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COAL LIQUEFACTION CATALYST DEVELOPMENT

Quarterly Progress Report No. 3, October 1—December 31, 1979

By
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R. J. Pellet
J. A. Mahoney

January 1980
Date Published

Work Performed Under Contract No. AC01-79ET14803

Amoco Oil Company
Research and Development Department
Naperville, Illinois

U. S. DEPARTMENT OF ENERGY

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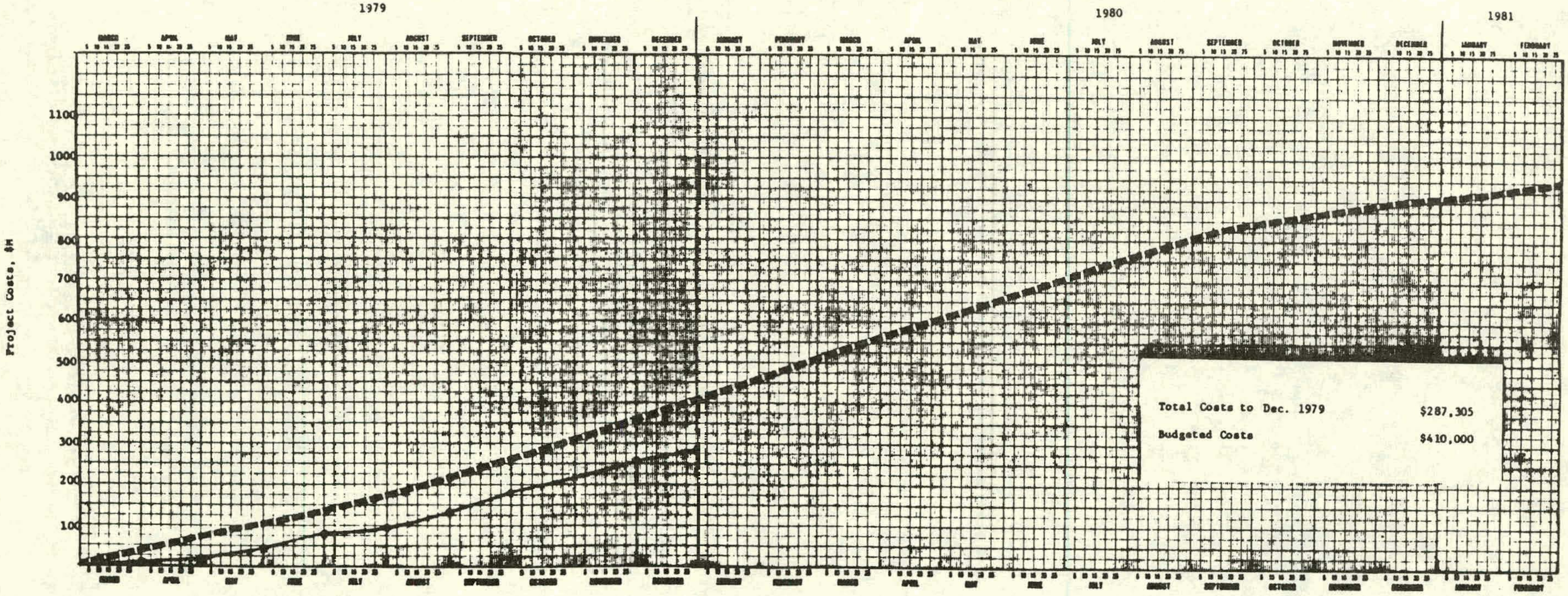
COST TRACKING CURVE
COAL LIQUEFACTION CATALYST DEVELOPMENT
AMOCO OIL RESEARCH & DEVELOPMENT



Total Costs to Dec. 1979	$287,305
Budgeted Costs	$410,000

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 contract 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 current contract 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 third quarter of the project (October 1 to December 31, 1979).

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QUARTERLY SUMMARY

This project is a continuation of the coal liquefaction program funded by the Electric Power Research Institute from 1975 to 1979. During the third quarter of DOE sponsorship (October 1 to December 31, 1979), progress was made in all tasks of the DOE contract.

Under Task 1--Catalyst Preparation and Screening, catalytic baseline runs continued with HDS-1442A in order to improve our baseline statistics as well as to monitor batch reactor performance. Testing of several new catalyst formulations was completed. No promising candidates for testing in the continuous aging unit were identified during the third quarter. Progress was limited this period by operational and manpower problems.

Tasks 2 and 3--Catalyst Aging Tests--Eastern and Western Coal centered around evaluation of the new SRC-II slurry oil as a hydrogen donor liquefaction solvent. Our data indicates that the SRC-II heavy distillate oil is not as effective a hydrogen donor solvent as the hydrogenated anthracene oil. It is possible that the catalyst plays a key role in the thermal liquefaction reactions by improving the hydrogen donor properties of the slurry oil through in-situ hydrogenation. Optimization of the H-Coal solvent composition and the effect of the catalyst on its composition during operation should be an important task for future research.

The differences in liquefaction behavior between Illinois No. 6 and Wyodak coal were determined. Wyodak coal is more difficult to liquefy than Illinois No. 6, however, the product quality should generally be better for Wyodak once it is liquefied.

A major portion of our effort this quarter was concerned with ascertaining the liquefaction behavior of a Western coal such as Wyodak with AMOCAT type catalysts. A run with Mo-G102B(14) was repeated because the catalyst in the original run was calcined at too high a temperature. the AMOCAT-1B catalyst was not as active as the AMOCAT-1A catalyst when processing Wyodak coal but the AMOCAT-1A catalyst, CoMo-G102B(14), was superior to HDS-1442A with the same feed. Larger micropores (APD ≥ 120 Å) are needed when processing Wyodak coal without the cobalt promoter.

These findings differ from earlier results under the EPRI contract with unpromoted molybdena catalysts (AMOCAT-1B) which utilized a good donor solvent as well as a catalyst support with micropores in excess of 120 Å pore diameter. In the EPRI work AMOCAT-1B was found to be a superior catalyst for processing Wyodak coal.

Product workups are in progress for several runs. Off-gas analysis was added to the product workup.

A two-month program to determine the feasibility of using the Amoco continuous aging unit for SRC-I product upgrading was outlined. Experimental work should begin in March of 1980 depending on receipt of material and catalyst. In this program, three NiMo catalysts will be tested in 150 hr continuous aging unit runs as well as a two-day solvent run and a two-day thermal run. The third NiMo catalyst will be a 1/32" AMOCAT type catalyst provided by W. R. Grace.

Under Task 4--Development Support Studies--Synthetic Coal distillation of the Panasol solvent to be used as a hydrogen donor for the pure compound studies was continued.

Task 5--Applications of New Catalysts--H-Coal continued to concentrate on the evaluation of the large 500 pound batch of AMOCAT-1A to be used in the HRI PDU tests. Final product analyses were completed and the large batch of AMOCAT-1A clearly exhibited improved performance over the H-Coal catalyst, HDS-1442A.

An Engelhard CoMo catalyst on a stabilized BaMo alumina was evaluated and found to have low initial conversion but also a low deactivation rate. Product workups for the resid and distillate portions are in progress.

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. Most of the experimental catalysts are prepared in our Amoco laboratories. 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. The most promising areas consist of the following:

Modified aluminas
Alternate catalytic materials
Multifunctional catalysts
Novel catalyst system

Base Case Runs

During the last quarter we completed several thermal and catalytic base runs with HDS-1442A as the reference catalyst. Toluene soluble conversion was selected as the basis for measuring liquefaction performance and the set of conditions listed in Table I was chosen for all runs.

Our base runs indicate that a 30 minute run time should be selected for screening experimental catalysts. From Figure 1, we can see two reasons for selecting this run length. First the difference between thermal and catalytic conversions appear to be greatest at this reaction 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. Having chosen the 30 minute run duration, base catalytic runs have been interspersed with the screening tests to more accurately determine conversion levels. This serves two purposes: (1) to improve to base case statistics, and (2) to constantly monitor reactor performance. The results of these base runs are presented in Table II. The average conversion at 30 minutes with HDS-1442A is 66.3% with an average deviation of 4.1%. The deviation should diminish as more base runs are completed.

Catalyst Preparations

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

Modified aluminas
Alternate materials
Two-catalyst systems (physical mixture)
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. Base case data will have to be generated for Wyodak coal.

FIGURE 1.

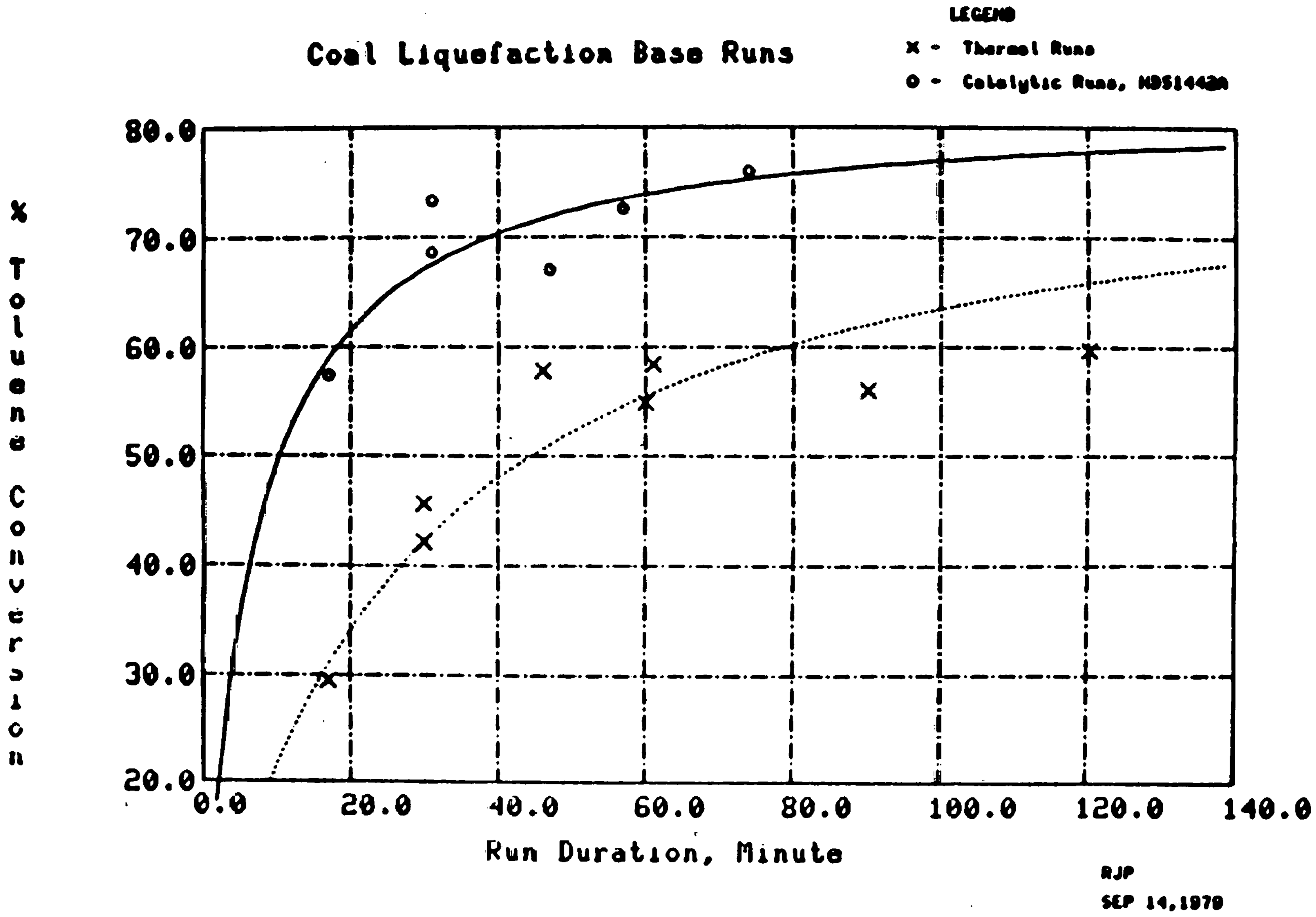
Coal Liquefaction Base Runs
LEGEND
x - Thermal Runs
o - Catalytic Runs, HDS1442A
% Toluene Conversion
80.0
70.0
60.0
50.0
40.0
30.0
20.0
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
Run Duration, Minute
RJP
SEP 14,1979

TABLE I

RUN CONDITIONS

Screening Test Conditions

Catalyst Charge	10g, dry basis
Catalyst Size	Through 60 on 100 mesh
Coal Charge	150g, as received
Coal Size	Through 60 mesh
Solvent	298 gm Panasol (AN-3R)
Pressure	137 atm (2000 psig)
Hydrogen Flow Rate	3 CF/hr
Mixing Speed	1800 rpm
Temperature (Maximum)	399°C (750°F)
Reaction Time (Nominal)	30 minutes

TABLE II

SUMMARY OF SCREENING RESULTS

October-December, 1979

Run No.	Cat #	Cat Des	% Conv.
Modified Aluminas			
110	4367-3	CoMo/3%U-Al_2O_3	53.4
116	4367-4	CoMo/3.6%BaO-Al_2O_3	52.6
Alternate Materials			
104	4367-1-3	2.6%CuB/11.4%MoN Al_2O_3	56.0
Mixed Catalysts			
105	2392-144 2392-135	CoO/B_2O_3-Al_2O_3 MoO_3/Al_2O_3	56.1
100	2392-138 2392-135	CoO/Al_2O_3 + MoO_3/Al_2O_3	55.4
Novel System			
96		10% Ni in Graphite	52.8
106		35% $AlCl_3$ in Graphite	33.5
Base Runs			
98	HDS-1442A	3%Co 16%MoO_3/Al_2O_3	67.3
99	"	"	61.7
114	"	"	61.4

TABLE III

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 + N_2/H_2O @ 1400°F

** 3% CoO 16% MoO_3/3% U-Al_2O_3 + N_2/H_2O @ 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)

*Catalyst Preparation Completed

**Tested

Catalyst Screening Results

System malfunctions and support staff illness limited progress this quarter. Modifications were made to the pressure and flow control systems to improve control of these process parameters after base case runs indicated problems in this area. Some catalyst from all categories have now been tested. The conversion levels observed for all catalysts tested in the third quarter are summarized in Table II.

Two-Catalyst Systems (Physical Mixtures)

Three mixed catalyst systems have been tested. A 10g charge of mixture was used in each test. Each mixture was composed of 80% MoO_3 on alumina and 20% CoO on a modified alumina. There were two questions to be answered by this line of experiment. First, will a cobalt promotional effect be observed when cobalt is physically separated from molybdenum? Secondly, will variations in cobalt support acidity affect the mixture performance?

In answer to the first question, it now appears that a direct interaction of cobalt-molybdenum is needed for optimal conversion. All three mixtures produced about 10% less toluene soluble material than the base HDS-1442A catlayst. However, to determine if cobalt component of the mixture has any promotional effect, a mixture composed of 80% molybdenum on alumina and 20% pure alumina will have to be run for comparison.

In answer to the second question, support acidity of the cobalt component has little effect on conversion levels since all three mixtures had identical activities within experimental error. In order to determine if diffusion limitations were responsible for the poor mixture performance one more catalyst must be tested. This catalyst should be a composite formed from very finely divided cobalt/alumina and molybdenum/alumina particles. This composite would have both components in close contact easing diffusion restrictions while avoiding any chemical interaction between cobalt and molybdenum.

Future work will test the effect of mixing supports with different pore size distributions. The proposed mixtures are summarized in Table IV.

Novel Catalyst Systems

Under this category, four catalysts have been tested. These catalysts consisted of metals intercalated into a graphite layered matrix. In testing these systems, it was hoped that the layered graphite support, which resembles the coal structure, would itself liquefy and render the intercalated metals readily accessible to the reaction mixture. Graphite systems containing Ni, $CrCl_3$, Co and $AlCl_3$ have been tested. The results of these tests are summarized in Table II. All intercalates performed extremely poorly. All except the nickel containing material gave conversions below the thermal conversion level. The results suggest that graphite is actually retarding liquefaction, perhaps by free radical scavenging. Before any other graphite catalysts are tested, two tests must be performed. First, graphite catalysts should be examined by X-ray diffraction to determine if the active metal is truly intercalated into the layered structure. Secondly, the effect of pure graphite on a known catalyst should be examined. This could involve testing a mixture of graphite and HDS-1442A. If graphite poisons the coal liquefaction process, conversion with HDS-1442A will be greatly reduced.

In the near future, we plan to test the molten salt catalyst described in Table IV.

TABLE IV

CATALYSTS FOR BATCH SCREENING: LIST 2
(to be prepared in 4th Quarter)

1) Modified Aluminas

Stabilized Supports - Rare Earth Doping

3% CoO 16% MoO_3/3% Pr-Al_2O_3

3% CoO 16% MoO_3/3% Sm-Al_2O_3

3% CoO 16% MoO_3/3% Gd-Al_2O_3

3% CoO 16% MoO/5% SiO_2-Al_2O_3 (Aero 105)

3% CoO 16% MoO_3/5% MgO-Al_2O_3

2) Alternate Materials

7.1% NiB,26.6%WC/Al_2O_3
7.1% NiB,26.1%WB/Al_2O_3
7.1% NiB,26.4%WN/Al_2O_3

3) Mixed Catalysts

3% NiO 16% MoO_3/High Surface Area Alumina
(for desulfurization)
+
16% MoO_3/Bimodal Alumina
(for conversion)

3% CoO 16% MoO_3/High Surface Area Alumina
+
16% MoO_3/Bimodal Alumina

3% CoO 16% $MoO_3$1.2% P/Aero 105 Alumina
+
16% MoO_3/Bimodal Alumina

4) Novel Catalyst Systems - Molten Salts

66% $SnCl_2$ - 34% Al_2O_3

42% $ZnNO_3$ - 58% Al_2O_3

Alternate Materials

Under this category, only one catalyst has been tested. It consists of 2.6% cobalt boride and 11.4% molybdenum nitride gelled into an alumina matrix. Borides, carbides and nitrides have been proposed for testing because of their possible stability under the hydrothermal conditions of coal liquefaction. The catalyst we tested was surprisingly active with a 56% conversion to toluene soluble materials. However, activity was still below that observed with HDS-1442A (66.3%) and could have been due to the alumina matrix used as a binder or due to a breakdown of the boride and nitride into the corresponding sulfide, oxide, or oxysulfide. Future runs will test the activity of the pure compounds in the absence of the alumina matrix and X-ray analysis of the spent catalyst will determine if the borides and nitrides have survived run conditions.

Modified Aluminas

Under this category, various components will be added to an alumina matrix to improve support stability against surface area loss under hydrothermal conditions. We propose to test the fresh modified catalyst in the batch unit to determine initial activity. We then plan to age the catalyst with steam at elevated temperatures and retest the aged catalyst in the batch unit to measure activity maintenance. Both fresh and aged catalyst will be submitted for pore size distribution analyses to determine how well the modified alumina has resisted sintering.

To date, a uranyl and a barium modified cobalt-molybdenum-alumina catalyst have been tested in the batch unit. Neither performed well at 52 to 53% conversion compared to 66.3% for the base catalyst under these conditions. A pore size distribution analysis may reveal the reasons for this poor performance.

TASKS 2,3 - CATALYST AGING TESTS--EASTERN AND WESTERN 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 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 V. 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 to be high due to the high oxygen content, which would have an unfavorable impact on the process economics.

TABLE V

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

The continuous-flow liquefaction unit, general procedures for catalyst testing, product workup and analysis methods were described in the first quarterly report. During the second 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 with Illinois No. 6 were completed 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. Significant differences in the liquefaction behavior between Illinois No. 6 and Wyodak coal were ascertained for both catalytic and thermal conversions. A run with Mo-G120B(14) which was inadvertently calcined at a very high temperature was also concluded. A short run of 47 hrs duration was completed to generate a used catalyst for characterization. Three runs with Wyodak coal were finished. The Mo-102B(14) catalyst was used in two of the runs while the third was a thermal base case run. The runs made so far employing SRC-II heavy distillate as the slurry oil are listed in Table VI for reference.

TABLE VI

SUMMARY OF AGING TESTS

Run No.	Catalyst	Note
Illinois No. 6		
5186	HDS-1442A	H-Coal catalyst
5187	Amocat-1A [CoMo-G108(16)]	500 lb. batch
5188	CoMo-G120B(11)	Experimental, control sample
5192	None	Thermal base run
5193	Mo-C102B(14)	18 lb. batch
5194	Engelhard CoMo	Lot #11015-26-1
5197	CoMo-G102B(14)	47 hr run for catalyst characterization
Wyodak Coal		
5189	HDS-1442A	H-Coal catalyst
5190	CoMo-G102B(14)	18 lb. batch
5191	Mo-G102B(14)	18 lb. batch
5192	None	Thermal base run
5195	Mo-G102B(14)	Aborted due to Magnedrive failure
5196	Mo-G102B(14)	Rerun of 5191

Slurry Oils

Slurry oil inspections are given in Table VII. The current slurry oil, FSN-10, has a lower specific gravity but higher endpoint than hydrogenated anthracene oil, FSN-6. Vacuum distillation of FSN-10 gives 2.9 wt% resid bottom at 970°F (520°C), while FSN-6 contains 1.1 wt% resid that boils above 935°F. Hydrogen content and atomic ratio of H/C are higher for FSN-10. It has been previously reported that solvent effectiveness is related to its H/C atom ratio (1). Solvent effectiveness decreases with increasing H/C for both coal and petroleum derived solvents. This suggests that hydrogenation alters the composition of the oil, e.g., removes oxygen and nitrogen compounds,

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(1) Catalyst Development for Coal Liquefaction, EPRI AF-1084, June, 1979.

so as to reduce its solvent power and that extensive hydrogenation is not necessary to provide adequate hydrogen donor capability. Therefore, we would expect FSN-10 to be a poorer hydrogen donor than FSN-6 because its H/C atom ratio is higher (0.992 vs. 0.792). Additionally, the high overall and basic nitrogen content of FSN-10 could also poison the active sites of the catalyst. The high oxygen content could also shield active sites as well as scavenge hydrogen radicals thereby prematurely terminating liquefaction type reactions. In the future we plan to determine the aromatic content of all our solvents.

TABLE VII

SLURRY OIL INSPECTIONS

Slurry Oil	FSN-10 SRC-II Hvy. Distillate	FSN-6 Hydrog. Anthracene Oil
Specific Gravity @ 25°C	1.079	1.124
Viscosity, cs	48.4 @ 40°C	21.9 @ 38°C
ASTM D-1160, Wt%		
IBP-650°F	39.3 (IBP ≅ 500°F)	43.9 (IBP ≅ 500°F)
650-935°F		55.0
650-970°F	57.8	
Resid bottom	2.9	1.1
Elemental Analysis, Wt%		
C	89.33	91.98
H	7.39	6.07
S	0.41	0.33
N	1.18	0.63
O	2.08	0.94
Atomic H/C	.992	.792
Basic Nitrogen	.7	.4
Moisture	.15	.049

Catalysts

Catalyst inspections are shown in Table VIII. HDS-1442A is the reference H-Coal catalyst with 56 Å average pore diameter. The next two catalysts are respectively 18 pound batches of CoMo and Mo supported on an identical Grace 102 Å bimodal alumina, denoted as G-102B(14) and prepared by W. R. Grace & Co. The average micropore diameter of these two batches turned out to be somewhat smaller than the originally intended 120 Å. The unpromoted molybdenum catalyst, Mo-G102B(14), was tested twice because of the uncertainty that the catalyst might have been mishandled in the first test.

TABLE VIII

CATALYST INSPECTIONS

Run No.	Catalyst	APD Å	SA m^2/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, -95,-96	Mo-G102B(14)	102	191	.704	14.1
5187	AMOCAT 1A(II-108/16)	108	186	.686	15.8
5194	Engelhard Stabilized CoMo	175	98	.352	17.9

The Engelhard catalyst had a considerable amount of macropores with an average pore diameter greater than 1000 Å (18%) as well as a large micropore average diameter (175 Å). Surface area and pore volume of this catalyst are low. This catalyst has a BaMo stabilized alumina base which may reduce asphaltene adsorption and help prevent sintering of the alumina in the presence of water at high temperatures.

Catalyst Pretreatment

All catalyst runs on the continuous aging unit are dried at 1000°F before they are loaded into the catalyst basket. There is considerable literature evidence that indicates that presulfiding wet hydrotreating catalysts is detrimental to catalyst activity. In run 5193 the Mo-G102B(14) was inadvertently calcined at 1500°F and the experiment was completed before we were aware of this fact. Calcination at 1500°F lowered the surface area of the fresh catalyst from 191 m^2/g to 99 m^2/g and increased the average pore diameter from 102 Å to 276 Å. Surprisingly, the pore volume was reduced from 0.704 cc/g to only 0.662 cc/g.

The Engelhard catalyst has similar surface properties but its average pore volume was only 0.352 cc/g. It appears that calcining with dry gases shrinks the pore structure without collapsing pores and losing volume.

Preliminary workup of the data with Illinois No. 6 coal feed indicates that the THF, benzene, and hexane soluble conversion for this catalyst are slightly better than HDS-1442A but not as good as AMOCAT 1A (II-108/16).

Experimental

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

TABLE IX

STANDARD TEST CONDITIONS

Catalyst Charge:	60 cc, 1/16" extrudates, 20cc, 3mm glass beads + glass wool
Coal Slurry Feed:	25 wt% coal in SRC II heavy distillate (FSN-10)
Pressure:	137 atm (2000 psig)
Temperature:	440°C (825°F)
H_2 Feed Rate:	225 liters/hr (8 SCFH)
Slurry Feed Rate:	422 g/hr
Reactor Holdup:	310 cc
Residence Time:	45 minutes
LHSV:	1.76 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, stationary basket. A 25 wt% powdered coal (35 micron) is slurried in SRC II heavy distillate (FSN-10) and pumped to 2000 psig. The slurry feed is combined with hydrogen flow and introduced to the bottom of the stirred autoclave reactor. The products are withdrawn through an overflow tube which extends about 8 cm from the reactor bottom to give a holdup volume of 310 cc.

During this period considerable operational difficulty was experienced with the Magnedrive II stirring assembly which drives the agitator that insures good mixing or CSTR behavior in the Autoclave reactor. Faulty welds caused hydrogen to slowly leak into the encapsulated Magnedrive assembly. The rare earth magnets used in the assembly swell in the presence of hydrogen which causes the agitator to seize sporadically during the run. Poor mixing causes dead zones in the reactor and allows the coal slurry to solidify at reaction conditions. Oscillations in internal reactor temperature appear as soon as any internal solids are formed because the solids insulate the temperature control thermocouple. Two runs were aborted due to Magnedrive failure. The Magnedrive II was replaced with a Magnedrive I which does not have hydrogen sensitive rare earth magnets.

A Perkin-Elmer Sigma I gas chromatograph system equipped with a thermal conductivity detector has been set up for routine analysis of gas compositions of the hydrogen-rich gas effluent from the reactor. The inlet gas stream to the reactor is pure hydrogen. Because of the simplicity of measuring carbon oxides and C_1-C_4 light hydrocarbons at the same time, the thermal conductivity detector was adopted instead of a flame ionization detector. Some of the G.C. analysis results are listed in Table X to illustrate the magnitudes of gas-make during the liquefaction of both Illinois No. 6 and Wyodak coal. Table X shows that the predominant component in the gas is methane followed by ethane and there are considerable amounts of carbon oxides produced during the liquefaction. In all cases hydrogen purity is above 95 volume percent. Wyodak coal appears to give slightly more light gases than Illinois No. 6 coal.

TABLE X

EFFLUENT GAS COMPOSITIONS DURING LIQUEFACTION OF ILLINOIS NO. 6 AND WYODAK COAL

	Illinois No. 6			Wyodak		
Sample I.D.	86-10	94-2	94-8	89-8	96-2	96-6
Catalyst	CoMo	CoMo	CoMo	CoMo	Mo	Mo
Catalyst Age, hrs.	120	24	92	97	20	66
Benzene Sol. Conv., Wt% maf	68.3	74.0	66.9	68.2	80.2	70.6
Exit Gas Composition, Vol%						
CO	NA	0.69	0.70	0.38	0.63	0.83
CO_2	NA	0.15	0.15	0.83	0.20	0.43
Methane	1.67	1.92	1.18	2.33	1.32	1.32
Ethane	0.70	0.93	0.48	0.78	0.71	0.57
Propane	0.24	0.14	0.14	0.50	0.13	0.09
Butane	0.20	0.13	0.07	0.13	0.09	0.09
Total	2.81	3.96	2.72	4.95	3.08	3.32
Wt% Total on Slurry Feed	1.47	1.74	1.46	2.69	1.58	1.88
(C_1-C_3) Wt% on a Dry Coal Basis	5.11	4.60	3.33	6.47	3.81	3.54

Non-Catalytic Liquefaction of Illinois No. 6 and Wyodak Coal

A thermal base run without a catalyst reveals an interesting contrast in liquefaction behavior between a bituminous Illinois No. 6 coal and sub-bituminous Wyodak coal, and perhaps gives some insight into the role that a catalyst plays during the liquefaction. The coal conversions to THF, benzene, and hexane soluble materials as well as to the ash free 520°C+ resid are shown in Table XI along with the product sulfur and nitrogen contents for two different types of slurry oils used for liquefaction of Illinois No. 6 and Wyodak coal. FSN-10 is the current slurry oil derived from SRC-II heavy distillate and FSN-6 is the topped, hydrogenated anthracene oil (HAO) which had been used prior to the present DOE contract. The test conditions were identical to those of our standard aging test (137 atm, 440°C) except for the catalyst basket which was filled with glass beads instead of catalyst. In the catalyst aging test the residence time is typically 45 minutes with a LHSV of 1.72 g coal/hr/cc-catalyst.

TABLE XI

THERMAL LIQUEFACTION OF ILLINOIS NO. 6 AND WYODAK COAL

Pressure:	137 atm
Temperature:	440°C
Coal Concentration:	25 wt%
Residence Time:	44 minutes

	SRC-II Heavy Distillate FSN-10 (Current)		Hydrogenated Anthracene Oil FSN-6 (HAO)	
Coal Conv., Wt% maf	Illinois No. 6	Wyodak	Illinois No. 6	Wyodak
THF soluble	86.5	73.1	92.6	79.6
Benzene soluble	58.4	55.8	62.0	64.8
Hexane soluble	23.6	18.2		
520°C+ resid	67.6	56.9	62.1	38.5
Sulfur, Wt%				
Total liquid	0.49	0.36	0.42	0.31
520°C+ resid	0.94	0.36	0.95	0.39
Nitrogen, Wt%				
Total liquid	1.23	1.14	0.85	0.71
520°C+ resid	1.89	1.68	1.84	1.60

The THF soluble conversion, which is a measure of a boiler fuel yield, is considerably lower for Wyodak coal indicating that Wyodak coal is much more difficult to liquefy than Illinois No. 6 coal. However, the benzene soluble conversions are comparable for both coals. The difference between THF and benzene soluble conversions, i.e. preasphaltene content, is lower with Wyodak coal suggesting that the product quality should be generally better for Wyodak coal once it is liquefied. The coal conversion to 520°C+ resid appears to be lower with Wyodak coal; but the product quality in terms of

520°C+ resid content of the THF soluble liquid appears to depend on the slurry oil used with FSN-6 (HAO) effecting much less resid content in the liquefied Wyodak coal than Illinois No. 6 coal. Hexane soluble conversions, although difficult to determine for the thermal liquefaction product, are higher with Illinois No. 6 coal in comparison to Wyodak coal. It is noted, however, that in the presence of a catalyst the Wyodak coal can be more readily liquefied to hexane soluble product than Illinois No. 6 coal.

Sulfur and nitrogen contents in the 520°C+ resid which consists mostly of liquefied coal oil, provide a more direct indication for heteroatom removal than those of total liquid. Illinois No. 6 coal shows a high concentration of sulfur in 520°C+ resid, whereas removal of sulfur from Wyodak coal is a less concern because of a low sulfur content in Wyodak coal. Nitrogen content is equally high for both Illinois and Wyodak coal.

When a hydrogenated anthracene oil (FSN-6) is used as slurry oil the THF soluble conversion of Illinois No. 6 coal is high at 92.6% and practically the same as the one obtainable with a catalyst, while that of subbituminous Wyodak coal is only about 80% without catalyst but increasing with an active catalyst. For the liquefaction of Illinois No. 6 coal the catalyst is primarily needed to remove sulfur and improve other product qualities, whereas for Wyodak coal the catalyst is required to increase liquefaction yield.

Compared to the results obtained with FSN-6 (HAO), the thermal liquefaction with SRC-II heavy distillate (FSN-10) gives much lower THF soluble conversions for both Illinois No. 6 and Wyodak coal as shown in Table XI. Apparently, SRC-II heavy distillate is a less effective hydrogen donor solvent compared with hydrogenated anthracene oil. It seems that maintenance of proper donor solvent quality through rehydrogenation is certainly one of the more important functions of catalyst for maximizing liquefaction yield.

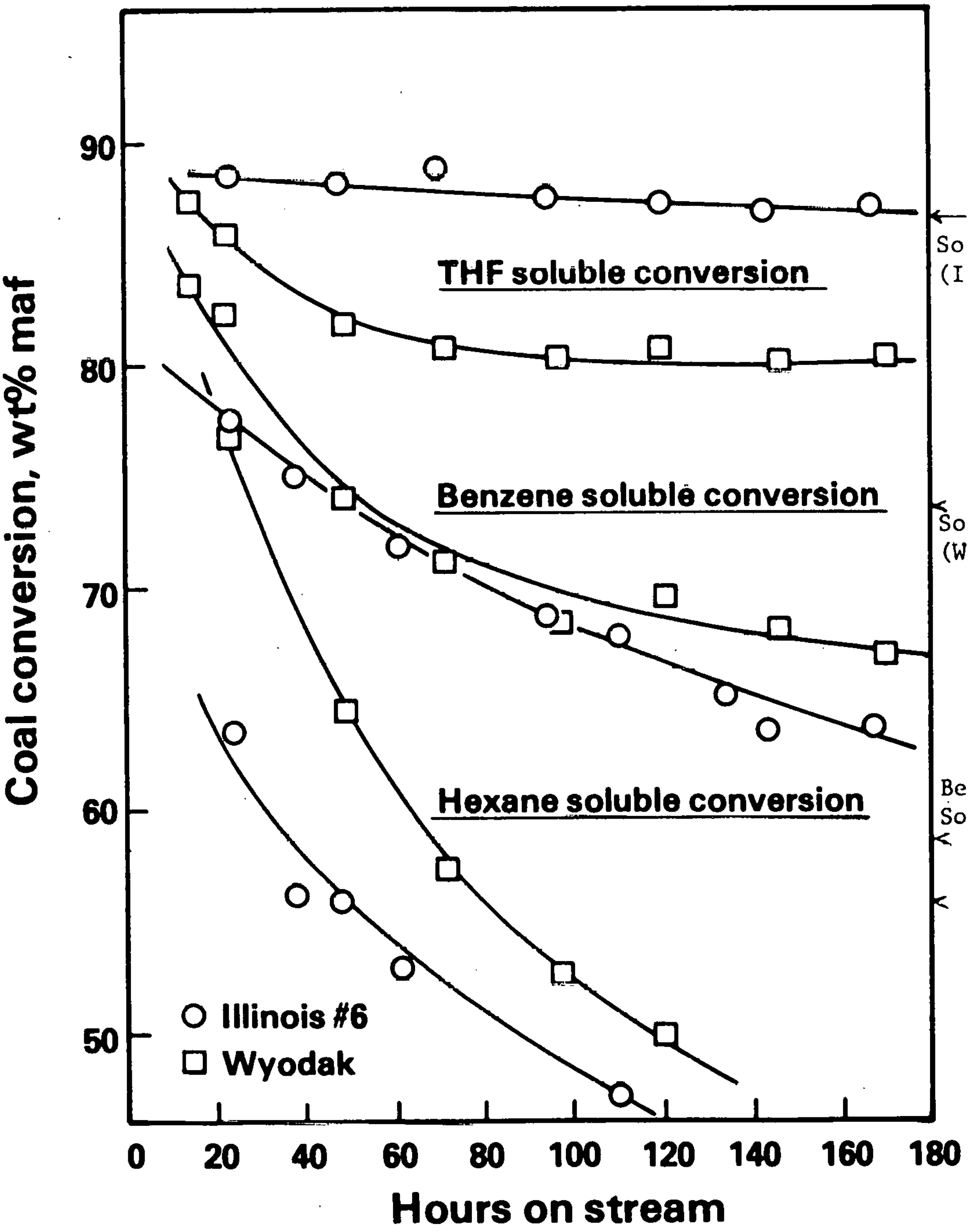
Comparison of Catalytic Liquefaction of Illinois No. 6 and Wyodak Coal

Catalytic liquefaction conversions to THF, benzene and hexane soluble products are compared in Figure 2 for Illinois No. 6 and Wyodak coal. The catalyst used is the CoMo on alumina HDS-1442A which is being used in H-Coal process development. The data were obtained from the standard aging test runs, 5186 and 5189, which employed SRC-II heavy distillate (FSN-10) as the liquefaction solvent.

Catalytic liquefaction of Wyodak coal results in a substantially higher THF soluble conversion when compared with thermal liquefaction, but it declines rapidly with catalyst age to a level much lower than that of Illinois No. 6 coal. THF soluble conversion of Illinois No. 6 coal is rather insensitive to whether catalyst is present or not. The catalytic conversions to benzene and hexane solubles are higher for Wyodak than Illinois coal, but the decline rates are faster with Wyodak coal. In summary, Wyodak coal is difficult to liquefy and catalyst is needed to increase the liquefaction yield of Wyodak coal. Once liquefied, Wyodak coal gives a product that contains a higher concentration of benzene and hexane soluble materials or better quality product than Illinois No. 6. However, such product qualities deteriorate rapidly with catalyst age. Wyodak coal appears to deactivate the catalyst more severely than Illinois No. 6 coal.

FIGURE 2

Liquefaction conversions of Illinois #6 and Wyodak coal with HDS-1442A catalyst



←—THF Thermal Soluble Conversion (Illinois No. 6)

< THF Thermal Soluble Conversior (Wyodak)

Benzene Thermal Soluble Conversior
< Illinois No.6

< Wyodak

The THF soluble liquid products from the two base runs (5186 and 5189) which used HDS-1442A catalyst to liquefy 25 wt% Illinois No. 6 and Wyodak coal respectively in SRC-II slurry oil, were fractionated and analyzed for elemental compositions of total liquid, 343-520°C (650-970°F) fraction and the 520°C+ resid cottom which consists mostly of liquefied coal. The results are summarized in Table XII and XIII with respect to catalyst age in days on stream.

The ASTM distillation shows that the liquid products from Wyodak coal contain smaller amounts of 520°C+ resid throughout the test periods. Compared to Illinois No. 6 coal, sulfur contents are lower in all fractions of liquid product from Wyodak coal. Nitrogen contents are above 1 wt% and there appears to be little denitrogenation achieved from either coal. The oxygen content in 520°C+ resid is surprisingly lower for the product derived from Wyodak coal rather than Illinois coal, although Wyodak coal contains considerably more oxygen than Illinois coal, 16% vs. 9%. The atomic H/C ratios appear to be equivalent initially for both coals, but those for Wyodak coal deteriorate faster.

TABLE XII

LIQUEFACTION OF ILLINOIS NO. 6 COAL WITH HDS-1442A (RUN 5186)
PRODUCT COMPOSITIONS

Days on Stream	1	2	3	4	5	6	7
Residence Time, Min.	45.3	44.3	44.4	45.0	46.0	44.0	42.9
ASTM D-1160, Wt%							
IBP-343°C	43.80	46.95	45.32	45.73	44.55	42.70	39.76
343-520°C	45.66	41.73	43.02	42.42	43.13	45.01	46.68
520°C+	10.54	11.32	11.66	11.85	12.32	12.29	13.56
Total Liquid (THF sol),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
Atomic H/C	1.032	1.024	1.020	1.027	0.999	1.014	0.982
343-520°C, Wt%							
S	0.22	0.26	0.27	0.29	0.30	0.34	0.36
N	1.09	1.06	1.11	1.06	1.10	1.15	1.12
O	1.12	1.95	1.43	1.21	1.58	2.77	2.27
Atomic H/C	0.960	.955	.951	.949	.954	.941	.945
520°C+ Resid, Wt%							
S	0.54	0.76	0.87	0.90	0.90	0.93	
N	1.83	1.81	1.90	1.94	1.97	1.95	2.07
O	3.18	5.05	6.65	7.65	5.21	6.69	7.06
Atomic H/C	.838	.825	.817	.814	.812	.802	.800

TABLE XIII

LIQUEFACTION OF WYODAK COAL WITH HDS-1442A (RUN 5189) PRODUCT COMPOSITIONS

Days on Stream	1	2	3	4	5	6	7
Resicence Time, min.	45.1	42.7	43.3	44.4	45.1	43.2	42.2
ASTM D-1160, Wt%							
IBP-343°C	47.72	46.54	45.27	45.83	46.38	42.78	41.05
343-520°C	45.39	45.29	44.92	44.30	43.49	45.47	47.12
520°C+	6.89	8.17	9.81	9.87	10.13	11.75	11.83
Total Liquid, Wt%							
S	0.14	0.17	0.19	0.20	0.21	0.23	0.22
N	0.99	1.06	1.01	1.01	1.07	1.08	1.10
O	1.63	1.53	1.76	0.97	1.27	1.01	1.44
Atomic H/C	1.038	1.015	0.901	0.871	0.891	0.911	0.891
343-520°C, Wt%							
S	0.16	0.21	0.23	0.24	0.25	0.29	0.26
N	1.13	1.19	1.17	1.23	1.22	1.20	1.17
O	1.02	0.46	1.70	1.60	1.60	1.64	1.42
Atomic H/C	0.977	0.947					
520°C+ Resid, Wt%							
S	0.35	0.37	0.32	0.31	0.30	0.32	0.29
N	1.57	1.72	1.66	1.77	1.76	1.79	1.74
O	3.55	3.17	2.50	2.30	5.53	2.01	4.45
Atomic H/C	0.833	0.810	0.788	0.761	0.762	0.772	0.774

Catalyst Ranking for Liquefaction of Wyodak Coal

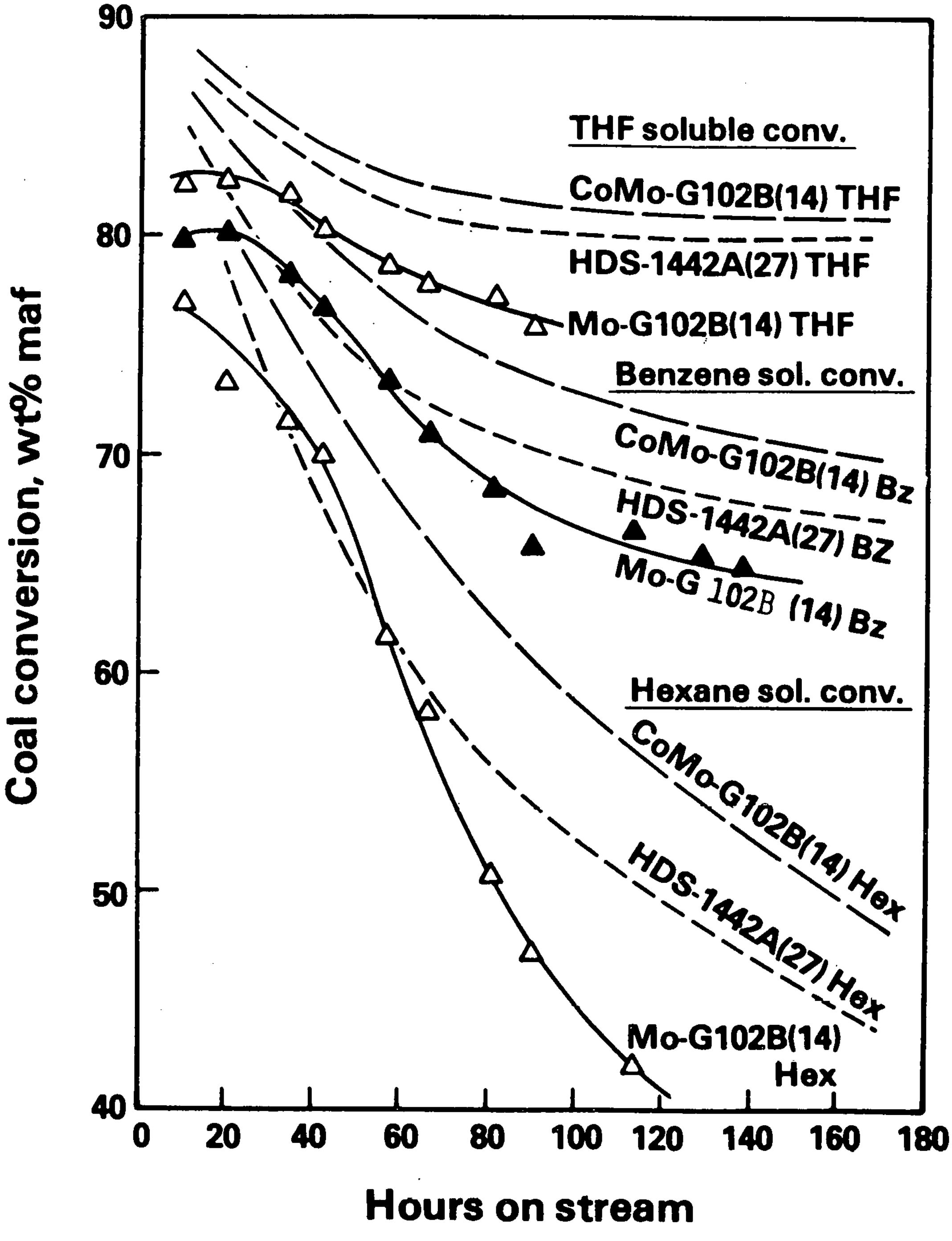
Three different types of catalyst have been tested for liquefaction of Wyodak coal. The purpose of these comparison tests was to assess preliminary effects of a large micropore diameter and to select a preferred catalytic metal between Mo and CoMo.

The liquefaction conversions to THF, benzene, and hexane soluble products are compared in Figure 3 for HDS-1442A (CoMo), CoMo-G102B(14) and Mo-G102B(14) catalysts. The conversions are based on the microresidue workup results and adjusted for small fluctuations in feed rate around the target value. The experimental CoMo-G102B(14) catalyst, which has a larger micropore diameter than HDS-1442A catalyst, exhibits a superior performance to HDS-1442A for all THF, benzene and hexane soluble conversions. However, the conversions with the unpromoted molybdenum version, Mo-G102B(14) are nowhere near the CoMo-G102B(14) and are slightly lower than those of HDS-1442A catalyst after 60 hrs on stream.

Some of the earlier work done for EPRI indicated that molybdenum catalyst supported on a 120 Å average pore diameter alumina showed as good a performance as CoMo on 120 Å alumina, and led to the conclusion that catalysts suitable for liquefying Wyodak coal should have larger micropores than those for Illinois coal (120 Å) and molybdenum was much preferred to

FIGURE 3

Liquefaction conversions of Wyodak coal



cobalt-molybdenum for reducing hydrogen consumption. In view of the disappointing performance of Mo-G102B(14) catalyst shown in Figure 3, the catalyst might simply have been prepared improperly as there was some concern expressed for dispersing molybdenum in the alumina support, or else the micropores are not large enough for unpromoted molybdenum case. On the other hand it is entirely possible that when hydrogen donor capacity of the liquefaction solvent is low as it is with SRC-II heavy distillate a hydrogenation component stronger than molybdenum may be needed. The effects of catalyst pore size, metals and hydrogen donor properties of SRC-II slurry oil will have to be characterized in the coming months in order to tailor-make a catalyst suited to liquefaction of Wyodak coal. While catalyst supports with 150 Å and 200 Å average micropore diameter are being prepared by W. R. Grace & Co., a laboratory scale batch of Mo on 140 Å alumina is ready for test.

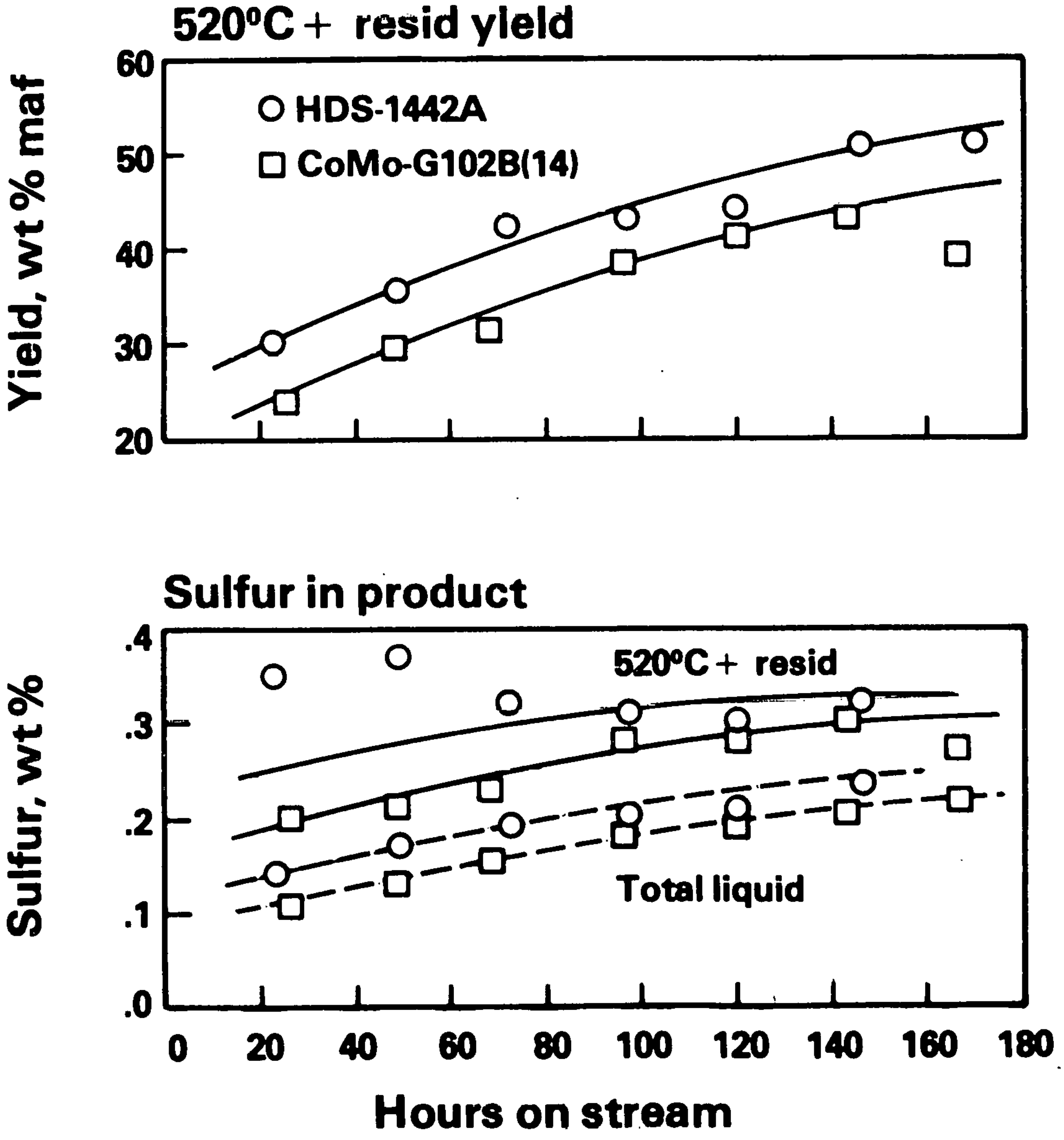
Turning to a further comparison of 56 Å HDS-1442A and 102 Å CoMo-G102B(14) catalysts, the 520°C+ resid yields and product sulfur contents are plotted vs. time on stream in Figure 4. The experimental batch of AMOCAT-1A type catalyst, CoMo-G102B(14), clearly shows lower 520°C+ resid yield and lower sulfur contents in both 520°C+ resid and total liquid than the small pore HDS-1442A catalyst.

Feasibility of Using the Continuous Aging Unit for Testing SRC Upgrading Catalysts

A two-month program to determine the feasibility of using the Amoco equipment for SRC-I product upgrading was outlined. Three NiMo catalysts will be tested. Two will be provided by Lummus and W. R. Grace will prepare a 1/32" AMOCAT type NiMo catalyst. Start-up procedures and analytical requirements for the products will be provided by Lummus and Cities Service. Experimental conditions were discussed. Space velocity will be determined by the maximum catalyst capacity of our basket. The test program will include three 150 hr continuous aging unit runs, a 2 day solvent run, and a 2 day thermal run. Lummus will provide 1 barrel of the SRC product ground into small pieces and 1 barrel of the solvent. Amoco will determine the optimum blend of SRC product and solvent that will provide a pumpable feed stream in our test equipment.

FIGURE 4

Comparison of 520°C + resid yield and product sulfur from liquefaction of Wyodak coal with HDS-1442A and CoMo-G102(14)



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 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 catalyst 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).

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. We have been attempting to distill the Panasol to recover the heavy, trimethylnaphthalene bottoms. Use of 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. This distillation has proved to very time consuming and difficult. The projected completion date for the distillation is late January.

We have begun preparation of some of the Eastern synthetic coal mixture to use as a feed in debugging the Development Support Unit (DSU). A new Ruska feed pump was added to the DSU to improve the accuracy of our feed rate and thereby improve overall accuracy of the kinetic rate constants.

The second purpose of running experiments with the raw Panasol solvent is to determine whether the hydrogen donor solvent capability of the Panasol is a function of the composition of this mixture. Since the Panasol solvent contains primarily substituted naphthalenes it is felt that the distillation will have little effect on the donor solvent capability.

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 objective 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 completed the evaluation of the large 500 lb batch of AMOCAT-1A. Using SRC-II heavy distillate as the slurry oil, the results from the aging test are quite clear. The 500 pound batch of AMOCAT-1A is good quality and exhibits highly improved performance over the H-Coal catalyst, HDS-1442A. The performance results of the large batch were equivalent to or better than those of earlier laboratory samples. The H-Coal Technical Advisory Committee voted in favor of a H-Coal PDU run based on these favorable results.

Samples of used catalysts from our aging tests were sent to PETC for catalyst characterization. Also, a sample of the Panasol solvent was provided to them.

During the period we continued to confer with Hydrocarbon Research, Inc. concerning their coal liquefaction catalyst development program. They will provide us with 3 catalyst samples for testing in our equipment.

Our subcontractor, W. R. Grace, is in the process of making a 150 Å and 200 Å version of AMOCAT-1A and 1B for testing in Tasks 2 and 3. They will also provide us with a 1/32" NiMo AMOCAT type catalyst for use in the SRC-II upgrading program. The bimodal catalysts with the 150 Å and 200 Å micropores should be available in January.

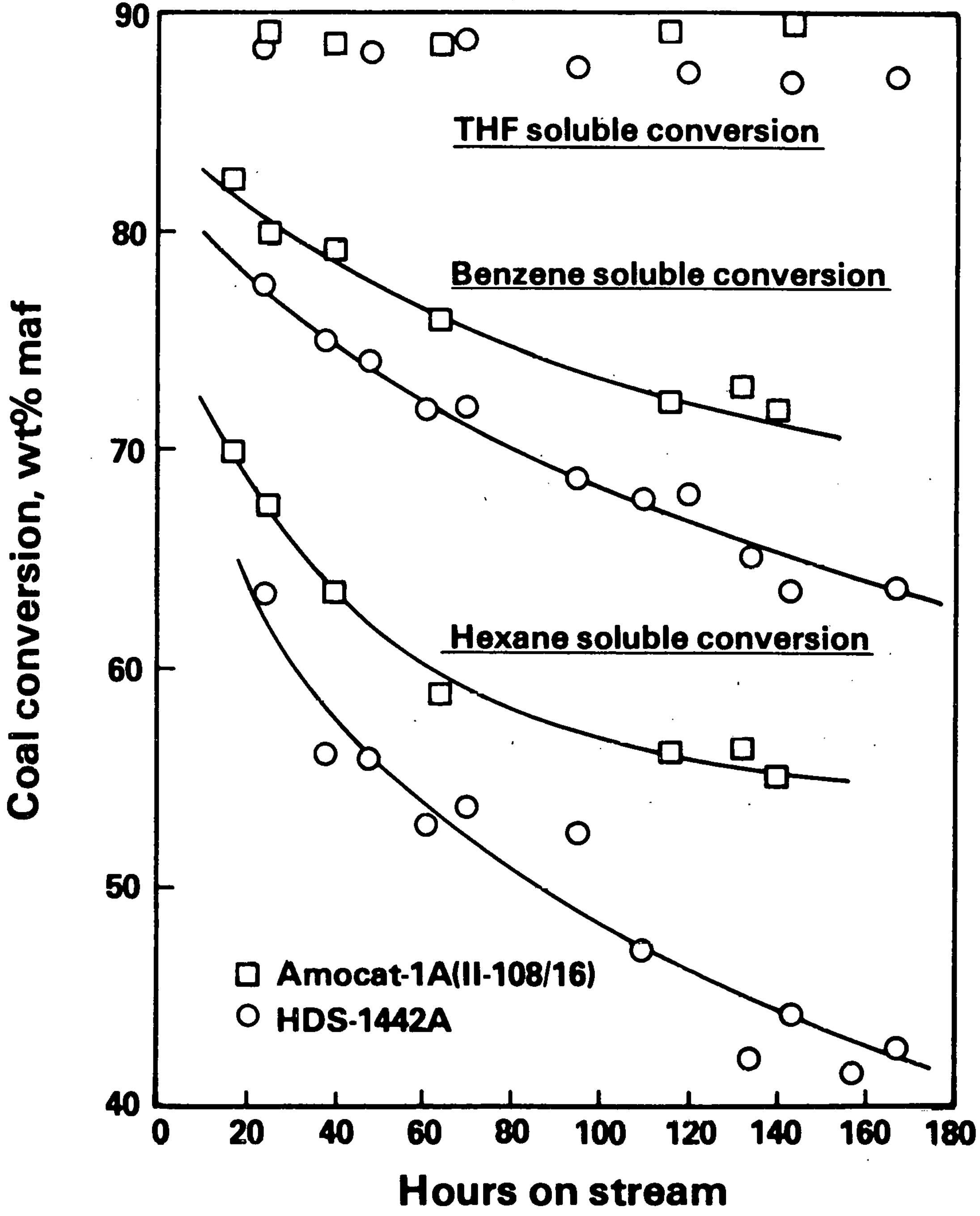
A catalyst submitted by Engelhard was tested and found to have low initial activity but a low activity decline rate.

Conversion and Product Quality Comparison, HDS-1442A Versus AMOCAT-1A (II-108/16)

The 500 lb batch of AMOCAT-1A (II-108/16) and HDS-1442A were tested and compared at the standard test conditions using Illinois No. 6 coal and SRC-II slurry oil. Complete conversion and product quality data will be presented in this section. First, the liquefaction performance based on product solubility are presented in Figure 5. 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.

FIGURE 5

Conversion of Illinois #6 coal



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 XIV.

TABLE XIV

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 THF soluble liquid products from Run 5186 and 5187, which used respectively HDS-1442A and AMOCAT-1A (II-108/16), (500 lb batch) catalyst to liquefy 25 wt% Illinois No. 6 coal in SRC-II heavy distillate, were fractionated and analyzed for elemental compositions of the total liquid , 343-520°C (650-970°F) fraction and 520°C+ resid bottoms. The elemental compositions of liquid products are summarized in Table XV and XVI.

The 520°C+ resid consists of mostly liquefied coal oil; whereas, the total liquid and 343-520°C cut contain substantial amounts of liquefaction solvent. Ideally, the resid bottom should be free of liquefaction solvent, but SRC-II heavy distillate contains 2.9 wt% of 520°C+ material whose sulfur content is 0.82%. The compositions of total liquid are on a solvent free basis.

AMOCAT-1A catalyst, which has given a higher liquefaction conversion, shows consistently lower sulfur contents in the resid as well as in the 343-520°C distillate cut and the total liquid than HDS-1442A catalyst. The resid nitrogen contents appear to be slightly lower with AMOCAT-1A than HDS-1442A, but as can be seen from total liquid nitrogen contents the extent of nitrogen removal is, in general, low for both catalysts. Oxygen contents in the 343-520°C distillate cuts are noticeably higher for AMOCAT-1A. Although there are large differences in hexane soluble content of the product between AMOCAT-1A and HDS-1442A catalysts, the atomic H/C ratios do not differ very much between catalysts and with catalyst age.

TABLE XV

PRODUCT QUALITY
(Run 5186, HDS-1442A)

Days on Stream	1	2	3	4	5	6	7
Residence Time, Min.	45.3	44.3	44.4	45.0	46.0	44.0	42.9
ASTM D-1160, Wt%							
343-520°C	45.66	41.73	43.02	42.42	43.13	45.01	46.68
520°C+	10.54	11.32	11.66	11.85	12.32	12.29	13.56
Total Liquid (THF Sol), 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
Atomic H/C	1.032	1.024	1.020	1.027	0.999	1.014	0.982
343-520°C, Wt%							
S	0.22	0.26	0.27	0.29	0.30	0.34	0.36
N	1.09	1.06	1.11	1.06	1.10	1.15	1.12
O	1.12	1.95	1.43	1.21	1.58	2.77	2.27
Atomic H/C	0.960	.955	.951	.949	.954	.941	.945
520°C+ Resid, Wt%							
S	0.54	0.76	0.87	0.90	0.90	0.93	
N	1.83	1.81	1.90	1.94	1.97	1.95	2.07
O	3.18	5.05	6.65	7.65	5.21	6.69	7.06
Atomic H/C	.838	.825	.817	.814	.812	.802	.800

TABLE XVI

PRODUCT QUALITY
(Run 5187, AMOCAT-1A)

Days on Stream	1	2	3	5	6
Resicence Time, Min.	44.6	43.5	44.0	43.3	43.4
ASTM D-1160, Wt%					
343-520°C	42.94	44.91	45.36	42.96	42.88
520°C+	9.78	11.91	11.04	10.55	11.43
Total Liquid (THF Sol), 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
Atomic H/C	1.029	1.033	1.033	1.013	1.016
343-520°C, Wt%					
S	0.24	0.26	0.26	0.29	0.33
N	1.09	1.08	1.12	1.11	1.18
O	3.55	2.25	2.44	2.41	
Atomic H/C	.963	.965	.954	.950	
520°C+ Resid, Wt%					
S	0.61	0.73	0.73	0.81	0.76
N	1.64	1.74	1.71	1.90	1.90
O	5.43	4.77	6.13	6.05	5.88
Atomic H/C	0.832	.822	.816	.803	

Test of Engelhard CoMo Catalyst for Liquefaction of Illinois No. 6 Coal

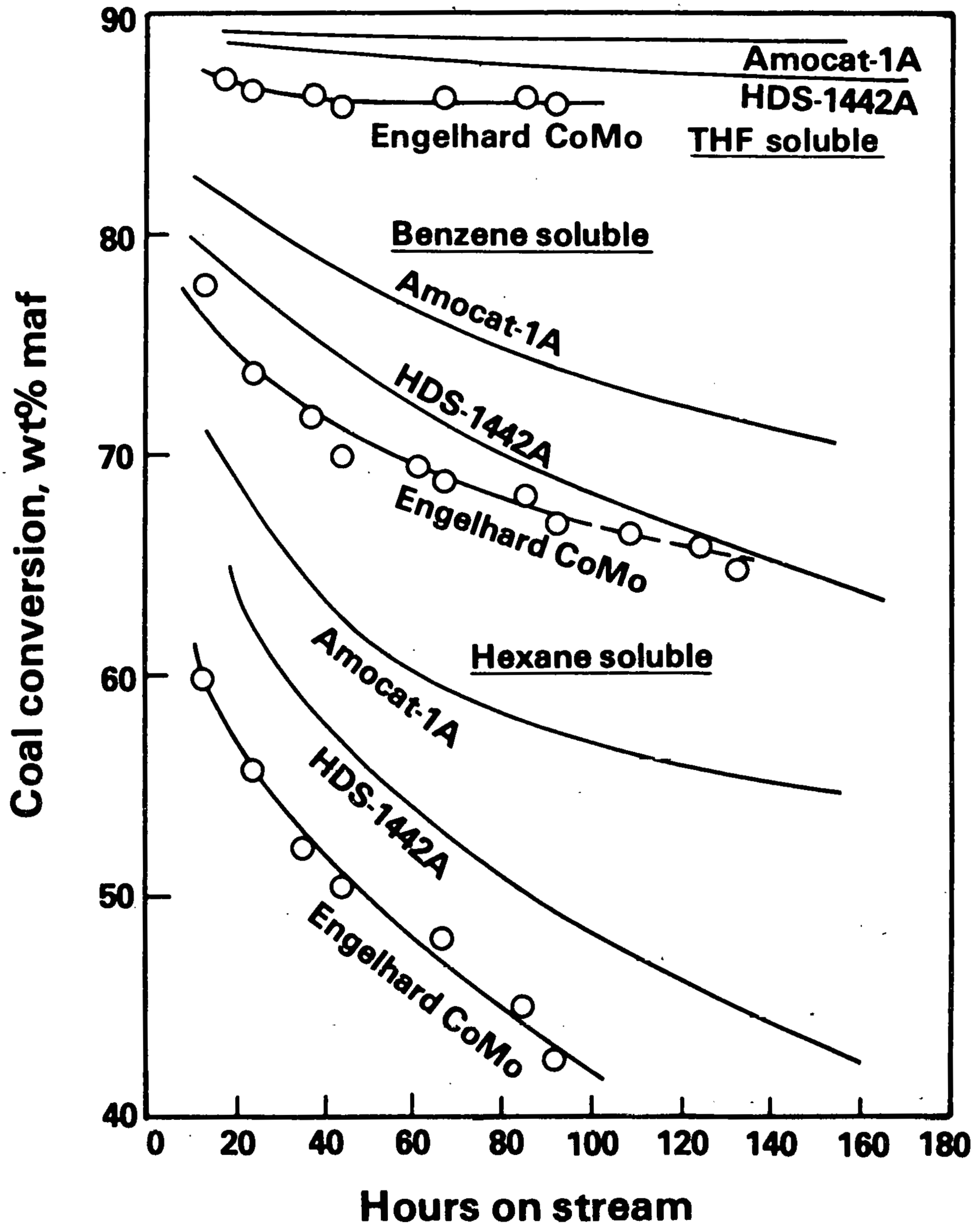
An Engelhard Cobalt-Molybdenum catalyst on a stabilized (BaMo) alumina (Lot 11015-26-1), whic was developed under DOE contract, was presulfided in situ and tested for liquefaction of Illinois No. 6 coal following our standard test procedure. The alumina was stabilized with BaMo to retard hydrothermal aging. The run started normally and proceeded well until the sixth day on stream when a unit upset occurred. The results of catalyst aging behavior up to the sixth day are compared with those of HDS-1442A and the 500 pound batch AMOCAT-1A (II-108/16) catalyst in Figure 6. It appears that the Engelhard catalyst is not as active initially as HDS-1442A catalyst for converting Illinois No. 6 coal to THF, benzene or hexane soluble product. The deactivation rate of the Engelhard catalyst is low for benzene conversion and at 125 hrs its activity level is comparable to HDS-1442A but is still far below AMOCAT-1A. Hexane soluble conversions are consistently below the base case catalyst.

Deactivation rates are low because the catalyst contains over 18% of macropores which are difficult to plug. The surface area of the catalyst is low (98 m^2/gm) and this probably accounts for the low initial activity.

Elemental analysis of the various boiling point fractions will be reported in the next quarterly.

FIGURE 6

Performance of Engelhard catalyst for liquefaction of Illinois coal



Future Work

Task 2

The following runs with Illinois No. 6 coal are planned:

Run No.	Catalyst
51102	Slurry Oil Effect Run
51103	Regenerated AMOCAT-1A Catalyst

Task 3

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 diameters will be undertaken in order to optimize the effect of micropore structure on liquefaction activity, heteroatom removal and activity decline rate.

The following runs are planned:

Run No.	Catalyst	Coal
51100	Mo-G150B	Wyodak
51101	Mo-G200B	Wyodak
51104	Regenerated AMOCAT-1A or 1B	Wyodak

Task 4

Blending of the Eastern and Western synthetic coal mixtures will begin as soon as the distilled Panasol solvent is available. Currently, we are limited by technician manpower and at this stage in our program we feel that Task 4 should have a lower priority relative to the other tasks.

Task 5

The following runs with Illinois No. 6 coal are planned:

Run No.	Catalyst
5198	Catalysis Research Corp. Catalyst
5199	Harshaw NiMo Catalyst

Testing of Hydrocarbon Research, Inc. Catalysts

Hydrocarbon Research, Inc. (HRI) has a DOE sponsored contract program entitled "Catalytic Evaluation for H-Coal." One of the subtasks of the Amoco program is the evaluation of the best catalysts of other DOE sponsored coal liquefaction catalyst development program. HRI will submit a sample of their vanadium, titanium, and magnesium NiMo H-Coal catalysts for testing in the Amoco batch screening unit. The most active catalyst determined from these experiments will then be tested in the continuous aging unit. The test would run under our standard screening procedure with Illinois No. 6 coal.

Another subtask of the DOE sponsored Amoco program is to develop a mathematical correlation between results obtained on the HRI and the Amoco test units. Joint testing of identical catalysts by both HRI and Amoco will provide the data base for the development of these mathematical expressions.

Preparation of Modified Aluminas--W. R. Grace Subcontract

W. R. Grace has been subcontracted to prepare modified aluminas to be used as supports for our coal liquefaction catalysts. In Task 3 of this Quarterly report we discussed the possibility that micropore size could be a critical variable in processing Wyodak coal. W. R. Grace is preparing two bimodal alumina supports, one with 150 Å average micropore diameter, the other with 200 Å. These catalysts will be used in aging tests with Wyodak coal during the coming quarter.

W. R. Grace will also attempt to prepare a 1/32" NiMo AMOCAT catalyst for use in the SRC upgrading effort. They have already prepared a 1/16" version of the same catalyst for the old EPRI contract.

W. R. Grace has also been contacted about preparing a large batch of AMOCAT-1B catalyst for testing by HRI in their large PDU ebullated bed pilot plant. They have been informed that we do not currently have the data for determining the optimum catalyst for processing Wyodak coal but we feel that it is crucial that the micropore diameter be greater than 120 Å. In contrast we do not feel that micropore diameter is as crucial in processing Illinois No. 6 coal and that the current AMOCAT-1A is the optimal catalyst for processing this coal.

DKK:RJP:JAM:sgj

APPENDIX A

PILOT PLANT RUN SUMMARY

During the third quarter of the current program, six runs were made on the continuous aging unit using the catalysts listed.

Run No.	Catalyst	
5192	Glass Beads	Wyodak coal for first half and Illinois No. 6 for balance of run. Uncatalyzed base run made at several residence times with both coals. Other test conditions and slurry oil were not changed.
5193	Mo-G102B(14) (3651-81)	Illinois No. 6 coal. Determining effect of co-promoter with Ill. #6 coal using W. R. Grace's molybdenum catalyst.
5194	Engelhard Lot No. 11015-26-1 (3651-109)	Illinois No. 6 coal. Evaluate a 100 gm sample of BaMo stabilized 3% CoO-15% MoO_3 on Al_2O_3 catalyst from Engelhard. This was one of the catalysts supplied by DOE through a contractor.
5195	Mo-G102B(14) (3651-81)	Wyodak coal. Continue evaluation of the unpromoted molybdenum catalyst with Western coal. The run was terminated prematurely when the agitator on the reactor failed which caused coke to be deposited throughout the reactor, and particularly on the catalyst bed.
5196	Mo-G102B(14) (3651-81)	Wyodak coal. Successful repeat of run 5195.
5197	CoMo-G102B(14) (3651-80)	Illinois No. 6 coal. Determine effect of Co promoter on Ill. #6 coal by comparing the results with those obtained with the unpromoted Mo-G102B(14) catalyst. Both catalysts use the same 102 A bimodal alumina base.

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