Surface Modified Coals for Enhanced Catalyst Dispersion and Liquefaction

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**SURFACE MODIFIED COALS FOR ENHANCED CATALYST
DISPERSION AND LIQUEFACTION**

Report for the Period

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ABSTRACT

The aim of this study is to enhance catalyst loading and dispersion in coal for improved liquefaction by preadsorption of surfactants and catalysts on to the coal. During this reporting period, liquefaction experiments were conducted with the raw coal and catalyst loaded samples. Pretreatment of the coal and catalyst-loaded samples were done using the surfactants presented in previous reports.

Liquefaction samples were tested using 6.6 g of solvent, 3.3 g coal, 6.9 MPa ambient hydrogen pressure, 425 °C and 30 minutes. The liquid and solid products were removed from the reactor using tetrahydrofuran (THF). Coal conversions were calculated based on THF and heptane solubility.

The results showed that in the absence of a catalyst, 33.8% heptane solubles was obtained with the parent coal compared to 27.8% and 27.3% with the SDS and DDAB surfactants. The presence of molybdenum, as expected, resulted in enhanced heptane solubles with or without surfactants. In the absence of surfactants, 50% heptane solubles was obtained compared to 40-47% with surfactants. Thus, it appears that pretreatment, unexpectedly, had a negative effect on liquefaction activity. It is unclear if the observed differences in results are significant. Clearly, additional experiments are needed before any firm deductions and conclusions can be drawn from the results.

INTRODUCTION

Coal surface contains both hydrophobic and hydrophilic sites. However, little work has been done to understand the effects of this dual character of the coal surface on catalyst loading and dispersion for coal conversion. When added from organic solution, the catalyst will be attracted to the organic sites on the coal but it will be repelled by the hydrophilic sites. This will produce low liquefaction activity.

By adsorbing appropriate surfactants onto coal, the hydrophilic heads of the surfactants will be adsorbed onto the oppositely charged sites on the coal while the organic portions will be oriented towards the organic solution. This should promote hydrophobic interaction between the hydrophobic catalyst solution and the catalyst precursor. The organic portion of the surfactant can also be adsorbed onto the hydrophobic site of the coal, with the hydrophilic head oriented towards the aqueous solution. This should enhance the uptake and dispersion of water-soluble catalyst precursors.

The high liquefaction activities of molybdenum compounds are well known (1,2). However, a major challenge which is facing the application of this catalyst on a commercial scale is the inability to achieve high levels of catalyst dispersion on coal. The need for high catalyst dispersion is especially important because of the high cost of molybdenum. Hence, improved

techniques for molybdenum dispersion in coal are needed for the enhancement of coal liquefaction activity.

The aim of this work is to enhance the liquefaction activities of coal by improving dispersion of molybdenum in coal by pretreatment with surfactants.

EXPERIMENTAL

The Illinois No.6 coal (DECS-24) used in this experiment was supplied by the Penn State Coal Sample Bank. The characteristics of the coal including proximate analysis and elemental analysis have been provided in previous reports (3,4).

The effectiveness of the catalyst loading technique was measured by liquefaction activities of the raw coal and the catalyst-loaded samples. Liquefaction studies were conducted in a stainless steel batch microautoclave reactor. The internal volume of the reactor including all tubing and connections was 60 mL. For continuous monitoring of pressure and temperature during the experiment, an internal thermocouple and pressure transducer were used. The samples were tested using 6.6 g of solvent, 3.3 g of coal and 6.9 MPa (1000 psi) ambient hydrogen pressure. The reactor was then attached to the rocker arm of a motor that vibrated at 180 cycles/min, and plunged into a pre-heated sandbath that was heated to 425°C in 40 minutes. This temperature was maintained for 30 minutes, after which the

reactor was removed and cooled with water. The liquid and solid products were removed from the reactor using tetrahydrofuran (THF). Coal conversions were calculated based on THF and heptane solubility.

RESULTS AND DISCUSSION

Measurements of the liquefaction activities produced results that were unexpected based on previously reported molybdenum uptake data. Although the technique being used has proven to be useful in increasing the amount of molybdenum uptake, it was unproductive in its ability to increase liquefaction activities.

The pretreatment of the coal surface with surfactants had relatively minor and unexpected effect on liquefaction activity. Table 1 shows all the results of the catalytic liquefaction experiments. Pretreatment of the coal with surfactants appears to have a negative effect on the liquefaction activities. In the absence of a catalyst, 33.8% heptane solubles was obtained with the parent coal, compared to 27.8% and 27.3% with SDS and DDAB, respectively. The presence of Triton, however did not show any significant difference.

The presence of molybdenum, as expected, resulted in enhanced levels of heptane solubles with or without surfactants. In the absence of surfactants 50% heptane solubles was obtained, compared to 44-47% with surfactants. Thus, again, the presence of surfactants appears to have a negative influence

on the production of heptane soluble material. It is still unclear if the observed differences in the results are significant.

In the case of the total coal conversion to liquids, as given by the THF solubles, no consistent trend was observed with respect to the effects of the surfactants. In some cases (eg. Triton), the surfactant appeared to enhance THF solubles while in other cases (eg. DDAB) THF solubles decreased. Clearly, additional data is required before firm trends and conclusions can be drawn from the liquefaction results.

It is our hypothesis, that the decrease in heptane solubles with surfactants may be due to a blockage of the coal surface from the molybdenum due to the coating of the surface with the surfactant. As a result, experiments will be conducted to determine the validity of this hypothesis, as it is critical to the results of this study.

Future studies will reveal new information regarding the usefulness of this technique for maximum catalyst dispersion. We hope to determine the validity of our hypothesis by modifying the method of surfactant-catalyst uptake on the coal surface. Further liquefaction studies should be able to refute or confirm our results.

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Sample	THF Solubles (Total Coal Conversion to Liquids)	Heptane Solubles (Oils)
Parent Coal	72.4%	33.8%
Coal + SDS	70.0%	27.8%
Coal + DDAB	66.0%	27.3%
Coal + Triton	77.9%	33.2%
Coal + Mo	90.0%	50.0%
Coal + Mo + SDS	95.4%	44.5%
Coal + Mo + DDAB	88.5%	46.9%
Coal + Mo + Triton	96.2%	46.7%

Table 1. Liquefaction Results