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COAL LIQUEFACTION CATALYST DEVELOPMENT

Quarterly Progress Report No. 1

By
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Amoco Research Center
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QUARTERLY PROGRESS REPORT NO. 1

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QUARTERLY SUMMARY

This project is a continuation of the coal liquefaction catalyst development program formerly funded by the Electric Power Research Institute. During the first quarter of DOE sponsorship, progress was made in the area of Task 1, Task 2, Task 3, and Task 5.

Work in Task 1--Catalyst Preparation and Screening--was concerned with modification of our product workup procedure and elimination or reduction of uncertainties in the analysis of data from batch autoclave screening runs. Toluene was substituted for benzene as a solvent in the product workup because of the health hazard associated with the use of benzene and was added to the product prior to filtration in order to expose both liquid and solid product to the solvent. The conversion was about the same, using either the old benzene or new toluene product workup.

The Engelhard dry coal charging device was used in an attempt to eliminate uncertainties in the batch screening data analysis. After considerable experimentation, use of the charging device was abandoned because of problems with plugging, temperature upsets, and catalyst coking.

The effort in Tasks 2 and 3--Catalyst Aging Tests - Eastern and Western Coal--was centered around preparation of enough liquefaction solvent for the DOE program. Initially, we attempted to distill 22 barrels of recycle SRC II solvent in order to prepare a suitable slurry oil, but the effort was abandoned because of the small amount of 260°C+ bottoms material. Subsequently, DOE arranged for nine barrels of SRC II heavy distillate, FSN-10, which we have tested suitable as slurry oil and will be used as our standard from now on.

In Task 5--Application of New Catalysts - H-Coal--our work centered around the 500 pound batch Amocat-1A (CoMo) that was received from W. R. Grace Company. Catalyst inspection data was acceptable, and according to a recent HRI report the performance results of the 500 pound batch were equivalent to or better than those of an earlier experimental Amocat-1A that HRI tested. The batch of catalyst was also tested in our continuous flow pilot plant, but results were inconclusive since lined-out slurry oil contained unconverted coal particles. At that point in time this was the only slurry oil available.

COAL LIQUEFACTION CATALYST DEVELOPMENT

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COST TRACKING CURVE
COAL LIQUEFACTION CATALYST DEVELOPMENT
AMOCO OIL RESEARCH & DEVELOPMENT

1979

1980

1981

FOREWORD

The H-Coal process, developed by Hydrocarbon Research, Incorporated (HRI), involves the direct catalytic hydroliquefaction of coal to low-sulfur boiler fuel or synthetic crude oil. The 200-600 ton/day H-Coal pilot plant is being constructed next to the Ashland Oil, Incorporated refinery at Catlettsburg, Kentucky under DOE contract to Ashland Synthetic Fuels, Incorporated. The heart of the process is the catalyst; therefore, it is desirable to optimize the specific functions of the catalyst as well as minimize its cost. The objective of this program is to develop improved catalysts for coal liquefaction with the overall objective of improving the H-Coal process. This project is the continuation of the catalyst development program previously funded by the Electric Power Research Institute (EPRI).

The program is divided into five project tasks:

- Task 1 - Catalyst Preparation and Screening
- Task 2 - Catalyst Aging Tests--Eastern Coal
- Task 3 - Catalyst Aging Tests--Western Coal
- Task 4 - Development Support Studies--Synthetic Coal
- Task 5 - Application of New Catalysts--H-Coal

The objective of this report is to outline progress in Tasks 1, Task 2, Task 3, and Task 5 during the first quarter of the project.

TASK 1 - CATALYST PREPARATION AND SCREENING

Under Task 1 of the Coal Liquefaction Catalyst Development Program, new experimental catalysts will be prepared, characterized and tested in a batch screening unit. The activities under Task 1 focus on the development of highly improved catalysts by structuring the experimental program to areas which offer the most promise. Most of the experimental catalysts would be prepared in our Amoco laboratories. The problem areas consist of the following:

- o Modified aluminas
- o Alternate catalytic materials
- o Multifunctional catalysts
- o Novel catalyst systems

Before engaging in our catalyst screening program, modifications of our testing procedure and apparatus were evaluated. The modification and used by Engelhard, involved the use of a dry coal charging device. The device would allow clear definition of the initial starting time for the liquefaction reaction avoiding reactions during the heat-up period.

The following sections describe Amoco's original screening unit and procedure as used for the EPRI funded program. Also described is the Engelhard modification to our procedure and our evaluation of the advantages and disadvantages of this modification. The procedure that we have finally adopted for screening is also discussed.

ORIGINAL CATALYST SCREENING UNIT

The catalyst screening unit, AU-47L, is located in Building 702 of the Amoco Oil process research facility. It was designed and constructed for a maximum working pressure and temperature of 2000 psig and 900°F in accordance with standardized instrumentation and control practice used throughout the Amoco Research laboratory.

The test unit consists of a gas supply module which provides a controlled flow of hydrogen to the reactor and nitrogen for purging. A gas compression station drawing from the central hydrogen supply is used to provide hydrogen of adequate pressure for operation.

The reactor module consists of a 1-liter Magnedrive packless autoclave (Autoclave Engineers, Inc.) and its associated piping. The reactor is piped into the hydrogen supply system and the gas withdrawal system. A view of the reactor, showing the reactor internals, is provided in Figure 1. The impeller and the thermocouple well are shown extending downward from the reactor head. Catalysts are mixed directly with the coal slurry and baffle bars are inserted into the reactor to prevent vortexing.

A split heater is used to heat the reactor. It can be removed from the reactor on completion of a run, thus allowing rapid cool-down. A typical temperature record obtained during a catalyst screening run is shown in Figure 2.

In the screening test, a continuous flow of gas through the reactor is maintained, thereby limiting the accumulation of water, hydrogen sulfide, ammonia, and light hydrocarbons in the reaction system. The reactor is provided with a small (40 cc) trap in the gas exit line to collect excess water and condensible hydrocarbons. The gas withdrawal module consists of the pressure letdown control valve, the wet test meter, and facilities for alternate gas venting and collection.

The control module for the unit is located inside an air-conditioned control corridor. This module contains the pressure, flow and temperature controllers and recorders, incrementing and switching timers, and safety monitoring equipment for both the catalyst screening unit and the continuous liquefaction unit. Inlet hydrogen pressure and flow and reactor pressure are maintained by Moore Syncro controller-recorders using the pneumatic signal from Foxboro pressure transmitters and d/p cells. Exit gas flow is recorded with a Sodeco digital printer using a photo-electric signal from the wet test meter. Iron-constantan thermocouples are used to sense temperatures. Reactor temperature is maintained using a Eurotherm controller with the thermocouple located within the reactor wall. Temperature inside the reactor is indicated on a Doric Trendicator 400 and recorded with a Leeds and Northrup Speedomax Azar recorder having a range of 650 to 850°F. Temperature in the heater jacket is recorded with a Honeywell Electronik 112 recorder. Release of combustible gases to the atmosphere is detected by a General Monitors, Inc., Model 1800 combustible monitor. A Ronan alarm station provides alarming and automatic safeguard actions when excessive deviations in pressure, flow, and temperature occur. A table of safeguard actions is included in Appendix A.

COAL

Illinois No. 6 coal from the Consolidation Coal Company's Burning Star Mine No. 2 at Pinkneyville, Illinois was used in this study. Approximately one ton of coal, ground to pass a 60 mesh screen and dried to about 3 percent moisture, was obtained from Hydrocarbon Research, Inc. (HRI). Eight drums, each containing about 250 pounds of coal in polyethylene bags, were received. The contents of drum #1 were broken down into smaller quantities and stored in polyethylene bags in 25 pound pails for easier access and to reduce exposure to air.

Figure 1. Reactor Internals

Figure 2. Typical Record of Reaction Temperature

4.

The proximate and ultimate analyses obtained on the coal are given in Table I.

TABLE I
ANALYSIS OF ILLINOIS NO. 6 COAL (HRI SAMPLE 3663)

<u>Proximate Analysis, Wt%</u>	<u>Amoco</u>				<u>HRI</u>	<u>CTE</u>
	1	2	3	Avg.		
Moisture					3.33	3.13
Ash					11.07	11.10
Volatile					36.50	37.87
Fixed Carbon					49.10	47.90
 <u>Ultimate Analysis, Wt%</u>						
Moisture	4.19	2.90	2.84	3.31	3.33	3.13
Carbon	67.36	66.95	66.39	66.90	68.30	
Hydrogen (organic)	4.63	4.81	4.78	4.74	4.38	
Nitrogen	1.15	1.23	1.23	1.20	1.37	
Sulfur	2.93	3.27	3.24	3.15	3.51	3.30
Ash	10.82	10.52	11.00	10.78	11.07	11.10
Oxygen (by difference)	8.92	10.32	10.52	9.92	8.04	
Atomic H/C				.844	.764	

Amoco sample 1 was taken from the top of drum #1. Samples 2 and 3 were taken at a later date from lower levels in drum #1. The HRI analysis is presumed to represent a composite of the coal before loading into drums.⁽¹⁾ The analysis obtained from CTE (Commercial Testing and Engineering Company, Chicago, Illinois) corresponds to Amoco sample 3. Where comparison can be made, there appears to be good agreement between the Amoco and CTE analyses of sample 3.

The proximate analyses of HRI and CTE also compare well. Except for a low carbon and correspondingly high oxygen, the average Amoco ultimate analysis is close to the HRI analysis. Noteworthy in the Amoco analyses is the high moisture content of sample 1, which was taken from the top of drum #1, compared to the moisture contents of the samples taken deeper in the drum.

A maceral analysis was obtained on a sample of coal from drum #1.⁽²⁾ The results are shown in Table II.

TABLE II
PENN STATE
MACERAL ANALYSIS
ILLINOIS NO. 6 COAL (HRI 3663)

<u>Component</u>	<u>Volume Percent</u>
Vitrinite	93.5
Pseudovitrinite	0.0
Fusinite	1.7
Semifusinite	1.8
Massive Micrinite	0.7
Granular Micrinite	0.9
Resinite	<u>1.4</u>
	100.0

It should be noted that this coal is very rich in vitrinite which is considered to be a reactive species in contrast to fusinite and micrinite. (3)

LIQUEFACTION SOLVENT

Various materials have been used as solvents in coal liquefaction. In general, these materials contain substantial quantities of condensed aromatic compounds. Such compounds when partially hydrogenated have the capability of transferring hydrogen to a hydrogen-poor substance, such as coal, thereby facilitating its dissolution. The simplest liquefaction solvent is tetralin while the most complex, excluding the liquefaction product itself, is coal tar distillate or anthracene oil. For the purpose of catalyst screening, we have chosen a material intermediate between these two extremes; namely, Panasol AN-3. This material is recovered from the distillation bottoms after high severity catalytic reforming of naphtha.

We see several advantages to using Panasol AN-3 as the liquefaction solvent.

- o It is available commercially and also internally from Amoco Chemicals.
- o It is free of sulfur, nitrogen, and oxygen compounds.
- o It is completely aromatic, consisting primarily of mono-, di-, and tri-methylnaphthalenes.
- o It contains very few side chains longer than methyl.
- o It has excellent potential for hydrogen transfer since it can be hydrogenated to tetralin type molecules.

Typical physical properties of Panasol AN-3, based on the analysis of an earlier sample, are presented in Table III.

TABLE III
PROPERTIES OF PANASOL AN-3⁽¹⁾

		Distillation ⁽²⁾	
		Wt%	°F
Specific Gravity (20°C)	0.993	0.5	388
API Gravity	10.6	1	390
		5	425
Viscosity, Cp at 100°F	2.08	10	429
Cp at 210°F	0.83	20	433
		30	436
Pour Point, °F	+5	40	439
		50	464
Flash Point, °F (Cleveland Open Cup)	230	60	471
		70	476
Ramsbottom Carbon, Wt%	0.4	80	499
		90	516
Heat Capacity at 550°F, Btu/lb/°F	0.59	95	536
		99	568
Aromatic Content, %	100	99.5	582

(1) Data obtained on a 1969 sample

(2) Gas chromatographic simulation

The hydrocarbon type distribution of Panasol AN-3, as determined by mass spectrometric analysis, is shown in Table IV. Dicyclic aromatics are the predominant species. Two- and three-ring aromatics constitute about 90 percent of the material while the remaining 10 percent is distributed between alkyl benzenes and partially hydrogenated polycyclics.

Properties of the current material, AN-3R, obtained from Amoco Chemicals Corporation, Texas City, Texas, and used in the catalyst screening program are listed in Table V. The two samples are very similar in composition. Analysis by gas chromatography shows that the current sample contains less than 0.4 percent C₈ and C₉ aromatics, primarily xylenes and trimethylbenzenes, and a total of 2.6 percent boiling below naphthalene.

TABLE IV
COMPOSITION OF PANASOL AN-3

Hydrocarbon Type, %	Carbon Number						
	10	11	12	13	14	15	16
Alkyl benzenes	0.4	1.8	0.7	0.3			
Naphthene benzenes		2.7	1.6	0.3			
Dinaphthene benzenes		1.0	0.7	0.3			
Naphthalenes	4.4	38.2	28.7	13.1	2.3	0.2	
Acenaphthenes			0.4	1.2	0.8	0.6	0.2
Fluorenes				0.1			

TABLE V
ANALYSIS OF COAL LIQUEFACTION SOLVENT
(Panasol AN-3R)

Specific Gravity (20°C)	0.992
API Gravity	10.7
Refractive Index, n_D^{20}	1.5948
Carbon, Wt%	92.06
Hydrogen, Wt%	7.89
H/C Atomic Ratio	1.02
Aromatic Content, %	100

Hydrocarbon Distribution⁽¹⁾

C ₈ , Wt%	.14
C ₉	.25
C ₁₀	9.16 (6.9% Naphthalene)
C ₁₁	42.94 (38.1% Methyl-naphthalene)
C ₁₂	31.12 (30.1% Dimethyl-naphthalene)
C ₁₃	10.34
Heavier	6.05

(1) Gas chromatographic analysis

ORIGINAL CATALYST SCREENING PROCEDURE

Operation of the catalyst screening unit involved the following steps:

- o Charging the reactor
- o Pressure testing and setting hydrogen flow
- o Reactor heat-up
- o Reaction at maximum temperature
- o Reactor cool-down
- o Depressuring and emptying the reactor

Charging the Reactor

The reactor head is provided with a 3/8" ID port for charging the sealed reactor. During the coal liquefaction runs, a slurry of catalyst and coal was admitted to the reactor through the charging port. A portion of the coal solvent was retained to wash down the slurry beaker and charging funnel, thus insuring quantitative transfer of catalyst and coal. As a result, approximately two grams of the AN-3R initially weighed out were lost due to wetting. The exact weight of AN-3R transferred to the reactor was determined by reweighing all wetted items.

Pressure Testing and Setting Hydrogen Flow

The reactor charge port was sealed and the reactor was purged first with nitrogen, then with hydrogen. Pressure was raised slowly with hydrogen to 137 atm (2000 psig). The reactor was blocked in for 15 minutes to check pressure integrity. Hydrogen flow was then set for 3 CF/hr. Stirring speed was set at the desired level.

Reactor Heat-Up

The reactor was brought to temperature by means of an electrical heating jacket. The split furnace was used for all catalyst screening runs. The intention was to have a uniform heat-up time from run to run. The most critical part of the heat-up period was in the upper temperature range where reaction could contribute to total conversion. In general, 40 minutes were required to reach 427°C (800°F) from 343°C while only 15 minutes were required to reach 399°C (750°F). Experiments showed that 399°C was a suitable temperature for catalyst screening so that the contribution of the heat-up period to conversion would be appreciably reduced.

Reaction at Maximum Temperature

When the desired reaction temperature was reached, temperature was maintained for a nominal reaction time, e.g., 60 minutes. The best control of temperature was obtained with the control thermocouple located in the body of the reactor. Control was such that a damped oscillation in temperature with a maximum amplitude of $\pm 3^\circ\text{C}$ was observed. Because of the oscillatory nature of the reaction temperature, as shown in Figure 2, the reaction time was defined as the interval starting at 5°C below the desired temperature during heat-up and ending at the same point during cool-down. This interval was measured precisely off the Azar recorder chart. Thus, for a nominal setting of 60 minutes, the recorded reaction time would be about 65 minutes.

Reactor Cool-Down

At the end of the nominal reaction time, the heat was shut off. When the temperature dropped to 5°C below the desired temperature, hydrogen flow was stopped and the reactor was isolated from the rest of the system. Stirring was continued. Using the split heater, cool-down was precipitous with only 2.5 minutes required to drop from 399° to 343°C. Cool-down to room temperature (with continued stirring) was effected in less than 90 minutes so that the reactor could be emptied and product work-up begun the same day as the run was made. During cool-down, pressure dropped from 137 atm to 59 atm.

Depressuring and Emptying the Reactor

At room temperature, the isolated reactor was depressured slowly, directly to vent. After depressuring, the contents of the reactor were removed by adding benzene to reduce viscosity and then draining through the flush valve. The stirrer was then stopped and the reactor opened up. The reactor internals, as well as the reactor cavity and flush valve, were thoroughly washed with benzene until all residual solids were recovered and the benzene washings collected separately. The reactor was then blown dry and closed up in preparation for the next run.

Original Product Work-Up Procedure

Solids, consisting of catalyst and coal residue, were separated from the oil by vacuum filtration using Whatman #42 filter paper. The filter cake was then washed with the reactor washings and finally with fresh benzene and allowed to dry to facilitate transfer to an extraction thimble. The benzene caught in a dry ice-acetone trap following the filter flask was added to the material drained from the reactor overhead trap to facilitate separation of the aqueous phase, which was weighed, from the organic phase, which was combined with the oil product.

The extraction thimble containing the recovered solids was placed in a Soxhlet extractor. All glassware, etc., was rinsed with benzene through the extraction thimble to ensure quantitative transfer of solids as well as oil. Extraction of the solids was carried out overnight using about 250 cc of benzene. Occasionally at low conversions it was necessary to divide the solid residue into two or more extractions. After extraction, the thimble containing filter paper, catalyst, and coal residue was allowed to air dry to evaporate most of the adsorbed benzene and then dried at 160°C for four hours in a vacuum oven (250 mm Hg).* The thimble was transferred to a vacuum desiccator to cool and then weighed.

Early in the experimental program, the oil product was handled as a benzene solution. The product oil was transferred to a one-liter volumetric flask to which the benzene washings were also added. The extraction apparatus was rinsed with benzene which was combined with the benzene extract and added to the volumetric flask. If there was excessive benzene extract, a portion of the benzene was removed by distillation before addition to the volumetric flask. Flask contents were diluted to the mark, the weight of the benzene solution was determined, and samples were then analyzed for benzene concentration by gas chromatography, as well as for Karl Fischer water and elemental composition.

* Initially, drying conditions were 110°C for 2 hours, but the more severe conditions were eventually adopted to ensure benzene removal.

Because of the large amount (nominally 60 wt%) of benzene present, however, the ultimate characterization of coal liquid was very sensitive to even small errors in the analysis of the benzene solution. Consequently, this policy was changed later in the program in favor of segregating the primary oil product and the benzene solution. The primary oil product was removed from the reactor, vacuum filtered, and the filtrate saved without dilution. The filter cake was then treated as before with the benzene washings from the reactor and extracted. This procedure is depicted in Figure 3. The benzene solution was distilled through a Claisen-Vigreux column to remove the benzene. Analysis of the primary oil and the benzene extract showed that the two oils were similar in composition. Therefore, the two materials were obtained to give a product usually containing less than one percent added benzene.

The use of benzene as the solvent in product work-up is based on:

- o Its extensive use in the industry for determining unreacted coal solids.
- o It introduced only carbon and hydrogen into the elemental analysis.
- o Its concentration is readily determined by gas chromatography using a normal paraffin, such as heptane or octane, as an internal standard.

Definition of Conversion

The definition of conversion is based on the measurement of unreacted coal and calculated on a moisture and ash-free basis as follows:

$$C = 100 \frac{S_i - S_f}{R}$$

where C = wt% maf conversion
 S_i = initial dry weight of catalyst and coal
 S_f = final dry weight of catalyst and coal residue
 R = weight of maf coal charged

The coal charged on an as-received basis was 150.0 grams. The dry and maf charge were calculated using an average of the HRI and the first Amoco ultimate analyses which indicated 3.76 wt% water and 10.95 wt% ash.* Thus, 150 g of as-received coal represented 144.4 g, dry, and 128.0 g, maf. Using the HRI analysis alone would give values of 145.0 g, dry, and 128.4 g, maf. These differences in the calculation of dry and maf coal result in an insignificant error of less than 0.3 wt% in conversion.

The coal residue was determined from the weight of dried solids after Soxhlet extraction with benzene. The reasons for using the benzene insolubles in defining conversion have already been enumerated. A comparison of benzene and

FIGURE 3

DETERMINATION OF INSOLUBLE RESIDUE,
BATCH SCREENING UNIT

pyridine extraction is discussed later. The solids recovered from the reactor also include catalyst. The weight of catalyst recovered cannot be determined with sufficient accuracy, therefore the weight of recovered solids was simply reduced by the catalyst charged. Because of the small amount of catalyst ultimately used in catalyst screening, any error due to changes in catalyst composition (e.g., sulfiding) should be insignificant.

DRY COAL CHARGING DEVICE

Engelhard's modification was designed to eliminate (or at least greatly reduce) uncertainties in the analysis of data from batch autoclave runs. These uncertainties result from coal conversion during both heating and cooling even in the absence of catalyst and high hydrogen pressures. Accordingly, provision was made to inject coal into the autoclave only after solvent and catalyst have been brought to operating temperature.

Thus, dry coal is injected from a pre-pressurized 250 ml cylinder (mounted above the autoclave) and fitted with a remotely operated fast-opening air actuated ball valve. The delivery tube (which extends through the autoclave cover and in close proximity to the internal liquid level) was made as short as possible and free of internal obstructions. The feed cylinder is fitted with an insert providing exponentially curved walls to facilitate complete discharge. The cylinder is tapped with a mallet after flushing and pressurizing to settle coal clinging to the walls. The packed coal occupies one-half of the charge cylinder volume.

Deliveries of 99% of the coal charged to the feeder were claimed by Engelhard, at differential pressures 1500 psi between feeder and autoclave at the time of discharge.

To avoid forcing coal and solvent into the feed and exit lines on injection, sintered metal filter elements were inserted into the gas (feed and vent).

In a typical run, solvent and catalyst are weighed and sealed in the autoclave. A weighed sample of coal is charged into the feeder. Appropriate line connections are made and both the autoclave and feeder are flushed with nitrogen, pressure tested, flushed with hydrogen and pressured with hydrogen (to 250 psi in the autoclave, 2000 psi in the feeder). The furnace is then elevated and the autoclave temperature is raised, with agitation to 30°C higher than the desired operating temperature. Coal is then injected from the feeder by opening the air actuated valve between the feeder and autoclave. When the pressures in the feeder and autoclave have equalized, the valve is closed, hydrogen is added rapidly to the autoclave until the desired operating pressure is reached and the temperature controllers are readjusted to the operating temperature.

Reaction time is now redefined as the interval starting with the injection of coal and ending when the temperature is intentionally cooled to 5°C below the lined out run temperature. This interval is again measured precisely off the Azar recorder chart. All other aspects of the unit and screening procedure were the same as described under our original procedure.

We have executed 12 practice runs with this dry coal charging device. The result of these runs is summarized in Table VI. Three severe problems associated with its use have been identified. They include:

- o temperature control
- o plugging of injection line
- o excessive catalyst deactivation

TABLE VI

THERMAL RUNS WITH DRY COAL CHARGING DEVICE

<u>Date</u>	<u>Notebook No.</u>	<u>Conditions</u>	<u>Comments</u>
4/27/79	4222-2	750°F, 300g Panasol	Valve malfunction; no coal injection
4/30/79	"	"	" "
5/2/79	"	Room T °F, No Panasol	99.7% Coal transfer
5/2/79	"	"	100% Coal transfer
5/3/79	"	Inlet heated to 200°F	Coal plugged in inlet line
		750°F, 300g Panasol	
5/4/79	4222-4	"	"
5/14/79	3660-60	"	"
5/15/79	3660-62	"	"
5/25/79	3660-63	"	70% Coal transfer, plug
5/25/79	3660-64	Predried coal	100% coal transfer
		750°F, 300g Panasol	
5/29/79	3660-65	"	"
5/30/79	3660-66	"	"
6/15/79	3660-68	"	Coal plugging, no transfer

First, there is a large temperature "upset" caused by the injection of the cold coal into the hot reactor. A temperature profile for a typical run using the charging device is shown in Figure 4. It is possible to partially compensate for this upset by preheating the reactor to a temperature about 30° higher than the desired run temperature. This aids in minimizing the time required to recover but a lag still occurs between injection time and temperature line out. So while the reaction start time has been defined, reaction conditions in the earlier stages of the run are uncertain, offsetting much of the advantages for using the device.

The second problem is more severe. Several of the practice runs were plagued by incomplete coal injection due to plugging associated with the charging device. Initial tests indicated that good transfer would occur if the reactor were cold and free of solvent. This suggested that solvent condensation in the tubing leading from the device to the reactor was responsible for the coal plugs. However, heating this inlet line to avoid condensation did little to remedy the problem. Partial success was achieved by predrying the coal at 100°F in a nitrogen atmosphere, but the procedure was still unreliable and occasional plugging occurred.

FIGURE 4

Finally, another potential problem exists which has a strong impact on the screening test. The solvent catalyst slurry must be heated to reaction temperature prior to coal injection, under reduced hydrogen pressure. These conditions usually lead to catalyst coking and deactivation, particularly when coal is first injected into the reactor and pressure is low (1000 psig). Because of these problems, use of the charging device was abandoned and the reactor was restored to its original condition.

Updated Product Work-Up Procedure

The original product work-up to obtain "benzene" soluble conversions has already been described. There are two problems associated with this procedure.

First, true benzene solubility is never determined. Only the unreacted solid residue is washed with benzene to remove any soluble material. The liquid product is never exposed to benzene and so benzene solubility is not measured. Secondly, there is a potential health hazard associated with the use of benzene. Both of these problems are avoided by the modified procedure we have adopted. Toluene is now used as a solvent and a five-fold excess is added to the product prior to filtration. Any toluene insoluble material is now precipitated and removed by filtration along with unreacted coal and catalyst. The residue is washed with toluene to remove solubles and conversion is determined from the amount of unreacted coal and toluene insolubles present in the filter cake. The updated procedure is shown in Figure 5. The procedure has now been tested in thermal runs and the results are presented in Figure 6. Here, conversion is plotted as a function of reaction time. Also shown for comparison are similar data obtained using the original "benzene soluble" conversions. Where data was available at similar reaction times, the conversion was about the same using either method of product work-up. This similarity is probably coincidental. Toluene is a better solvent for coal liquids than benzene but the new procedure inherently produces more insoluble materials. The two effects most likely offset each other.

FUTURE WORK

Now that a suitable product work-up procedure has been selected, testing will continue to establish base conversion levels; both thermal and catalytic. The base catalytic runs will employ the commercial catalyst, HDS-1442A, and conversion will be measured as a function of run time. This data is needed for comparison with new experimental catalysts soon to be tested.

Screening will begin by testing "Modified Aluminas" and "Two Catalyst Systems" previously outlined in the Technical Proposal under Task I.

FIGURE 5

UPDATED PRODUCT WORKUP FOR
BATCH SCREENING UNIT

FIGURE 6

TASK 2 - CATALYST AGING TESTS--EASTERN COAL

Promising catalysts screened in a batch unit are evaluated further for aging behavior in a continuous-flow stirred reactor where a mixture of powdered coal slurry and hydrogen is contacted with the catalyst contained in a stationary basket on a once-through basis at fixed test conditions. The continuous flow pilot plant equipments, test procedure, product workup and analysis are reviewed in detail in the following. The runs made since March, 1979 will be summarized later.

PILOT PLANT UNIT AND OPERATION

Unit Flow Diagram

The continuous coal liquefaction pilot plant consists of sections for coal slurry feed, hydrogen feed, stirred autoclave reactor, slurry product collectors, and gas scrubber. Also included are instrumentation, back-up systems and automation features for control monitoring, metering and safeguarding for continuous operations 24 hours a day, 7 days a week to obtain catalyst life data.

A schematic flow diagram is given in Figure 7. The slurry oil is drawn off from the storage drum, mixed with pulverized coal and transferred to the slurry feed tank which is placed on a high accuracy electronic scale. The coal slurry is vigorously stirred in the feed tank and constantly circulated with a Moyno pump. The circulation loop provides the suction for a Bran & Luebbe metering pump. The coal slurry feed is combined with a controlled hydrogen flow and continuously introduced into the bottom of a one liter stirred autoclave reactor containing a stationary catalyst basket. No pre-heater is employed. Reaction products are withdrawn through an internal vertical overflow tube into one of the two high pressure separators. The slurry product collected in the separator is drained manually into a product receiver. The exit gas from the separator is passed through an ammonium salt scrubber filled with water, depressured through a letdown valve, metered, and either vented or sampled. An analytical procedure utilizing a gas chromatograph equipped with dual detectors (FID and thermal conductivity) is currently under development and will be used for all future tests to allow a better estimate of gas yields. Operation is once through with respect to both hydrogen and coal slurry feed.

The catalyst aging test is typically run for a 6-10 day period. Samples are taken for two hours during the day and also collected overnight; the overnight operation is unattended. Product recovery ranges between 98 to 102 wt% on feed. Slurry pumping is consistently within 5% of a target rate, and unit shutdown due to plugging seldom occurs.

Fig 7 Unit flow diagram

Fig 8 Liquefaction reactor

Reactor

The one-liter stirred autoclave which has been used as reactor for four years was recently replaced by a new but identical autoclave with Magnedrive II stirrer (see Figure 8). The internal dimensions are 7.6 cm I.D. and 22.9 cm deep with a conical bottom. The stirred autoclave reactor has a stationary annular shape catalyst basket which can be slid and fitted against the reactor wall, as shown in Figure 8. The annular shape basket is 10 mm thick and 10.2 cm high, which can hold up to 100 cc catalyst in 5-6 pellet thickness. Baffles are provided in and outside of the annulus to prevent vortexing. A well-defined slurry and gas interface is established at the tip of the overflow tube which extends about 8 cm from the reactor bottom and 2.5 cm below the top of the catalyst basket. The reactor holdup is set at 295 cc, but it can be varied by the overflow tube height so that the residence time for thermal reaction (relative to catalytic reaction) can be adjusted. A high stirring rate with a six blade homemade impeller is used to mix the reactor contents and to provide a high interfacial area between the hydrogen gas and the slurry. After each test the catalyst basket is removed and is typically very clean showing no signs of plugging or bridging on the basket screen.

The reactor is heated up by a split-type electric furnace surrounding the reactor wall which is 1.75 cm thick. The flat reactor outside bottom is insulated by a fitted transite plate. The reactor internal temperatures are measured and controlled within 1°C by the thermocouple extended from the reactor head through a thermocouple into slurry phase.

FEEDSTOCKS

Coal

The original inventory of Illinois No. 6 Burning Star Mine Coal received from HRI is still the supply source for the current study on Eastern coal. The subbituminous Wyodak coal mined by Wyodak Resources Development Company, Gillette, Wyoming, and dried to about 6 wt% moisture by HRI, is also used to study Western coal. For pilot plant aging tests, these coals were ground further to pass 400 mesh (<38 micron) in a nitrogen atmosphere and stored in polyethylene bags. The proximate and ultimate analyses and inspection on particle size distribution are given in Table VII.

Slurry Oil

Ten drums of SRC II heavy distillate was received from the Pittsburgh and Midway Coal Mining Company (sample shipment No. 1576) on May 22, 1979. The ten individual drums were blended in two batches, with the first batch stored in five 55-gallon drums and the second batch in four drums. They are designated as FSN-10 and meet our specification required for reasonable slurry pumping operation. FSN-10 will be used as our standard slurry oil and good for one year supply. The complete analytical inspection data are not available yet.

TABLE VII
ANALYSES OF COALS

<u>Proximate, Wt%</u> <u>Moisture Free</u>	<u>Illinois No. 6</u> <u>Burning Star</u>	<u>Wyodak</u> <u>Gillette, Wy.</u>
Ash	11.29	9.35
Volatile	38.47	45.26
Fixed Carbon	50.17	45.39
<u>Ultimate Analysis, Wt%</u>		
Moisture	3.32	5.85
Ash	10.92	8.80
Carbon	67.60	62.83
Hydrogen (organic)	4.56	4.65
Oxygen (by difference)	8.98	15.97
Nitrogen	1.29	0.92
Sulfur	3.33	0.98
Atomic H/C	.809	.888
<u>Sulfur Types, Wt%</u>		
Inorganic	0.08	0.05
Pyritic	1.17	0.12
Organic	2.08	0.81
	3.33	0.98
<u>Particle Size, Wt%</u>		
16-30 U.S. Mesh	0.2	0.0
30-50	0.8	0.4
50-100	1.7	0.9
100-200	5.8	3.5
200+	91.5	95.2

Prior to FSN-10, a total of 22 barrels of SRC II light and heavy distillate (FSN-9) was received, but the material was not viscous enough to be used as a slurry oil. This earlier shipment was in the process of atmospheric and vacuum distillation for 1-1/2 months when FSN-10 was received. The distillation work was stopped and the vacuum bottom obtained so far was designated as FSN-9A and stored for future use. A 40% yield of heavy distillate, FSN-9A, was obtained during the fractionation of the full boiling range SRC II product.

TEST PROCEDURE

Catalyst performance is compared on the same volume basis. A total of 60 cc whole pellets, typically 1/16" (2mm) extrudates is compactly measured in a graduate, mixed with 40 cc of 3 mm glass beads and loaded into the annular 10 mm thick catalyst basket. The remaining space of the basket is filled with 3 mm glass beads and a layer of glass wool to prevent catalyst spillover.

The reference catalyst is Cyanamid 1/16" cobalt-molybdenum on alumina (HDS-1442A) obtained from Hydrocarbon Research, Inc.

Standard Test Conditions

The test conditions for measuring catalyst activity are set as follows:

TABLE VIII

STANDARD TEST CONDITIONS

Catalyst Charge:	60cc, 1/16" extrudate
Coal Slurry:	25 Wt% coal in SRC II heavy distillate
Reactor Holdup:	295 cc
Pressure:	137 atm (2000 psig)
Temperature:	440°C (825°F)
H ₂ Feed Rate:	225 liters/hr (8 SCFH)
Slurry Feed Rate:	402 g/hr
Residence Time:	44 minutes
LHSV:	1.68 g-coal/hr/cc-catalyst
Mixing Speed:	1500 rpm

The test conditions are the same as the high severity conditions employed last year under EPRI's sponsorship, except for a change in LHSV from 1.79 to 1.69 due to a small reduction of reactor holdup. The slurry concentration of 25 wt% is comparable to that used in H-Coal bench scale unit. The residence time is a nominal value calculated from reactor holdup divided by slurry feed rate. The residence time of 44 minutes is selected to correspond benzene soluble conversions in the range of 70-80% which allows catalyst effects to be seen more clearly. Consistent slurry pumping is an important factor for obtaining good quality data.

Test Procedure

Prior to startup, catalyst is sulfided in situ at 260°C, and temperature is brought to 400°C with wash oil only in order to avoid the plastic state of coal which otherwise might foul catalyst. A detailed procedure is summarized in Table IX.

TABLE IX

REACTOR STARTUP PROCEDURE

1. Purge with nitrogen and heat reactor to 260°C (500°F)
2. Sulfide catalyst at 260°C with 8 vol% H₂S in hydrogen in excess of the stoichiometric amount of sulfur. Typically, a total of 0.15 grams of sulfur per each gram of cobalt-molybdenum catalyst is passed at about 3 atm in 30 minutes. An exotherm less than 20°C is usually observed during the sulfiding.
3. Pressure up the reactor and set hydrogen flow at 260C in 30 minutes.
4. Start a wash oil (hydrogenated anthracene oil, HAO) spiked with dimethyldisulfide to 0.5 wt% S and rapidly heat reactor to 400°C (750°F).
5. When temperature reaches 400°C, switch to coal slurry and raise temperature to 440°C (825°F) to commence testing.

When the test is over, the hydrogen flow and slurry feed pumping are briefly interrupted and the reactor contents are emptied to a blowdown drum. Then, the operation is switched from coal slurry to wash oil (HAO) pumping for a minimum of a two-hour period during which reactor cooldown begins. When temperature reaches about 260°C (500°F), the wash oil pumping together with hydrogen flow is stopped and the reactor holdup is again emptied. With the hydrogen flow restored, the reactor continues to cool down to ambient temperature. Finally, the unit is depressured and purged with nitrogen prior to recovery of the used catalyst. The catalyst basket usually shows no plugging or bridging on either the basket screen or in the catalyst bed. To prepare for further analyses, the used catalyst is washed with tetrahydrofuran in an ultrasonic bath followed by Soxhlet extraction and vacuum oven dried at 110°C. We plan to analyze the extract from the bath to determine whether any inorganic material is being removed from catalyst particles.

PRODUCT WORKUP AND ANALYSISMajor Performance Indicators

Various types of information are generated from product workup and analysis. The specific information needed to assess catalyst performance fall into the following general categories:

TABLE X

CATALYST PERFORMANCE INDICATORS

Total Liquefaction Yield	Conversion to THF Solubles
Product Selectivity	Conversion to Benzene Solubles
	Conversion to Hexane Solubles
	Conversion to 520°C - liquid
Product Quality (total liquid and 520°C+ Resid)	S, N, O, H contents, Specific Gravity
Hydrogen Consumption	From Elemental Balance

Total liquefaction yield or boiler fuel production is represented by the conversion of coal to the materials soluble in tetrahydrofuran (THF). The benzene soluble conversion is, in essence, a measure of the extent of pre-asphaltene conversion; it provides a much more sensitive performance indicator than the THF soluble conversion. Hexane soluble conversion is indicative of secondary hydrogenation. Product qualities such as S, N, O, H contents are measured on both total THF soluble liquid and 520°C+ vacuum distillation resid bottom. Since the total THF soluble liquid product contains slurry oil as well as liquefied coal oil, the qualities of 520°C+ resid are considered more important. Vacuum distillation of the new heavy distillate slurry oil, FSN-10, shows about 2 wt% 520°C+ resid.

Product Workup

The slurry product recovered is stripped with nitrogen to remove hydrogen sulfide and ammonia before it is allocated for various types of product workup. Product workups are carried out to determine coal conversion based on solubility to a specific workup solvent and to generate enough quantity of liquid sample needed for product quality analysis and estimation of hydrogen consumption. Largely, two product workup methods are employed; macro-THF workup method and micro-residue method.

The macro-THF workup method is the usual vacuum filtration followed by Soxhlet extraction with THF, and is performed only on the slurry products obtained daily for two-hour sampling period to determine the following comprehensive data: a) THF insoluble content, b) ash content in THF insoluble residue, c) THF soluble liquid product for analysis, and d) 520°C+ resid fraction of the total liquid by vacuum distillation. The micro-residue method is used to determine benzene and hexane soluble conversions by millipore filtration of a small sample of slurry product diluted with the respective workup solvent. The method is fast and has been used to monitor the pilot plant runs on both the two-hour cuts and overnight samples. The detailed product workup procedures are described below and are depicted in Figure 9.

FIGURE 9

PRODUCT WORKUP FOR
CONTINUOUS PILOT PLANT

THF Macro-Residue Method

About 350g of slurry product sample is diluted with tetrahydrofuran in 1:1 volume ratio, and vacuum filtered through Whatman No. 42 filter paper on a Buchner funnel at room temperature. The filter cake is washed with THF and then air dried in situ for easy transfer to a Whatman cellulose extraction thimble. The thimble containing the residue and filter paper is Soxhlet extracted overnight (18 hours) with 500 ml THF, followed by vacuum drying for three hours at 110°C. The filtrate and extract are combined and distilled to remove THF. The total liquid product usually contains less than 2 wt% THF.

Because THF is a powerful solvent, the filtration is quite efficient and usually complete in two hours; handling loss of the insolubles during the workup is negligible. The method agrees well with THF micro-residue workup employing a millipore filtration cartridge as seen in the table below.

TABLE XI

COMPARISON OF THE WORKUP METHODS

<u>Sample No.</u>	<u>THF Insoluble, Wt% of Product</u>	
	<u>Macro Residue</u>	<u>Micro Residue</u>
1	3.91	3.92
2	3.90	3.93
3	3.87	3.87
4	4.12	4.10

Ash Determination in Insoluble Residue

The THF soluble conversion may be calculated based on the THF insoluble content or alternatively using ash content of the THF insoluble residue. To do this, a high temperature ashing is performed; about 6 grams of dry THF insoluble residue is calcined in a muffle furnace in flowing air with the temperature gradually raised to 480°C for one hour and then subsequently raised to 815°C (1500°F) where it is held for three additional hours to completely combust the residue and leave only ash.

Vacuum Distillation, 520°C+ Resid

Since the THF soluble total liquid contains both slurry oil and coal liquid, it is distilled to obtain 520°C+ resid bottom fraction which consists essentially of liquefied coal oil. Using an ASTM D-1160 apparatus, a 200g sample is distilled at atmospheric pressure to remove the low boiling fraction until the vapor temperature reaches 315.5°C (650°F). Then, the remaining atmospheric residue is vacuum distilled at 1.0 mm Hg until vapor temperature is 293.3°C (560°C). Distillation is stopped by filling the apparatus with nitrogen, shutting off heaters and removing the sample pot as soon as possible. The residue in the pot is recovered as 520°C+ resid fraction in terms of atmospheric temperature.

The 520°C+ resid bottom fraction in the hot flask is fluid but solidifies upon cooling. It is ground to powder, homogenized and sent for elemental analyses. According to ASTM D-1160 method, the cut point may be in error by 10°C. When the slurry oil alone, FSN-10, was distilled in the same manner, 520°C+ resid bottom was approximately 2 wt% of the slurry oil. Increase in the vacuum distillation end point beyond 520°C is not practical.

Benzene Micro-Residue Method

1. Sampling: Slurry product in a pint bottle is vigorously shaken on a paint shaker before sampling. Weigh out approximately 8 grams of sample into a preweighed 40 ml vial.
2. Dilution: Add 20 ml benzene into vial to dilute the sample. Shake and pour into millipore cell with a 10 micron teflon filter. Wash vial with another 20 ml benzene. Wash vial cap with benzene using a squeeze bottle. Pour washings into cell.
3. Initial Filtration: Obtain filtrate 40 ml by applying 25 psig N₂ pressure.
4. Additional Washings: Relieve cell pressure, add 40 ml benzene into cell and then obtain 40 ml filtrate. Repeat once more.
5. Final Washing: Add 50 ml benzene into cell and obtain filtrate until nitrogen breaks through.
6. Drying: Let nitrogen flow for ten minutes to predry filter cake. Collect the filter cake and filter into an aluminum weighing pan and dry in vacuum oven for one-half hour at 110°C.

Duplicate analyses of six separate coal liquefaction products showed a standard deviation of difference, 0.045. The precision of the millipore filtration method is equivalent to a Soxhlet extraction method, but much faster. The above micro-residue method, except for 5 micron size filter, is used to determine THF micro-residue in the absence of THF macro-residue data.

Hexane Micro-Residue Method

1. Place a 12 μ teflon filter in an aluminum weighing dish and dry in a vacuum oven for 30 minutes to weigh. Assemble the millipore cell. Insert a cork into the stem of the holder and add 10 ml hexane.
2. Sampling: Shake slurry product sample on a paint shaker. Pour about 5 gms of sample into a dry, preweighed, 20 ml vial.
3. Dilution: Add about 5 drops of n-hexane to the vial and shake vigorously to disperse hexane in the sample. Repeat two more times. Add 5 ml more hexane, shake and pour into millipore unit. Wash vial and vial cap using squeeze bottle. Pour washings into the unit.

28.

4. Fill the unit full of hexane, release the cork from the stem and allow the hexane to flow. Keep adding hexane making sure that the filter is not allowed to dry out at any time.
5. Once 300 ml hexane has passed through the unit, allow the cake to drain dry. Pressurize the holder with 10 lbs of nitrogen for 10 minutes to predry.
6. Disassemble the holder. Place the filter cake and filter into the weighing pan. Brush into the pan any insolubles that cling to the walls of the holder.
7. Dry the insolubles, sample vial, and cap in a vacuum oven for 30 minutes at 110°C. Remove, cool and weigh. Include the weight of insolubles in the sample vial with the weight of insolubles on the filter,

The present method differs from the previously used hexane millipore procedure particularly in sample dilution step and gives more consistent results.

Coal Conversion Calculation

The liquefaction conversion on a moisture and ash free basis (maf) is calculated from the insoluble residue obtained with a specific workup solvent:

$$X = \frac{(100-Mo) - 100 (R/Co) y}{100-Mo-Ao} \times 100$$

where

X = Wt% maf conversion
Mo = Wt% moisture content of feed coal
Ao = Wt% ash content of feed coal
Co = Wt% coal in slurry feed
R = Wt% dry insoluble residue in slurry product
y = fractional recovery of slurry product

Any uncertainties in feed coal concentration or product recovery translate to imprecision in the conversion calculation when it is based on insoluble. An alternative method which does not depend on slurry feed concentration and product recovery rate is to measure ash content of the insoluble residue and calculates conversion as follows:

$$X(\text{THF}) = \frac{(100-Mo - 100 Ao/A_t)}{100-Mo-Ao} \times 100$$

$$X(\text{benzene}) = \frac{(100-Mo) - 100 (A_1/A_t)(B/T)}{100-Mo-Ao} \times 100$$

$$X(\text{hexane}) = \frac{(100-Mo) - 100 (A_1/A_t)(H/T)}{100-Mo-Ao} \times 100$$

where X = THF, Benzene or Hexane soluble conversion
 A_o = Wt% ash in feed coal
 A_t = Wt% ash in dry THF insoluble residue
 T = Wt% dry THF insoluble in slurry product
 B = Wt% dry benzene insoluble in slurry product
 H = Wt% dry hexane insoluble in slurry product

Ash content is measured by the high temperature ashing method described earlier. The ash method can also provide a means of checking out operational consistency such as coal concentration in feed which may be estimated by $Co = (A_t/A_o) \cdot T \cdot y$.

Product Analysis

There are two main product streams that leave the liquefaction reactor: the hydrogen rich off-gas and the slurry product withdrawn from the high pressure separator which is held at 65°C. The slurry product is stripped with nitrogen to remove hydrogen sulfide and ammonia, and then separated into THF insoluble residue and total liquid product by the macro-residue workup method. A portion of the total liquid product essentially free of THF is vacuum distilled to obtain 520°C+ resid fraction. Analyses on total liquid are reported on a THF-free basis.

TABLE XII

PRODUCT ANALYSIS

Exit Gas	Light Hydrocarbons (C ₁ -C ₅), Carbon oxides
THF - Soluble Liquid	C, H, O, N, S, THF, Water, Specific Gravity
520°C+ Resid	C, H, O, N, S
THF-Insoluble Residue	C, H, O, N, S, ash content

ANALYTICAL METHODS

Elemental

C, H, O	High accuracy combustion
N	Kjeldahl
Basic Nitrogen	Nonaqueous acidimetry
S	X-ray fluorescence for liquids; High temperature method (ASTM D-1552) for solids

Other Analyses

Water	Karl Fischer titration
THF	G.C. component analysis
C ₁ -C ₅	Isothermal G.C. (H ₂ flame)
CO, CO ₂	G.C. (Thermal conductivity)
Trace Metals	Emission spectrography, EDAX

The analyses regularly performed to assess product qualities and analytical methods employed are summarized in Table XII. The hydrogen-rich exit gas usually contains very little C_1 - C_5 light hydrocarbons. Analysis of carbon oxides contents is a new addition and calibration of thermal conductivity G.C. is underway. Elemental analyses of THF-insoluble residue is performed to reconstitute more accurately the slurry product composition needed for hydrogen consumption. Sulfur in 520°C+ resid is measured by a high temperature combustion method. The high temperature sulfur analyzer measures $0.54 \pm 0.03\%$ sulfur for a reference coal sample obtained from National Bureau of Standards.

Used catalysts as well as fresh catalysts are characterized for surface properties, coke content and trace metals deposition during the liquefaction test. Prior to analysis, used catalysts are cleaned in an ultrasonic bath filled with THF for at least four hours followed by Soxhlet extraction for 18 hours. Loss on ignition (LOI) is measured by calcination of a used catalyst sample in air for three hours. Carbon, hydrogen, and sulfur contents are also analyzed for comparison with LOI. Nitrogen desorption isotherms using Digisorb 2500 and mercury porosimetry are used to measure surface area and pore size distribution.

PILOT PLANT RUN SUMMARY

Beginning in March, 1979, the priority for pilot plant activity under DOE sponsorship is to prepare enough liquefaction solvent needed throughout the two-year contract term, and to check the quality of 500 pound batch Amocat-1A (II-112) (CoMo) catalyst as soon as the sample becomes available from W. R. Grace Company. Main run events are summarized below:

<u>Run No.</u>	<u>Date</u>	<u>Test Length, Days</u>	<u>Run Events</u>
5181	4/16/79	10	To test coal slurry pumping under liquefaction condition with the initial shipment of 22 barrels of SRC II distillate (FSN-9) received on 3/21/79. Two small batches of heavy fractions, approximately 500°F+ and 570°F+, both gave a pumpable coal slurry, thus establishing distillation cut point.
5182	5/6/79	7	While the new slurry oil was being prepared by distillation, a base run with HDS-1442A was established using a line-out slurry at hand (FSN-8) as the liquefaction solvent. The run was to be compared with 5183. The catalyst was loaded in the new catalyst basket with 10 mm annular thickness instead of the worn out 6 mm basket.

<u>Run No.</u>	<u>Date</u>	<u>Test Length, Days</u>	<u>Run Events</u>
5183	6/1/79	2	A new stirred autoclave reactor, identical in design to the previously used reactor, was installed while awaiting arrival of 500 batch Amocat-1A sample. The activity test of Amocat-1A was started at the same conditions as Run 5182, but aborted after two days on stream due to reactor pressure loss through a crack in 1/4" thermocouple well caused by mechanical and thermal stress.
5184	6/5/79	8	<p>Amocat-1A (500 pound batch sample) was tested again at the same conditions as Run 5182 using the line-out slurry oil (FSN-8) which contained solid particles. The operation was reasonably smooth, but there were a few items in testing method and strategy which could have adversely affected the results. They will be discussed later.</p> <p>At the end of the run, slurry pumping was tested for the 10-barrel shipment of SRC II heavy distillate (FSN-10) which would replace FSN-9 as the new standard slurry oil. FSN-10 was found to give a satisfactory pumping of coal slurry.</p>
5185	6/19/79	8	The SRC heavy distillate (FSN-10) was used as the slurry oil to test Amocat-1A catalyst again.

Slurry Oil Production

A preferred slurry oil to be used in our pilot plant operation is a hydrogenated coal derived oil with viscosity and gravity high enough to achieve consistent coal slurry pumping. A hydrogenated coal oil with boiling range of 250-450°C (500-850°F) usually fulfills these requirements. The end point is chosen well below 520°C in order to be able to separate 520°C+ resid consisting entirely of liquefaction product free of slurry oil, and also to avoid unduly rapid catalyst deactivation due to too high boiling components of slurry oil.

The slurry oil used in the past was the hydrotreated topped anthracene oil such as FSN-6 listed in Table XIII. In the current DOE program, we have decided to use a recycle solvent from SRC II process. The initial shipment was 22 barrels of light and heavy distillates of SRC II which we designated

as FSN-9. The material as received was not suited for slurry oil, so it was distilled sequentially in atmospheric and vacuum stills to recover 260°C+ heavy fractions. As shown in Table XIII, the 260°C+ bottoms have a lower specific gravity but higher enough viscosity than those of FSN-6 to be used as the slurry oil. However, fractionation of FSN-9 for 1-1/2 months has yielded only one barrel of the 260°C+ bottoms. Subsequently, DOE has arranged for nine barrels of heavy distillate from SRC II, FSN-10, which we have tested suitable as slurry oil. FSN-10 will be used as a standard slurry oil from now on.

TABLE XIII

SLURRY OIL INSPECTION

<u>I.D.</u>	<u>Material</u>	<u>Sp. Gr. at 24°C</u>	<u>Viscosity c.s. at 40°C</u>
FSN-6	Hydrotreated Anthracene Oil	1.124	21.9
FSN-9	SRC II (representative product)		
	As received	0.986	4.2
	210°C+	0.992	8.6
	260°C+	1.058	34.6
	300°C+	1.091	77.1
FSN-10	SRC II Heavy Distillate	1.075	46.1

Aside from the physical property, FSN-10 contains about 1.2 wt% moisture which might be detrimental to catalyst activity maintenance, compared with 0.3% moisture in FSN-6. FSN-10 also contains solid particles insoluble in THF. However, removal of the solid fines by distillation would be time consuming and not practical. A complete characterization of FSN-10 is under way. Under the standard aging test conditions, FSN-10 is expected to give enough differential between thermal and catalytic liquefaction conversion. Run 5181 where 25 wt% Illinois No. 6 was slurried in 260°C+ fraction of FSN-9, which would be similar to FSN-10, resulted in thermal benzene soluble conversion of 55-60 wt% maf that are considered to be adequate.

TASK 5 - APPLICATION OF NEW CATALYSTS--H-Coal

Preliminary Results of 500 Pound Batch Amocat-1A-(II-112) Catalyst

A composite sample of 500 pound batch Amocat-1A-(II-112) (CoMo) was received from W. R. Grace Company. Inspections by N_2 desorption and mercury porosimetry showed that the pore size distribution was within the specification when compared to various versions of small experimental batches which we made and previously tested out to be all superior to HDS-1442A catalyst. Based on this, the catalyst was recommended for H-Coal bench scale test, and according to a recent HRI report the performance results of the 500 pound batch were equivalent to or better than those of earlier Amocat-1A-(I-120) that HRI tested.

The 500 pound batch Amocat-1A-(II-112) sample was also tested in our continuous flow pilot plant, Run 5184, using a line-out slurry as the liquefaction solvent. The line-out slurry was the coal liquefaction slurry products collected last year as slop and contained unconverted coal particles. It was used because at that point in time no other solids-free slurry oil was available. The preliminary results for Amocat-1A (II-112) showed that not only benzene insoluble but also THF insoluble contents of the products were higher than those of Run 5181 for HDS-1442A, indicating lower coal conversions with Amocat-1A sample. However, conversion of Illinois No. 6 coal to THF soluble material should be the same regardless of catalyst type and in fact without a catalyst in our test conditions. Therefore, we strongly suspect that the slurry oil used for Run 5181 and 5184 may not have been of uniform quality, perhaps due to solid settling in the storage drum, which in turn could make one to one comparison of catalyst performance impossible. In fact, ash content measurement indicates there is an increase in ash content of feed slurry for Run 5184 compared to Run 5181.

Besides the irregularity in slurry oil quality, the new catalyst basket with a wider annular thickness and reduced baffle size employed in the tests might have created more vortexing and reduced mixing efficiency so that defining reaction times was difficult. Several steps are being taken to resolve these uncertainties in catalyst comparison test. The run data, together with catalyst inspection data will be presented in the next monthly report.

Ebullation Characteristics

The 500 pound sample of Amocat 1A-(II-112) was prepared from six smaller batches in pilot plant equipment. This catalyst has a very distinctive bimodal pore size distribution with 18% of the total pore volume in macropores greater than $1000^{\circ}A$ diameter. Some of the key properties are listed below.

<u>Sample</u>	<u>Diameter</u> <u>in</u>	<u>Length</u> <u>in</u>	<u>Pore Volume H₂O)</u> <u>cc/gm</u>	<u>CoO</u> <u>%</u>	<u>MoO₃</u> <u>%</u>
R11092	.057	.164	.71	3.12	16.10
R11093	.056	.161	.73	2.95	15.84
R11094	.057	.160	.74	3.03	16.41
R11095	.057	.158	.73	3.12	15.87
R11096	.057	.155	.74	3.12	15.81
R11097	.057	.167	.75	3.12	15.77

Detailed analytical inspections of the six batches and composite can be found in Appendix C. The composite sample of Amocat 1A-(II-112) (identified as R11091) had a pore volume of .73 cc/gm using water titration and .717 cc/gm by combining the micropore volume of the BET measurement with the macropore volume from mercury porosimetry. In our new Amocat nomenclature II indicates the catalyst batch number and 112 is the average pore diameter. An experimental determination of the terminal velocity in water was made for the Amocat 1A-(II-112) and HDS-1442A; an average of 15 separate determinations was made. The terminal velocity of the smaller Amocat 1A was 14.38 cm/sec compared to 16.94 cm/sec for HDS-1442A. Based on this, the ebullation velocity for Amocat 1A would be about 85% of HDS-1442A. However, there were some very small particles in the Amocat 1A which would tend to lower the ebullation velocity.

For both spherical and nonspherical particles the terminal velocity u_t can be obtained from Figure 9, an experimental correlation of the dimensionless groups $C_d Re_p^2$ versus Re_p , where

$$Re_p = \frac{d_p \rho_g u_t}{\mu}$$

and the velocity independent group,

$$C_d Re_p^2 = \frac{4g d_p^3 \rho_g (\rho_s - \rho_g)}{3\mu^2}$$

The sphericity ϕ_s is also used as a parameter in Figure 9 and is defined as

$$\phi_s = \left(\frac{\text{surface of sphere}}{\text{surface of particle}} \right)_{\text{both of same volume}}$$

$$\phi_s (\text{cylinder}) = \frac{4 \left(\frac{3d_p L}{16} \right)^{2/3}}{d_p L + d_p^2/2}$$

ϕ_s = sphericity

Re_p = particle Reynolds number

d_p = particle diameter

L = particle length

u_t = terminal velocity

ρ_g = fluid density

ρ_s = solid density

μ = viscosity

FIGURE 9

CHART FOR CALCULATING THE TERMINAL VELOCITY
OF PARTICLES FALLING THROUGH FLUIDS (4)

$$C_d Re_p^2 = \frac{4(980 \text{ cm/sec}^2)(.237 \text{ cm})^3(\text{gm/cm}^3)(1.66-1.0)}{3(.1 \text{ gm/cm-sec})^2}$$

$$C_d Re_p^2 = 1148$$

$$\phi_s (\text{Amocat 1A}) = .7837$$

From Figure 7 the particle Reynolds number is:

$$Re_p = 11 = \frac{d_p \rho_g u_t}{\mu}$$

$$\therefore u_t = \frac{11\mu}{d_p \rho_g} = \frac{(.1)}{(.237) 1} = 4.64 \text{ cm/sec}$$

If the viscosity of the coal liquid product produced by Amocat 1A were 25% less (HRI reports considerably less), the terminal velocity would increase by 40%. Therefore, improved product quality can easily offset smaller size as far as ebullation characteristics.

HRI have already tested the 500 pound batch of Amocat and found its performance to be quite good; the test was terminated after six days due to ash plugging the upper portion of the reactor. Since the Amocat 1A achieves more viscosity reduction of the residual oil than HDS-1442A, it should probably be ebullated in the H-Coal reactor at the same recycle rate as the HDS-1442A catalyst. From the standpoint of ebullation and pore transport properties, it does not seem logical to increase the size of the Amocat 1A. Once the liquefaction performance of this catalyst has been confirmed by a test in the Amoco pilot plant, we will strongly recommend it for a test on the H-Coal FDU.

FUTURE WORK

Immediately after refinements of test procedures, the following runs are planned:

Run No.	Catalyst	Coal
5186	HDS-1442A	Illinois No. 6
5187	Amocat-1A-(I-120)(experimental batch)	Illinois No. 6
5188	Amocat-1A-(II-112)(500 pound batch)	Illinois No. 6
5189	Amocat-1B-(I-120)(experimental batch)	Illinois No. 6
5190	Thermal	Illinois No. 6 and Wyodak
5191	HDS-1442A	Wyodak
5192	Amocat-1A	Wyodak
5193	Amocat-1B (Mo)	Wyodak

REFERENCES

1. Brooks, J. A., Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., "Catalyst Development for Coal Liquefaction," Electric Power Research Institute Report AF-190, February, 1976.
2. *ibid*
3. P. H. Given, et al., Dependence of Coal Liquefaction Behavior on Coal Characteristics, Research and Development Report No. 61, Interim Report No. 9, Contract No. 14-01-0001-390, Pennsylvania State University, June 14, 1974.
4. G. G. Brown, et al., Unit Operations, John Wiley and Sons, New York, 1950.

APPENDIX A
SCOPE OF AUTOMATIC SAFEGUARD ACTIONS--CATALYST SCREENING UNIT

38.

Alarm Station Iden.	Trouble	Safeguard Actions	Alarm Switch	Override Switch	Scope of Override
PAH-1 HIGH PRESS HYDROGEN FEED	Pressure of hydrogen feed is too high.	Alarm	PSH/L-1	PAS-1H	Alarm.
PAL-1 LOW PRESS HYDROGEN FEED	Pressure of hydrogen feed is too low.	Alarm; after a 30-second delay, stop hydrogen flow by closing FSV-1. (Valve must be reopened manually.)	PSH/L-1	PAS-1L	Alarm; safeguard actions.
PAH-2 HIGH PRESS AUTOCLAVE #1	Pressure in Autoclave is too low.	Alarm; after a 30-second delay, additionally stop hydrogen flow by closing FSV-1. (Valve must be reopened manually.)	PSH/L-2	PAS-2H	Alarm.
FAH-3 EMERG SHUTOFF HYDROGEN SUPPLY	Major hydrogen leak has shut off the hydrogen feed to plant AU-47L.	Alarm; stop H ₂ flow immediately by closing FSV-3. (Valve must be reopened manually.)	FSH/L-3	FAS-3H	Alarm.
FAL-3 EMERG SHUTOFF HYDROGEN SUPPLY	Bypass valve left open.	Alarm after 10 minutes (failure to close bypass valve); after 20 minutes stop H ₂ flow by closing FSV-3. (Valve must be reopened manually.)	FSH/L-3	FAS-3L	Alarm; safeguard actions.
FAH-1 HIGH TEMP AUTOCLAVE #1	Temperature in Autoclave is too high.	Alarm; after a 10 minute delay, cut power to heaters JE-1 and JE-3. (Heater power must be restored manually.)	TIS-1	TAS-1	Alarm; safeguard actions.

APPENDIX B

SURFACE PROPERTIES OF AMOCAT 1A (I-112)

39.

- WAPERVILLE, IL

PORE SIZE DISTRIBUTION VIA MERCURY PENETRATION

CALCULATED JUN 1, 1979

R11091

AMOCAT 1A 500# BATCH

PORE RADIUS (A)	CUMULATIVE PORE VOLUME CC/G.	PORE VOLUME CC/G.	VOLUME PERCENT	AREA PERCENT
50000.0-20000.0	0.0211	0.0017	0.24	0.00
20000.0-5000.0	0.0220	0.0008	0.12	0.00
5000.0-2500.0	0.0383	0.0163	2.29	0.04
2500.0-1000.0	0.1113	0.0730	10.27	0.43
1000.0-600.0	0.1278	0.0165	2.32	0.21
600.0-500.0	0.1318	0.0040	0.57	0.08
500.0-400.0	0.1364	0.0046	0.64	0.10
400.0-300.0	0.1422	0.0058	0.81	0.17
300.0-250.0	0.1452	0.0030	0.43	0.11
250.0-225.0	0.1467	0.0015	0.21	0.07
225.0-200.0	0.1496	0.0029	0.41	0.14
200.0-175.0	0.1530	0.0034	0.47	0.18
175.0-150.0	0.1563	0.0034	0.47	0.21
150.0-140.0	0.1592	0.0029	0.41	0.20
140.0-130.0	0.1632	0.0040	0.56	0.30
130.0-120.0	0.1672	0.0040	0.56	0.33
120.0-110.0	0.1712	0.0040	0.56	0.36
110.0-100.0	0.1792	0.0080	1.12	0.78
100.0-90.0	0.1967	0.0175	2.46	1.89
90.0-80.0	0.2380	0.0414	5.81	4.99
80.0-75.0	0.2840	0.0459	6.46	6.08
75.0-70.0	0.3359	0.0519	7.30	7.34
70.0-65.0	0.3935	0.0577	8.11	8.76
65.0-60.0	0.4609	0.0674	9.47	11.05
60.0-55.0	0.5370	0.0761	10.70	13.57
55.0-50.0	0.6147	0.0778	10.93	15.19
50.0-47.5	0.6477	0.0330	4.64	6.95
47.5-45.0	0.6756	0.0279	3.92	6.17
45.0-42.5	0.6962	0.0207	2.91	4.84
42.5-40.0	0.7090	0.0128	1.80	3.18
40.0-37.5	0.7190	0.0099	1.40	2.63
37.5-35.0	0.7221	0.0031	0.44	0.88
35.0-32.5	0.7252	0.0031	0.44	0.95
32.5-30.0	0.7284	0.0031	0.44	1.02
30.0-27.5	0.7306	0.0022	0.31	0.79
27.5-25.0	0.7306	0.0	0.0	0.0
25.0-22.5	0.7306	0.0	0.0	0.0
22.5-20.0	0.7306	0.0	0.0	0.0
20.0-17.5	0.7306	0.0	0.0	0.0

- * SPECIFIC SURFACE AREA BY MERCURY PORE METHOD 201.50 M/GRAM
- * AVERAGE PORE RADIUS 72.5 ANGSTROMS

- * NOTE THESE LAST TWO VALUES ARE INTENDED AS USEFUL APPROXIMATIONS ONLY, ASSUMING A MODEL OF UNIFORM CYLINDRICAL PORES. MORE ACCURATE SURFACE AREAS MAY EASILY BE DETERMINED BY REQUESTING A "SOCO" OR "DIGISORB" NITROGEN ADSORPTION BET PROCEDURE.

DESORPTION PORE VOLUME DISTRIBUTION

PORE RADIUS, A	PORE VOL. (CC/G)	CUM. PV	SURF. AREA (SQ. M/G)	CUM. SA	PORE VOL. (CC/G)	SURF. AREA (SQ. M/G)
+500.0-500.0	+0.0051	+0.0051	+0.145	+0.145	+0.74	+0.14
+500.0-700.0	+0.0070	+0.0121	+0.312	+0.457	+1.02	+0.11
+700.0-1000.0	+0.0055	+0.0176	+0.317	+0.774	+0.41	+0.11
+1000.0-2500.0	+0.0030	+0.0206	+0.215	+0.989	+0.43	+0.08
+2500.0-2250.0	+0.0031	+0.0237	+0.262	+1.251	+0.28	+0.07
+2250.0-2000.0	+0.0022	+0.0266	+0.271	+1.521	+0.22	+0.10
+2000.0-1750.0	+0.0037	+0.0303	+0.397	+1.918	+0.54	+0.14
+1750.0-1500.0	+0.0040	+0.0343	+0.439	+2.357	+0.58	+0.17
+1500.0-1400.0	+0.0017	+0.0360	+0.239	+2.596	+0.28	+0.09
+1400.0-1300.0	+0.0023	+0.0383	+0.336	+2.932	+0.33	+0.12
+1300.0-1200.0	+0.0033	+0.0416	+0.528	+3.460	+0.48	+0.14
+1200.0-1100.0	+0.0032	+0.0455	+0.634	+4.094	+0.87	+0.28
+1100.0-1000.0	+0.0070	+0.0525	+1.328	+5.422	+1.02	+0.48
+1000.0-900.0	+0.0100	+0.0625	+2.111	+7.533	+1.78	+0.77
+900.0-800.0	+0.0230	+0.0915	+6.826	+14.359	+2.23	+2.28
+800.0-750.0	+0.0256	+0.1171	+6.610	+21.108	+3.73	+2.37
+750.0-700.0	+0.0321	+0.1493	+8.865	+29.973	+4.72	+3.14
+700.0-650.0	+0.0511	+0.2003	+15.135	+45.108	+7.78	+5.63
+650.0-600.0	+0.0600	+0.2603	+19.186	+64.295	+7.78	+6.34
+600.0-550.0	+0.0663	+0.3266	+23.061	+87.356	+7.78	+6.28
+550.0-500.0	+0.0725	+0.3992	+27.631	+114.987	+13.57	+9.72
+500.0-475.0	+0.0396	+0.4385	+16.145	+131.132	+5.76	+5.70
+475.0-450.0	+0.0271	+0.4657	+20.483	+151.615	+6.87	+7.32
+450.0-425.0	+0.0290	+0.5146	+13.243	+164.858	+4.22	+4.78
+425.0-400.0	+0.0323	+0.5469	+15.654	+180.512	+6.71	+5.00
+400.0-375.0	+0.0374	+0.5844	+19.328	+199.840	+5.76	+6.36
+375.0-350.0	+0.0245	+0.6124	+15.711	+215.551	+4.15	+5.56
+350.0-325.0	+0.0121	+0.6249	+7.159	+222.710	+1.78	+2.87
+325.0-300.0	+0.0144	+0.6397	+2.689	+225.399	+2.18	+3.41
+300.0-275.0	+0.0114	+0.6512	+7.956	+233.355	+1.67	+2.58
+275.0-250.0	+0.0062	+0.6574	+4.737	+238.092	+0.91	+1.70
+250.0-225.0	+0.0067	+0.6641	+5.653	+243.745	+0.94	+2.03
+225.0-200.0	+0.0040	+0.6681	+3.749	+247.494	+0.88	+1.35
+200.0-175.0	+0.0028	+0.6729	+5.135	+252.629	+0.70	+1.74
+175.0-150.0	+0.0046	+0.6775	+5.696	+258.325	+0.67	+2.04
+150.0-125.0	+0.0034	+0.6813	+5.499	+263.824	+0.58	+1.77
+125.0-100.0	+0.0045	+0.6854	+8.008	+271.832	+0.66	+2.47

TOTALS

+100.00 +100.00

AVERAGE PORE RADIUS BASED ON VOLUME = +53.874 A
 (HALF OF THE PORE VOLUME HAS RADIUS SMALLER OR GREATER THAN THIS RADIUS)
 AVERAGE PORE RADIUS BASED ON VOLUME & AREA = +49.244 A
 SURFACE AREA (BET SCHEME) = +186.389 SQ. M/GRAH
 BET SLOPE = +0.023105
 SUM OF PORE SURFACE AREA (BET SCHEME) = +278.544 SQ. M/GRAH

INCREMENTAL PORE VOLUME DISTRIBUTION (CFST 0.2110)

41

2 OF MAXIMUM PORE VOLUME (+0.072543 CC/G)
VERSUS AVERAGE PORE RADIUS, Å, ANGSTROMS

APPENDIX C

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST COMPOSITE
SAMPLE R-11091

PHYSICAL PROPERTIES:

Avg. diameter, inches
Avg. length, inches
Avg. crush strength, lb/mm
Bulk density, gm/cc

SUPPORT

0.058
0.168
1.5
0.53

CATALYST - Amocat 1A
(II-112)

0.058
0.165
1.8
0.62

SURFACE PROPERTIES:

Surface area, m²/gm
Avg. micropore diameter, Å
Min. micropore diameter, Å
Total pore volume, cc/gm
% pore volume >600 Å diameter

206
116
80
0.88
17

177
112
60
0.71
20

CHEMICAL ANALYSIS:

CoO, wt %
MoO₃, wt %
Na₂O, wt %
GaO, wt %

-
-
0.03
0.01
2.93
16.25
0.03
0.01

MICROPORE ANALYSIS:

Pore volume in pores having
diameters between 600 Å and

580 Å	.0008 cc/gm	.0004 cc/gm
560	.0017	.0008
540	.0023	.0012
520	.0029	.0016
500	.0042	.0025
480	.0051	.0034
460	.0061	.0042
440	.0071	.0051
420	.0081	.0059
400	.0096	.0072
380	.0107	.0086
360	.0119	.0099
340	.0131	.0112
320	.0152	.0130
300	.0172	.0153
280	.0199	.0176
260	.0228	.0211
240	.0260	.0253
220	.0311	.0317
200	.0385	.0381
180	.0489	.0460
160	.0768	.0753
150	.1134	.1024
140	.1665	.1356
130	.2242	.1734
120	.3341	.2400
110	.4191	.2959
100	.5329	.3696
90	.6525	.4485
80	.7291	.5173
70	-	.5675
60	-	.5716
Total micropore vol., cc/gm	.73	.57
Avg. micropore diameter, Å	116	112

MACROPORE ANALYSIS:

Pore volume in pores having
diameters between 10,000 Å and

9000. Å	.0004 cc/gm	.0000 cc/gm
8000.	.0014	.0000
7000.	.0111	.0030
6000.	.0225	.0159
5000.	.0478	.0376
4000.	.0771	.0665
3000.	.1035	.0918
2000.	.1285	.1090
1000.	.1455	.1291
700.	.1499	.1372
600.	.1502	.1413
Total macropore vol., cc/gm	.15	.14

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST R-11092

<u>PHYSICAL PROPERTIES:</u>	<u>SUPPORT</u>	<u>CATALYST</u>
Avg. diameter, inches	0.056	0.057
Avg. length, inches	0.154	0.164
Avg. crush strength, lb/mm	1.8	1.7
Bulk density, gm/cc	0.53	0.65

<u>SURFACE PROPERTIES:</u>		
Surface area, m ² /gm	202	180
Avg. micropore pore diameter, Å	120	112
Min. micropore pore diameter, Å	80	70
Total pore volume, cc/gm	.86	.68
% pore volume > 600 Å diameter	15	15

<u>CHEMICAL ANALYSIS:</u>		
CoO, wt. %	--	3.12
MoO ₃ , wt. %	--	16.10
Na ₂ O, wt. %	0.03	0.03
CaO, wt. %	< 0.01	< 0.01

MICROPORE ANALYSIS:

Pore volume in pores having diameters between 600 Å and

580 Å	.0005 cc/gm	.0005 cc/gm
560	.0011	.0010
540	.0017	.0015
520	.0023	.0019
500	.0029	.0028
480	.0041	.0038
460	.0053	.0053
440	.0066	.0060
420	.0073	.0070
400	.0087	.0083
380	.0098	.0095
360	.0114	.0108
340	.0125	.0114
320	.0141	.0131
300	.0168	.0147
280	.0193	.0163
260	.0227	.0182
240	.0262	.0202
220	.0327	.0241
200	.0412	.0278
180	.0563	.0362
160	.0992	.0582
150	.1458	.0834
140	.2019	.1191
130	.2657	.1629
120	.3650	.2429
110	.4543	.3055
100	.5629	.3817
90	.6689	.4712
80	.7299	.5555
70	--	.5839
Total micropore vol, cc/gm	.73	.58
Avg. micropore diameter, Å	120	112

MACROPORE ANALYSIS:

Pore volume in pores having diameters between 10,000 Å and

9000. Å	.0007 cc/gm	.0004 cc/gm
8000.	.0007	.0004
7000.	.0007	.0017
6000.	.0007	.0041
5000.	.0061	.0079
4000.	.0287	.0194
3000.	.0578	.0423
2000.	.0873	.0694
1000.	.1100	.0930
700.	.1206	.1008
600.	.1277	.1013
Total macropore vol, cc/gm	.13	.10

APPENDIX C (cont.)

44.

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST R-11093

<u>PHYSICAL PROPERTIES:</u>	<u>SUPPORT</u>	<u>CATALYST</u>
Avg. diameter, inches	0.056	0.056
Avg. length, inches	0.154	0.161
Avg. crush strength, lb/mm	1.8	1.6
Bulk density, gm/cc	0.51	0.64

<u>SURFACE PROPERTIES:</u>		
Surface area, m ² /gm	211	184
Avg. micropore diameter, Å	120	109
Min. micropore diameter, Å	70	(a)
Total pore volume, cc/gm	.90	(a)
% pore volume > 600 Å diameter	17	(a)

<u>CHEMICAL ANALYSIS:</u>		
CoO, wt. %	--	2.95
MoO ₃ , wt. %	--	15.84
Na ₂ O, wt. %	0.03	0.03
CaO, wt. %	< 0.01	< 0.01

MICROPORE ANALYSIS:

Pore volume in pores having diameters between 600 Å and

580 Å	.0004 cc/gm	(a)
560.	.0008	
540.	.0012	
520.	.0016	
500.	.0026	
480.	.0036	
460.	.0045	
440.	.0055	
420.	.0064	
400.	.0080	
380.	.0095	
360.	.0111	
340.	.0126	
320.	.0147	
300.	.0175	
280.	.0204	
260.	.0239	
240.	.0274	
220.	.0320	
200.	.0471	
180.	.0565	
160.	.0990	
150.	.1526	
140.	.2131	
130.	.2804	
120.	.3721	
110.	.4526	
100.	.5576	
90.	.6549	
80.	.7371	
70.	.7485	

Total micropore vol, cc/gm	.75
Avg. micropore diameter, Å	120

MACROPORE ANALYSIS:

Pore volume in pores having diameters between 10,000 Å and

9000 Å	.0009 cc/gm	.0006 cc/gm
8000.	.0014	.0035
7000.	.0066	.0069
6000.	.0148	.0169
5000.	.0325	.0340
4000.	.0647	.0606
3000.	.0937	.0922
2000.	.1182	.1049
1000.	.1392	.1241
700.	.1522	.1309
600.	.1532	.1342

Total macropore vol., cc/gm	.15	.13
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APPENDIX C (cont.)

45.

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST R-11094

<u>PHYSICAL PROPERTIES:</u>	<u>SUPPORT</u>	<u>CATALYST</u>
Avg. diameter, inches	0.057	0.057
Avg. length, inches	0.155	0.160
Avg. crush strength, lb/mm	1.8	1.7
Bulk density, gm/cc	0.52	0.63
<u>SURFACE PROPERTIES:</u>		
Surface area, m ² /gm	(a)	185
Avg. micropore diameter, Å	(a)	108
Min. micropore diameter, Å	(a)	70
Total pore volume, cc/gm	(a)	73
% pore volume > 600 Å diameter	(a)	21
<u>CHEMICAL ANALYSIS:</u>		
CoO, wt. %	-	3.03
MnO ₃ , wt. %	-	16.41
Na ₂ O, wt. %	0.03	0.03
CaO, wt. %	< 0.01	< 0.01
<u>MICROPORE ANALYSIS:</u>		
Pore volume in pores having diameters between 600 Å and		
580 Å	(a)	.0009 cc/gm
560		.0017
540		.0026
520		.0034
500		.0043
480		.0052
460		.0066
440		.0070
420		.0075
400		.0092
380		.0103
360		.0110
340		.0121
320		.0138
300		.0153
280		.0172
260		.0202
240		.0229
220		.0264
200		.0317
180		.0405
160		.0597
150		.0832
140		.1167
130		.1591
120		.2282
110		.2771
100		.3621
90		.4592
80		.5446
70		.5809
Total micropore vol, cc/gm		.58
Avg. micropore diameter, Å		108
<u>MACROPORE ANALYSIS:</u>		
Pore volume in pores having diameters between 10,000 Å and		
9000. Å	(a)	.0007 cc/gm
8000.		.0007
7000.		.0060
6000.		.0228
5000.		.0525
4000.		.0860
3000.		.0990
2000.		.1205
1000.		.1364
700.		.1438
600.		.1510
Total macropore vol., cc/gm		.15

(a) Missing values are being repeated.

APPENDIX C (cont.)

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST R-11095

PHYSICAL PROPERTIES:

	<u>SUPPORT</u>	<u>CATALYST</u>
Avg. diameter, inches	0.057	0.056
Avg. length, inches	0.159	0.158
Avg. crush strength, lb/mm	2.1	1.7
Bulk density, gm/cc	0.53	0.64

SURFACE PROPERTIES:

Surface area, m ² /gm	(a)	182
Avg. micropore diameter, Å	(a)	117
Min. micropore diameter, Å	(a)	70
Total pore volume, cc/gm	(a)	.71
% pore volume >600 Å diameter	(a)	18

CHEMICAL ANALYSIS:

CoO, wt. %	--	3.12
MoO ₃ , wt. %	--	15.87
Na ₂ O, wt. %	0.03	0.03
CaO, wt. %	<0.01	<0.01

MICROPORE ANALYSIS:

Pore volume in pores having diameters between 600 Å and

580. Å	(a)	.0004	cc/gm
560.		.0004	
540.		.0016	
520.		.0023	
500.		.0037	
480.		.0044	
460.		.0053	
440.		.0062	
420.		.0062	
400.		.0072	
380.		.0079	
360.		.0087	
340.		.0094	
320.		.0096	
300.		.0103	
280.		.0144	
260.		.0186	
240.		.0191	
220.		.0271	
200.		.0335	
180.		.0357	
160.		.0445	
150.		.0755	
140.		.1108	
130.		.1380	
120.		.2666	
110.		.3304	
100.		.4136	
90.		.4903	
80.		.5525	
70.		.5761	
Total micropore vol., cc/gm		.58	
Avg. micropore diameter, Å		117	

MACROPORE ANALYSIS:

Pore volume in pores having diameters between 10,000 Å and

9000. Å	(a)	.0007	cc/gm
8000.		.0011	
7000.		.0055	
6000.		.0120	
5000.		.0309	
4000.		.0554	
3000.		.0822	
2000.		.0986	
1000.		.1133	
700.		.1270	
600.		.1281	
Total macropore vol., cc/gm		.13	

(a) Missing values are being repeated.

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST R-11096

<u>PHYSICAL PROPERTIES:</u>	<u>SUPPORT</u>	<u>CATALYST</u>
Avg. diameter, inches	0.056	0.057
Avg. length, inches	0.161	0.155
Avg. crush strength, lb/mm	1.6	1.8
Bulk density, gm/cc	0.52	0.63

SURFACE PROPERTIES:

Surface area, m ² /gm	204	183
Avg. micropore diameter, Å	121	111
Min. micropore diameter, Å	80	(a)
Total pore volume, cc/gm	.95	(a)
½ pore volume > 600 Å diameter	21	(a)

CHEMICAL ANALYSIS:

CoO, wt. %	--	3.12
MoO ₃ , wt. %	--	15.81
Na ₂ O, wt. %	0.03	0.03
CaO, wt. %	< 0.01	< 0.01

MICROPORE ANALYSIS:

Pore volume in pores having diameters between 600 Å and

580 Å	.0005 cc/gm	(a)
560	.0010	
540	.0015	
520	.0020	
500	.0033	
480	.0047	
460	.0060	
440	.0066	
420	.0080	
400	.0097	
380	.0111	
360	.0120	
340	.0145	
320	.0154	
300	.0181	
280	.0210	
260	.0240	
240	.0276	
220	.0346	
200	.0434	
180	.0603	
160	.1008	
150	.1524	
140	.2090	
130	.2762	
120	.3877	
110	.4795	
100	.5931	
90	.7023	
80	.7500	
Total micropore vol., cc/gm	.75	
Avg. micropore diameter, Å	121	

MACROPORE ANALYSIS:

Pore volume in pores having diameters between 10,000 Å and

9000. Å	.0021 cc/gm	.0011 cc/gm
8000.	.0111	.0047
7000.	.0369	.0129
6000.	.0617	.0305
5000.	.0892	.0558
4000.	.1118	.0853
3000.	.1354	.1051
2000.	.1545	.1235
1000.	.1797	.1419
700.	.1903	.1526
600.	.1975	.1564
Total macropore vol., cc/gm	.20	.16

(a) Missing values are being repeated.

APPENDIX C (cont.)

CHARACTERIZATION OF COAL LIQUEFACTION CATALYST R-11097

<u>PHYSICAL PROPERTIES:</u>	<u>SUPPORT</u>	<u>CATALYST</u>
Avg. diameter, inches	0.057	0.057
Avg. length, inches	0.159	0.167
Avg. crush strength, lb/mm	1.5	1.7
Bulk density, gm/cc	0.51	0.62

SURFACE PROPERTIES:

Surface area, m ² /gm	207	186
Avg. micropore diameter, Å	114	111
Min. micropore diameter, Å	80	70
Total pore volume, cc/gm	.93	.77
% pore volume > 600 Å diameter	22	22

CHEMICAL ANALYSIS:

CoO, wt. %	-	3.12
MnO ₃ , wt. %	-	15.77
Na ₂ O, wt. %	0.03	0.03
CaO, wt. %	< 0.01	< 0.01

MICROPORE ANALYSIS:

Pore volume in pores having
diameters between 600 Å and

580 Å	.0000 cc/gm	.0004 cc/gm
560	.0000	.0007
540	.0000	.0011
520	.0002	.0015
500	.0005	.0025
480	.0010	.0036
460	.0019	.0052
440	.0029	.0060
420	.0044	.0069
400	.0056	.0078
380	.0068	.0087
360	.0083	.0100
340	.0092	.0113
320	.0110	.0127
300	.0139	.0147
280	.0165	.0171
260	.0201	.0199
240	.0229	.0228
220	.0299	.0278
200	.0361	.0334
180	.0483	.0447
160	.0836	.0696
150	.1170	.0952
140	.1541	.1328
130	.2156	.1711
120	.3095	.2432
110	.3936	.3069
100	.5222	.4067
90	.6498	.5054
80	.7271	.5809
70		.6003
Total micropore vol., cc/gm	.73	.60
Avg. micropore diameter, Å	114	111

MACROPORE ANALYSIS:

Pore volume in pores having
diameters between 10,000 Å and

9000. Å	.0021 cc/gm	.0008 cc/gm
8000.	.0152	.0079
7000.	.0485	.0219
6000.	.0741	.0485
5000.	.1012	.0748
4000.	.1232	.1024
3000.	.1427	.1209
2000.	.1612	.1367
1000.	.1795	.1522
700.	.1933	.1599
600.	.2005	.1671
Total macropore vol., cc/gm	.20	.17

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