CATALYTIC COAL LIQUEFACTION

MASTER

Quarterly Report for the
Period January-March, 1981

Sol W. Weller
State University of New York at Buffalo

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for the United States
Department of Energy
Under Contract No. DE-AC2276-ET-10518

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. Objectives and Scope of Work

This research has the following scope and objectives:

1. To develop improved coal liquefaction catalysts containing supported molybdena, by establishing the effects of pore size and composition in particulate catalysts, composition in monolith catalysts, and shell thickness in shell catalysts.
2. To extend the O_2 chemisorption technique for determination of specific surface area of molybdena to a temperature of -78°C rather than -195°C , to sulfide catalysts, to monolith and "shell" catalysts, and to used, regenerated catalysts.
3. To explore the role of unsupported catalysts in coal liquefaction.
4. To use hydrotreating of methylnaphthalene and/or other aromatic compounds as a convenient means of screening several catalytic functions of liquefaction catalysts.

II. Summary of Progress to Date

A new tubing bomb micro reactor has been designed, constructed, and tested. It is suitable for catalyst comparisons in experiments of widely differing nature. The reactor is capable of initial pressurization with H_2 , heating, pressure monitoring during a run, and G.C. analysis of gaseous products.

An extensive series of runs has been completed on the hydrotreating of 1-methylnaphthalene as a multifunctional catalyst screening test at 500°C . Six Co/Mo/ Al_2O_3 catalysts from four suppliers have been tested (after presulfiding), along with a comparison run with stannous chloride. At a catalyst level of 0.5 wt.%, the rank-ordering of activity for ring hydrogenation (RHG) was Cyanamid HDS-1442B > Amocat 1A > Harshaw 0402T > Akzo PA-23924 > Amocat 1B > Akzo 77-RAM-3. Ring hydrocracking (RHC) activity decreased in the order Amocat 1A > Amocat 1B > Akzo PA-23924 > Harshaw 0402T > Akzo 77-RAM-3 > Cyanamid HDS-1442B. Hydrodemethylation (HDM) is almost unaffected by Co/Mo/ Al_2O_3 catalysts. At 500°C , the extent of RHC and HDM is much greater than at 450°C , but the extent of RHG is much less.

III. Detailed Description of Technical Progress.

Task No. 1: Improved Supported Catalysts.

No new data are available for this Report.

Task No. 2: Specific Surface Area of Molybdena.

No data are available for this Report.

Task No. 3: Role of Unsupported Catalysts.

To permit more convenient testing of catalysts in the presence of $H_2(g)$, a new tubing bomb reactor has been designed, constructed, and successfully tested. The reactor is in the shape of an inverted tee. It is capable of initial pressurization, heating, pressure monitoring during a run, and G.C. analysis of gaseous products after a run. It is intended for catalyst comparison, not for rapid kinetic studies.

Figure 1 shows the design and dimensions of the tubing bomb reactor. Stainless steel tubing (type 316) and high pressure fittings were purchased from Autoclave Engineers. Pressure is monitored by a pressure transducer (J. P. Semiconductor JPX series) in conjunction with a strip chart recorder Linear Instruments Model 555). Excitation current to the transducer is supplied by a strain-gage amplifier (Action Instruments AP4251). A typical pressure profile during a run is shown in Figure 2.

The heated region of the reactor is limited to the horizontal section of the inverted tee. The long vertical stem is unheated and exposed to ambient air. This serves to prevent both heat buildup and condensation of products in the pressure transducer and valve. By maintaining the transducer at room temperature, even during a run at $400^\circ C$, temperature effects on the transducer output are eliminated. Coned and threaded fittings are used for the 9/16" and 3/8" O.D. tubing, to prevent leakage which might occur during cyclic use of the reactor.

The total volume of the reactor is ca. 29 cm^3 . Of this, the heated horizontal section makes up 21.8 cm^3 . A typical charge to the reactor is 10g tetralin, 2g coal, and 1000 psi (cold) H_2 .

End-to-end mixing is achieved by shaking the reactor around a pivot point on the vertical section. As presently set up, the reactor is shaken through an angle of $\pm 20^\circ$ (with reference to the horizontal) by a motor (Dayton A.C. Induction Motor Model 5K339K) plus speed reducer (Dayton Model 22152B) operating at 67RPM.

Fig. 1 Tubing Bomb Reactor

Fig. 2 Pressure Profile (Run without catalyst)

Heating of the reactor is accomplished with a flexible electric heating tape (Briskheat) wrapped around aluminum foil. The entire horizontal section is then enclosed in a thin steel cylinder lined with ceramic fiber insulation. Two thermocouples, directly in contact with the reactor tubing, serve to monitor and control (via a temperature controller) the reactor temperature.

Results obtained with this apparatus will be reported in the next Quarterly Report.

Task No. 4: Multifunctional Screening Tests.

In FE-2013-14, exploratory studies were reported on hydrotreating of 1-methylnaphthalene at 450°C. A number of Co/Mo/Al₂O₃ catalysts obtained from Harshaw, Cyanamid, and Akzo Chemie were rank-ordered with respect to ring hydrogenation activity. SnCl₂, also tested, was found to be quite inactive for ring hydrogenation but unusually active for hydrodemethylation.

These studies have now been extended to 500°C. for a number of the Co/Mo/Al₂O₃ catalysts. Also included in the present study were Amocat 1A and Amocat 1B; these samples were obtained through the courtesy of Amoco. The properties of the as-received catalysts are summarized in Table 1.

All the catalysts were presulfided (15% H₂S-85% H₂, 2 hrs., 450°C) before testing. The tests were made in a 1L stirred autoclave (MagneDrive) for 30 min. at 500°C. The charge to the autoclave was 200 g 1-methyl naphthalene (1-MN), 1g catalyst (ground), and 1000 psia (cold) H₂. Two blank runs with no catalyst and one run with SnCl₂ (1g) were also made. 1-MN was obtained from two

Table 1.
Properties of As-Received Catalysts

	Harshaw 0402T	Akzo PA-23924	Akzo 77-RAM-3	Cyanamid HDS-1442B	Amocat 1A	Amocat 1B
% CoO	3.0	4.0	2.5	3.2	3.2	--
% MoO ₃	15.0	11.5	8.1	16.0	16.2	14.9
% SiO ₂	5.0	--	--	0.2	--	--
Surf. area, m ² /g	200	150	86	330	154	167
Pore volume, cc/g	0.40	0.50	0.55	0.80	0.47	0.51

sources, Eastman Kodak and Fisher Scientific; these differed somewhat in purity (see below). As previously reported, interpretation of results was based on (1) final autoclave pressure after cooling, (2) G. C. analysis of the autoclave gas, and (3) G. C. analysis of the liquid in the glass liner.

A total of 14 runs were made; these are listed in Table 2 in chronological order. Also listed for each run in Table 2 are the source of 1-MN, the final (cold) pressure, and the moles of CH_4 and C_2H_6 produced per 200g 1-MN. Runs 4 and 5 are duplicates, as are 10 and 11. Runs 1 and 2 differed in that autoclave glass liner was omitted in Run 2. Gas analyses are not presented except for the CH_4 and C_2H_6 contents; C_3H_8 and higher hydrocarbons were not present in measurable quantity.

The analyses (G.C., area %) of the liquid products are listed in Table 3. For simplicity, the contents of alkyl benzenes are lumped in the table.

The results shown in Table 3 have been grouped in Table 4 in order to bring out more clearly the extent to which three types of reaction were occurring:

TABLE 2 Summary of Runs

RUN no.	Catalyst	Source of 1-methyl naphthalene	P_f (psia)	CH_4 (moles)	C_2H_6 (moles)
1	None (blank)	Kodak	955	0.31	0.01
2*	None (blank)	Kodak	880	0.35	0.01
3	Harshaw 0402T	Kodak	697	0.3	0.03
4	Harshaw 0402T	Fisher	706	0.3	0.02
5	Harshaw 0402T	Fisher	710	0.3	0.02
6	Akzo-Chemie 77-RAM-3	Kodak	731	0.3	0.02
7	Akzo-Chemie 77-RAM-3	Fisher	749	0.32	0.02
8	Akzo-Chemie PA-23924	Kodak	728	0.32	0.02
9	Akzo-Chemie PA-23924	Fisher	715	0.31	0.02
10	Amocat 1A	Fisher	650	0.33	0.02
11	Amocat 1A	Fisher	645	0.33	0.02
12	Amocat 1B	Fisher	715	0.32	0.03
13	Sn Cl_2	Fisher	900	0.37	0.01
14	Cyanamid HDS-1442B	Fisher	671	0.34	0.02

*Glass liner was not used

TABLE 3 Analyses of Liquid Product (Area %)

RUN no.	Alkyl benzenes	T	N	1-MT	5-MT	6-MT	1-MN	X
1	0.7	0.1	19.2	0.6	0.1	-	78.1	1.2
2	1.1	0.3	23.7	1.0	0.1	-	72.9	0.9
3	5.0	2.3	20.1	1.7	2.3	0.1	66.1	2.4
4	3.5	2.0	18.6	2.6	2.3	0.2	69.0	1.8
5	3.4	2.1	18.6	2.1	2.6	0.2	69.0	2.0
6	4.6	2.0	18.0	1.4	2.0	trace	69.2	2.8
7	2.9	1.8	19.4	1.9	2.1	0.1	69.7	2.1
8	4.5	1.7	18.4	1.8	2.4	trace	68.7	2.5
9	3.9	2.0	19.7	2.1	2.8	trace	68.7	1.4
10	4.2	2.8	18.5	2.6	3.3	0.1	66.1	2.4
11	4.3	2.6	19.3	2.3	3.2	0.1	66.0	2.2
12	4.2	1.8	19.4	1.8	2.9	0.1	68.3	1.5
13	0.3	0.2	23.4	2.3	0.2	-	73.4	0.2
14	2.7	3.2	18.8	3.6	3.6	0.1	66.8	2.3

Key: T = tetralin, N = naphthalene

1-MT = 1-methyltetralin, 5-MT = 5-methyl tetralin

6-MT = 6-methyl tetralin, 1MN = 1-methylnaphthalene

X = 2-methylnaphthalene and compounds with retention time greater than that of 1-MN.

TABLE 4 Reaction Summary

RUN no.	HDM	RHC	RHG
1	19.3	0.7	0.8
2	24.0	1.1	1.4
3	22.4	5.0	6.4
4	20.6	3.5	7.1
5	20.7	3.4	7.0
6	20.0	4.6	5.4
7	21.2	2.9	5.9
8	20.1	4.5	5.9
9	21.7	3.9	6.9
10	21.3	4.2	8.8
11	21.9	4.3	8.2
12	21.2	4.2	6.6
13	23.6	0.3	2.7
14	22.0	2.7	9.4

Key: HDM = hydrodemethylation = naphthalene + tetralin

RHC = ring hydrocracking = lumped alkylbenzenes

RHG = ring hydrogenation = tetralin + methyltetralins

these are hydrodemethylation (HDM), ring hydrocracking (RHC), and ring hydrogenation (RHG). The sum of naphthalene and tetralin is taken as the measure of HDM; lumped alkyl benzenes are the measure of RHC; and the sum of tetralin and methyltetralins (principally 1- and 5-MT) is the measure of RHG. The use of "area %" in the liquid analyses distorts the absolute values of these three reactions, but comparisons of catalysts are unaffected by this complication.

A number of conclusions may be drawn from the data in Tables 2-4:

1. A small amount of liquid is always found outside the glass liner which is routinely used in the autoclave. Analysis of this liquid always indicates a somewhat higher conversion than in the main liquid product (inside the liner). The possibility that the outside liquid is the result of splashing was ruled out by a blank run with stirring but no heating; in this case no liquid was found outside the liner. The possibility that it results from simple dripping of reflux condensate is not borne out by Run 2 (no liner used), which showed higher conversion than its duplicate, Run 1. It is probable that the higher conversion in the outside liquid reflects exposure of this liquid to the autoclave walls, which are higher in temperature than the main body of liquid. As a result, all analyses and conversions shown in Tables 3 and 4 are based on analysis of the liquid inside the glass liner.

2. The two supplies of 1-MN differed slightly in purity; the Eastman Kodak sample analyzed as 99.2% purity (nature of impurity peak unknown), and the Fisher Scientific sample was ~100%. Comparison of Runs 3, 4 and 5 for Harshaw 0402T, of Runs 6 and 7 for Akzo 77-RAM-3, and of Runs 8 and 9 for Akzo PA-23924 indicates a small systematic difference in the RHG and RHC results as a function of feedstock. RHG tended to be less by ca. 0.5-1% for the Eastman Kodak sample, and RHC to be ca. 0.5-1.5% higher for this feedstock. Further research would be necessary to determine whether the impurity might be such as to slightly inhibit catalytic ring hydrogenation and enhance ring hydrocracking. Differences in HDM are asystematic.

3. The extent of hydrodemethylation is almost the same with all Co/Mo/Al₂O₃ catalysts as it is in absence of catalyst. This is true for the present experiments at 500°C as it was at 450° (see Quarterly Report FE-2013-14).

4. SnCl₂ is exceptional at 500°C, as it is at 450°C (FE-2013-14). Inspection of the data for Run 13 in Tables 2-4 shows that SnCl₂ is an extremely poor catalyst for both RHG and RHC, but it increases HDM somewhat.

5. For the Co/Mo/Al₂O₃ catalysts tested, the order of decreasing ring hydrogenation activity was Cyanamid HDS-1442B>Amocat 1A>Harshaw 0402T~Akzo PA-23924>Amocat 1B >Akzo 77-RAM-3.

6. The order of decreasing ring hydrocracking activity is Amocat 1A~Amocat 1B>AkzoPA-23924>Harshaw-0402T>Akzo 77-RAM-3~Cyanamid HDS-1442B.

7. At 500°C the extent of hydrodemethylation is about five times higher, and the extent of ring hydrocracking almost 7 times higher, than at 450°C.

8. By contrast, at 500°C the extent of ring hydrogenation is about 4 times lower than at 450°C. This is presumably the result of the less favorable thermodynamic equilibrium for hydrogenation of aromatics at the higher temperature.

9. Of the three catalytic functions studied, HDM does not result in a net pressure change (one CH₄ molecule produced per H₂ molecule consumed). RHG consumes 2 molecules of H₂ per molecule of methyl naphthalene (or naphthalene) hydrogenated to methyl tetralin (or tetralin); and RHC can be shown to consume 3 molecules of H₂ per molecule of alkyl benzene formed. It is logical, therefore, to attempt to correlate pressure drop (or final cold pressure) with the sum of RHG plus $\frac{3}{2}$ RHC. Such a plot (p_f vs. RHG + 1.5 RHC) is shown in Figure 3. The plot is indeed linear, with an extrapolated intercept of 1000 psia, and a slope corresponding to a pressure drop of ca. 23 psi per 1% feed converted by RHG.

The interpretation of Figure 3 may be checked by an a priori calculation of the slope. The net gas volume of the autoclave (when glass liner and 1-MN are present) is ca. 700 cc.; at the initial pressure of 1000 psia, the initial H₂ charge is 1.98 moles. If 1 mole % of the initial charge of 1-MN (1.43 moles) undergoes RHG, the theoretical pressure drop should be

Figure 3. Relation of Final Autoclave Pressure to Extent of Ring Hydrogenation & Ring Hydrocracking.

$$\frac{(0.01 \times 1.43 \times 2)}{1.98} \times 1000 = 14.4 \text{ psi.}$$
 This is only about 2/3 of the observed slope (23 psi/% RHG) of Figure 3. Part of this discrepancy may originate in the use of area ratios rather than mole ratios in the G. C. analysis of the liquid product.