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DEVELOPMENT OF SIGNIFICANTLY IMPROVED CATALYSTS FOR
COAL LIQUEFACTION AND UPGRADING OF COAL EXTRACTS

Quarterly Progress Report No. 7 for April 1—June 30, 1983

By

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Work Performed Under Contract No. AC22-81PC40091

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1. SUMMARY

This Quarterly Progress Report covers work on Tasks 3, 4, 5, 6, and 8 during the period April-June, 1983.

- 1.1 Task 3: On the basis of the ebullation study conducted for Task 3 on a 3-inch column at Stamford and a 6-inch column at Hydrocarbon Research, Inc., it is concluded that 2mm median diameter, -6 +16 mesh, beads are equivalent in behavior to HDS 1442A, 1/16 inch extrudates, and 1.4mm, -8+20 mesh, beads are equivalent to HDS 1442B, 1/32-inch extrudates. The range of bead sizes that would be satisfactory for coal liquefaction and coal extract upgrading ebullated bed reactors has been selected.
- 1.2 Tasks 4 and 5: A series of twenty-five experimental bead catalysts were tested for coal liquefaction activity in batch screening trials. Six factors relating to support preparation and composition, molybdenum, nickel, and cobalt levels, and additives, were varied according to a statistical design. Molybdenum (MoO_3) and NiO/CoO promoter levels were found to correlate most closely with coal conversion and sulfur removal. Support composition and additive variables had detrimental effects only at particular levels.
- Batch testing with coal extracts was initiated. Runs were done to gain experience in processing extracts as well as to develop satisfactory work-up procedures. Results of baseline runs are given.

- 1.3 Task 6: Commissioning of the CSTR test unit continued during the quarter. The reactor system was operated at process temperature and pressure using flush oil and the product collection system was tested. Hydrogen leak testing was successfully completed and a short thermal coal slurry run was made. Several equipment problems persist.
- 1.4 Task 8: Surface characterization of experimental bead catalysts continued. X-ray photoelectron and electron microprobe techniques were used. Results are compared to activity test data.

2. INTRODUCTION

During 1979-80, a new generation of very active long-lived catalysts for hydrotreating was discovered at the Stamford Research Laboratories of the American Cyanamid Company. The catalysts are based on a unique substrate prepared in bead form from a rehydratable alumina. Their spherical shape, crush strength, and abrasion resistance make them ideal candidates for use in ebullated bed reactors. The beads have internal pore structures that are controllable over a wider range than conventional alumina supports, leading to active catalysts that are resistant to poisoning.

In September, 1981 the Department of Energy granted a 3-year contract to the American Cyanamid Company for the development of significantly improved catalysts for coal liquefaction and for upgrading coal extracts, utilizing bead substrates. During the first year of the contract (FY 1982) a facility for catalyst activity testing was constructed. An associated laboratory for carrying out specialized analytical procedures was established. Cold-flow studies were conducted and methods for studying the details of catalyst surfaces were developed.

3. OBJECTIVES AND SCOPE

The primary objective of this project is to develop one or more catalysts for coal liquefaction and/or for upgrading coal extracts which will be superior to the best currently known catalysts. The superiority will be judged by considering both the activity and the life of the catalysts. Catalysts will first be screened in a batch reactor to identify promising candidates. The latter will be tested in a continuous aging reactor to evaluate their resistance to deactivation under coal-liquefaction and extract upgrading conditions. In addition, a program of cold flow ebullation tests is being carried out to determine the median size and size range of beads compatible with operation of ebullated bed reactors. Furthermore, special analytical methods will be used to characterize catalysts before and after performance testing to elucidate the mechanism of catalyst deactivation. The work of the contract has been divided into the following eight tasks:

- Task 1: Project Work Plan - Completed
- Task 2: State-of-the-Art Assessment - Completed
- Task 3: Cold-Flow Ebullation Tests
- Task 4: Bead Catalyst Characterization
- Task 5: Catalyst Batch Screening
- Task 6: Continuous Aging Tests
- Task 7: Catalyst Regenerability
- Task 8: Analytical Methods Review

This Quarterly Progress Report covers work on Tasks 3, 4, 5, 6 and 8 during the period April-June, 1983.

4. Task 3: COLD FLOW EBULLATION TESTS

This section summarizes the results of the ebullation tests on the 6-inch diameter column, conducted by Hydrocarbon Research, Inc. (HRI), under a subcontract from American Cyanamid, and lists the conclusions of the entire study vis-a-vis the purpose of the task.

4.1. Ebullation Tests - 6-inch Column

As a part of Task 3 of the contract, the American Cyanamid Company had subcontracted with HRI to test 9 bead-fluid combinations in HRI's 6-inch diameter cold flow ebullation column. HRI's report on the cold flow work subcontracted to them concluded that the 2mm median diameter beads (-6 +16 mesh) would be acceptable for coal liquefaction and that the 1.4mm median diameter beads, which displayed acceptable carry-over only at gas velocities of 0.1 ft/sec and lower, would be satisfactory for coal extract upgrading with a slightly narrower distribution than that tested (-8 +20 mesh). In general, the operation was easier and more predictable with beads than it is with extrudates, and with the disengagement zone, any of the beads tested in this program (0.5mm to 2mm median diameter) would operate acceptably in an ebullated bed reactor.

4.2 Conclusions from the Ebullation Study

The purpose of the cold flow ebullation study was to aid in selecting suitable particle sizes and particle size distributions for coal liquefaction and coal extract upgrading catalysts. On the basis of the work conducted for Task 3 the following conclusions can be drawn:

1. 2mm median diameter beads are equivalent to HDS 1442A, 1/16-inch extrudates.
2. 1.4mm median diameter beads are equivalent to HDS 1442B, 1/32-inch extrudates.
3. Bead diameters in the 0.84mm to 2.38mm (20 to 8 mesh) range would be well within the acceptable range for coal extract reactors and, therefore, could be tested in the aging studies.
4. Since with appropriate disengagement devices carry-over of beads could be eliminated, aging tests with even smaller beads (as low as 60 mesh, 0.25 mm diameter) should be considered in order to test the effect of particle size on catalyst activity and life.
5. The ebullation behavior of beads is generally similar to that of extrudates. The dependence of bed porosity on liquid and gas rates parallels that of extrudates.
6. With gas rates in excess of 0.05 ft/sec and a bed expansion of 30% or more there is no segregation of beads by size. Also the solids appear well-mixed axially.
7. The interface is a function of bead size distribution and the operating conditions and for smaller beads (1.4mm and lower) appears visually to be more diffuse than with extrudates. The interface spread is less than 18 inches even at gas velocities of 0.15 ft/sec at bed expansions up to 100%.

8. In HRI's 6-inch column there was no carry-over of beads (as small as 60 mesh) into the product withdrawal line, with or without internal recycle of the liquid phase. The extent of carry-over, therefore, will depend on the presence or absence of a disengagement device above the catalyst bed.

5. Tasks 4 and 5: CATALYST CHARACTERIZATION AND
BATCH SCREENING TESTS

5.1 Introduction

During the past quarter, a substantial number of catalyst screening runs were made using the 1-liter autoclave Batch Test unit. Experimental bead catalysts were tested for coal liquefaction performance with Illinois No. 6 as feed. Results of this work as well as that from ongoing baseline runs with HDS 1442A and Amocat 1A are presented. Work with coal extract feed was initiated and results of initial baseline tests with Shell 324M are given.

5.2 Coal Conversion Runs

5.2.1 Test Procedures

The conditions used for Batch Screening tests with Illinois #6 coal are summarized in Table 5.1. These conditions closely follow those used by workers at PETC (1) and Amoco (2). As described in Section 5.2.2., they give results with baseline catalysts comparable to previously published work. The criteria used to establish the agitator speed and gas flow were described in Quarterly Progress Report No. 6 (3).

Batch product workup, shown schematically in Figure 5.1, is a modification of the "Benzene Macro-Residue" procedure (PR-1) described by Amoco (2) and currently referred to by Amoco as "Original Product Work-Up Procedure" (4). The major difference is the use of toluene instead of benzene for

TABLE 5.1
SCREENING CONDITIONS
COAL CONVERSION RUNS

Pressure	2000 PSI
Temperature (Max)	399°C
Gas Flow	5.5 CFH
Agitator Speed	1400 RPM
Reaction Time	30 Min
Solvent Charge	300g PANASOL AN-3R
Coal Charge*	150g Illinois No. 6
Coal Particle Size	-100 Mesh (97%)
Catalyst Charge**	10g
Catalyst Particle Size	60-100 Mesh

* Coal dried to approximately 2% moisture

** Catalyst presulfided

FIGURE 5.1

BATCH PRODUCT ANALYSIS FLOW CHART

washes and extractions. All analytical results are stored on-line in databases on a Digital Equipment Corporation DECSys-10 computer.

Conversion is calculated from the weight of the "Solid Residue" using equation 5.1:

$$\text{Toluene-soluble Conversion \%} = \frac{W_C + W_{\text{cat}} - I}{W_C (1 - A_C)} \times 100 \quad (5.1)$$

where: W_C = Dry weight of coal charged (g)

W_{cat} = Dry weight of catalyst charged (g)

I = Weight of toluene insolubles ("Solid Residue") after liquefaction(g)

A_C = Ash content of coal (weight fraction)

A discussion of conversion calculations was included in Quarterly Progress Report No. 3 (5).

Sulfur, nitrogen and direct oxygen are among the analyses applied to the "Combined Liquid Product" recovered from Batch runs. Sulfur is quantified by X-ray fluorescence while both nitrogen and oxygen are determined with a Perkin-Elmer Model 240C CHN analyzer. Nitrogen is run in the CHN mode of the instrument with samples encapsulated in Perkin-Elmer Differential Scanning Calorimetry pans. This encapsulation prevents any loss of the viscous but volatile samples during the purge cycle of the instrument. The contribution of atmospheric nitrogen in the head space of the sealed pan is subtracted via highly reproducible blank runs. Although

workers at Engelhard (using an older model Perkin-Elmer unit) felt that nitrogen analysis by a CHN analyzer was insufficiently precise (6), experience in this laboratory indicates that a precision of $\pm 0.07\%$ absolute for duplicate runs is achievable. Direct oxygen, also determined with the 240C, involves a change of reagents in the instrument but yields more reliable results than the usual oxygen by difference calculations. Samples for oxygen analysis are encapsulated in the same manner as samples for nitrogen analysis.

It is desirable to express the heteroatom content of products in a way that accurately reflects only the liquid formed by liquefaction of coal. Amoco approached this by adjusting sulfur and nitrogen values in the liquid product for water, residual extraction solvent and Panasol, assuming no losses (2). An improvement in this approach has been developed by assuming that slurry solvent (Panasol) and coal liquid are subject to the same losses in recovery while no losses occur in the recovery of the solids after a Batch run. With these assumptions, a fractional recovery of the liquid phase can be calculated and used to correct the contribution of Panasol to the total liquid product. Since Panasol contains no appreciable nitrogen, sulfur or oxygen, all heteroatoms detected in the combined liquid product are assumed to be contributed by the coal liquid and adjusted to reflect "sulfur in coal liquid", etc.

The coal liquid make, determined using the above assumptions, can be used to calculate a value for conversion to coal liquid (ratio of coal liquid make to weight of maf coal charged) which can be compared to conversion calculated using equation 5.1 (solids conversion). Fig. 5.2 is a plot of solids conversion vs. conversion to coal liquid for numerous runs including thermal runs, baseline runs (see Section 5.2.2) and catalytic runs (see Section 5.2.4). The plot points out the strong correlation between the two methods of calculating conversion. It also illustrates that the conversion to coal liquid is generally some 2% lower than the solids conversion. The bias is the loss expected due to gas make. No correlation was found between conversion and product recovery.

5.2.2. Baseline Runs

Throughout the operation of the Batch Test unit, periodic testing of baseline catalysts was done to verify the consistency of the test results and to develop measures of reproducibility which could be used in the statistical evaluation. For coal conversion, the baseline catalysts are HDS-1442A and Amocat 1A. The averaged results of these baseline runs are shown in Table 5.2. The table includes conversion of solids to toluene soluble material, and %S, %N, %O in coal liquid. Methods for obtaining these results are given in Section 5.2.1.

FIGURE 5.2

CORRELATION OF COAL LIQUID FORMATION
TO SOLIDS CONVERSION

TABLE 5.2

BATCH SCREENING TESTSBASELINE RUNSILLINOIS NO. 6 COAL AT 399°C

<u>Catalyst</u>	<u>Tolune Soluble Conversion %</u>	<u>Sulfur in Coal Liquid %</u>	<u>Nitrogen in Coal Liquid %</u>	<u>Oxygen in Coal Liquid %</u>
HDS 1442A	70.4+ 1.08*	1.02+ 0.02*	1.00+ 0.15*	7.32+ 0.51*
Amocat 1A	75.0	0.83	1.08	6.82

* 95% Confidence Intervals

In the course of baseline testing, a sudden downward shift in conversion results was observed (see Table 5.3). This occurred just prior to the start of experimental catalyst testing. By studying data acquired by computer during each run, the cause of the loss of conversion was determined to be a sudden decrease in time of 5 minutes, yet unaccounted for, during the reactor heat-up from 375°C-399°C. (The heat-up profile has remained consistent since this change has occurred.) Two runs were made to confirm the hypothesis: one was heated to 385°C and held for 1 minute and another was heated to 385°C and held for 6 minutes before cool down. Table 5.3 shows the effect on conversion of this change in heat history. The results are consistent with the observed shift in baseline values and are indicative of the large amount of conversion taking place during heat up.

5.2.3 Bead Catalyst Testing

Twenty-five experimental bead catalysts were prepared according to a fractional factorial design based on six parameters of 4 or 5 levels each, expected to be critical for catalyst performance. The design targets are given in Table 5.4. The first parameter, support process, consists of five proprietary variations in the support preparation. The second parameter, support composition, reflects variations in treatments and use of additives which influence the chemical and physical properties of the catalysts. The third parameter, molybdenum level, has four different target values from 2%-15%. The fourth parameter involves five different

TABLE 5.3

BATCH SCREENING TESTS

EFFECT OF HEAT-UP ON CONVERSION

Illinois No.6 Coal
HDS 1442A

	Run Time (Min)				Toluene Soluble Conversion (%)
	<u>25°-350°C</u>	<u>350°-375°</u>	<u>375°-399°</u>	<u>375°-375°</u>	
First Baseline Series	54-59	4-5	10	40	74.3 ± 1.6
Second Baseline Series	54-59	4-5	5-6	36	70.4 ± 1.1
	<u>25°-350°</u>	<u>350°-385°</u>	<u>385° Hold</u>	<u>350°-350°</u>	
First Heat-Up Trial	57	7	1	10	23.6
Second Heat-Up Trial	56	8	6	15	32.9

TABLE 5.4

STATISTICAL DESIGN TARGET VALUES

<u>Design #</u>	<u>I</u> <u>Support</u> <u>Process</u>	<u>II</u> <u>Support</u> <u>Composition</u>	<u>III</u> <u>MoO₃</u> <u>Level (%)</u>	<u>IV</u> <u>Promoters</u> <u>NiO:CoO (%)</u>	<u>V</u> <u>Catalyst</u> <u>Modifiers</u>	<u>VI</u> <u>Catalyst Preparation</u>
1	1	1	10	3:0	-	2
2	1	2	15	1.5:1.5	Cr	2
3	1	3	5	-	P(1)	1
4	1	4	2	0:3	Na	4
5	1	5	10	1.5:0	P(2)	3
6	2	1	15	0:3	P(1)	3
7	2	2	5	1.5:0	Na	2
8	2	3	2	3:0	P(2)	2
9	2	4	10	1.5:1.5	-	1
10	2	5	10	-	Cr	4
11	3	1	5	1.5:1.5	P(2)	4
12	3	2	2	-	-	3
13	3	3	10	0:3	Cr	2
14	3	4	10	1.5:0	P(1)	2
15	3	5	15	3:0	Na	1
16	4	1	2	1.5:0	Cr	1
17	4	2	10	3:0	P(1)	4
18	4	3	10	1.5:1.5	Na	3
19	4	4	15	-	P(2)	2
20	4	5	5	0:3	-	2
21	5	1	10	-	Na	2
22	5	2	10	0:3	P(2)	1
23	5	3	15	1.5:0	-	4
24	5	4	5	3:0	Cr	3
25	5	5	2	1.5:1.5	P(1)	2

ratios of NiO and CoO promoters. The fifth parameter, catalyst modifiers, reflects the use of various additives to the catalyst composition including two methods for addition of phosphorus. The sixth parameter, catalyst preparation, involves variations in the process used to convert supports to finished catalysts.

A list of catalyst properties and test results is given in Table 5.5. Measured values for molybdenum, nickel and cobalt contents as well as surface area (SA) and water pore volume (WPV) are included. The analytical methods used to determine these properties were previously outlined in Quarterly Report No. 5 (7). For each catalyst, model pore diameter is given, and in cases where the catalyst is bimodal, the location of the second mode is indicated. These values are obtained from differential pore size distribution plots based on mercury porosimetry data. An example is shown in Figure 5.3. A few of the catalysts have complex distributions which complicates determining the location of the modes in the ordinary sense. These cases are noted on the table.

A number of catalysts were run in duplicate to establish the reproducibility of bead catalysts screens. A pooled standard deviation of 2.3% was calculated based on six replicate runs. (One pair of runs not in Table 5.5.) This is somewhat higher than for HDS 1442A baseline runs. This may be due to slight differences in sample handling characteristics or inhomogeneity in catalyst samples.

TABLE 5.5

BATCH SCREENING TESTS

DEAD CATALYST PROPERTIES AND RESULTS

Catalyst	Statistical Number	MoO ₃ %	NiO %	CoO %	SA m ² /g	PV (H ₂ O) cc/g	MPD Å	Conversion %	S	N	O
									In Coal	Liquid (%)	
14454-20	1	10.5	3.1	-	161	.73	200	72.5	.77	1.14	7.09
14454-36	2	17.9	1.4	1.2	122	.54	240	72.4	.82	1.03	6.25
14454-25	3	4.6	-	-	162	.81	140*	67.3	1.40	1.01	6.89
13501-136	4	1.8	-	2.9	208	.81	140	62.1	1.36	.95	7.78
14454-33	5**	9.5	1.9	-	105	.64	400	69.9, 70.0	1.00, 1.00	.72, 1.17	6.94, 7.38
13501-111	6	14.2	-	2.8	111	.71	220, 4000	72.4	1.04	.80	6.66
13501-103	7	5.3	1.5	-	124	.92	200, 4000	55.7	1.28	.88	6.73
14454-38	8	1.9	2.9	-	151	.84	120*	65.6	1.22	.87	7.52
13501-130	9	9.8	1.5	1.4	225	.84	160*	72.7	.84	.92	7.28
13501-137	10	10.1	-	-	108	.83	800, 14,000	58.3	1.27	.81	8.16
13501-138	11**	4.9	1.5	1.4	137	.71	140, 8000	68.9, 72.1	1.01, .94	1.10, .73	7.76, 6.64
13501-149	12	1.8	-	-	157	.75	160, 4000	63.0	1.32	.89	8.32
13501-110	13	9.9	-	2.7	148	.65	200	72.3	.93	.73	7.10
13501-147	14	10.9	1.6	-	181	.71	140*	72.0	.85	1.05	6.36
13501-158	15**	13.1	3.0	-	169	.59	150, 8000	72.8, 72.3	.91, 1.06	.91, .94	7.34, 7.21
13501-131	16	2.0	1.5	-	168	.85	190, 20,000	61.9	1.30	.90	7.79
13501-151	17**	9.6	2.8	-	135	.76	210, 20,000	73.3, 76.7	1.01, 1.08	1.13, .81	8.37, 7.74
14454-23	18	10.8	1.5	1.5	156	.82	140, 8000	67.8	1.29	.65	8.07
13501-109	19	16.0	-	-	156	.78	170, 3000	71.1	1.52	.86	7.49
13501-148	20	4.7	-	2.8	199	.99	410*	67.9	1.09	.93	7.96
13501-104	21**	11.2	-	-	140	.80	90, 140,000	63.2, 66.6	1.45, 1.34	.82, .91	6.81, 8.37
13501-155	22	10.0	-	2.8	113	.72	130	63.1	1.07	.76	7.21
13501-139	23	16.0	1.5	-	100	.61	290, 30,000	70.3	1.15	.94	6.80
14178-186	24	5.2	2.8	-	193	.78	120	66.4	1.00	.82	7.03
13501-70	25	1.8	1.4	1.4	130	.77	100	61.0	1.19	.88	7.56

* Complex PSD

** Duplicate Screening Test

PORE SIZE DISTRIBUTION

FIGURE 5.3
TYPICAL CURVE

5.2.4 Results and Discussion

Results of the bead catalyst screens have been evaluated in three ways: (1) individually in comparison to baseline catalyst performance, (2) as a group to determine useful correlations, and (3) on a statistical basis with reference to the experimental design. Conversion performance of HDS 1442A was met or exceeded by 12 of the 25 bead catalysts tested. One of these catalysts was comparable to Amocat 1A. It is of interest to note that many of the bead catalysts showing good performance have significantly lower MoO_3 contents than the baseline catalysts (HDS 1442A - 16.5% MoO_3 , Amocat 1A - 15.7% MoO_3).

Evaluation of catalysts on the basis of product heteroatom content is meaningful only for sulfur. Four bead catalyst showed performance comparable to Amocat 1A. This corresponds to approx. 75% reduction in sulfur content in comparison to sulfur in the feed coal (3%). Furthermore little or no nitrogen removal is seen in any of the screens, within the reproducibility of the tests. Values of nitrogen in coal liquid higher than nitrogen in the feed coal (1.0%) are seen in some cases. Results of oxygen analyses are similarly inconclusive.

Test results were also evaluated on a statistical basis. For each factor in the experimental design, average values for conversion and heteroatom content were computed at each level, disregarding differences in the other factors. These results are given in Table 5.6.

TABLE 5.6

CALCULATED AVERAGE VALUES FOR DESIGN FACTORS

Factor	Level	% Conversion	%S	%N	%O
I. Support Process	1	68.84	1.070	1.016	7.034
	2	69.80	1.014	.856	7.270
	3	68.94	1.130	.902	7.251
	4	68.40	1.168	.862	7.873
	5	64.80	1.172	.853	7.238
II Support Composition	1	67.78	1.114	.914	7.266
	2	67.50	1.100	.906	7.314
	3	68.66	1.208	.840	7.276
	4	68.86	1.040	.920	7.188
	5	67.98	1.092	.900	7.624
III. Molybdenum Level	2%	62.72	1.278	.898	7.794
	5%	67.24	1.156	.912	7.162
	10%	69.51	1.053	.894	7.408
	15%	71.80	1.014	.912	6.896
IV. NiO:CoO	0:0	66.58	1.318	.888	7.690
	1.5:0	67.96	1.116	.944	6.968
	3:0	70.12	.982	.946	7.396
	1.5:1.5	68.56	1.030	.885	7.272
	0:3	67.56	1.108	.834	7.342
V. Additives	None	69.28	1.034	.964	7.490
	Na	66.32	1.258	.866	7.490
	Cr	68.26	1.074	.858	7.266
	P(1)	69.20	1.098	.942	7.106
	P(2)	67.72	1.090	.872	7.316
VI Catalyst Preparation	1	67.56	1.104	.904	7.290
	2	68.37	1.080	.924	7.165
	3	67.90	1.130	.842	7.448
	4	68.58	1.160	.918	7.600

Repeat runs in Table 5.5 were not included in the analysis in Table 5.6. Of the six parameters in the design, MoO_3 level and promoter level (NiO +/ or CoO) had the greatest effect on conversion and sulfur level. Increased conversion of solids and lowering of product sulfur content were observed steadily as MoO_3 content increased in the range 2%-15%, with some leveling off in the response curve. The nickel-containing catalysts appeared to outperform cobalt-containing catalysts for both solids conversion and sulfur removal. In general, little effect of support physical properties was observed in the results. Support process level 5 resulted in lower conversion values than for other four levels. Addition of Na_2O (Additives factor) had the adverse effect of decreasing conversion and increasing sulfur levels in the liquid product. None of the six factors had a significant effect on nitrogen or oxygen content.

A striking aspect of the data is the close correlation ($r = 0.89$) between conversion and sulfur-content. Figure 5.4 illustrates the relationship observed in the combined data for experimental catalysts, baselines, and thermal runs. It suggests a mechanistic link between coal conversion and desulfurization.

Attempts to correlate catalyst performance with catalyst physical properties yield only a weak relationship between surface area and sulfur level, i.e., higher surface area catalysts yield products with somewhat lower sulfur contents (See

FIGURE 5.4

RELATIONSHIP BETWEEN SULFUR CONTENT
AND CONVERSION TO COAL LIQUID

Figure 5.5). Furthermore, empirical equations relating the conversion and sulfur content results of these tests to key factors discussed above, excluding surface area, pore volume, or pore mode yield residual standard deviations comparable to the standard deviation estimates based on repeat runs of HDS 1442A. The equations are as follows:

$$\begin{aligned} \text{Solids} \\ \text{Conversion } (\%) &= 74.63 - \frac{65.6}{\% \text{ MoO}_3 + 3.7} + 1.06(\% \text{ NiO}) + 0.35(\% \text{ CoO}) \\ &\quad - 0.57(\% \text{ Na}_2\text{O}) - 4.43(\text{Support Process } 5) \end{aligned} \quad (5.2)$$

$$\begin{aligned} \text{Sulfur in} \\ \text{Coal Liquid } (\%) &= 1.053 + \frac{2.05}{(\% \text{ MoO}_3) + 3.7} - 0.112(\% \text{ NiO}) \\ &\quad - 0.071(\% \text{ CoO}) + 0.041(\% \text{ Na}_2\text{O}) \end{aligned} \quad (5.3)$$

Failure to observe strong pore texture effects on the results, pointed out by Ocampo et al. (8), is indicative of the limitations of the test procedures used. The referenced work suggests that coal liquefaction catalysts, particularly with respect to hydrogenation performance, deactivate very rapidly due to build up of coke, with longer range aging effects due to deposit of metals. Thus, the results observed in batch screening tests are based on the performance of a catalyst already partially deactivated by the first mechanism, which brings about a reduction in surface area and total pore volume. It is therefore not surprising that fresh catalyst physical properties fail to correlate strongly with performance.

FIGURE 5.5
EFFECT OF SURFACE AREA ON
SULFUR IN COAL LIQUID

5.2.5 Conclusions

Screening of the first set of experimental bead catalysts for initial liquefaction activity with Illinois No. 6 coal at 399°C has been completed. Catalysts with initial activities comparable to Amocat 1A were in the group. Aging characteristics will be determined for some of these catalysts in CSTR tests. In addition, a new series of preparations will be specified on the basis of results from the initial set of coal catalyst screens.

5.3 Extract Upgrading Runs

5.3.1 Test Procedures

During this quarter, extract upgrading tests were initiated. The coal extract being tested is crushed, deashed, solvent refined coal from Wilsonville Run #242. Two slurry solvents, both Stage I recycle oil (Tray 8) from Wilsonville Run #243 were received. Analyses of both solvents, along with analysis of the solvent refined coal, are included in Table 5.7. It was decided that sample V-178 (collected directly from the distillation tower) would be used instead of V-177 (same material after storage) since large differences in viscosity between the materials suggested deterioration, perhaps polymerization, on storage.

The workup of batch extract-upgrade product entails a heated vacuum filtration (under a nitrogen blanket) through Whatman #42 filter paper to remove ground catalyst.

TABLE 5.7ANALYSIS OF EXTRACT-UPGRADING FEEDS

		<u>Recycle Solvents</u>	
	<u>SCT-SRC</u>	<u>V-177</u>	<u>V-178</u>
%C	88.53	88.78	87.12
%H	6.57	9.73	10.31
%N	1.17	0.38	0.28
%O	3.56	1.94	1.86
%S	0.57	0.25	0.19
Basic N	-	0.24	0.22
Viscosity(40°C)	-	80.4	20.0
% H ₂ O	0.22	0.049	1.17
Density(20°C)	-	0.985	0.958
% Ash	0.14	-	0.01
% THF insolubles	0.0	0.0	0.0
% Ethyl acetate insolubles	13.1	0.0	0.0
% Cyclohexane insolubles	50.4	0.7	0.3

The filtrate is then analyzed by pressure filtration (see Section 5.3.3) to determine % conversion for the run. The filtrate is further analyzed for C,H,N,O,S,H₂O and also examined by simulated distillation.

Equation 5.4 is used for calculating conversion for extract runs. The value used for I_{Feed}^{EA} is an average number from 4 different feed samples.

$$X^{EA} = \frac{I_{Feed}^{EA} - I_{Prod}^{EA}}{I_{Feed}^{EA}} \times 100^A \quad (5.4)$$

where:

X^{EA} = % conversion of ethyl acetate insolubles to solubles

I_{feed}^{EA} = % ethyl acetate insolubles in feed

I_{Prod}^{EA} = % ethyl acetate insolubles in product

* Similarly for cyclohexane and tetrahydrofuran

5.3.2 Baseline Runs

Conditions for extract upgrading screens were determined on the basis of a series of baseline runs with Shell 324M catalyst, obtained from Wilsonville. Catalyst properties are given in Table 5.8. Initial results obtained at 425°C showed extremely high conversions as determined by pressure filtration tests with ethyl acetate and cyclohexane (See Table 5.9). (Pressure filtration tests with THF were not done since extract

TABLE 5.8CATALYST PROPERTIESSHELL 324M

MoO₃ 20.4%

NiO 3.5%

P 3.0%

Surface Area 164 m²/g

Pore Volume 0.47 cm³/g

TABLE 5.9

EXTRACT UPGRADING TESTS

BASELINE RUNS

SHELL 324M CATALYST

<u>Temperature</u> °C	<u>Conversion of Insolubles</u> <u>Pressure Filtration Tests</u>		<u>Product Analysis</u>		
	<u>Ethyl</u> <u>Acetate</u>	<u>Cyclo-</u> <u>Hexane</u>	<u>S</u>	<u>N</u>	<u>O</u>
	%	%	%	%	%
425	92.9	81.6	0.05	0.57	2.06
399	89.8	61.8	0.06	0.61	1.99
380	83.8	45.0	0.09	0.67	2.19
360	75.4	35.7	0.13	0.62	2.18

feeds being used have essentially no THF insolubles). Runs were then made at several lower temperatures and screening results compared. A temperature of 380°C was chosen for further runs, mainly on the bases of sample handling characteristics. However, nitrogen removal at 380°C is low. Some higher temperature screens may be done to better determine this performance characteristic.

At this point, a limited study of the effects of H₂ flow rate (5.5 cfh vs 10 cfh) and agitator speed (1400 rpm vs 1800 rpm) on conversion was done. A diagram showing the experimental matrix and the results is given in Figure 5.6. None of the effects observed are statistically significant for any of the cases. On the basis of these results, it was decided to select the conditions which have been used in the coal liquefaction screens for work with extracts (5.5 cfh and 1400 rpm). A complete list of screening conditions is given in Table 5.10.

Extract-upgrading tests will continue with screening of experimental bead catalysts and periodic baseline runs with Shell 324M. Eighteen bead catalysts were selected from the 25 in the original group. Eliminated were catalysts containing only 2% MoO₃, except for #8 (14454-38), and catalysts made by Support Process 5, except for #23 (13501-139).

5.3.3 Analytical Methods

Pressure Filtrations

Pressure filtration is used to determine % insolubles of extract upgrading product in ethyl acetate,

FIGURE 5.6

PROCESS VARIABLES STUDY
STATISTICAL DESIGN

Extracts

TABLE 5.10BATCH SCREENING CONDITIONSEXTRACT-UPGRADING RUNS

Pressure	2000 psi H ₂
Temperature (Max.)	380°C
Gas Flow	5.5 cfh
Agitator Speed	1400 rpm
Reaction Time	60 min
Solvent Charge	150g
Extract Charge	150g
Catalyst Charge*	10g
Catalyst Particle Size	60 -100 mesh

* Catalyst presulfided

toluene and cyclohexane. These values are used to calculate % conversion for each of the solvents (equation 5.4). The unit is similar to that used by workers at PETC (1). It consists of a 1000-mL Whitey stainless steel cylinder connected to a Millipore pressure filter holder containing a 47-mm Millipore TEFLON[®] filter (10- μ m pores). In use, a 1-3g sample of upgraded extract is dispersed in 30 mL of the appropriate solvent (with sonication). The mixture is poured into 70 mL of the same solvent with stirring. The 1000-mL reservoir (stainless-steel cylinder) is then charged with 900 mL of fresh solvent and the 100-mL sample/solvent mixture is introduced into the Millipore pressure filter holder. The reservoir is pressurized to 40 psi with nitrogen which flushes the sample mixture and the fresh solvent through the filter. The filter and residues are dried and weighed. The percent insolubles in the sample is calculated.

Simulated Distillation

Simulated distillation is done to determine the distillation range of the sample tested. The method used is a modification of the ASTM D2887 method for "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography". A sample (diluted with CS₂ if necessary) is injected into a Varian 3200 gas chromatograph and separated on an 18"x 1/8" stainless steel column packed with 3.8% silicone rubber UC-W98 on Chromasorb WHP. Conditions are adjusted to allow separation of C₅-C₄₀ hydrocarbons in a calibration mixture. The chroma-

togram of the sample is integrated by time slicing and the distillation curve is constructed by comparison with the chromatogram of the standard sample.

5.4 References

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6. Task 6: CONTINUOUS AGING TESTS

6.1 Unit Start-Up

Commissioning of the CSTR Test Unit continued during the quarter. Pumping of oil and gas through the system (ex-reactor) was achieved. Burn-in of the reactor heater was begun and final modifications to the product receivers were made. Failed solenoid valves were replaced by more rugged units from another vendor. Following this, slurry pumping trials were begun. The slurry recirculation loop was modified to eliminate solids build-up and the check-valve springs were removed from the high pressure pumps. The product collection vessels were insulated and brought to operating temperature. Finally, hydrogen pressure testing of the system was successfully completed.

Operation of the CSTR Test Unit began with a one-day thermal run. Start-up was accomplished by initially pressurizing the system with hydrogen and filling the reactor with flush oil. The reactor was heated to 400°C and hydrogen flow started at 3776 sccm. Slurry feed (33% Illinois No. 6 coal in hydrogenated creosote oil) was diverted to the reactor after 15 minutes and the operating temperature of 425°C was achieved. Reactor hold-up was approx. 330 mL. Product was collected in the main receiver for 1-1/2 hours before switching to the smaller sample receiver for 1-1/2 hours. The receivers were let down and a sample obtained for workup.

A second, short thermal run is planned to evaluate a modified temperature control strategy, since cascade control used on the first run was poor. This will be followed by an extended thermal run to check-out feasibility of unattended operation.

While mechanical operation of the CSTR has proved to be satisfactory, two major equipment problems remain. The weigh scale, needed for determination of slurry feed rate, was removed and returned to the vendor after numerous attempts to correct its faulty operation. An alternative system was purchased, with delivery expected in August. Also, attempts to obtain satisfactory level probes for the product receivers have not been successful. The originally installed units were returned to the vendor and an alternative probe for the main receiver only was purchased and checked out. While the device could be spanned and zeroed at atmospheric pressure, it lost calibration at operating conditions. Discussions with the new vendor were initiated to determine the source of the problem. Installation of a differential pressure device is also being investigated.

6.2 Analytical Plan

The analytical sampling plan for Task 6 encompasses analyses of feeds and products for continuous aging tests.

6.2.1 Feeds

Coals are statistically samples and analyzed as follows upon receipt:

- a) Ultimate analysis
- b) Proximate analysis
- c) Colorific value
- d) Sulfate sulfur*

* These analyses will be performed periodically during storage.

Slurry solvents are statistically sampled and analyzed as follows:

- a) C,H,N*
- b) O
- c) Moisture
- d) Ash
- e) Viscosity*
- f) Density
- g) Basic N
- h) Analytical distillation (D1160)
- i) Flash and fire point

These feeds are additionally analyzed as part of the coal slurry. Each batch of slurry prepared is sampled and analyzed for the following:

- a) C,H,N
- b) Moisture
- c) Ash
- d) Density
- e) Viscosity

6.2.2. Product

Product from the reactor is collected daily over a two-hour period. A portion of each day's sample is analyzed by pressure filtration (see Section 5.3.3). The bulk of the sample is split into tetrahydrofuran (THF) soluble and insoluble fractions. The THF insolubles are analyzed for ash content. The THF solubles are stripped of THF and analyzed as follows:

- a) C,H,N,O
- b) Sulfur
- c) Moisture
- d) Basic nitrogen
- e) Residual THF

A portion of the THF solubles is distilled using a modified ASTM D1160 procedure. The fraction boiling below 972°F (760 torr) is analyzed as follows:

- a) C,H,N,O
- b) S
- c) Basic N
- d) Composition (gas chromatography)

The 972°F⁺ fraction is analyzed for C,H,N,O,S and viscosity (if possible).

Spent catalyst from the reactor will also be analyzed.

6.2.3 Analytical Procedures

A short summary of the analytical procedures used for this task is included below. A more complete compendium of procedures will be included in a later report.

Elemental Analysis by High Temperature Combustion

See Section 5.3.3

Water

Water is quantified on a Photovolt Aquatest IV moisture analyzer which utilizes coulometrically generated iodine to complete the Karl Fischer reagent. The sample is injected into the sample chamber and the instrument generates Karl Fischer reagent until the water is consumed. Water detection is accomplished with a dual platinum sensing electrode. Percent water is then automatically calculated and displayed.

Ash

Ash is determined in accordance with ASTM Method D482 "Standard Test Method for Ash from Petroleum Products". The sample is ignited and allowed to burn. The residue is reduced to ash in a muffle furnace and then weighed.

Density

Density is determined using a Mettler/Paar Model DMA 10 digital densimeter. A U-shaped hollow oscillating tube is filled with the sample and the period of the natural frequency of oscillation is measured automatically by the instrument. By comparing the period obtained with those obtained using air and water, the density of the sample can be quickly and accurately calculated.

Kinematic Viscosity

Kinematic viscosity is determined according to ASTM Method D445 "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)". The sample is introduced into the calibrated viscometer. The time it takes to flow through a capillary is measured. Kinematic viscosity is calculated from this value.

Microfiltration

See Section 5.2.3

X-ray Fluorescence Sulfur (XRF)

X-rays are emitted from a chromium target at 40kv. They impinge on the sample which absorbs the radiation and fluoresces. The sulfur fluorescence line is separated from the spectrum with a crystal monochromator and its intensity is measured with a proportional counter. The sulfur content is then calculated relative to a series of standards.

Parr Bomb Sulfur

The sample is fired in a Parr oxygen bomb calorimeter. The SO_2 formed is precipitated as barium sulfate and quantified with a Dionex ion exchange chromatograph.

Basic Nitrogen

Basic nitrogen compounds are determined by potentiometric titration on a Metrohm E636 Titroprocessor with perchloric acid in acetic acid/toluene. The electrode system consists of a glass electrode and a saturated calomel electrode. The titrator automatically locates the equivalence point and calculates the final results.

Ultimate, Proximate and Calorific Value Analyses

These will be performed by an outside laboratory according to ASTM methods D3176, D3172, and D2015 respectively.

Sulfate Sulfur

The coal is extracted with hydrochloric acid to remove the sulfates. The sulfates are quantified with a Dionex ion exchange chromatograph.

7. Task 8: ANALYTICAL METHODS REVIEW

7.1 Introduction

In this quarter surface characterization of experimental bead catalysts continued. The work focused on X-ray photoelectron spectroscopy (XPS or ESCA) and electron microprobe analysis of fresh catalysts. An overview of those results and some comparisons with conversion results in the batch test which relate to catalyst activity are included.

7.2 Results and Discussion

In the last quarterly report the microprobe results for most of the fresh bead catalysts were compiled (1). Since that time, all of the fresh bead catalysts have been examined by electron microprobe analysis and the trends are the same. Generally the Ni, Co and Cr are uniformly distributed across the catalyst bead diameter while the Mo and P are not generally uniformly dispersed. The first group of catalysts examined are the samples labelled 1-1E in Table 7.1 and they showed the poorest Mo distributions. However, the Mo and P distributions were more uniform in catalysts made after the initial group. In spite of the non-uniform distributions in the first group of catalysts, the catalyst activity was as expected based on Mo content in the batch tests. It may be that the uniformity of the Ni and Co is more important than the non-uniformity of the Mo with respect to conversion in the batch reactor.

TABLE 7.1

COMPILATION OF SURFACE ANALYSIS DATA WITH
BULK METAL LOADINGS AND CONVERSION VALUES

SAMPLE	MICROPROBE	ESCA DATA FRESH POWDERS						METALS LOADING						BATCH TEST ³ TOLUENE SOLUBLE CONVERSION(%)
	Mo c/e ¹	MoO ₃	NiO	CoO	P ₂ O ₅	Cr ₂ O ₃	Na ₂ O	MoO ₃	NiO	CoO	P ₂ O ₅	Cr ₂ O ₃	Na ₂ O	
1	.46	12.8	3.2	Δ				10.5	3.1					72.5
1A	.47	11.4	2.8					10.2	3.0					72.4
1B	.63	12.0	1.2	1.2				10.3	1.5	1.5				73.7
1C	.56	10.9	2.8					10.3	3.1					72.2
1D	.68	13.8	2.6					10.7	3.0					72.5
1E	.50	11.9	3.1					10.6	3.0					72.2
2	.82	21.0	*	*		5.2		17.9	1.4	1.2		4.6		72.4
3	.68	8.1			4.3			4.6			2.2			67.3
4	.70	2.4		1.3			3.0	1.8		2.9			2.0	62.1
5	.80	9.9	.8		4.1			9.5	1.9		2.7			69.9, 70.0
6	.72	17.3		2.3	2.4			14.2		2.3	2.0			72.4
7	1.01	8.5	1.3				3.5	5.3	1.5				1.8	65.7
8	.57	5.8	2.6		4.5			1.9	2.9		2.8			65.6
9	.63	12.6	1.8	1.8				9.8	1.5	1.4				72.7
10	.78	13.1				2.1		10.1				4.8		68.3
11	.94	7.7	1.4	2.2	3.1			4.9	1.5	1.4	2.3			68.9, 72.1
12	.88	2.0						1.8						63.0
13	.73	9.1		2.4		2.4		9.9		2.7		4.6		72.3
14	.80	10.1	1.3		5.3			10.9	1.6		2.2			72.0
15	.78	12.3	1.4				3.5	13.1	3.0				2.8	72.8, 72.3
16	.84	3.9	*			5.8		2.0	1.5			5.0		61.9
17	.65	8.9	1.9		3.5			9.6	2.8		2.4			73.3, 76.7
18	.55	9.3	.9	*			2.1	10.8	1.5	1.5			2.0	67.8
19	.66	21.8			2.0			16.0			2.2			71.1
20	.90	6.1		1.6				4.7		2.3				67.9
21	.71	13.8					4.0	11.2					2.0	63.2, 66.6
22	.75	9.0		2.0	1.9			10.0		2.8	2.5			63.1
23	.70	19.4	1.3					16.0	1.5					70.3
24	.87	5.3	3.2		1.1	5.2		5.2	2.8			4.6		66.4
25	.92	3.0	1.5		4.0			1.8	1.4	1.4	2.5			61.0

Δ - All blanks left in the table indicate elements not present in that catalyst

* - Indicates that an element was not observed in the ESCA spectrum although present in bulk metal loadings

¹ c/e - is center to edge ratio

² - This is the first group of catalysts made and examined. See Reference 1

³ - Toluene soluble conversion is a measure of catalyst activity. See Section 5.
catalyst is.

The batch test is run primarily with powdered samples. In order to compare conversion numbers with surface characterizations ESCA spectra of the powdered fresh catalysts were collected. ESCA results are normally reported as atomic percents. A computer program was written to convert from atomic to weight percents so that comparisons could also be made with bulk metals loadings determined by EDX and DC Plasma. The results are compiled in Table 7.1. Generally, the ESCA results and the bulk weight percents are very similar. It is of interest to study samples where the ESCA results are very different from the bulk metal loadings and to determine whether these samples show significantly better or poorer conversions than the norm. Samples 2, 3, 7, 8, 16 and 18 all show ESCA weight percents different from the bulk metal loadings. In Samples 2, 3, 16 and 18 promoters (NiO or CoO or both) are not observed in the ESCA spectra. However, this may be due to the very high noise levels present.

To compare conversion values an uncorrected average of the values for given MoO_3 levels was calculated (see Table 7.2). This is a very simplistic comparison since no corrections have been made for the differences between catalysts which might effect the results. (See Sec. 5) Samples 2, 3, and 16 show conversions very near the

TABLE 7.2

COMPARISON OF BATCH TEST RESULTS WITH MoO_3 LEVELS

<u>MoO_3 LEVEL¹</u>	<u>Average Uncorrected Toluene Soluble Conversion (%)²</u>
2	62.7
5	67.2
10	69.5
15	71.8

¹ MoO_3 levels are given in weight percents and are based on the design rather than the determined metal loadings.

²Toluene soluble conversion is a measure of catalyst activity, that is the higher the percent the more active the catalyst is.

average value. The conversion value for sample 18 is lower than the average, but sample 18 also contains Na_2O which has been shown to lower conversions.

Samples 7 and 8 show higher MoO_3 levels in the ESCA study than the bulk metals loadings. Sample 7 shows poorer conversion than the average, but like sample 18 it contains Na_2O . However, sample 8 shows better conversion than the average and would be interesting to study further.

At least with the fresh catalysts there are not very many differences between bulk metals loadings and the ESCA results for powdered samples. This data will provide a baseline for future work to be done.

7.3 References

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