**PROCESS AND ANALYTICAL STUDIES OF ENHANCED LOW
SEVERITY CO-PROCESSING USING SELECTIVE COAL
PRETREATMENT**

DOE/PC/88812--T9

DE92 001638

001 1 0 1991

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**Quarterly Technical Progress Report for the Period
March - May, 1991**

DOE Contract No. DE-AC22-88PC88812

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ABSTRACT

This report describes progress on research during the eleventh quarter of this contract dealing with applications of coal pretreatment techniques in coal/oil co-processing and direct hydroliquefaction. The objectives of the project are to investigate various coal pretreatment techniques and to determine the effect of these pretreatment procedures on the reactivity of the coal. Reactivity enhancement will be evaluated under both direct hydroliquefaction and co-processing conditions. Coal conversion utilizing low rank coals and low severity conditions (reaction temperatures generally less than 350 °C) is the primary focus of the liquefaction experiments, as it is expected that the effect of pretreatment conditions and the attendant reactivity enhancement will be greatest for these coals and at these conditions.

This document presents a summary of results for the first set of a series of runs intended to simulate operation of a two-stage integrated liquefaction reactor train. These studies were designed to investigate the effect of the severity of the first stage liquefaction process on the required severity and resulting yields from the second stage. Process conditions were varied between thermal and catalytic for both stages, and from temperatures of 350 to 400 °C at a nominal residence time of 30 minutes. These data will provide background information that will be useful in comparing the effect of mild chemical pretreatment on the yield (quantity) and quality of distillate from the simulated two-stage reaction scheme.

Preliminary results have indicated that the severity of the first stage has a very significant impact on coal conversion and distillate yield from the second reactor stage. For low rank coals, higher overall coal conversion and distillate yield can be obtained by operating the first stage thermally (no added catalyst) and at low severity when compared to the catalytic/catalytic mode operated at high

severity. These data indicate that total conversion (THF solubles) and distillate yield (hexane solubles) for liquefaction of Wyodak subbituminous coal in tetralin are 13% and 14% higher respectively when the first stage is operated at low severity (350 °C) and thermally (no added catalyst).

TECHNICAL DISCUSSION

Introduction

The objective of this experimental study was to investigate the effect of reaction severity on conversion of coal to hexane and THF solubles in order to provide background information that can be used in subsequent studies. The concept under development holds that the reactivity of the material derived from first stage coal liquefaction/dissolution processes is directly related to the severity of the primary conversion step. Hence, carrying out these reactions at lower temperature will give rise to more reactive coal-derived intermediates, which will in turn facilitate operation of the stage II hydroprocessing reactor at lower severity conditions. This combination of low severity in both stages will minimize hydrocarbon gas make and catalyst deactivation leading ultimately to improved process economics.

During the past quarter, a series of runs were initiated that were intended to simulate the operation of an integrated two-stage liquefaction train. This is being carried out using batch tubing-bomb microautoclave reactors to mimic the operation of an actual two-stage system. Operation of both stages under thermal (no added catalyst) and catalytic conditions was investigated over a broad temperature range intended to span low (reaction temperature of 350 °C) and moderate (reaction temperature of 400 °C) severity conditions for both stages. Both thermal/catalytic (stage I/stage II) and catalytic/catalytic modes of operation were simulated. Total coal conversion (THF solubles), gas make, and distillate yield (hexane solubles) from both the first and second stage reactors were monitored for these experiments.

Experimental

Two coals (Wyodak subbituminous and Illinois #6 high volatile bituminous) from the Argonne Premium Coal Sample Bank were utilized for this study. A 20 cc 1/2" diameter microautoclave tubing bomb reactor system was used to carry out the liquefaction experiments. Tetralin (1,2,3,4-tetrahydronaphthalene) was used as the vehicle for all experiments in order to mimic operation under direct hydroliquefaction conditions. Industrial grade hydrogen gas (General Air Services Inc.) was used as the reaction gas. Powdered Shell 324 Ni-Mo/Al₂O₃ was used as a catalyst. Prior to use, the catalyst was presulfided following a prescribed temperature program in an external tube furnace using a mixture of 10% H₂S in H₂.

The micro reactor was filled with a weighed amount of coal sample (0.5 gr) and carrier solvent (tetralin) in 1:2 weight ratio. Two 3mm stainless steel balls were placed inside the reactor to facilitate mixing. Reactions were run utilizing two reactors in parallel under identical operating conditions, with one reactor containing catalyst. Following reaction and cool-down, the reactors were weighed, depressurized and then weighed again to give a quantitative measure of the gas make. For the simulated two-stage runs, catalyst was added (if needed for the thermal/catalytic mode where the first stage was operated thermally), and the reactor was re-sealed, pressurized and run at the prescribed second stage conditions. Under catalytic/catalytic operation, the reactor was depressurized and repressurized between runs, but fresh catalyst was not added. All runs were carried out for a time period of 30 minutes (each stage). This reaction period represents the elapsed time at isothermal conditions, and does not include an initial 90 to 120 second non-isothermal heat-up period.

The reaction products were first extracted with tetrahydrofuran (THF) and the soluble and insoluble fractions separated by centrifugation. The insolubles were

oven dried overnight and the solubles subsequently extracted with hexane to precipitate hexane insolubles. The insoluble hexane mass was also oven dried overnight and then both THF and hexane insolubles fractions were weighed. The micro reactors were also weighed after extraction so as to ensure that residual insolubles had not been left behind in the reactor. A few experiments were duplicated to verify the reproducibility of the data. It was observed that the reproducibility of the numbers was generally within $\pm 3\%$. Further run and analytical procedures have been described in detail elsewhere (1).

Conversions (THF and hexane) were calculated using the following expressions:

$$\text{THF conversion} = \frac{\text{THF insols in} - \text{THF insols out}}{\text{THF insols in}}$$

$$\text{Hexane conversion} = \frac{\text{Hex. insols in} - \text{Hex. insols out}}{\text{Hexane insols in}}$$

An additional parameter, hexane selectivity, was developed and utilized to aid in the elucidation of the effect of catalyst on coal conversion. This parameter was defined by the following expression:

$$\text{Hexane selectivity} = \frac{\% \text{ Hexane sols}}{\% \text{ THF sols}}$$

Essentially, hexane selectivity provides a quantitative measure of that fraction of THF solubles which is also hexane soluble. All values in the above expressions are on a moisture and ash-free basis.

Results and Interpretations

Wyodak Coal: Results of simulated two stage experiments using Wyodak subbituminous coal are listed in

Table I and represented schematically in Figures 1a (THF conversion) and 1b (hexane conversion). Several important observations are apparent from this data set. First, both total conversion and distillate yield (hexane solubles) for liquefaction of Wyodak coal in a two stage configuration are reasonably sensitive to temperature staging and operational conditions. As shown, increasing severity in the catalytic/catalytic mode does produce an increase in both total coal conversion and distillate yield. For example, a comparison of run combinations 4 and 6 for the catalytic/catalytic mode indicates that increasing the severity of stage I from 350 °C to 400 °C (with stage II fixed at 400 °C) increases total conversion and distillate yield by 10 and 21% respectively. Further, operation of the stage II reactor below 400 °C (run combinations 2 and 8) results in a very significant decrease in overall conversion and distillate make, probably due to the low activity of the catalyst at temperatures below 400 °C. The most significant observation from this data set is, however, seen in a comparison of run combination 3 with run combinations 4, 5, and 6. Run combination 3 represents a simulated thermal/catalytic mode of operation, with the first stage operating at low severity (350 °C) and stage II at moderate severity (400 °C). For Wyodak subbituminous coal, both total coal conversion and distillate yield are higher from this run combination than for the catalytic/catalytic mode at the same severity or thermal/catalytic or catalytic/catalytic modes at higher levels for first stage reaction severity (400 °C). Comparing the thermal/catalytic mode at 350 °C/400 °C to the thermal/catalytic mode at 400 °C/400 °C (run combinations 3 and 5), both total conversion and distillate make are 13 and 14 % higher respectively when the first stage is operated at low severity. At these levels of conversion (>85%), even a 5 % increase is considered highly significant to the overall economics of

the operation (2). Hexane selectivities reflect little difference between the two modes of operation.

Illinois #6 coal: Data for simulated two-stage conversion of Illinois #6 coal under direct hydroliquefaction conditions (tetralin vehicle) is shown in Table II and Figures 2a (THF conversion) and 2b (hexane yield). Interestingly, the benefits seen above for the lower rank coal are now absent. Increased conversion and distillate yield track exactly with increasing reaction severity. These data (hexane conversion) also indicate that at low severity the thermal/catalytic mode is in general superior to the catalytic/catalytic mode, with higher yields found for hexane solubles.

These observations would seem to lend strength to the hypothesis that has been offered by this author and others concerning the inherent reactivity of low rank coals and the influence of liquefaction conditions on the ultimate yields that can be attained. McMillen and coworkers (3) and Moroni (4) have illustrated the influence of the reactivity of oxygen functional groups on coal conversion. Stohl (5) has shown that condensation reactions involving phenolic oxygen can take place at temperatures well below 300 °C, hence pointing out the importance of these functional groups during the initial stages of coal conversion (reactions that are probably taking place in the preheater where insufficient hydrogen transfer capability exists to suppress these reactions). Published results of the previous investigations funded under this contract (see for example Baldwin et al. (6)) have shown that selective oxygen alkylation is an effective means for passivating phenolic oxygen, thus increasing the reactivity of low rank coals.

Plans for the Coming Months

These data illustrate that low severity liquefaction practiced in the first stage of a two-stage liquefaction system does have a significant impact on the overall

conversion and distillate make achieved. These results will be expanded during the coming months to include reactions carried out under coal/oil coprocessing conditions, and first and second stage reactions incorporating a disposable catalyst (pyrite) and synthesis gas (CO/H₂) under both direct hydroliquefaction and coprocessing operational modes. Finally, conversion of coals that have been chemically pretreated following the mild alkylation procedures utilized during the earlier stages of this program will be investigated.

An experimental program to investigate the effect of mild alkylation on the global kinetics and activation energy for liquefaction of Wyodak coal is also in progress. Results of these studies will be reported during the next quarter.

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TABLE I
SIMULATED TWO-STAGE PROCESSING OF WYODAK COAL

<u>No.</u>	<u>Conditions</u> ¹	<u>THF</u> ²	<u>Hexane</u> ³	<u>Select.</u> ⁴
1	T/C (350/350)	46	37	80.4
2	C/C (350/350)	51	42.5	83.3
3	T/C (350/400)	95.6	88.6	92.6
4	C/C (350/400)	83.5	73	87.5
5	T/C (400/400)	85.4	76.7	89.7
6	C/C (400/400)	91.7	87.6	95.6
7	T/C (350/375)	73.8	69.3	93.9
8	C/C (350/375)	67.1	62.6	93.3

NOTES:

All runs carried out using tetralin as the vehicle.

1. The nomenclature identifies either thermal (T) or catalytic (C) mode of operation for stage I or II. The temperature for that stage is also indicated.

2. Conversion of coal to THF solubles plus gas (%).

3. Conversion of coal to hexane solubles (%).

4. Hexane selectivity (%).

TABLE II
SIMULATED TWO-STAGE PROCESSING OF ILLINOIS #6 COAL

<u>No.</u>	<u>Conditions</u> ¹	<u>THF</u> ²	<u>Hexane</u> ³	<u>Select.</u> ⁴
1	T/C (350/350)	66.2	46.8	70.7
2	C/C (350/350)	60.3	37.1	61.5
3	T/C (350/400)	79.6	67.6	84.9
4	C/C (350/400)	72.4	53.1	73.3
5	T/C (400/400)	89.9	87.5	97.3
6	C/C (400/400)	91	86.4	95
7	T/C (350/375)	64	41.9	65.3
8	C/C (350/375)	66.9	40.2	60

NOTES:

All runs carried out using tetralin as the vehicle.

1. The nomenclature identifies either thermal (T) or catalytic (C) mode of operation for stage I or II. The temperature for that stage is also indicated.

2. Conversion of coal to THF solubles plus gas (%).

3. Conversion of coal to hexane solubles (%).

4. Hexane selectivity (%).

FIGURE 1a

FIGURE 1b

FIGURE 2a

FIGURE 2b

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