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ADVANCED COAL LIQUEFACTION CATALYST DEVELOPMENT

Quarterly Progress Report No. 8, July 1–September 30, 1983

By
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ADVANCED COAL LIQUEFACTION CATALYST DEVELOPMENT

QUARTERLY PROGRESS REPORT NO. 8

JULY 1 - SEPTEMBER 30, 1983

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FORWARD

The objective of this program is to identify advanced coal liquefaction catalyst and operating conditions for use in optimized, two-stage direct coal liquefaction process applications and to experimentally test catalysts in a two-stage reaction system for supporting the improvement of this process.

Further improvements in direct liquefaction technology will rely on a program plan aimed at developing two-stage processes. Use of Amocat™ bimodal catalysts will permit solid separation after the second stage where good quality, low viscosity coal liquid product eases solid-liquid separation problems. Optimization of two-stage process conditions as well as second-stage catalysts will permit substantial improvement of direct coal liquefaction technology. Conditions and catalyst will be optimized to permit maximum production of donor solvent boiling point material, low in sulfur, nitrogen, and oxygen content.

A development plan consisting of eight project tasks has been formulated and is summarized as follows:

- Task 1 - Project Work Plan
- Task 2 - Literature Survey
- Task 3 - Feed Materials Specification
- Task 4 - Continuous Aging Unit Modification
- Task 5 - Thermal Reaction Process Variable Study
- Task 6 - Two-Stage Optimization
- Task 7 - Project Coordination
- Task 8 - Ebullated Bed Testing

Under Task 1, a Project Work Plan will be prepared which will present in detail all activities which will be performed during the three-year program. Under Task 2, Literature Survey, a state-of-the-art review on direct coal liquefaction catalysts and catalytic processes will be completed. In Task 3, Feed Materials Specification, slurry oil will be

hydrogenated and characterized. In Task 4, Continuing Aging Unit Modification, the existing experimental facilities will be modified for two-stage processing with a preheater. Task 5, Thermal Reaction Process Variable Study, is geared to determining the thermal liquefaction behavior of the two coals selected for study. Task 6, Two-Stage Optimization, second-stage reaction temperatures, space velocities, and catalyst compositions will be optimized. Task 7, Project Coordination, will provide technical support to other DOE contractors working in the two-stage coal liquefaction and analytical testing areas. In Task 8, Ebullated Bed Testing, two 15-day bench-scale runs will be run by subcontractors.

The objective of this report is to outline and summarize progress in Tasks 3, 5, and 6 during the last quarter.

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TASK 3--FEED MATERIALS SPECIFICATION

Under Task 3 of the Advanced Coal Liquefaction Catalyst Development Program, raw creosote oil will be hydrogenated and then fractionated to recover material boiling in the range 550+°F for use as donor solvent. The characterizations of the primary solvent, FSN-30 (6.86% hydrogen), plus secondary solvents FSN-31 (7.01% hydrogen) and FSN-32 (6.54% hydrogen), have previously been reported. Additionally, a quantity of very severely hydrotreated creosote oil was also produced. This material, identified as FSN-38, was analyzed for carbon, hydrogen, oxygen, sulfur, nitrogen, and basic nitrogen. These data, together with those of FSN-30 for comparison, are shown in Table 3-1.

TABLE 3-1

ANALYSES OF DONOR SOLVENTS

	<u>FSN-30</u>	<u>FSN-38</u>
Carbon, Wt%	91.64	91.85
Hydrogen, Wt%	6.86	7.19
Oxygen, Wt%	0.94	0.64
Sulfur, Wt%	0.17	0.01
Nitrogen, Wt%	0.68	0.44
Basic Nitrogen, Wt%	0.36	0.18

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TASK 5--THERMAL REACTION PROCESS VARIABLE STUDYMICROREACTOR RUNSSummary of Microreactor Data

Baseline tests were conducted using the microautoclave unit to determine the effects of solvent hydrogen content and reaction pressure on the thermal liquefaction of Illinois No. 6 coal to toluene-soluble products. Conversion was plotted versus reaction severity using the STTU scale⁽¹⁾. Over the range 6.54-7.19% hydrogen content of the solvent, retrograde reactions decrease with increasing hydrogen content. Conversion is slightly higher under 2,000 psi nitrogen than under 500 psi nitrogen, presumably due to the physical effect of keeping more solvent in the liquid phase thereby increasing the solvent-to-coal ratio. Dehydrogenation of the solvent at high temperature and low hydrogen pressure is thought to be occurring.

Effect of Solvent

Previously⁽²⁾ it was found that for hydrogenated creosote oil solvents having hydrogen contents of 6.54, 6.86, and 7.01% (solvents FSN-32, -30, and -31, respectively) conversion to toluene-soluble products at high reaction severity increases with increasing hydrogen content of the solvent. Additional experiments with these solvents plus experiments with solvent FSN-38, hydrogenated creosote oil containing 7.19% hydrogen (described herein, Task 3), were run. The data are shown in Figure 5-1.

Conversion with FSN-38 solvent was experimentally indistinguishable from FSN-31 solvent at about 40 STTU. Both were higher than FSN-30 solvent. However, at very high severity, about 80 STTU, conversion increased with increasing hydrogen content of the solvent over the range 6.54-7.19% hydrogen. Conversion increases because retrograde reactions decrease with increasing hydrogen content of the solvent.

Effect of Pressure

The conversions of Illinois No. 6 coal to toluene-soluble products in FSN-30 solvent under 500 and 2,000 psi nitrogen were determined. These data are compared with the conversions under 500 and 2,000 psi hydrogen in Figure 5-2. The objectives of these experiments were to isolate the physical effect of pressure and also to separate the solvent-hydrogen effect from the gaseous-hydrogen effect.

Conversion under 2,000 psi nitrogen is slightly higher than the conversion under 500 psi nitrogen. This increase with pressure is a physical effect. The higher pressure keeps more material in the liquid phase. This is equivalent to increasing the ratio of solvent to coal. FSN-30 is a high boiling solvent so this pressure effect is small. In other systems the magnitude of this effect will depend on the volatility of the solvent.

The identical conversions obtained under 500 psi nitrogen and 500 psi hydrogen indicate that only solvent-derived hydrogen is utilized in coal liquefaction under 500 psi hydrogen.

The increase in conversion with 2,000 psi hydrogen over 2,000 psi nitrogen indicates that gaseous hydrogen makes a real contribution to donatable hydrogen, but the contribution is important only at higher pressure with a good quality solvent.

These pressure effects on conversion could be rationalized if hydrogen gas solubility were increasing exponentially with increasing pressure. However, calculations based on American Petroleum Institute tables show that hydrogen solubility increases by only a factor of three in going from 500 psi to 2,000 psi at 850°F.

The effects of pressure on conversion could be explained if operation at high severity and low pressure were promoting the dehydrogenation of the hydrogenated creosote oil solvent, resulting in a poorer quality solvent. We do not have experimental proof of this hypothesis.

However, (1) the reaction of hydrogen with an aromatic solvent to form hydrogenated solvent is a reversible process; (2) the position of equilibrium for the hydrogenation and dehydrogenation reactions is dependent on both temperature and pressure, and (3) similar dehydrogenation is known to occur in the hydrotreatment of petroleum oils at high severity.

CONTINUOUS FLOW UNIT RUNS

Three runs were performed to examine the effect of first-stage catalysts on the characteristics of the coal liquid. All three runs were performed in the one-stage catalytic mode in the continuous coal liquefaction unit described in the first annual report of this contract⁽³⁾. The conditions chosen for these runs were 810°F, 2,000 psi, and a nominal residence time of 35 minutes. This set of conditions matches those used in one of the experiments in the study of the thermal liquefaction of coal. Thus, the results between these catalytic runs and the noncatalytic experiments are directly comparable. The thermal results are described in Quarterly Report No. 7 of this contract⁽²⁾. The space velocity was approximately 5 grams coal per gram of catalyst per hour. This relatively high space velocity was chosen to simulate short residence time conditions in a first-stage reactor and because extensive catalytic data in the one-stage mode has been collected at lower space velocities in previous contracts.

Run 51149 was run with Wyodak coal and medium-level hydrogenated creosote oil (FSN-30) with a 3/1 solvent-to-coal ratio. The catalyst (7457-172) was a wide-pore alpha alumina with 1.4% Mo. The average pore radius of the fresh catalyst is 205 Å and the surface area is 17 sq. meters/gram. The nominal objective of the catalyst is to provide a large-pore medium to act as a getter for metal deposition. The Mo was added to provide some hydrotreating activity in the first stage with an inexpensive catalyst.

The conversion of maf coal is shown in Figures 5-3 through 5-5. Figure 5-3 is a plot of the THF-soluble conversion as a function of hours on stream. The value obtained for the noncatalytic conversion of Wyodak coal at these conditions is shown on the graph as a line of "T"s at 78%. The THF conversion during this run ranged from 75% to 83% with one outlier on the third sample at 58%. There is no significant trend in the numbers, and they generally lie about the thermal value, indicating that the catalyst has no effect on the THF conversion of Wyodak coal.

Toluene-soluble conversion for this run is shown in Figure 5-4. It ranges from 57% to 65% about the thermal value of 60%. As in the case of THF-soluble conversion, there is no identifiable trend in the data with time and no significant conversion advantage associated with the use of this catalyst. The values for hexane-soluble conversion, shown in Figure 5-5, range from 6% to 44% compared to the thermal value of 22%. The samples from the first six days all have a conversion advantage of 5% or greater than the thermal sample. Thus, it seems that the catalyst enhances the production or stabilization of the hexane-soluble portion of the oil to some degree.

Run 51150 was run with Illinois No. 6 coal with the same conditions and same catalyst as Run 51149. The conversions are shown in Figures 5-6 through 5-8 for this run. The noncatalytic values shown in "T"s on these graphs are the average values from three thermal runs with residence times of 30, 34, and 35 minutes. The THF-soluble conversions, shown in Figure 5-6, range from 93.5% to 94.5% around the thermal value of 94.0%. There is no trend in the data with time. Thus, as is the case for Wyodak coal, the presence of this catalyst exhibits no influence on the conversion of lom to THF-soluble liquids. Both the toluene- and hexane-soluble conversions exhibit significant improvement over the thermal baseline at the beginning of the run (Figures 5-7 and 5-8). The toluene conversion for the first-day sample is 64.5%. The conversion decreased over the course of the five-day run to the thermal value of approximately 58%. The same general trend is observed for hexane-soluble conversion in Figure 5-8. It ranges from

32% at the beginning of the run to 16% on the fifth day. This can be compared to the thermal value of 22%. Due to the uncertainty of the hexane millipore analysis, it is difficult to say whether or not the decrease of the hexane conversion below the thermal baseline is real or not. However, it is certainly conceivable that the catalyst might enhance retrograde reactions or direct available hydrogen to other fractions. In any case, the monotonic decrease of both the toluene and hexane conversions over the five days of the run indicate strongly that the presence of the catalyst does significantly affect the course of the reaction.

Run 51151 was run with Illinois No. 6 coal and FSN-30 solvent at the same reactor conditions as the previous two runs. The catalyst used was AMOCAT 1B with impregnated SnCl_2 . The THF-soluble conversions range from 94% on the second day down to 91% on the final (seventh) day of the run (see Figure 5-9). The numbers follow a general downward trend over the course of the run. All of the results fall below the average value of 94% for the noncatalytic runs. In this case, there appears to be some disadvantage associated with the use of this catalyst. The toluene-soluble conversion shown in Figure 5-10 ranges from 62% on the first day to 56% on the last day compared to the thermal value of 58%. Again, the influence of the catalyst is indicated by the monotonic decline in conversion throughout the run. There may be a small conversion benefit associated with the presence of the catalyst at the outset of its use, but this benefit deteriorates over the first few days to the thermal level. Figure 5-11 shows the hexane conversion as a function of hours on stream. The first day's sample exhibited a hexane conversion of 35% compared to the thermal value of 22%. For the second through the sixth day, the values were in the range of 25%-26%. On the final day of the run, the hexane conversion dropped to the thermal baseline. Thus, the hexane conversion exhibits the same trends for this catalyst as the THF and toluene conversion.

REFERENCES

1. Hydrocarbon Research, Inc., FE-10152-84, October, 1982; 1 STTU=1 minute of reaction at 840°F.
2. J. A. Mahoney, M. M. Schwartz, and T. S. Wittrig, Quarterly Report No. 7 for DOE Contract No. DE-AC22-81PC40009, "Advanced Coal Liquefaction Catalyst Development", October, 1983.
3. J. A. Mahoney, M. M. Schwartz, and T. S. Wittrig, Annual Report No. 1 for DOE Contract No. DE-AC22-81PC40009, "Advanced Coal Liquefaction Catalyst Development", February, 1983.

Microreactor data: effect of solvent on conversion of IL. No. 6 coal to toluene-soluble products

Microreactor data: effect of nitrogen on conversion of IL. No. 6 coal to toluene-soluble products

RUN 51149

TTTTTTT CORRESPONDS TO THE VALUE IN THE ABSENCE OF CATALYST

FIGURE 5-3

FIGURE 5-4

RUN 51149

TTTTTT CORRESPONDS TO THE VALUE IN THE ABSENCE OF CATALYST

FIGURE 5-5

RUN 51150

TTTTTT CORRESPONDS TO THE VALUE IN THE ABSENCE OF CATALYST

FIGURE 5-6

FIGURE 5-7

RUN 51150

FIGURE 5-8

RUN 51151

TTTTTT CORRESPONDS TO THE VALUE IN THE ABSENCE OF CATALYST

FIGURE 5-9

FIGURE 5-10

RUN 51151

TTTTTT CORRESPONDS TO THE VALUE IN THE ABSENCE OF CATALYST

FIGURE 5-11

TASK 6--TWO-STAGE OPTIMIZATION

Following the three first-stage catalyst runs, it was decided that a more meaningful test of the effectiveness of a first-stage catalyst would be to test it in the two-stage integrated mode against a thermal base case. Consequently, the unit was switched to the two-stage mode to establish optimum conditions for catalyst testing in this configuration for Illinois No. 6 and Wyodak coals. It is proposed that each coal will be run at three different noncatalytic first-stage conditions with fixed conditions in the second stage. This set of experiments will allow the evaluation of the effect of first-stage conditions on coal liquid characteristics. One of these runs for Illinois No. 6 was completed during this period as discussed below. The conditions chosen for the catalytic second stage are 700°F, 2,500 psi, and a space velocity of 0.5 grams coal per gram of catalyst per hour. The catalyst chosen for the base case runs was AMOCAT 1C. The pressure in the first stage will be 2,500 psi for all the experiments in this set. The other operating conditions (temperature and residence time) are shown below:

<u>Temperature</u>	<u>Residence Time</u>	<u>Run Number</u>
770°F	35 min.	51153
850°F	35 min.	51154 (in progress)
850°F	10 min.	Proposed

Run 51152 was run on Illinois No. 6 coal with a first-stage temperature of 770°F and a first-stage residence time of 35 minutes. During startup of the run, there was a temperature excursion in the catalytic reactor to approximately 900°F. The temperature rise appeared to be the result of an exothermic reaction on the freshly sulfided catalyst. Since it is well known that temperatures in this range will cause sintering in NiMo catalysts, it was presumed that the catalyst was destroyed under these conditions. The run was continued for two days for operating experience and for comparison with the next run at the same conditions.

Figures 6-1 and 6-2 show the THF- and toluene-soluble conversions, respectively, for the run. The average result for the THF conversion is 95.4%. The corresponding result for the toluene conversion is 85.4%. The THF result is in the same range as those obtained for a medium severity, single-stage thermal experiment. However, toluene conversion for this configuration is approximately 5% higher than the maximum toluene conversion obtained for single-stage noncatalytic experiments.

Run 51153 was a repeat run of the conditions used for Run 51152. Startup was performed by the following procedure. Flow of wash oil was brought onstream with the two reactors at approximately 500°F. The temperature on the first reactor was brought up to 770°F. The heat carried from the first reactor to the second via liquid flow brought the second reactor to some nominally higher temperature (about 550°F). From this point, the heaters to the second stage were brought on in small increments to heat the catalyst bed to 700°F over a period of approximately 1 hour. During heatup of the second-stage reactor, coal slurry was introduced to the reactors. This procedure eliminated the problem of overheating the catalyst in an exotherm generated by introducing feed directly onto fresh catalyst.

Significant problems experienced in the course of this run included the integrity of the catalyst basket and difficulty in filtering the liquid product in the THF workup. A larger catalyst basket (7 inch length compared to standard 3 inch length) was necessary to accommodate the catalyst loading required to achieve a space velocity of 0.5 in the catalytic reactor. Difficulty was encountered in affixing the baffles to the inside of the annulus without warping the baffles. This problem, together with some looseness in the bearing for the stirrer, caused a collision between the stirrer and the basket which resulted in a hole in the basket of about 2 sq. cm. This resulted in loss of approximately 20-30% of the catalyst at some point during the run. The major effect of this loss is an increase of the nominal space velocity in the second stage from 0.5 g coal/g catalyst/hour to between 0.6 and

0.7. As experience is gained in the fabrication of the larger baskets, the baffle problem will be corrected.

The standard THF workup procedure for coal liquid samples begins with filtration of 400 ml of coal liquid with an equal volume of THF through Grade 94 Eaton-Dikeman filter paper in a Buchner funnel. This filtration is performed at room temperature and typically requires less than an hour for completion. In the case of the coal liquids produced under the conditions of Run 51153, the filters plugged within several minutes leaving approximately 80% of the liquid above the filter. This problem was not resolved by direct heating with a heat lamp to the point of boiling off the THF nor by letting the heated apparatus stand overnight. The analysis and appropriate fractions were obtained from these samples by introducing the unfiltered liquid directly into the soxhlet extraction and running the THF extraction directly on the liquid. The THF-soluble conversion for the samples collected over this seven-day run are shown in Figure 6-3. It is apparent from the range of values obtained (93.5%-96.5%) that the filter plugging is not due to a low solubility of the coal liquid in THF. A change in the size distribution of the solid particles could facilitate plugging of filters and seems the most likely candidate for the cause of this problem. If the problem persists for other sets of two-stage conditions, other filters of different mesh size will be explored. Detailed analytical results from these runs will be reported in the next quarterly report.

RUN 51152

FIGURE 6-1

RUN 51152

FIGURE 6-2

RUN 51153

FIGURE 6-3