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CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

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CATALYSTS FOR UPGRADING COAL DERIVED LIQUIDS
(DE-14876-2)

ABSTRACT

Construction of the new trickle-bed reactor was completed and one experiment was conducted. The experimental run was made using a Pamco coal-derived liquid containing 0.40% sulfur and 0.95% nitrogen. The catalyst utilized was an American Cyanamide HDN-30, Ni-Mo-Al₂O₃. Run conditions were at 399C (750F), 1500 psig and space times up to two hours. Sample analyses are not yet available from this experiment.

Two runs were completed in the Catalyst Life Test Unit (CLTU) utilizing a liquid containing 50% Synthoil and 50% Raw Anthracene oil. This fluid has a 0.54% sulfur and 1.21% nitrogen. Two Ni-Mo-Al₂O₃ catalysts were used--Shell-324, and H-Oil. Both experiments were terminated prematurely because of equipment malfunction. Sample analyses are not yet available from these two experiments.

OBJECTIVE AND SCOPE OF WORK

The goal of this program is to investigate catalysts for upgrading liquids derived from coal-to-oil processes.

This research has the following technical objectives:

1. Investigate mechanisms responsible for rapid initial catalyst deactivation.
2. Study use of "throw away" catalysts and staged catalyst beds in hydroprocessing of coal liquids.

The investigation shall consist of the following tasks:

- Task 1-a. Inexpensive "throw away" type catalysts for coal liquids upgrading shall be investigated for reactor guard chamber service.
- Task 1-b. Reactors packed with mixtures of catalyst types and zoned catalyst configurations shall be evaluated.
- Task 2-a. Catalyst life tests shall be conducted using a standard Ni-Mo/alumina hydroprocessing catalyst in the existing catalyst life test unit.
- Task 2-b. Changes in catalyst properties, including surface area, pore size distribution, pore volume, and coke and inorganics accumulation shall be measured as a function of coal-liquid contact time.
- Task 2-c. The Ni-Mo/alumina catalyst tested in Task 2-a shall be regenerated by oxidation, and tested for activity recovery.

SUMMARY OF PROGRESS TO DATE

The following chart summarizes the progress to date.

The three tasks (1-a, 1-b, and 2-a) show scheduled progress. This progress in the three task areas has involved equipment preparation, familiarization of all new personnel, experimental design, and procuring chemicals, supplies and feedstock.

As of March 31, 1980, 7% of the total budget has been spent (\$12,956 of \$181,060). This is rather low, and reflects the "start-up" phase of the project.

PROGRESS SUMMARY AS OF MARCH 31, 1980

Scheduled

Progress

* Project start date is October 1, 1979

DESCRIPTION OF TECHNICAL PROGRESS

Task 1 - Throw Away and Zoned Catalyst Systems (O. Bhan)

The construction of the new trickle-bed reactor as mentioned in the previous quarterly report was completed. The new system incorporates improved pressure and temperature control and utilizes a somewhat smaller quantity of catalyst loading.

One experimental run was conducted in the new reactor system to obtain data as part of the experimental design in the zoned catalyst bed studies. A Pamco coal-derived liquid was the feedstock and a vendor catalyst from American Cyanamide Company was used. The properties of both the feedstock and the catalyst are shown in Tables I and II. Note that the feedstock has a sulfur and nitrogen concentration of 0.40% and 0.95%, respectively. The catalyst is American Cyanamide HDN-30 and is a nickel-molybdenum-alumina type. Run conditions were maintained at 399C (750F), 1500 psig nominal pressure, and space times of from 0.5 to 2.0 hours, volume basis.

This experimental run was also used for testing equipment and to familiarize personnel. The experiment was conducted for a total of 96 hours continuous operation and with no significant pressure drop or indication of reactor plugging during the period. Shut down was scheduled. The liquid samples from this experimental run are presently being analyzed.

During the next quarter, three more experimental runs are scheduled and are to involve another vendor catalyst of a cobalt-molybdenum-alumina type plus two zonal catalyst bed experiments.

TABLE I
PROPERTIES OF FEEDSTOCK

<u>Oil</u> <u>Composition; Wt%</u>	<u>Pamco Process</u> <u>Solvent</u>
Carbon	89.08
Hydrogen	7.41
Nitrogen	0.95
Sulfur	0.40
Oxygen	2.16*
<u>Normal boiling point**</u>	
Initial	93C (200F)
10%	114C (238F)
30%	122C (251F)
50%	148C (298F)

* By difference

** Determined from ASTM D 1160 Data

Task 2 - Catalyst Life Studies (H. J. Chang)

Run Series CNB and CNC

The feedstock used in these two experimental runs was Rasyn liquid which is a mixture of 50% Synthoil II liquid and 50% Raw Anthracene oil (see Table II). This liquid has been tested extensively in previous studies. The properties of the catalysts used in these two reactors are shown in Table III. These two catalysts are nickle-molybdenum-alumina types, are extrudates and offer promise for upgrading coal liquids. The H-Oil catalyst is bi-dispersed and has a most frequent micropore diameter of 44 Å. The Shell-324 catalyst shows significant promise in upgrading coal-derived liquids*. It has a most frequent pore diameter of 118 Å. Pore structure properties of these two catalysts are shown in Figures 1-6.

The objectives of these two experimental runs were to obtain experience for new undergraduate personnel serving as technician support, to test Reactors 1 and 3 in the CLTU and to characterize the activities and short-time aging characteristics of these two new catalyst candidates.

The designed run conditions were as follows:

<u>Run Series</u>	<u>CNB</u>	<u>CNC</u>
Reactor	1	3
Catalyst	Shell-324 (Table III)	H-Oil (Table III)
Feedstock	Rasyn (Table II)	Rasyn (Table II)
Temperature	371C (700F)	371C (700F)
Pressure	1500 psig	1500 psig
Space time (Vol. Hrly.)	2 hrs	2 hrs
Hydrogen flow	10,000 SCF/Bbl	10,000 SCF/Bbl

During the experimental operations equipment problems were encountered that resulted in operation at non-designed conditions and premature shut down. Large pressure fluctuations beyond the accepted values were experienced and we believe they were caused by malfunctioning of pressure control valves. Reactor No. 1, oil feed pump, also malfunctioned and resulted in a flow rate of oil much lower than desired. This reactor was terminated after only 44 hours of continuous operation.

* "Commercial Scale Expanded Bed Hydroprocessing of Solvent Refined Coal Extract", Cities Service Company., FE-2038-25, August, 1978.

TABLE II
PROPERTIES OF FEEDSTOCK

<u>Oil</u> <u>Composition; Wt%</u>	<u>Rasyn Oil*</u>
Carbon	84.92
Hydrogen	6.57
Sulfur	0.54
Nitrogen	1.21
Oxygen**	5.71
Ash	1.05
<u>Normal boiling point***</u>	
Initial	160C (320F)
10%	233C (451F)
30%	303C (577F)
50%	356C (673F)

* Equal volume mixture of Raw Anthracene oil and Synthoil II liquid (Western Kentucky Blend).

** By difference

*** Determined from ASTM D 1160 Data

TABLE III
CATALYST PROPERTIES

Catalyst Code	Shell-324	H-oil	HDN-30
Manufacturer	Shell	Armak	American Cyanamide
Chemical Composition, wt%			
NiO	2.7*	4.8*	5.0*
MoO ₃	13.2*	12.0*	20.5*
Physical Properties (1/16" Extrud.)			
surface area m ² /gm	146 (150*)	276 (277*)	122 (160*)
pore volume cc/gm	0.42 (0.48*)	0.57 (0.65*)	0.44*
Most frequent			
pore diameter	118	44	84
$\overset{\circ}{\text{A}}$ diameter		<u>% pore volume in pore</u>	
35-70	12	53	22
70-100	21	8	45
100-150	57	3	9
150-200	2	2	3
200-400	1	5	7
400-600	1	6	3
>600	6	23	11
TOTAL	100	100	100

* Vendor's data

Unstable, and unusual, reactor temperature was experienced in Reactor No. 3 during the experiment resulting in termination of that run after only 70 hours of operation. The cause of this unstable temperature is being investigated.

In summary, these two experimental runs were only marginally successful and partial analysis of the liquid samples will be made at a later date. Improvements to eliminate the above problems will be made on the equipment during the coming quarter. In addition to these equipment improvements at least one more experimental run will be conducted.

Figure 1. Pore Size Distribution

Cumulative Pore Volume, cc/gram

Figure 2. Cumulative Pore Volume

Figure 3. Pore Size Distribution.

Figure 4. Cumulative Pore Volume

Figure 5. Pore Size Distribution

Cumulative Pore Volume, cc/gram

Figure 6. Cumulative Pore Volume