, 2500 psig, 500 ppm Mo (added as AHM), Hondo Resid to Illinois 6 Coal