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COMPOSITE-BED REACTOR FOR UPGRADING
COAL-DERIVED LIQUIDS

Quarterly Progress Report for the Period April 1—June 30, 1984

By
Billy L. Crynes
Mayis Seapan

July 9, 1984

Work Performed Under Contract No. FG22-83PC60787

Oklahoma State University
Stillwater, Oklahoma

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School of Chemical Engineering
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Stillwater, Oklahoma 74078

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COMPOSITE-BED REACTOR FOR UPGRADING COAL-DERIVED LIQUIDS

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ABSTRACT

Five experimental runs were conducted as a part of the temperature and catalyst zoned reactor study. Four experiments were made using the temperature zoned concept. These experiments were conducted at 10.3 MPa (1500 psig), with the bottom zone reactor at 400°C (752°F), LHST of 1.9 h, with 20% (wt) of the catalyst in the top zone and utilizing a variable temperature in the top zone 400-500°C (752-932°F). Excessive reactor plugging occurred when the top zone was operated at 500°C (932°F). This suggests an upper limit when utilizing the feedstock of 15% (wt) mixture of SRC in a coal liquefaction process solvent, and with a commercial grade catalyst, Armak KF-153-S, a Ni-Mo type. All temperature zoning combinations showed a loss in catalyst activation over the experimental run durations of 72 h. Activity loss was rapid in the first 30 to 40 h and gradual thereafter. This activity loss was caused by carbonaceous material and metals deposition. Increasing the top zone temperature from 400 (752°F) to 450°C (842°F) provided a beneficial effect on HDN and HDM activity. A further temperature increase was detrimental because of excessive coking and possible thermodynamic equilibrium limitations.

The one reference run that was conducted for the catalyst zone study utilized 400°C (752°F) in both zones, the same feedstock, catalyst, and operational conditions as reported above. Sample analyses are not yet completed.

INTRODUCTION

In upgrading steps for coal-derived liquids the heterogeneous catalysts are known to experience rapid activity decay. The emphasis in this research is directed toward hydrotreatment, including hydrocracking, of coal-derived liquids. The heteroatoms present in coal-derived liquids must be reduced; the liquids may require reduction in molecular weight and viscosity, and small quantities of inorganic components may need to be reduced.

This study incorporates a two zone, packed bed reactor with the capability of sampling between the zones. The zones will contain catalysts of different properties and will be operated at different temperatures. This is a highly flexible system that offers possibilities for maintaining catalyst activity and for "tuning" reactions to achieve liquids upgrading with reduced hydrogen consumption.

TASK STATEMENTS

The overall objective of this study is to assess the advantage of composite-bed reactors with respect to the maintenance of catalyst activity while processing coal-derived liquids. The following subtasks will be addressed:

1. Using a reference catalyst and liquid, a set of experiments will be conducted to evaluate the advantage of operating a two zone, fixed-bed reactor at different temperatures in each zone.
2. A set of experiments on a reference liquid and at reference conditions will be conducted to evaluate the advantage of having catalysts of differing types (active metal species).

3. A set of experiments will be conducted to evaluate the advantage of maintaining catalysts in two separate zones wherein the pore properties of the catalysts vary significantly.
4. The kinetics of heteroatom removal, asphaltene or residue conversion, and hydrogenation in the single- and composite-bed studies will be investigated using the experimental data.
5. The activity-time profiles for the various reactor systems will be evaluated and characterized.

ACCOMPLISHMENTS

During this report period four experimental runs were completed as part of the temperature zoned reactor study, and one was made as a reference experiment for the catalyst zoned reactor study. The individual task activities are summarized here:

Task 1 (John R. Beazer) A total of six experimental runs were conducted in a two-stage trickle-bed reactor. The sixth run was a duplicate of the fourth run as a check on precision and reproducibility. In each run, the operating pressure was maintained at 10.3 MPa (1500 psig). The reactors were loaded with 20% of the total catalyst in the top zone and the remainder in the lower zone. The temperature in the top zone was operated in 25° increments from 400 to 500°C (752-937°F) while the temperature in the lower zone was always maintained at 400°C (752°F). The space time (based on total bed volume) was held at 1.9 h and the hydrogen flow rate was kept at 1781 std m³/m³ of oil (10,000 SCF/bbl). The feedstock was a 15% (wt) SRC solids in a process solvent and the catalyst was a Ni-Mo-Al₂O₃ catalyst (Armak KF-153-S).

Feedstock and catalyst properties were given in Quarterly Report DOE/PC/60787-1, January 17, 1984.

Table I summarizes the experimental run conditions and gives a brief comment on operating problems. Run TZE was shut down after only six hours of operation due to excessive reactor plugging; no liquid, catalyst or gas analyses were taken from this run. Excessive plugging due to interstitial deposits indicate that 500°C (937°F) is too high a temperature to attempt hydrotreating this feedstock.

Liquid samples taken every 6-12 h were analyzed for N, H and C content by a Perkin-Elmer 240B elemental analyzer. Figures 1-5 show the N% (wt) for each sample as a function of time on stream. In each case, the catalyst lost a significant amount of HDN activity. Rapid activity loss occurred until 48-60 h, after which the activity loss leveled off. Similar loss in HDN activity when processing coal liquids was observed by Chang (1982), Ahmed (1979), and Bhan (1983). The catalyst activity loss can be attributed to coking and metals deposition (Chang, 1982).

The HDN activity of the catalyst showed a dependence on the top zone temperature. As the temperature in the top zone increased from 400°C (752°F) to 450°C (842°F), the N removal also increased; a kinetics effect.

However, for the temperature increase to 475°C (887°F), the final product N content was greater than that for any other run. At 475°C (887°F), more coke (carbonaceous material) was deposited on the catalyst surface. Coke blocks pores and covers active sites which severely reduce the effective area for hydrotreating. Also, at 475°C (887°F), the top bed contained large amounts of interstitial deposits. A carbonaceous ash residue "glued" the catalyst pellets together which caused poor catalyst wetting and mass transfer, thus reducing the HDN activity.

The effect of top zone temperature was also evident in the liquid sample H contents. Table II lists the H% (wt) for each run. Runs TZA, TZB, and TZC (400-450°C) (752-842°F) all showed consistent H contents of about 10.2% (wt). Run TZD (475°C) (887°F), however, showed a marked decline in hydrogen content after 26 h of operation and resulted in only 9.3% (wt) H by the end of the run. Here, the reaction kinetics effect was overcome by the equilibrium limits of hydrogenation. Ahmed (1979) and Ternan et al. (1982) reported that hydrotreating coal-derived liquids at too high of a temperature can cause dehydrogenation due to unfavorable thermodynamic equilibrium. Also, coke deposits and poor reactor performance due to interstitial deposits could also contribute to the decreased hydrogen activity.

Figure 6 presents the N% (wt) of the interstage samples for each run, and Table III lists the H% (wt) of the interstage samples. These samples are withdrawn by a special device between the two catalyst zones. The interstage samples showed only slight HDN and exhibited little or no catalyst deactivation. However, these samples did contain more H than the feedstock (7.3% wt) and the H content gradually decreased with time on stream.

Liquid samples collected between 48-60 h on stream were vacuum distilled according to the ASTM D-1160 procedure. As the top zone temperature increased, the normal boiling point curve slightly shifted. This shift was due to a temperature effect on increasing cracking and hydrocracking. This effect was also illustrated in the vol % of the three distillate types. As the top zone temperature increased, the light oils increased from 2 to 8% (vol), and the heavy ends decreased from 40 to 30% (vol). The shift in the normal boiling point curve and changes in vol % light oil and heavy ends were not excessive since only 20% (wt) of the total catalyst was in the high temperature top zones.

Spent catalysts were Soxhlet extracted with tetrahydrofuran for 24 h and dried in a vacuum oven. These aged catalyst samples were analyzed for coke content which was defined as the % wt loss in catalyst upon combustion at 475°C (887°F). Aged catalyst sample weight reduction occurs not only by the combustion of carbonaceous deposits but also by oxidation of the active (Ni, Mo) and deposited metals (Fe, Ti) sulfides. Bhan (1983) reported a 3.3% (wt) reduction due to active metal oxidation for the KF-153-S catalyst. Catalyst coke content data are reported with correction for active metal oxidation; no estimate could be made for the weight reduction associated with deposited metals oxidation.

Table V presents the coke content of the aged catalyst for each run. The coke content for each individual zone from top to bottom was relatively constant. Chang (1982) reported that coke content is greater at the top section of a reactor zone if the coking rate is still rapidly increasing. Once a maximum coking rate has been attained, the reactor zone will show constant coke content in each section. This result, along with the profile of HDN activity loss, shows that in each run the maximum coking rate was attained before 72 h and probably began leveling off at 40-60 h.

The hydrotreating temperature of the top zone showed definite effects on the catalyst coke content in the top zone (Figure 8). For the temperature range of 400-450°C (752-842°F) only a small increase in coke content was reported (3.7% wt). However, for the change from 450 (842°F) to 475°C (887°F), a large increase in the catalyst coke content was observed (7.3% wt). Ternan et al. (1979) hydrotreated a heavy gas oil from hydrocracking bitumen and found similar coking activity. They found the coke content increased with temperature up to approximately 375°C (707°F); it remained constant from 375 (707°F) to 440°C (824°F); above 440°C (824°F), the coke

content increased markedly with temperature. Ternan et al. hypothesized that the flat spot in the coking profile was related to a phenomenon of adsorption or reactivity of hydrogen on the catalyst surface counteracting the tendency for increased coke formation. This effect of temperature on coke content was also reported by Ahmed (1979) who hydrotreated FMC coal oil at 10.3 MPa (1500 psig) and 3.0 h over a commercial Co-Mo catalyst. He ran experiments at 371, 427, and 454°C (700, 800, 850°F) and reported coke contents of 21.3, 20.8, and 38.0% (wt), respectively.

The catalyst coke content of the lower zone slightly increased with increasing top zone temperature. For a top zone temperature of 400°C (752°F) the lower zone coke content was 21.8% (wt) while at a top zone temperature of 475°C (887°F), a coke content of 26.6% (wt) was reported. This indicated that even though the top bed hydrotreated some of the coke precursors, the feed to the second stage was still high in polynuclear aromatic compounds.

Spent catalysts were examined for metals by Energy Dispersive X-ray Analysis (EDAX) in a Scanning Electron Microscope (SEM). Although the EDAX analyses are only semi-quantitative, they are helpful in determining the types of metals present and where the deposits concentrate.

Table VI lists the average metal deposition in the reactor zones in terms of area %. The amount of Fe deposited was approximately the same for each run indicating that removal of Fe compounds was relatively temperature independent. Ti deposits, however, showed a dependence on operating temperature. As the reactor temperature increased from 400 (752°F) to 475°C (887°F), the relative amount of Ti increased. Tamm et al. (1981) hydrotreated Arabian heavy oil and found organometallic compounds to follow the Arrhenius law where increases in temperature exponentially increased HDM rates.

Task 2 (Robert T. Newton) One experimental run was completed to establish reference data. Run CA was operated at 400°C (752°F) and 10.3 MPa (1500 psig). The catalyst and feedstock were the same as those used in Task 1. For this reference run, the same catalyst was used in both reactor zones.

Liquid samples were taken every 6 h for the first 48 h and every 12 h thereafter up to end of run, 72 h. The liquid samples will be analyzed for H, N, and C content and ASTM distillations will be performed on selected samples.

Severe plugging occurred throughout the run, sometimes requiring a pressure drop of 3.4 MPa (500 psi) to regain normal operation. Plugging was probably caused by a glass packing bead which was found in the intermediate sampling valve after the run.

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TABLE I
EXPERIMENTAL RUN PARAMETERS

Reactor: two-stage trickle bed		Hydrogen flow rate: 1781 std m ³ /m ³		
Pressure: 10.3 MPa (1500 psig)		Space time: 1.9 h		
Run Name	Temperature (°C)		Time on Oil (h)	Comments on Operation
	Top Zone	Bottom Zone		
TZA*	400	400	72	no problems during run
TZB	425	400	72	no plugging problems, maximum pressure drop across reactor was 0.4 MPa
TZC**	450	400	72	slight plugging problems occurred at about 58 h, maximum pressure drop across reactor was 0.7 MPa
TZD	475	400	72	slight plugging at about 30 h, progressively worse plugging, maximum pressure drop across reactor was 5.5 MPa
TZE	500	400	6	severe reactor plugging caused shut down after 6 h, maximum pressure drop across reactor was 10.3 MPa
TZF	475	400	72	slight plugging at about 36 h, progressively worse plugging, maximum pressure drop across reactor was 6.9 MPa

* Previously named TD in Quarterly Report DOE/PC/60787-2, April 17, 1984.

** Previously named TB in Quarterly Report DOE/PC/60787-2, April 17, 1984.

TABLE II
HYDROGEN CONTENT OF LIQUID SAMPLES
(wt%)

<u>Time on Stream (h)</u>	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
6	10.5	10.3	--*	10.6
12	10.8	9.9	10.3	10.8
18	10.6	9.8	---	10.2
24	10.0	10.1	10.5	10.2
30	10.3	10.0	---	9.9
36	9.3	9.6	10.2	9.7
48	10.0	9.3	10.0	9.2
60	10.1	10.1	10.1	9.2
72	9.8	10.0	10.0	9.5

* Samples taken every 12 h
Feedstock contained 7.3 % (wt) H

TABLE III

HYDROGEN CONTENT OF INTERSTAGE SAMPLES
(wt%)

<u>Time on Stream (h)</u>	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
6	7.5	9.1	--	8.7
12	8.1	8.2	8.1	8.3
18	7.9	8.6	--	8.1
24	8.0	8.6	8.4	8.1
30	8.0	8.1	--	8.1
36	8.0	8.2	8.6	8.0
48	7.7	8.5	8.8	7.8
60	8.0	8.3	8.5	8.3
72	8.1	8.2	8.5	7.8

* Feedstock contained 7.3 % (wt) H

TABLE IV
DISTRIBUTION OF LIQUID SAMPLES AS A
FUNCTION OF BOILING POINT RANGE

<u>Volume % distilled</u>	<u>TZA</u>	<u>TZB</u>	<u>Temperature (°C)</u>		<u>FEED</u>
			<u>TZC</u>	<u>TZD</u>	
initial	195	160	150	155	250
10	250	245	237	237	275
20	273	270	265	271	291
30	290	286	280	287	305
40	305	297	295	298	323
50	323	310	310	313	337
60	343	328	328	332	360
70	378	350	355	352	395
80	425	385	395	393	450
wt residues (grams)	9.9	11.0	5.0	8.1	21.7
light oil (vol%) T<216°C	2.0	5.5	7.0	7.5	0.0
mid-distillate (vol%) 216<T<343°C	58.0	62.5	60.0	60.5	52.0
heavy ends (vol%) T>343°C	40.0	32.0	33.0	32.0	48.0

TABLE V
CATALYST COKE CONTENT

<u>Section</u>	Weight Percent			
	<u>TZA (400°C)</u>	<u>TZB (425°C)</u>	<u>TZC (450°C)</u>	<u>TZD (475°C)</u>
<u>TOP ZONE</u>				
Top	28.6	29.0	29.6	35.8
Middle	25.5	29.1	31.2	41.5
<u>Bottom</u>	<u>27.1</u>	<u>25.3</u>	<u>31.2</u>	<u>36.8</u>
Average	27.0	27.8	30.7	38.0
<u>LOWER ZONE</u>				
Top	23.6	23.9	25.8	26.8
Upper Middle	23.5	19.2	24.3	25.5
Lower Middle	19.1	24.1	24.8	26.4
<u>Bottom</u>	<u>21.1</u>	<u>19.7</u>	<u>24.5</u>	<u>28.0</u>
Average	21.8	21.8	24.8	26.6

TABLE VI
AVERAGE METAL DEPOSITION IN REACTOR ZONES

Run	Zone	Area Percent		
		Fe	Ti	Cr
TZA (400°C)	Top	26.8	0.8	3.6
	Lower	9.8	3.5	0.6
TZB (425°C)	Top	30.1	2.3	5.3
	Lower	10.2	1.9	0.4
TZC (450°C)	Top	32.3	3.9	5.1
	Lower	9.5	2.6	0.2
TZD (475°C)	Top	32.4	7.4	2.0
	Lower	11.9	6.0	0.1

Figure 1. Effect of Time on Stream on Nitrogen Content, TZA.

Figure 2. Effect of Time on Stream on Nitrogen Content, TZB.

Figure 3. Effect of Time on Stream on Nitrogen Content, TZC.

Figure 4. Effect of Time on Stream on Nitrogen Content, TZD.

Figure 5. Effect of Time on Stream on Nitrogen Content, all runs.

Figure 6. Effect of Time on Stream on Nitrogen Content, interstage samples.

Figure 7. Boiling Point Distribution of Run TZA, TZB, TZC, and TZD.

Figure 8. Effect of Top Zone Temperature on Catalyst Coke Content.

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