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COAL LIQUEFACTION CATALYST DEVELOPMENT

Quarterly Progress Report No. 2, July 1—September 30, 1979

By
D. K. Kim
R. J. Pellet
K. K. Robinson
J. A. Mahoney

October 1979
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Research and Development Department
Amoco Oil Company
Naperville, Illinois

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P.O. Box 400
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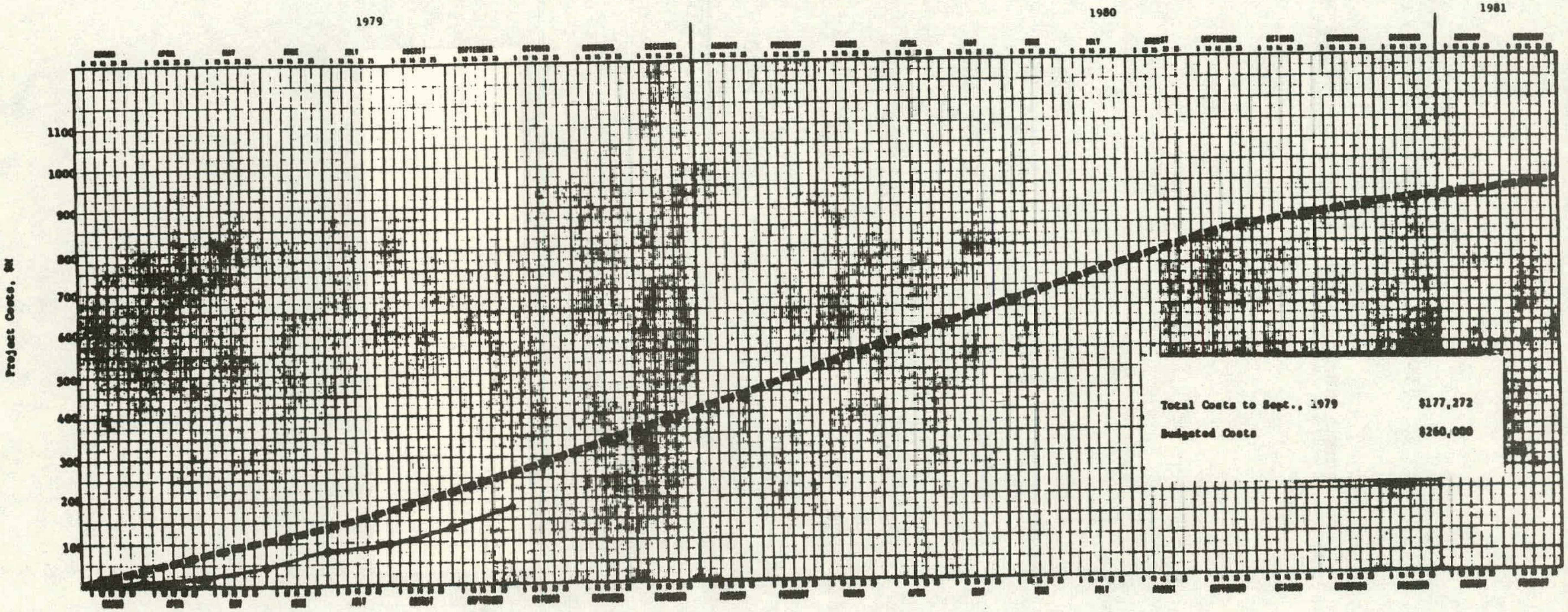
COST TRACKING CURVE
COAL LIQUEFACTION CATALYST DEVELOPMENT
AMOCO OIL RESEARCH & DEVELOPMENT



FOREWARD

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 all the project tasks during the second quarter of the project.

QUARTERLY SUMMARY

This project is a continuation of the coal liquefaction catalyst development program formerly funded by the Electric Power Research Institute. During the second quarter of DOE sponsorship, progress was made in all the task areas.

Under Task I -- Catalyst Preparation and Screening, the thermal and catalytic baseline runs continued with HDS-1442A as the reference catalyst and toluene soluble conversion as the basis for liquefaction performance. Results from these experiments suggested that a 30-minute run time should be selected for screening experiments. Test results of several new catalyst formulations are reported. No promising candidates for testing in the continuous aging unit were identified during the second quarter.

Task 2 -- Catalyst Aging Tests -- Eastern Coal was centered around evaluation of the new SRC II slurry oil as a liquefaction solvent as well as a design change in the catalyst basket for the continuous aging unit. Uncertainties in Run 5188 clouded the assessment of the slurry oil effect. Subsequent runs with the new SRC II solvent indicated that slurry oil effects are small.

Task 3 -- Catalyst Aging Tests -- Western Coal concentrated on ascertaining the liquefaction behavior of a Western Coal such as Wyodak with AMOCAT type catalysts. A run with H-Coal reference catalyst, HDS-1442A, was completed as well as runs with AMOCAT 1A and 1B type catalysts. Product workups are in progress.

Under Task 4 -- Development Supports Studies, simplifications were made in the composition of our synthetic coal feed to improve analytical and kinetic accuracy. The Panasol solvent was distilled into two fractions and the bottom fraction containing primarily trimethylnaphthalenes will be used as the hydrogen donor solvent for the synthetic coal feed.

Task 5 -- Application of New Catalysts--H-Coal concentrated on the evaluation of the large 500 pound batch of AMOCAT 1A.

Using SRC II heavy distillate as the slurry oil and Illinois No. 6 coal feed, the results from the aging test are quite clear. The recently prepared 500 pound batch of AMOCAT 1A is good quality and exhibits highly improved performance over the H-Coal catalyst, HDS-1442A. Benzene and hexane soluble conversion are markedly higher with hexane soluble conversion declining less rapidly with time. Furthermore the yield of $520^{o}C^{+}$ resid is about 5% lower with AMOCAT 1A indicating that more high quality lower boiling material is being produced. Finally the sulfur content of the $520^{o}C^{+}$ resid is also lower. The highly improved catalyst should be considered for future evaluation in the larger H-Coal process development unit (PDU) and recently the H-Coal Technical Advisory Committee voted in favor of an H-Coal PDU run with AMOCAT 1A catalyst.

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 are prepared in our Amoco laboratories. The problem areas consist of the following:

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

Before engaging in our catalyst screening program, modifications of our testing procedure and apparatus were evaluated. The modification of the apparatus, developed 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. After considerable experimentation, use of the charging device was abandoned because of problems with temperature control, injection line plugging, and excessive catalyst deactivation. In the modification of the testing procedure toluene was substituted for benzene as a solvent in the product workup.

The following sections describe thermal and catalytic baseline runs which were required because of the new product workup procedure as well as the use of a new baseline catalyst, HDS-1442-A. Test results of several new catalyst formulations are reported as well as detailed composition of new catalysts that will be tested in the initial phase of the DOE program.

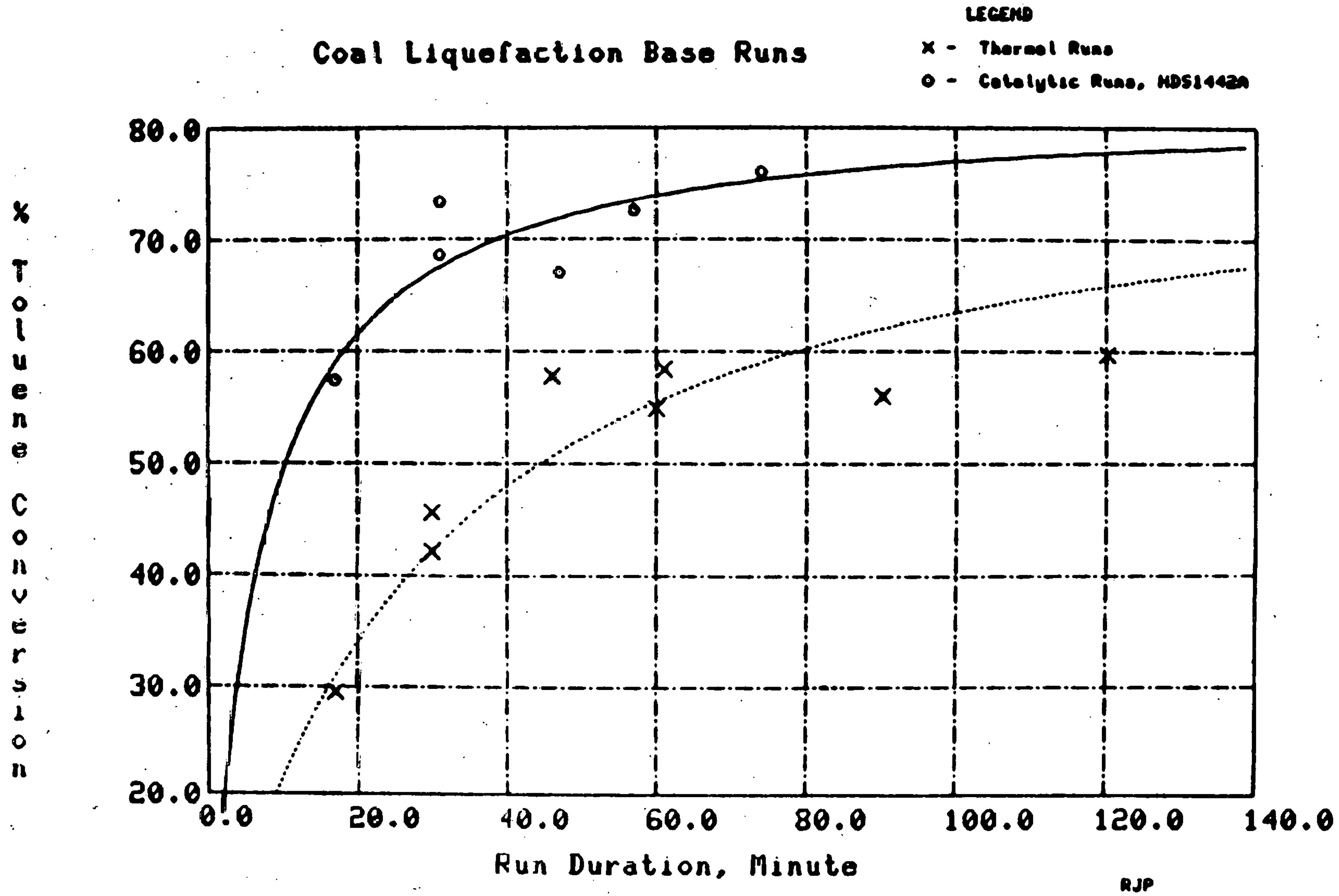
Base Case Runs

Several base runs have been completed on the batch screening unit. These runs have measured the extent of both catalytic and thermal conversion as a function of batch run duration. Both thermal and catalytic base conversion levels had to be reestablished because of the change in product work-up procedure and the use of a new base case catalyst. Our base catalytic runs were made with HDS-1442A ($CoO:MoO_3/3:16$) catalyst. Conversion results obtained to date are summarized in the accompanying Figure 1.

All base case runs have been made at 750°F, 2000 psig total pressure, 10 g. of catalyst, 2 to 1 solvent to coal ratio, and range in duration from 17 minutes to 2 hours with Illinois No. 6 coal feed and Panasol solvent. Conversion levels were determined from the amount of toluene insoluble material. The results indicate that as the run time increases from 0 to 40 minutes, the percent conversion increases rapidly. But after 40 minutes there is only a slight increase in conversion suggesting that the system has approached a pseudo-equilibrium state both in the thermal and catalytic cases. The reaction time is defined as the interval starting at 5°C below the desired temperature during heat-up and ending at the same point during cool-down.

While more base runs are needed to accurately determine conversion levels, our data suggests that a 30-minute run time should be selected for screening experimental catalyst. There are two reasons for selecting this run length. First,

FIGURE 1.



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the difference between thermal and catalytic conversion appears to be the greatest at this time. Thus, the catalytic contribution to the overall conversion will be maximized. Secondly, at 30 minutes the total conversion is far from complete, and catalysts, more active than HDS-1442A, should be easily detectable. Screening tests will be interspersed with thermal and catalytic base runs to more accurately determine conversion levels around the 30-minute run duration.

Catalyst Preparations

Catalyst preparations scheduled for the initial phase of the DOE contract are listed in Table I. They encompass all four categories described in the work statement and include:

Modified aluminas
Alternate material
Two-catalyst systems (physical mixtures)
Novel catalyst systems

Illinois No. 6 coal will continue to be used as the feed material for the batch screening runs. Wyodak coal will be used to test successful candidates in the batch screening runs. Base case data will have to be generated for Wyodak coal.

Experimental Catalysts

Adequate base information was available to begin testing experimental catalyst formulations in mid-September. Four catalysts were tested at a constant run duration of about 30 minutes. The results obtained with these experimental catalysts as well as the thermal and base catalyst conversion levels obtained by regression are shown in Figure II. Here we have plotted conversion to toluene soluble products as a function of run duration. The lines are the best least squares fit of the base case data shown in Figure I. The experimental catalysts tested fall into two categories:

a) mixed-catalyst systems
b) intercalated catalysts

The mixtures were formed by blending a 16% MoO_3 on alumina (60/100 mesh) with 3% CoO on either an acidic support ($B\text{-}Al_2O_3$) or a basic support ($Na\text{-}Al_2O_3$). The alumina used was provided by Grace (R11084) and had some bimodal pore characteristics. The observed conversion levels suggest that support acidity or basicity has little effect on the cobalt catalysts activity or selectivity. The results also show that the cobalt and molybdenum functions can be separated with no loss in activity relative to the base $CoO\text{-}MoO_3$ catalyst (HDS-1442A).

The intercalated catalysts consisted of either chromium chloride (15%) or cobalt (5%) intercalated into the graphite layered structure. Both catalysts were available commercially through the Alpha division of Ventron. The results obtained with these intercalates is rather disappointing. In fact the conversion levels observed were even below the expected thermal conversion level. This suggests that the graphite catalyst either retard thermal conversion or catalyze a polymerization reaction that produces toluene insoluble material.

A summary of all the experimental catalysts tested in the batch screening unit during the second quarter is shown in Table II.

FUTURE WORK

Screening will continue with other catalyst formulations shown in Table I. Base conversion levels for Wyodak coal with HDS-1442A as a function of run duration will be determined.

FIGURE II.

COAL LIQUEFACTION ACTIVITY
EXPERIMENTAL CATALYSTS

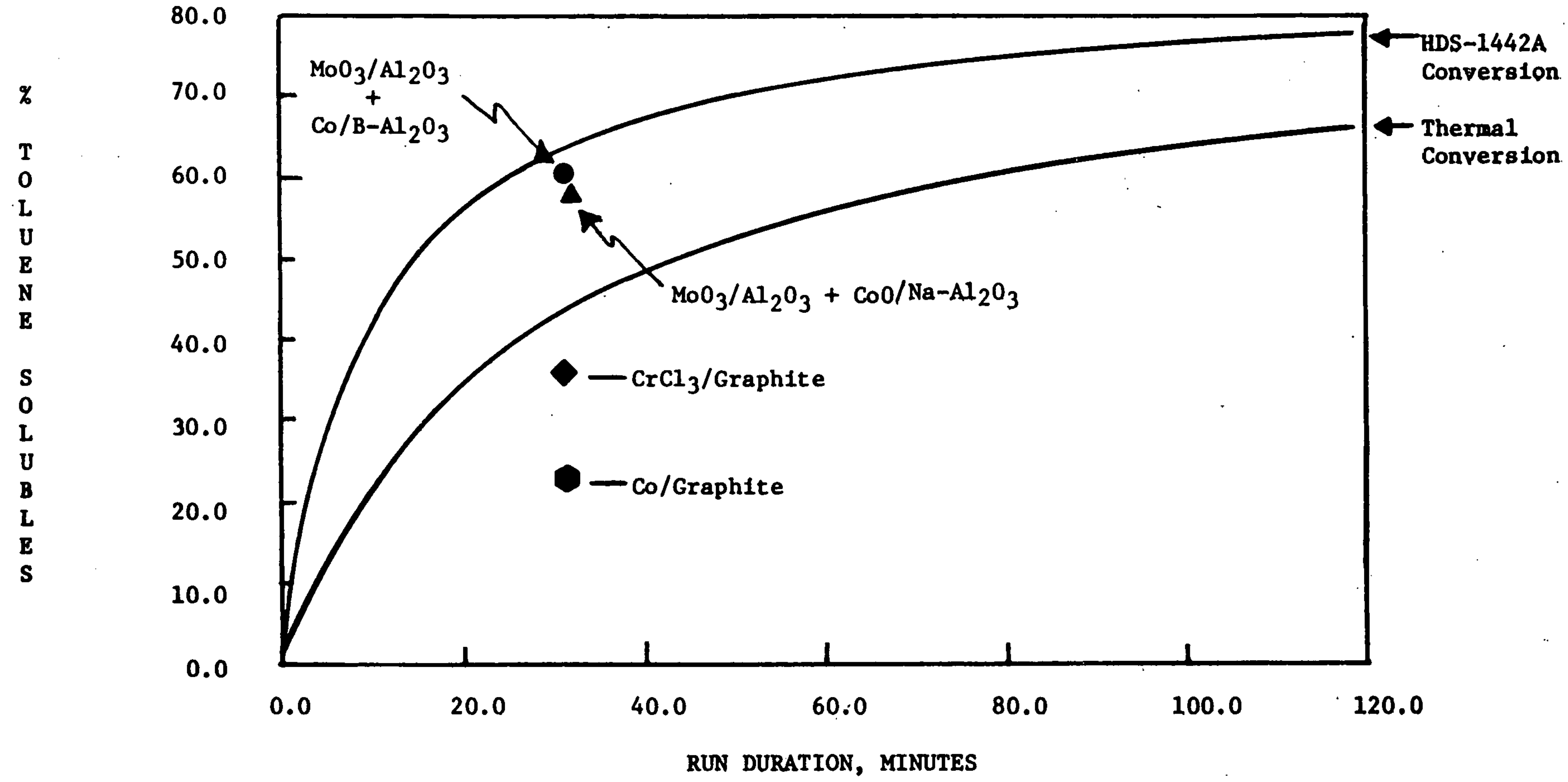

TABLE I

CATALYSTS FOR BATCH SCREENING

1) Modified Aluminas

3% CoO 16% MoO_3/carbonized G120 B-Al_2O_3

3% CoO 16% MoO_3/10% BaO-Al_2O_3 (neutralized)

Stabilization

AMOCAT 1A + N_2/H_2O @ 1400°F

3% CoO 16% MoO_3/3% Ce-Al_2O_3 @ 1400°F

3% CoO 16% MoO_3/3% U-Al_2O_3 @ 1400°F

2) Alternate Material

2.6% Co_2B 13.2% MoB_2/Al_2O_3

2.7% Co_2N 13.2% MoB_2/Al_2O_3

2.6% Co_2B 11.4% Mo_2C/Al_2O_3

2.7% Co_2N 11.4% Mo_2C/Al_2O_3

2.6% Co_2B 11.4% Mo_2N/Al_2O_3

2.7% Co_2N 11.4% Mo_2N/Al_2O_3

3) Two Catalyst Systems

20% [3% CoO/Al_2O_3] 80% [16% MoO_3/Al_2O_3]

20% [3% CoO/1% Na-Al_2O_3] 80% [16% MoO_3/Al_2O_3]

20% [3% CoO/1% B-Al_2O_3] 80% [16% MoO_3/Al_2O_3]

20% [3% CoO/Al_2O_3] 80% [16% WO_3/Al_2O_3]

20% [3% NiO/Al_2O_3] 80% [16% WO_3/Al_2O_3]

20% [3% NiO/Al_2O_3] 80% [16% WO_3/Al_2O_3]

4) Novel Catalyst Systems

5% Co in Graphite (intercalated)

15% $CrCl_3$ in Graphite (intercalated)

10% Ni in Graphite (intercalated)

35% $AlCl_3$ in Graphite (intercalated)

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TABLE II

SUMMARY OF BATCH SCREENING RUNS
SEPTEMBER, 1979

Run No.	Catalyst	Conditions	%Conversion
3660-87	HDS-1442A	750°F for 46 min	62.7
-88	"	750°F for 61 min	68.4
-89	"	750°F for 11 min	42.5
-91	"	750°F 21.5 min	49.4
-92	$CrCl_3$ in Graphite	750°F for 31 min	35.4
-93	$(MoO_3/Al_2O_3$ $(CoO/Na\text{-}Al_2O_3$	750°F for 31.5 min	57.2
-94	$(MoO_3/Al_2O_3$ $(CoO/B\text{-}Al_2O_3$	750°F for 31 min	60.1
-95	Co in Graphite	750°F for 31 min	21.5

TASK 2 - CATALYST AGING TESTS--EASTERN COAL

Aging behavior is the critical test for an improved coal liquefaction catalyst. Once promising candidates have been identified in Task 1, Catalyst Preparation and Screening, and Task 4, Development Support Studies--Synthetic Coal, they are tested further in a 150-hour aging test in a continuous pilot plant unit.

The specific objectives of Task 2 include the following:

1. Establish aging behavior of new or modified Amoco catalysts at higher severity test conditions with Eastern coal.
2. Develop a better understanding of the catalyst deactivation through extensive characterization of spent catalysts.
3. Perform aging tests on other DOE contractors' catalysts, when requested.

The continuous-flow liquefaction unit, general procedures for catalyst testing, product workup and analysis methods were described in the first quarterly report. During this period, the new slurry oil to be used as a liquefaction solvent throughout the project was selected, and a design change was made on the catalyst basket which had presented some uncertainties in assessing catalyst performance. Using the new slurry oil and the improved catalyst basket, two runs (5186, 5188) were completed with Illinois No. 6 comparing liquefaction performance of the H-Coal catalyst, HDS-1442A and a control sample, CoMo-G120B(11). A third run with the 500 lb batch of AMOCAT 1A catalyst was also completed. Details are reported in the Task 5 section of this quarterly report.

Experimental

The test conditions for measuring catalyst aging behavior are as follows:

TABLE III

STANDARD TEST CONDITIONS

Catalyst Charge: 60 cc, 1/16" extrudates, 20cc, 3mm glass beads + glass wool
Coal Slurry Feed: 25 wt% coal in SRC 11 heavy distiallate (FSN-10)
Pressure: 137 atm (2000 psig)
Temperature: 440°C (825°F)
H_2 Feed Rate: 225 liters/hr (8 SCFH)
Slurry Feed Rate: 413 g/hr
Reactor Holdup: 310 cc
Residence Time: 45 minutes
LHSV: 1.72 g-coal/hr/cc/catalyst
Mixing Speed: 1500 rpm

Catalyst performance is compared on the basis of the same volumetric loading, 60 cc of 1/16" extrudates contained in an annular shape, stationery basket. A 25 wt% powdered coal (<35 micron) is slurried in SRC II heavy distillate

(FSN-10) and pumped to a high pressure. The slurry feed is combined with hydrogen flow and introduced to the bottom of the stirred autoclave reactor which is at 137 atm and 440°C. The products are withdrawn through an overflow tube which extends about 8 cm from the reactor bottom to give a holdup of volume of 310 cc.

Efficient mixing and contacting between the slurry and catalyst particles are accomplished by a high stirring rate (1500 rpm) and proper design of catalyst basket. Several baskets of different design have been tried before the current annular shape basket was selected; it has 5 mm wide slab baffles in and outside with a 10 mm thick annulus. By increasing annular thickness from the previous 6 mm to current 10 mm, fabrication of basket became easier and channeling was eliminated. The baffles in an earlier version of 10 mm annular basket (used in Run 5182 through 5185) were made of 2 mm thick wire which created vortexing.

The wider slab baffles in the current design eliminated vortexing and established a well-defined liquid and gas interface in a glass mockup study, thus allowing more accurate estimation of residence time and space velocity. The impeller diameter was reduced slightly from 3.78 cm to 2.86 to accommodate the wider basket baffles.

The slurry oil, FSN-10, is a uniform blend of the 10-barrel shipment of SRC II heavy distillate received from Pittsburgh & Midway Mining Co. Inspection data are shown in Table IV . The high viscosity more than compensates for the relatively low gravity to give a pumpable coal slurry. Slurry pumping has been reasonably consistent. Initial boiling point of FSN-10 is estimated in the neighborhood of 238°C (460°F). Using the same ASTM distillation method as the one routinely performed for liquid products, the resid fraction of FSN-10 boiling above 520°C (970°F) is approximately 2.9 wt%. The slurry oil contains very little THF and benzene insolubles so they are to be neglected for coal conversion concentration. Sulfur content is low (0.41%) but nitrogen content is somewhat high (1.18%).

TABLE IV

SLURRY OIL (FSN-10) INSPECTIONS

Specific Gravity @ 25°C	1.079
Viscosity @ 40°C, cs	48.4
ASTM D-1160, Wt%	
IBP-650°F	39.3
650-970°F	57.8
970°F+	2.9
(IBP ∿460°F)	
Wt% Insolubles	
THF	<0.05
Benzene	<0.07
Hexane	∿8.21
Elemental, Wt%	
C	89.33
H	7.40
S	0.41
N	1.18
Atomic H/C	0.994

Comparison Runs

Three runs were made at standard test conditions using Illinois No. 6 Coal and the new FSN-10 slurry oil solvent (see Table V).

TABLE V

COMPARISON RUNS

Run No.	Catalyst	Comments
5186	HDS-1442A	Base run
5187	AMOCAT-1A(II-108/11)*	500 lb. batch
5188	CoMo-G120B(11)	Experimental AMOCAT-1A type control sample

* Numbers in parentheses indicate the following information (batch number - APD /% macropores).

There have been several versions of AMOCAT 1A but they are typified by having a bimodal pore size distribution with an average micropore diameter around 120 Å and at least 7% of total pore volume occupied by macropores greater than 1000 Å in diameter. The 500 lb. batch of AMOCAT 1A catalyst was prepared by W. R. Grace according to Amoco specifications. Chemical analysis of a composite sample (R11091) showed 15.3 wt% MoO_3 and 3.1 wt% CoO. The surface properties are compared in Table VI with those of H-Coal reference catalyst HDS-1442A and three other small experimental batches of AMOCAT 1A type catalysts prepared in our Amoco laboratories.

TABLE VI

COMPARISON OF AMOCAT 1A TYPE CATALYSTS WITH HDS-1442A

				10^3-10^5 Å Pores					
Catalyst	APD Å	SA m^2/g	PV cc/g	PV, cc/g	% of tot.	g/cc	Diam. mm.	L/D	Note
HDS-1442A	56	332	.741	.191	27.6	.571	1.54	(2.8)	H-Coal
AMOCAT 1A (II-108/16	108	186	.686	.112	15.8	.622	1.39	(2.5)	500 lb. batch
AMOCAT 1A (1-120/7)	122	158	.636	.044	7.3	.670	1.45	(2.0)	HRI #177-137
CoMo-G120B (A-122/11) Grace 100 Alumina	122	154	.609	.071	11.1	.688	1.47		High Activity
CoMo-G120B (B-111/17) Grace 100 Alumina	111	162	.615	.101	17.3	.683			High Activity

The macropore volume of the current 500 lb. batch AMOCAT 1A (II-108/16) is higher than that of AMOCAT 1A (I-122/7) tested in 1978 in H-Coal bench scale unit, but it is within the range of other AMOCAT 1A type catalysts. Average pore diameter of the micropores (measured by nitrogen desorption method) appears to be slightly smaller than the targeted 120 Å intended for the 500 lb. batch AMOCAT 1A; however, the catalyst contains virtually all the micropores that other experimental AMOCAT 1A catalysts have. The average pore diameter is defined such that half of the pore volume has diameter smaller or greater than this diameter. Apparent bulk density, ABD, is generally higher for AMOCAT 1A type catalysts than HDS-1442A. However, it should be pointed out that very high density does not necessarily imply higher catalyst activity on a constant volume basis.

The pore size distribution by mercury porosimetry is plotted in Figure III as the frequency of pores versus pore diameter to illustrate biomodality of both HDS-1442A and AMOCAT 1A catalysts. The 500 lb. batch AMOCAT 1A (II-108/16) shows a more pronounced bimodal pore distriubtion than the experimental batch AMOCAT 1A (I-122/7). A more detailed micropore distribution obtained by nitrogen desorption method are compared in Figure IV. The 500 lb. AMOCAT 1A (II-108/16) contains more smaller pores but the micropore size distribution is almost identical to that of AMOCAT 1A (I-122/7). The pores in HDS-1442A are much smaller than either of AMOCAT catalysts and are more susceptible to plugging by coke.

CoMo-G120B(11) has previously shown better liquefaction performance than HDS-1442A when Illinois No. 6 coal was slurried in a hydrotreated anthracene oil at conditions similar to the current test conditions (see Figure V). The purpose of the current run was to determine if the new SRC slurry oil has any effect on liquefaction performance. Since both AMOCAT 1A (II-108/16) and CoMo-G 120B(11) have similar surface properties, it was expected that their liquefaction performance would be comparable.

Contrary to this expectation and also the earlier performance ranking, the recent test result shows disappointingly low benzene soluble conversions for CoMo-G120B(11) as shown in Figure VI.

There were several uncertainties in the present test:

1. Coal drum was changed during the run.
2. Slurry oil (SRC II heavy distillate) drum was changed.
3. Moyno circulation pump broke down in the middle of the run.

Since this catalyst had been stored for over a year it also had adsorbed a considerable amount of water. It has been reported in the literature recently that the presence of water is bad for the optimum presulfiding of hydrotreating catalysts. Also, we know that water at high temperatures can alter the pore size structure of the alumina support. The results shown in Figure VI for CoMo-G120B(11) are very similar to earlier results with 120 Å unimodal CoMo catalysts. The 11% macropore volume of the CoMo-G120B(11) was low initially and pretreating the wet catalyst at 400°F could have caused a significant reduction in macropore volume. We plan to obtain pore size distributions of CoMo-G120B(11) in the wet state as well as after it has been dried in an oven at 900°F. This particular run may give us some insight into the pretreatment and handling of bimodal type catalyst.

Results with the 500 lb. batch of AMOCAT 1A (II-108/16) were extremely favorable. Details will be discussed in Task 5 of this quarterly report.

FIGURE III

PORE SIZE DISTRIBUTION (Hg Porosimetry)

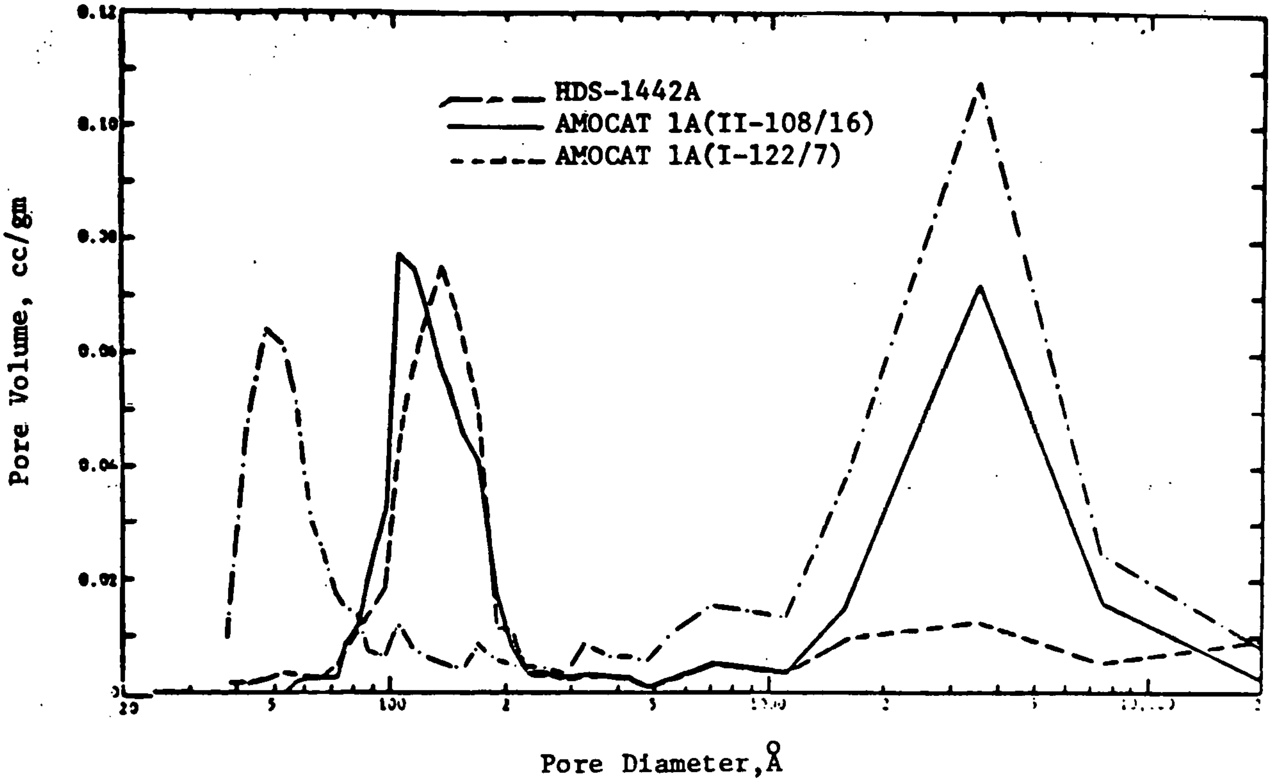


FIGURE IV

PORE SIZE DISTRIBUTION (N_2 Desorption)

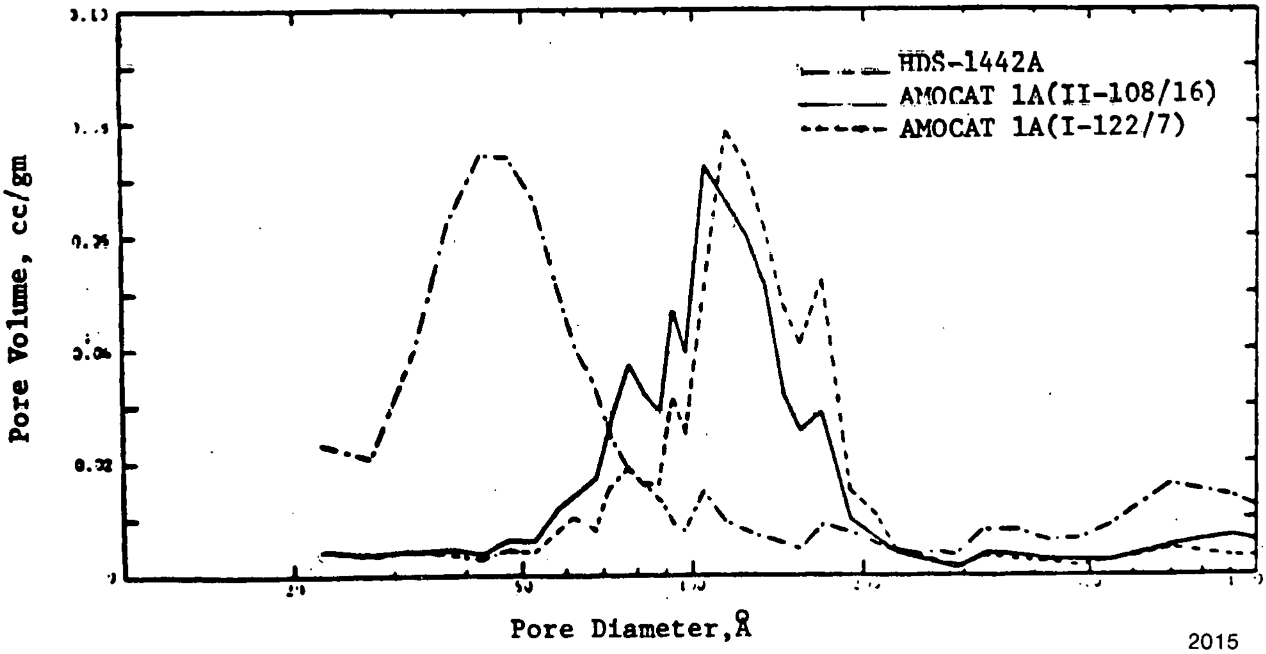


FIGURE V

RELATIVE RANKING OF CoMo-G120B(11) vs. HDS-1442A FOR LIQUIFYING ILLINOIS NO. 6 COAL IN A HYDROTREATED ANTHRACENE OIL.

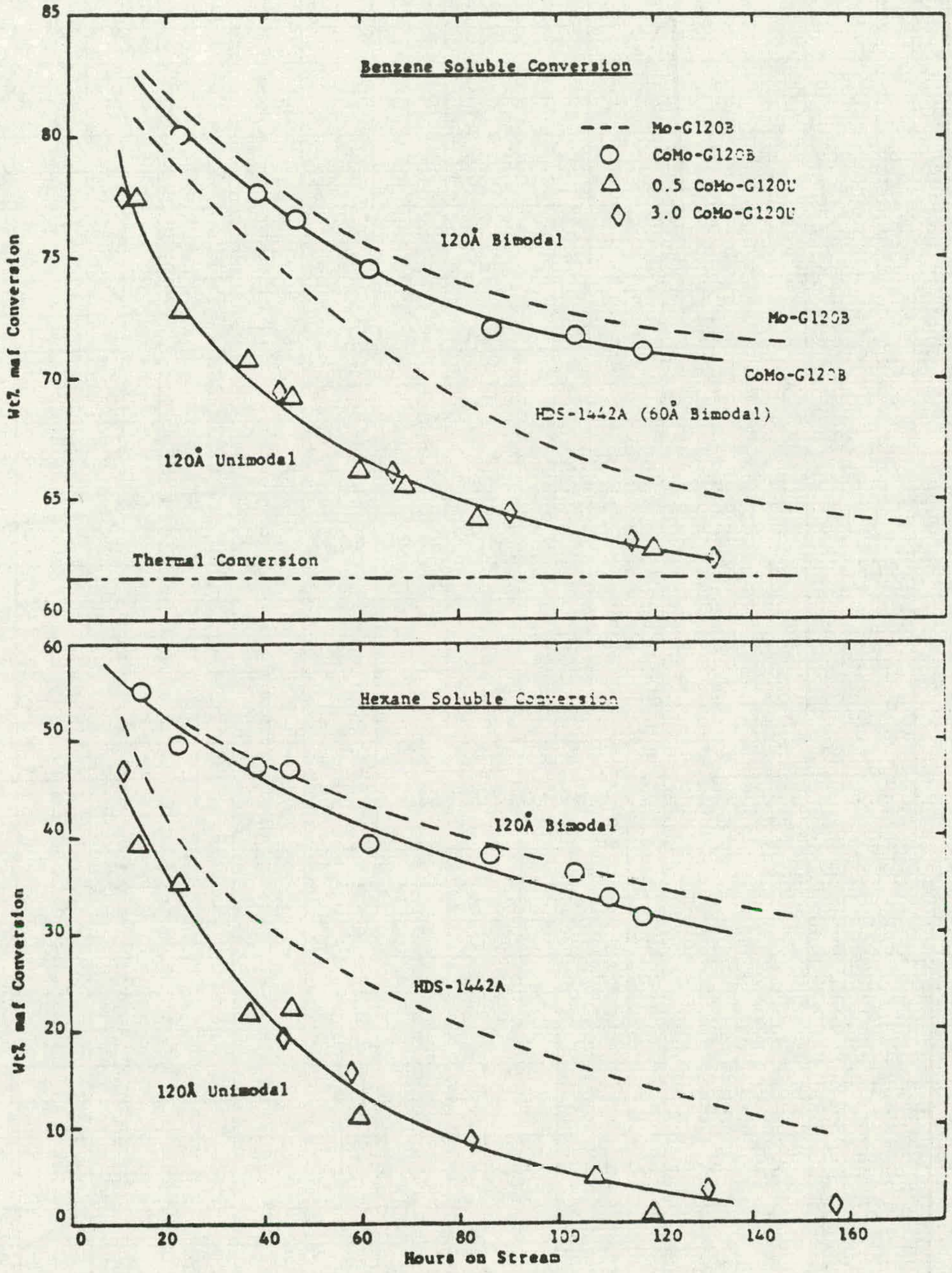
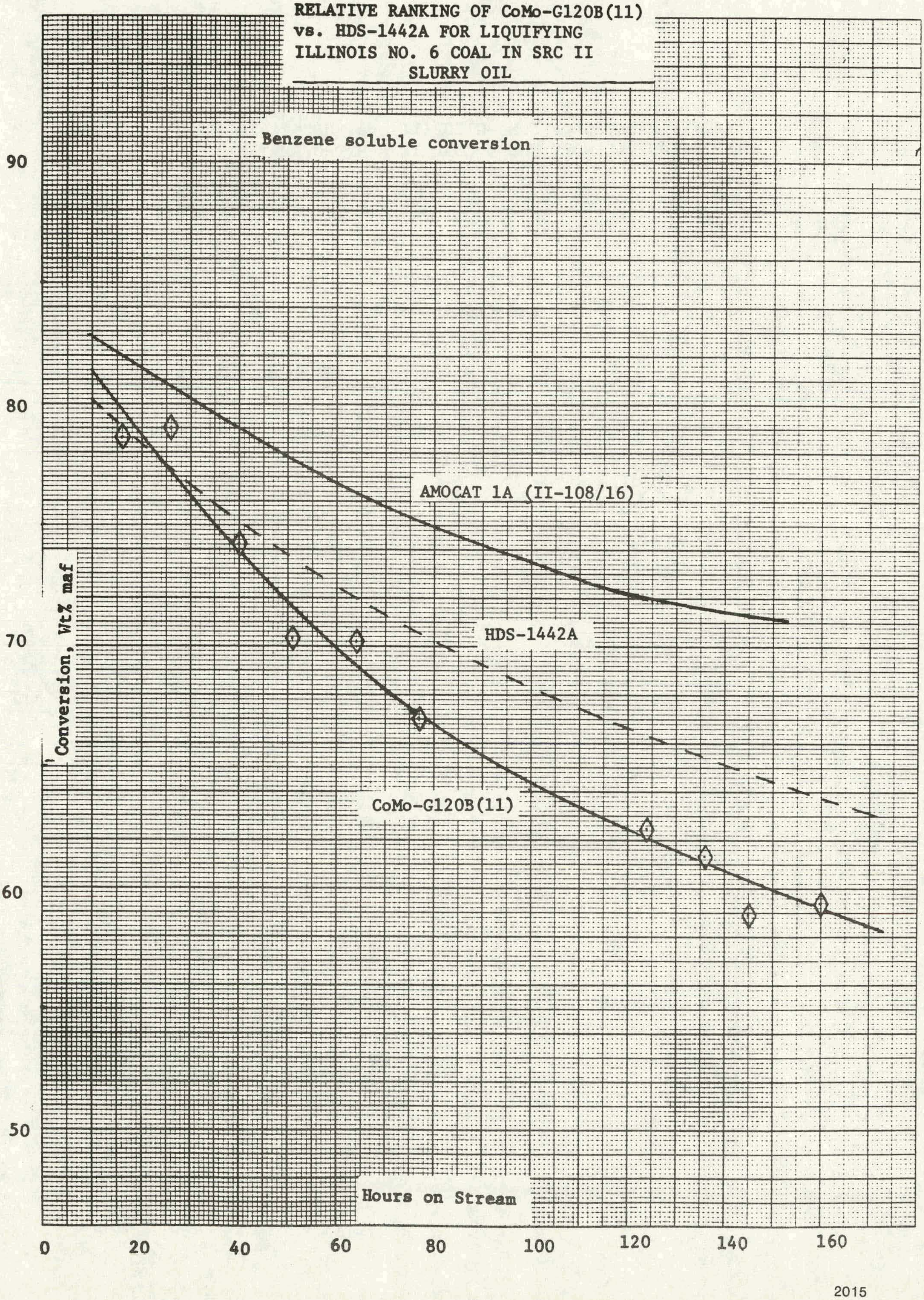


FIGURE VI



RELATIVE RANKING OF CoMo-G120B(11) vs. HDS-1442A FOR LIQUIFYING ILLINOIS NO. 6 COAL IN SRC II SLURRY OIL

Future Work

The following runs are planned:

Run No.	Catalyst	Coal
5192	Thermal	Illinois No. 6 and Wyodak
5193	AMOCAT-1B(18 lb. batch)	Illinois No. 6
5194	Engelhard	Illinois No. 6
5195	Grace 150Å Bimodal	Illinois No. 6
5196	Grace 200Å Bimodal	Illinois No. 6
5197	New Catalyst	Illinois No. 6

TASK 3. CATALYST AGING TESTS--WESTERN COAL

The objective of Task 3 is to characterize liquefaction of subbituminous Western coal such as Wyodak coal and to develop catalysts uniquely suited to that coal. Some of the key points to consider include the following:

- Liquefaction yield
- Product quality
- Catalyst aging behavior
- Hydrogen consumption

The maceral composition of Wyodak coal, low huminite and high fusimite contents relative to Illinois No. 6 coal, might have some relations to the liquefaction yield. Although sulfur content is low, nitrogen content of Wyodak is high as shown in Table VII . Catalyst aging is an important concern when considering the higher moisture content of Wyodak coal and the high concentration of alkaline-earth in the mineral matter. Hydrogen consumption is expected high due to the high oxygen content, which would have an unfavorable impact on the process economics.

TABLE VII

ANALYSES OF COALS

Ultimate Analysis, Wt%	Illinois No. 6 Burning Star	Wyodak Gillette, Wy.
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
Sulfur Types, Wt%		
Inorganic	0.08	0.05
Pyritic	1.17	0.12
Organic	2.08	0.81
	3.33	0.98

Three runs with Wyodak coal were completed at the same test conditions used for Illinois No. 6 coal, i.e. 137 atm, 440°C and 25 wt% coal in SRC II heavy distillate. Catalyst properties are listed in Table VIII .

TABLE VIII

CATALYST INSPECTIONS

Run No.	Catalyst	APD Å	SA m2/g	PV cc/g	Macropore Volume % of total Hg PV
5189	HDS-1442A	56	332	.741	27.6
5190	CoMo-G102B(14)	102	188	.681	14.2
5191	Mo-102B(14)	102	191	.704	14.1

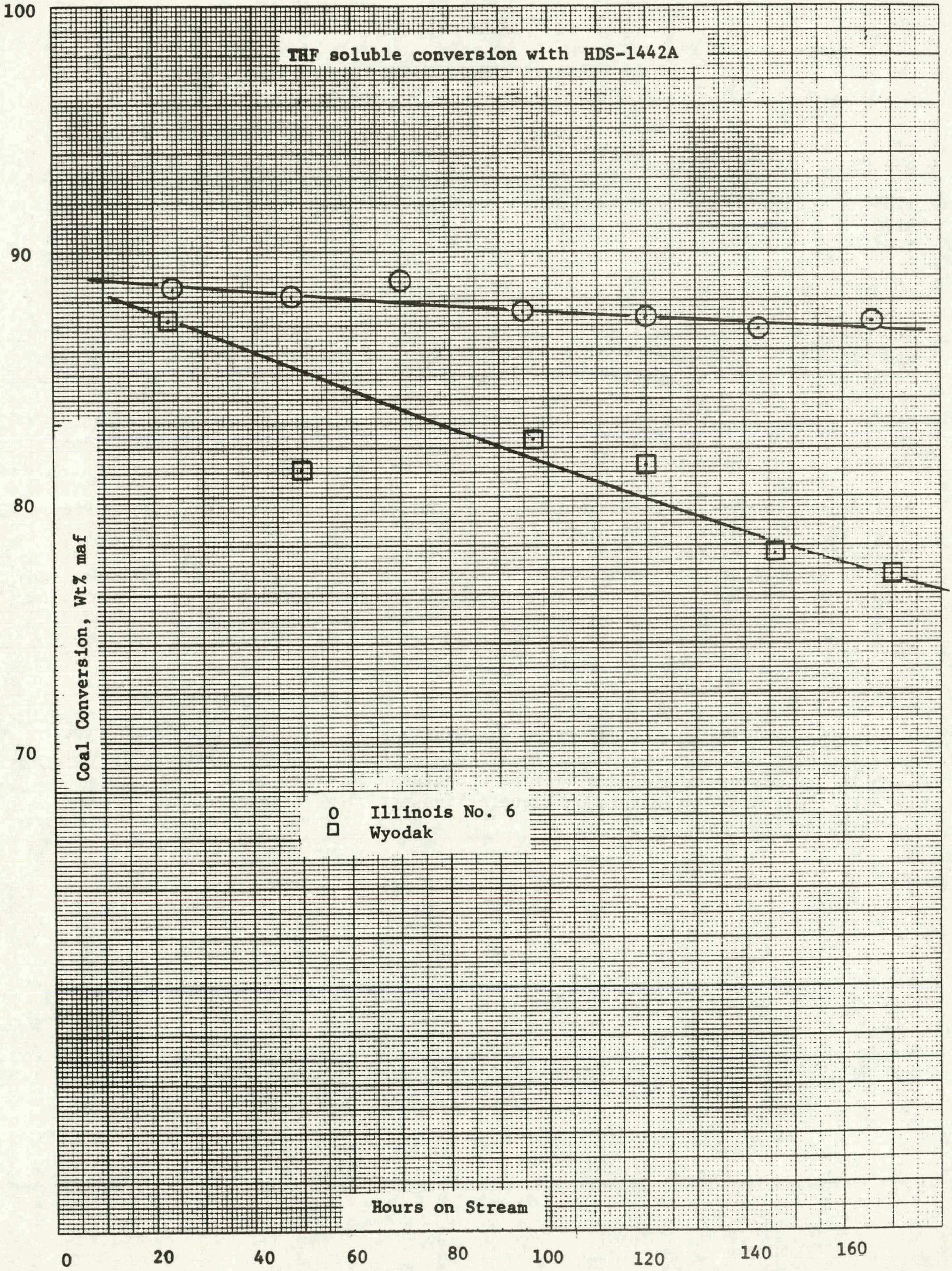
HDS-1442A is the reference H-Coal catalyst. The other two catalysts, CoMo-G102B(14) are respectively 18-pound batches of cobalt-molybdenum and unpromoted molybdenum supported on an identical Grace 102 Å bimodal alumina prepared by W. R. Grace. The average pore diameter of these two batches are slightly smaller than the intended 120 Å, but the majority of micropores are in the 70-200 Å range. The two catalysts would reveal the metals effect on liquefaction of Wyodak coal as well as the pore size effect when compared to HDS-1442A.

Preliminary results of liquefaction yield from Wyodak catalyst is given in Figure VII where the THF conversion is plotted vs. time on stream. THF soluble conversion of Illinois No. 6 coal is high and fairly constant throughout the run, whereas the THF soluble conversion of Wyodak coal is lower and declines with catalyst age. This indicates that Wyodak coal is more difficult to liquefy than Illinois No. 6 coal and causes more severe catalyst deactivation. More detailed comparisons of liquefaction behavior will be presented when product analyses are complete.

Future

A detailed analysis of the data from the runs with Wyodak coal and AMOCAT type catalyst will be completed. Additional runs with other Grace bimodal supports with larger micropore diamters will be undertaken in order to optimize the effect of micropore structure on liquefaction activity, heteroatom removal and activity decline rate.

FIGURE VII


THF soluble conversion with HDS-1442A
Coal Conversion, Wt% maf
Hours on Stream
100
90
80
70
0
20
40
60
80
100
120
140
160
O Illinois No. 6
□ Wyodak

TASK 4 - DEVELOPMENT SUPPORT STUDIES--SYNTHETIC COAL

Deliverability of an improved catalyst for the H-Coal process is a primary objective of the program. To achieve this goal the catalyst development program will be supplemented with work aimed at answering fundamental questions. Significant advances in catalyst technology frequently require a blend of fundamental and applied work; the catalyst development programs in the petroleum industry have successfully used this approach on numerous occasions.

The mechanism studies by Curran et al (1) have been tremendously valuable in understanding hydrogen donor reactions involved in non-catalytic coal liquefaction. However, the presence of a catalyst in the liquefaction medium adds a new dimension to the picture. Although certain theories have been advanced on the function of the liquefaction catalyst, there is an obvious need to more clearly define its role.

Some significant strides in coal liquefaction can be accomplished in a fundamental study using synthetic coal mixtures. Two types of synthetic coals will be used--one representing Eastern coal and the other Western. Differences in sulfur and oxygen content will reflect the two types of coal. It should be pointed out that the specific compounds which comprise the synthetic coals are not as large as those present in coal; however, they should adequately represent units of functionality found in coal. This reasoning is based on the excellent work by Whitehurst, et al, at Mobil Oil. The specific catalytic functions that we believe are important in coal liquefaction include:

1. hydrogenation,
2. cracking,
3. hydrogenolysis to remove sulfur, nitrogen, and oxygen,
4, isomerization.

The first three listed catalytic functions are the most important, and these will be examined by an appropriate mixture of model compounds in a hydrogen donor solvent.

Deactivated catalysts will also be investigated with the synthetic coal system to assess which catalytic functions have been altered and to what extent. For example, it is quite possible that the fresh catalyst performance has little if any, relation to the performance of a liquefaction catalyst after it has been aged only one hour. To clarify this possibility, catalysts which have been aged only one hour will be examined in the development support unit along with catalysts aged for longer periods of time (150 hours).

DEVELOPMENT SUPPORT UNIT

Activities under Task 4 center around tests in a 300 cc continuous stirred reactor. This is a smaller version of the multiphase gradientless reactor developed by Amoco researchers (2). Operation is once through with respect to both hydrogen and the synthetic coal feed.

Spinning Basket Reactor Description

The spinning catalyst basket of the reactor is shown in Figure VIII. The catalyst is held in place by wire mesh in an annular space inside the basket, where internal baffles are between the catalyst space and the center support shaft. The basket is also surrounded by a baffle system which directs the fluid flow and prevents liquid vortexing. A 300 cc autoclave designed and built by Autoclave Engineers serves as the basis for the reactor system and is equipped with a packless magnetic drive to rotate the basket.

Good contacting is provided by the liquid and entrained gas bubbles flowing rapidly past the catalyst. This highly turbulent gas-liquid mass is a liquid continuous bubble swarm. Backmixed (gradientless) operation is assured by good mixing in the reactor. The flow pattern, shown in Figure IX, is as follows: (1) Fluid enters near the center of the basket through the cutouts at the top and bottom; (2) the fluid inside the basket rotates at the same rate as the basket and moves by centrifugal force into the catalyst; (3) fluid exits the catalyst and moves up or down between the basket and autoclave wall; (4) the fluid moves into the spaces above and below the basket where it then re-enters the basket.

Process Description

The overall flow scheme is shown in Figure X. Hydrogen is metered to the reactor from the pilot plant feed system. Liquid feed is pumped to the reactor by a Ruska pump which regulates the flow rate.

Hydrogen, hydrogen sulfide, and vaporized hydrocarbon are removed from the vapor space above the spinning basket. It is heated to reaction temperature to prevent condensation and refluxing, then cooled to room temperature in a condenser where it enters a separator. The liquid hydrocarbon is recycled with an air driven Haskel pump to the reactor. The uncondensed gas, hydrogen, ammonia and hydrogen sulfide, passes through the unit pressure control valve to the wet test meter, which measures the gas flow rate.

The liquid exits the reactor to a high-pressure separator with an overflow pipe positioned inside. Liquid level in the reactor is maintained at the same level as the top of the overflow pipe in the separator. The liquid overflows from the pipe into the body of the separator. The liquid level in the body of the separator is maintained below the top of the overflow pipe.

Residence Time Distribution

For analysis of the data, the residence time distribution of the liquid must be clearly defined; the spinning basket reactor should approximate a single backmixed reactor. Highly vaporized feeds work against this objective, however. To maintain the partial pressure of the reaction species (e.g. hydrogen sulfide) at the desired level, hydrogen is constantly fed and withdrawn from the reactor. As hydrogen is withdrawn, so is the vaporized liquid. This results in the residence time of the lighter components being less than the rest of the reaction

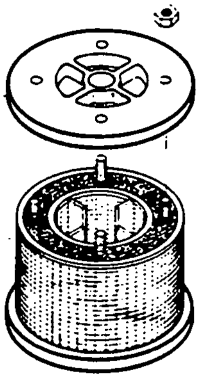


FIGURE VIII. Annular catalyst basket

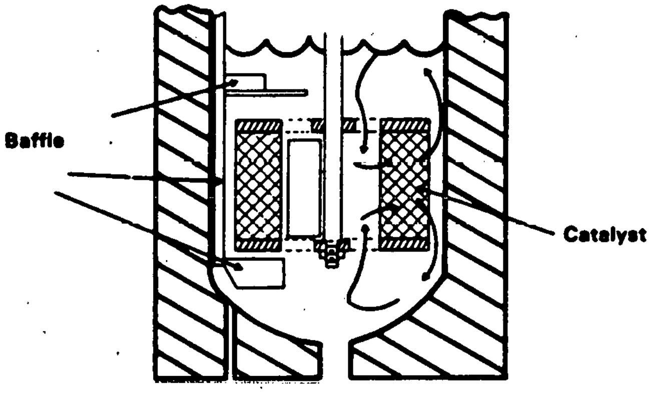
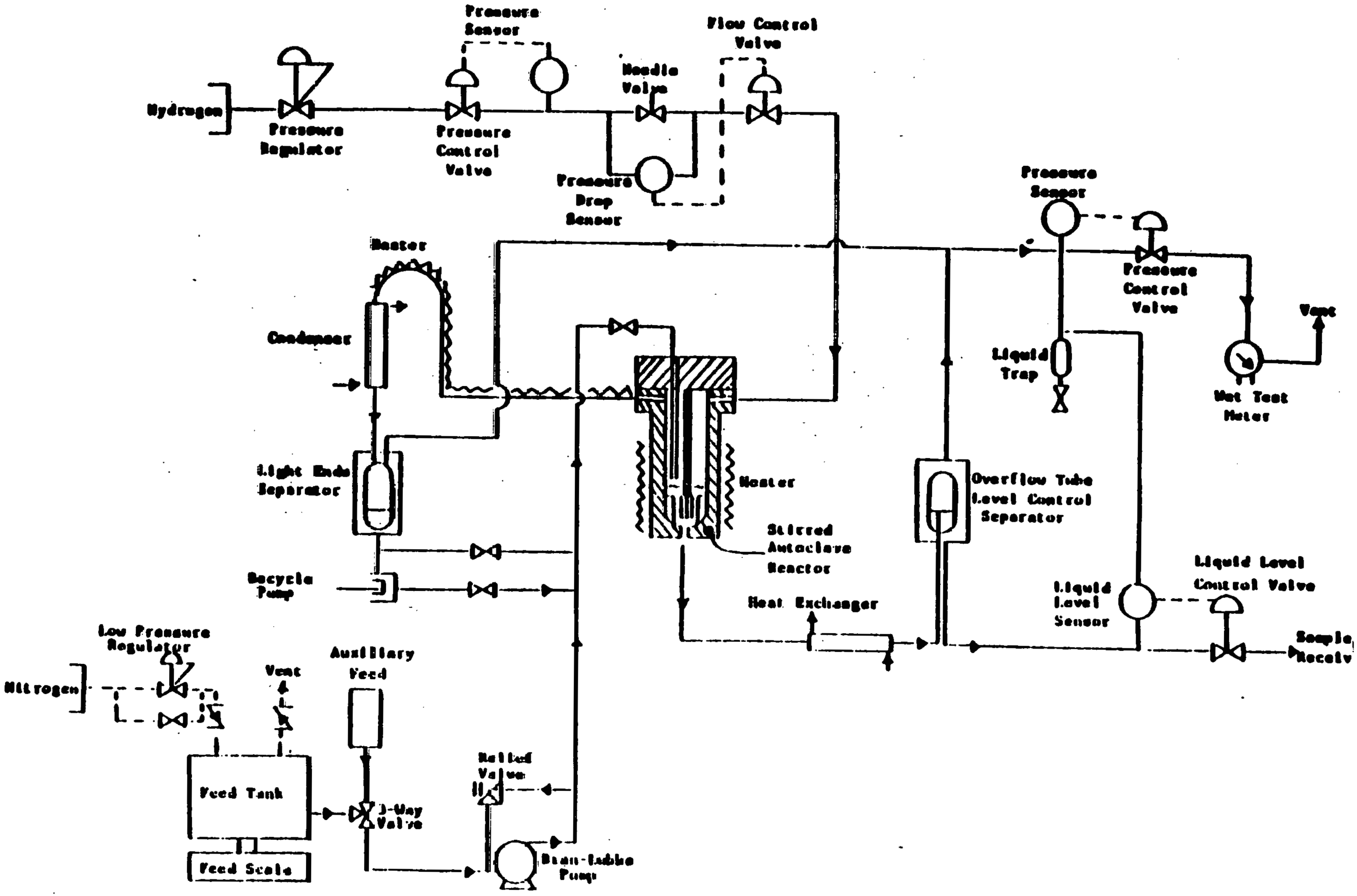


FIGURE IX. Multiphase spinning basket reactor

FIGURE X

FLOW DIAGRAM OF DEVELOPMENT SUPPORT UNIT



mixture. To prevent this, vaporized liquid leaving the reactor with the gas stream should be condensed and then recycled back to the reactor. This controls and defines the residence time distribution of the liquid in the reactor by requiring all of it which enters to exit the reactor as liquid assuming hydrocracking reactions are negligible. More specifically, the off-gas is cooled to amient temperature to condense the light hydrocarbons before being vented. Then the light hydrocarbons are returned to the reactor with an air-driven recycle pump.

Feed and Test Conditions

Test conditions consist of:

Operating Conditions - Development Support Unit

Catalyst Charge:	10 gm, 1/16" extrudate
Feed:	Synthetic coal - 12 compounds in Panasol
Pressure:	68 atm (1000 psig)
Temperature:	329°C (625°F)
H_2 Feed Rate:	.57 liter/gm feed
Liquid Feed Rate:	50 gm/hr
WHSV:	5 gm oil/hr-gm catalyst
Mixing Speed:	750 rpm

Initially a twelve-component mixture, containing compounds with the units of functionality found in coal, was used to separately analyze the catalytic functions of hydrogenation, hydrocracking, hydrodesulfurization, hydrodenitrogenation, and hydrodeoxygenation. Although the compounds are not as large as those found in coal, Whitehurst, et al (3) at Mobil have pointed out that the unique molecular bonding can still be adequately represented by careful selection of the "units of functionality."

The composition of this synthetic coal mixture is as follows:

Compounds	Eastern Synthetic Weight %	Western Synthetic Weight %
Oxygen Containing:		
p-cresol	5.2	10.2
dibenzofuran	8.0	9.0
phenyl ether	8.2	8.9
Nitrogen Containing:		
indole	1.2	1.0
quinoline	1.3	1.0
Sulfur Containing:		
benzothiophene	1.0	.3
dibenzothiophene	1.4	.2
n-butylsulfide	1.5	.2
Hydrocarbons:		
anthracene	1.5	1.5
bibenzyl	2.5	2.5
hexadecane	3.0	3.0
isopropylbenzene	3.0	3.0
Solvent:		
Panasol AN-3 (trimethylnaphthalene)	62.2	59.2

The composition of the synthetic coal mixtures reflects differences in Western and Eastern coal by the sulfur and oxygen content.

Product characterization will consist of:

- Capillary Chromatograph
- Infrared Spectroscopy
- Ultraviolet Spectroscopy
- Elemental Analysis for C, H, S, N, O

Conversion Index

Because the gradientless reactor permits reaction studies at isothermal conditions with uniform concentrations, it eleminates the need for integral and partial differential equations, whose solution often requires complex and lengthy computer programming and processing. Instead, each steady-state experiment with integral conversion yields a reaction role for a first order reaction that is simply calculated from the ordinary difference equiation:

$$\frac{W}{F} = \frac{(X_o - X_i)}{r_p} = \frac{(X_o - X_i)}{kX_o}$$

where W is the mass of catalyst, F is the feed rate of reactant, X is the concentration of reactant, and subscript o and i refer to outlet and inlet concentration.

$$\frac{W}{F}k = \frac{X_o - X_i}{X_o} = \text{CI} = \text{Conversion Index}$$

Use of a conversion index is based on the assumption that all experiments are run in a narrow range of process conditions so that adsorption and temperature effects may be neglected.

Solvent Production

Various materials have been used as hydrogen donor solvents in coal liquefaction. In general, these materials contain substantial quantities of condensed aromatic compounds. The solvent must have the capability of transferring hydrogen to a hydrogen- deficient substance, such as coal feed. For the purpose of catalyst screening and synthetic coal model compound studies Panasol AN-3 was chosen as a solvent. This material is recovered from the distillation bottoms after high severity reforming of naphtha.

Panasol is completely aromatic and consists primarily of mono-, di-, and trimethylnaphthalene. The trimethylnaphthalenes boil between 278°C and 289°C and are the highest boiling fractions of this particular solvent. Seven barrels of Panasol were distilled to recover the heavy, trimethylnaphthalene bottoms. Use of a narrow boiling range solvent will improve analytical accuracy of the model compound study by minimizing interaction between the solvent and model compound gas chromatographic spectra.

Future Work

We plan to begin the model compound studies utilizing a pure compound mixture of six compounds in addition to the Panasol bottoms solvent. The boiling point of the reactants on the approximate composition are shown in Table IX.

TABLE IX

SIMPLIFIED SYNTHETIC COAL MIXTURE

Compound	Boiling Point °C	Mixture 1 (Eastern)	Mixture 2 (Western)
anthracene	354	10.0	10.0
dibenzothiophene	332	4.0	1.0
quinoline	237	1.0	1.0
indole	254	2.0	1.0
dibenzofuran	285	10.0	14.0
p-cresol	202	10.0	14.0
Panasol (trimethylnaphthalenes)	275-289	63.0	59.0

Dibenzothiophene will interact to some extent with the solvent however this is the key sulfur functional group found in coal and therefore we felt that it was important to include it. The relative composition of the oxygen, nitrogen, and sulfur compounds are approximately the same in the 6 compound and 12 compound synthetic coal feed.

The test pressure for the model compound study will be increased to 2000 psig to more closely approximate H-Coal conditions. The test temperature will be increased to the 430°C (800°F) range again to approximate H-Caol conditions. The WHSV will be set at a value to give about 50% conversion at H-Coal conditions with the reference catalyst, HDS-1442A; a small catalyst charge will allow us to increase space velocity.

Blending of the synthetic feed will begin in October followed by testing to establish base conversion index. Base conversion runs will employ the commercial catalyst, HDS-1442A as well as AMOCAT type catalysts, CoMo-G102B(14) and Mo-G102B(14).

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

Most of the effort by the participants in the H-Coal project is directed at process development and reactor improvements. However, it is important to note that catalyst performance has a strong impact on product quality, operating strategy (catalyst replacement, reactor conditions) and economics.

The objectives of Task 5 include the following:

1. Provide technical support on H-Coal tests run at HRI.
2. Correlate performance between H-Coal and Amoco test units.
3. Provide large scale samples of liquefaction catalyst for evaluation in H-Coal PDU or upgrading processes.
4. Coordinate activities with other DOE facilities.

In Task 5 we concentrated on the evaluation of the large 500 pound batch of AMOCAT 1A during the second quarter. A previous test on rerun slurry oil had led to inconclusive results on the conversion performance. We now are certain that the solids content varied over the test series and introduced errors in the determination of insoluble residue, used to calculate conversion. A reanalysis of the data in terms of preasphaltene (THF sol-bz insol) and asphaltene (bz sol-hex insol) content shows that the AMOCAT 1A is better than HDS-1442A catalyst.

Using SRC II heavy distillate as the slurry oil, the results from the aging test are quite clear. The recently prepared 500 pound batch of AMOCAT 1A is good quality and exhibits highly improved performance over the H-Coal catalyst, HDS-1442A. Benzene and hexane soluble conversion are markedly higher with hexane soluble conversion declining less rapidly with time. Furthermore the yield of 520°C$^+$resid is about 5% lower with AMOCAT 1A indicating that more high quality lower boiling material is being produced. Finally, the sulfur content of the 520°C$^+$ resid is also lower. The highly improved catalyst should be considered for future evaluation in the larger H-Coal process development unit (PDU). Details of the two runs with AMOCAT 1A(II-108/16) are reported.

Continuous Aging Unit Results with 500 Pound AMOCAT 1A(II-108/16) Catalyst

Two runs were made with AMOCAT 1A(II-108/16) in the Continuous Aging Unit with Illinois No. 6 Coal. In the first run, No. 5184, lined-out or rerun slurry oil was used as the liquefaction solvent. The lined-out slurry oil was the coal liquefaction slurry products collected last year as slop and contained unconverted coal particles. It was used at that point in time because no other solids-free slurry oil was available. The results for AMOCAT 1A(II-108/16) showed that not only benzene insoluble but also THF insoluble contents of the products were greater than those of Run 5182 for HDS-1442A.

Since liquefaction of Illinois No. 6 coal results in the same amount of the THF insoluble content regardless of catalyst type and with or without a catalyst, the difference in THF insoluble content must be due to irregularity in solid fines content of the rerun slurry oil. As proof, measurements of ash content of the slurry products which have been otherwise constant varies from run to run and day to day as shown in Table X .

TABLE X

ASH CONTENT OF PRODUCT SLURRY (WT%)

Days on Stream	HDS-1442A Run 5182	AMOCAT 1A(II-108/16) Run 5184
1	2.78	3.18
2	2.79	3.45
3	2.90	3.70
4	2.91	3.48
5	2.95	3.44

In spite of the difficulty caused by solid fines in rerun slurry oil, some assessment of the liquefaction performance of the two catalysts is still possible. To do this the preasphaltene and asphaltene contents are compared. Preasphaltenes are the fraction of product soluble in THF but insoluble in benzene. Asphaltenes are the benzene soluble and hexane insoluble fractions. Figure XI shows that both preasphaltene and asphaltene contents are lower for AMOCAT 1A(II-108/16) than HDS-1442.

When the new SRC II slurry oil was received the 500 lb batch AMOCAT 1A(II-108/16) and HDS-1442A were retested and compared at the standard test conditions using Illinois No. 6 coal and SRC-II slurry oil. First, the liquefaction performance based on product solubility are presented in Figure XII. The THF soluble conversion which may be termed as boiler fuel yield is high and essentially the same for both HDS-1442A and AMOCAT 1A(II-108/16) catalysts. This is characteristic of bituminous Illinois No. 6 coal. However, benzene soluble and hexane soluble conversions, the more sensitive performance indicators, are higher for AMOCAT 1A (II-108/16) than HDS-1442A throughout the entire run length. The difference in hexane soluble conversion is especially large. The catalyst ranking for liquefaction conversion turned out as expected for AMOCAT 1A type catalysts. We conclude that the quality of 500 lb. batch AMOCAT 1A(II-108/16) catalyst is acceptable.

Product qualities also appear to be better for AMOCAT 1A(II-108/16) than HDS-1442A catalyst. Specific gravities of the total THF soluble liquid products containing slurry oil are lower with AMOCAT 1A(II-108/16) than HDS-1442A as shown in Table XI .

FIGURE XI

COMPARISON OF PRODUCT WORKUP RESULTS

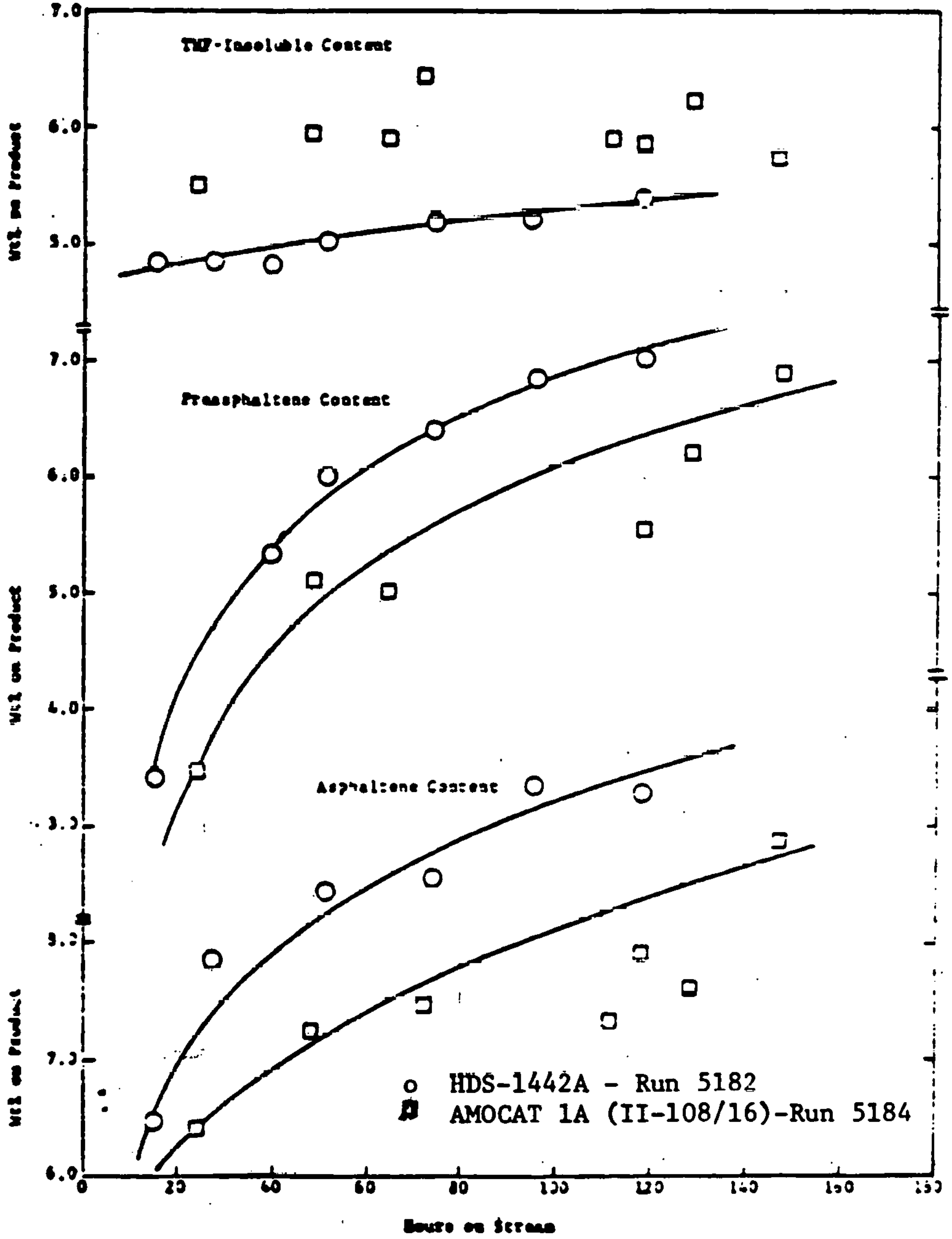


FIGURE XII

CONVERSION OF ILLINOIS NO. 6 COAL

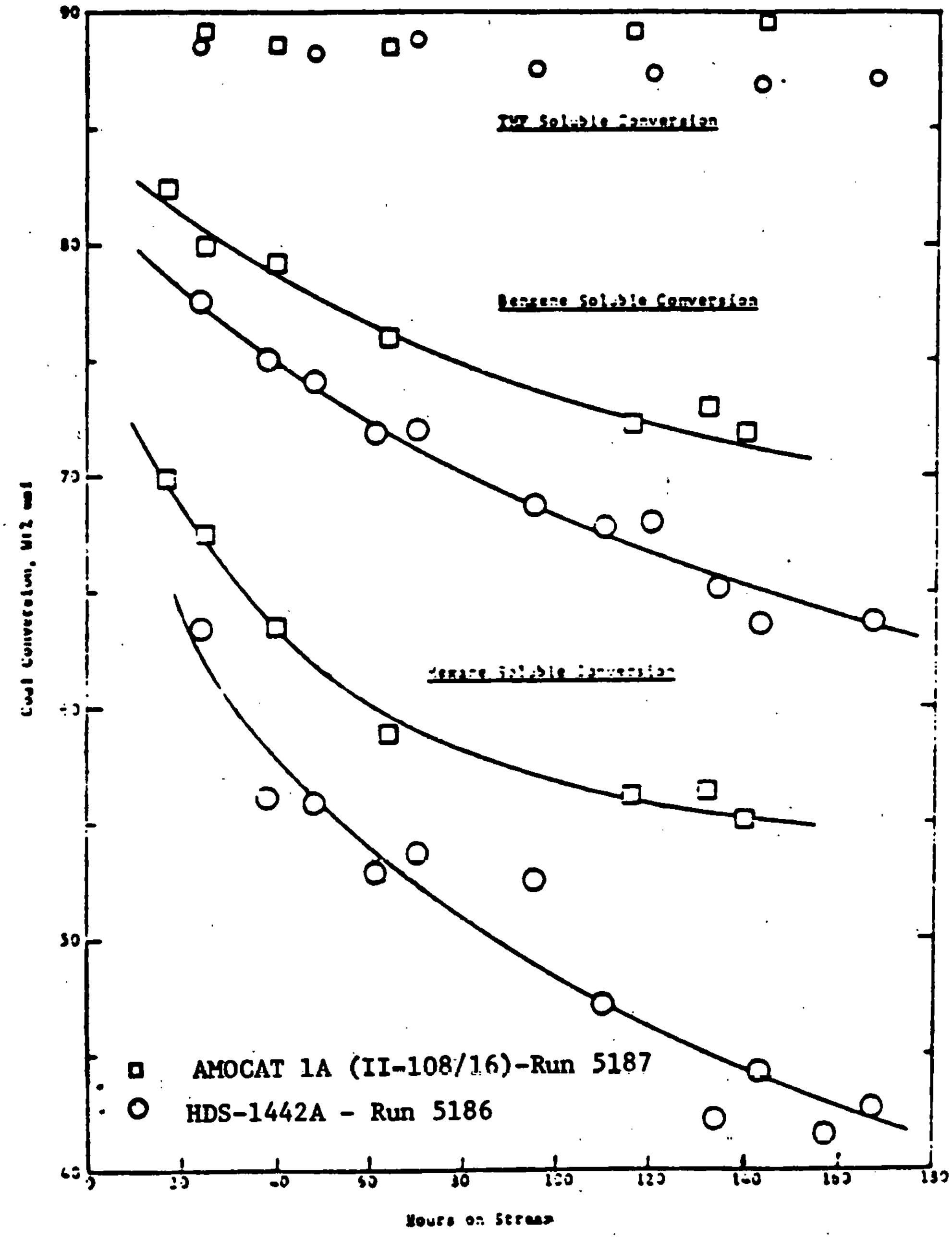


TABLE XI

SPECIFIC GRAVITY OF THE SOLUBLE LIQUID

Days	Run 5186 HDS-1442A	Run 5187 AMOCAT 1A (II-108/16)
1	1.070	1.064
2	1.073	1.070
3	1.073	1.068
4	1.074	---
5	1.072	1.068
6	1.078	

The total THF soluble liquid was vacuum distilled to obtain 520^oC^+ resid fraction which consisted essentially of liquefied coal oil. The slurry oil alone contained approximately 2.9 wt% 520^oC^+ resid material, some of which would certainly undergo hydrogenation to lower boiling materials at the liquefaction condition, but the extent of that reaction was not determined. Nevertheless, the 520^oC^+ resid yield was calculated based on moisture-ash free coal and the results were presented in Figure XIII along with sulfur contents in the resid.

The 520^oC^+ resid yield obtained with AMOCAT 1A(II-108/16) is lower than that of HDS-1442A; AMOCAT 1A (II-108/16) gives more low-boiling distillate product than HDS-1442A catalyst. The sulfur contents in 520^oC^+ resid are also lower for AMOCAT 1A (II-108/16), indicating better desulfurization activity.

Sulfur contents in liquid product are lower with AMOCAT 1A (II-108/16) than with HDS-1442A. Sulfur removal is better with AMOCAT 1A (II-108/16) catalyst. Nitrogen contents of the liquid product also appear to be slightly lower for AMOCAT 1A (II-108/16), but in general, are not much different from the feed nitrogen content. Nitrogen contents of the slurry oil and Illinois No. 6 coal are respectively 1.2 and 1.3 wt%. Nitrogen removal is much more difficult to achieve than desulfurization at coal liquefaction conditions. The nitrogen and sulfur contents in Table XII correspond to 20-30% denitrogenation and 60-75% desulfurization based in total slurry feed. Hydrogen contents are steadily higher for the products obtained with AMOCAT 1A (II-108/16) catalyst than HDS-1442A. Oxygen contents in general are slightly lower for AMOCAT 1A (II-108/16).

TABLE XII

PRODUCT QUALITY COMPARISON

	AMOCAT 1A(II-108/16)-Run 5187				
Days On Stream	1	2	3	5	6
THF Soluble Liquid, wt%					
S	0.24	0.27	0.27	0.31	0.31
N	1.01	1.02	1.06	1.03	1.09
O	2.44	1.68	1.40	0.60	2.55
H	7.68	7.70	7.68	7.56	7.52
Atomic H/C	1.029	1.033	1.033	1.013	1.016
$520^\circ C^+$ Resid, wt%					
S	0.61	0.73	0.73	0.81	
N	1.64	1.74	1.71	1.90	
O	5.43	4.77	6.13	6.05	
H	6.09	5.98	5.89	5.81	
Atomic H/C	.832	.822	.816	.803	

	HDS-1442A - Run 5186						
Days On Stream	1	2	3	4	5	6	7
THF Soluble Liquid, wt%							
S	0.22	0.27	0.30	0.32	0.32	0.37	0.38
N	1.06	1.00	1.01	1.04	1.05	1.12	1.13
O	2.53	2.64	2.51	2.80	2.19	2.55	4.38
H	7.68	7.62	7.59	7.59	7.43	7.58	7.26
Atomic H/C	10.32	1.024	1.020	1.027	0.999	1.014	0.982
$520^\circ C^+$ Resid, wt%							
S	0.54	0.76	.87	0.90	0.90	0.93	
N	1.83	1.81	1.90	1.94	1.97	1.95	
O	3.18	5.05	6.65	7.65	5.21	6.69	
H	6.13	5.98	5.90	5.86	5.85	5.76	
Atomic H/C	.838	.825	.877	.814	.812	.802	

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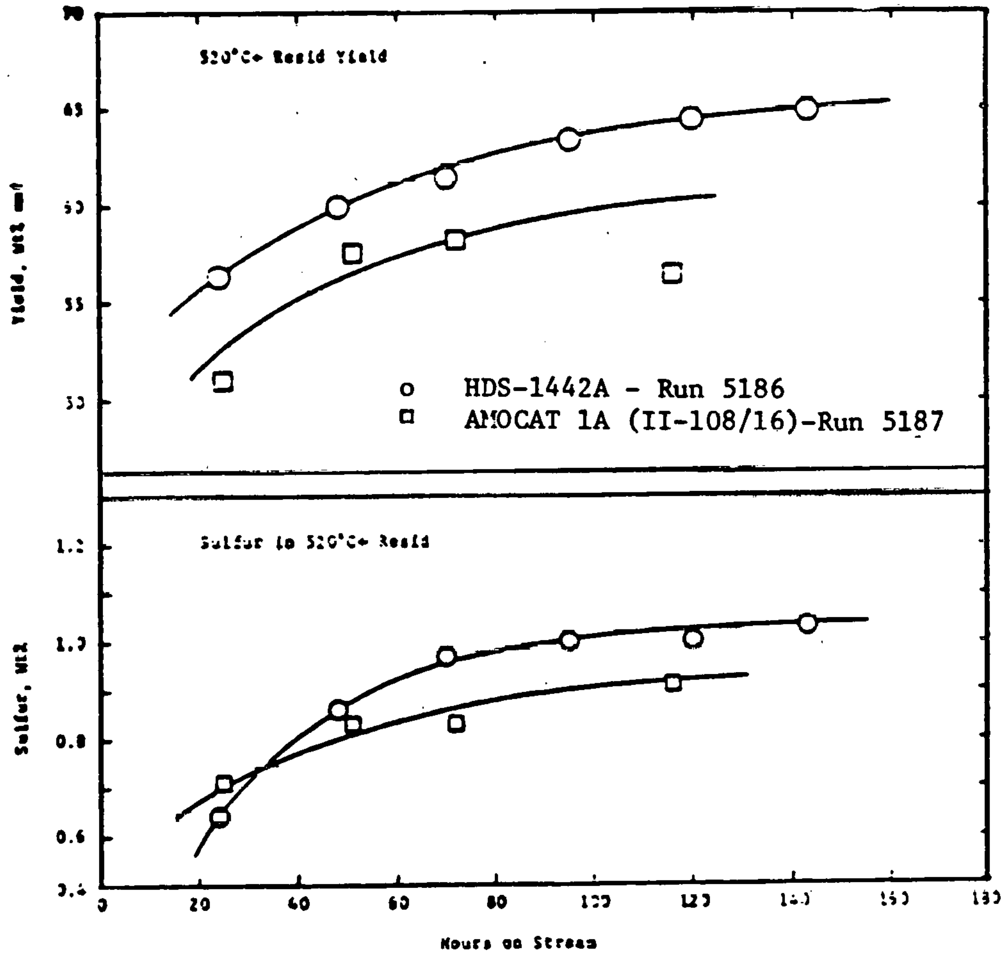
FIGURE XIII

RESID YIELD AND SULFUR CONTENT



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APPENDIX A.

Pilot Plant Run Summary

During the second quarter of the program 6 runs were on the Continuous Aging Unit, Main run events are summarized below:

Run No.	Catalyst	Run Events
5186	HDS-1442A (2392-5)	7/12-7/18/79 A base run for Illinois No. 6 coal at standard test conditions with SRC-II heavy distillate (FSN-10, Bbl #1) as the slurry oil. Catalyst was loaded in the redesigned basket with 10 mm annular thickness and slab baffles to prevent vortexing.
5187	AMOCAT-1A(II-108/16) (2392-147)	7/28-8/3/79 A composite sample of the 500 pound batch CoMo AMOCAT-1A type catalyst prepared by W. R. Grace was tested for comparison with Run 5186. Impeller diameter of the reactor stirrer was reduced from 3.17 cm to 2.86 cm to give more clearance between impeller and baffles of the catalyst basket.
5188	CoMo-G120B(11) (2392-120)	8/14-8/21/79 To obtain performance ranking of the previously proven experimental batch vs. 500 pound AMOCAT-1A catalyst relative to HDS-1442A. Changes in coal drum (Illinos No. 6, FCL-13, Drum #3) and slurry oil (FSN-10, Bbl #2) during the run. Temporary unit upset in the middle of the run due to product separator overflow.
5189	HDS-1442A (2392-5)	8/23-8/30/79 A base run for Wyodak coal. Test conditions and slurry oil remain unchanged.
5190	CoMo-G102B(14) (3651-80)	9/6-9/13/79 An 18 pound batch of CoMo on 102 Å bimodal alumina with 14% macropore volume prepared by W. R. Grace was tested to determine pore size effect on Wyodak coal liquefaction, as compared with Run 5189.
5191	Mo-G102B(14) (3651-81)	9/19-9/26/79 Another 18 pound batch by W. R. Grace of unprpmoted molybdenum version on the same alumina support as 3651-80. Tested with Wyodak coal to determine metals effects, Mo vs. CoMo.

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DOE/HQ

U. S. Dept. of Energy

Washington D. C. 20545

John Shen (MS GTN E-338) (7)

Pittsburgh Energy Technology Center

4800 Forbes Avenue
Pittsburgh, PA 15213

L. Polinski

Arthur Churm
Chief Office of Patent Council
U. S. Department of Energy
9800 S. Cass Avenue
Argonne, Illinois 60439

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