BATCH SCREENING OF COAL LIQUEFACTION CATALYSTS WITH A FALLING BASKET REACTOR

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The Harshaw Chemical Company and Battelle Columbus Laboratories have been studying coal liquefaction catalysts in a joint program sponsored by the Dept. of Energy. Its objective is the development of catalysts of improved life and selectivity for direct liquefaction processes.

Harshaw's specific objective is to identify catalysts of superior activity and selectivity, i.e. those that most efficiently use hydrogen in forming coal liquids with low heteroatom content. These will then be tested by Battelle for longer term aging characteristics. This paper is a report of progress with about half of the planned screening tests completed.

Experimental System

The test system, diagrammed in Figure 1, is based on an Autoclave Engineers 1-liter Magnedrive reactor and is designed to run whole formed catalysts in an environment of coal slurry with continuous hydrogen flow.

Illinois No. 6 coal from Consolidation Coal Company's Burning Star Mine No. 2 was analyzed as follows after grinding and drying.

	Wt %
Moisture	1.3
Ash	12.0
Carbon	68.3
Hydrogen	4.7
Nitrogen	1.2
Sulfur	3.2
Oxygen (by diff.)	9.3

The coal is charged to the reactor as 30% MAF coal in a vehicle. Two vehicles have been used. The first is a "heavy oil" cut of a coal tar from Koppers Co. Analyses of this vehicle and the coal are shown below.

	Wt % Components	
	Coal	Heavy Oil
Oil	1.0	76.9
Asphaltenes	0.3	22.8
Pre-asphaltenes	7.8	} 0.3
Residue	90.9	
	100.0	100.0
% Sulfur	3.2	0.44
% Nitrogen	1.2	0.96

In the second series of runs the vehicle is tetralin. Run conditions for the two series are as follows:

Vehicle	Heavy Oil	Tetralin
Pressure, psig	4000	2500
Temperature, °C	425	425
Activation in H_2/H_2S, hr	1.5	1.5
Thermal Reaction Period, hr*	0.5	1.0
Catalytic Reaction Period, hr	2.0	2.0
Inlet H_2 Flow, SCFH	5	10
Catalyst Charge, cc	25	25
Wt Coal, g	188	162
Wt Vehicle, g	355	306
Volume of Slurry, cc	471	471

*After heatup to 425°C

Falling Basket Reactor

It is desirable that a catalyst screening test simulate continuous operating conditions as far as possible. In this case, five requirements were set in advance.

1. Batch operation for rapid screening.
2. Pre-activate the catalyst *in situ* with H_2/H_2S.
3. Use formed catalyst (tablets and extrudates) rather than powder.
4. Avoid contact of catalyst with slurry during heatup.
5. Separate thermal from catalytic conversion experimentally.

The Falling Basket Reactor, illustrated in Figure 2, was developed to meet these requirements. With this device, the catalyst is suspended in the gas phase during the initial stages of the run, then lowered into the liquid for the catalytic reaction portion. Catalyst (25 cc) is loaded in the four arms of the basket assembly which moves along a grooved sleeve attached to the agitator shaft. In operation the basket is held at the top of the shaft by a horizontal notched groove as long as the shaft is rotated at a constant RPM. (Rotation speed was set at 300 RPM after a preliminary mixing study.) When rotation is stopped and momentarily reversed, the basket travels down the groove to the bottom position where it remains for the rest of the run. The point at which the basket drops is recorded by a temporary drop in batch temperature.

Pre-activation of the catalyst, heatup, pressurization, and a period of thermal reaction are accomplished after sealing the reactor, but before contacting catalyst and slurry. The catalytic period starts when the basket is dropped into the liquid and stops when the heater is removed from the autoclave. Figure 3, a typical temperature history of a run, shows that this sequence results in a well defined reaction period. Figure 3 also shows the endotherm that always occurs during heatup as the coal undergoes thermal dissolution.

Product Analysis

Product analysis schemes are similar for the two vehicles except for the addition of a distillation step in the tetralin runs (Figure 4). The vehicle remained with the coal liquefaction products in the heavy oil runs. The techniques used to separate oil (pentane soluble),

asphaltenes (benzene soluble, pentane insoluble), and pre-asphaltenes (pyridine soluble, benzene insoluble) are well known.

Effluent gas was monitored by GC for 50 runs, enough to establish that there were no significant differences among catalysts in the gases formed, nor between catalysts and no catalyst. It was concluded that light hydrocarbons come from the coal (not the vehicle) at the test operating conditions, whether or not catalyst is present.

Samples of the separator condensate and the distillate obtained during product workup were analyzed by GC for the tetralin runs. Particular attention was paid to the relative amounts of decalin, tetralin, and naphthalene as indicators of hydrogenation activity.

The results are presented in terms of elemental analyses of product (%S, %N, and H/C atomic ratio); extraction analyses (oil/asphaltene ratio and % pre-asphaltenes); the decalin/naphthalene ratios of distillate and separator product (for tetralin runs); and conversion. Conversion is defined as 100 less the percent MAF coal charged that remains benzene insoluble. Note that the chemical analyses refer to coal plus vehicle in the heavy oil runs, but only to coal products in the tetralin runs.

Catalysts

Eight 1/8 in. tabletted catalysts were tested in the heavy oil series at 4000 psig. Four of these tablets and ten 1/16 in. extrudates have been tested to date in the runs with tetralin at 2500 psig. Various blank and duplicate runs were made with both vehicles.

The reference catalyst is Harshaw's CoMo-0402 T 1/8, which has been reported in connection with work on the Synthoil process and other studies. Other catalysts are designated either by their commercial name (as HT-400) or by a simple chemical notation (as NiMo). The catalysts tested to date represent a variety of chemical compositions and support structures. For example, two sets of NiMo extrudates were made to have systematically varying pore structure; these are designated on Table 2 as A-1, B-1, etc.

Catalysts are loaded on a volume basis (25 cc). Packed densities cover a wide range, tablets running 1.0 - 1.1 g/cc and extrudates 0.6 - 0.8 g/cc. Weight of catalyst charged therefore ranges from about 15 to 28 g.

General Results

Test results from runs with heavy oil vehicle are summarized in Table 1, and from tetralin runs in Table 2. All runs were at the operating conditions given above except for the few special run times indicated by notes to the tables. The runs are listed in order of decreasing oil/asphaltene ratio in the product.

Mass recoveries typically run 97 to 99% with heavy oil and higher with tetralin; the small variations do not affect the conclusions. "Conversion" of coal to liquids also falls within a narrow range for standard runs and does not differentiate among catalysts. Thermal conversion (no catalyst present) is about 2-3% lower than the average catalytic conversion with heavy oil, and about 6-7% lower with tetralin. The fact that the catalytic conversions are close attests to the reproducibility of the test, for conversion varied widely when time was varied as in Runs 18, 19, and 20. Excellent reproducibility

is also demonstrated by the similar results found in duplicate Runs 32 and 50, and 29 and 52 (Table 2).

As noted earlier, the amount and composition of effluent gases do not appear to be influenced by the presence of a catalyst. Similarly, the amount of separator condensate is essentially constant for a fixed run time. However, its composition is related to the activity of the catalyst used, as may be seen from the decalin/naphthalene ratios given in Table 2. The data show that separator product is more saturated than the solvent which remains in the reactor and becomes "distillate".

Special Runs

The marked effect of a catalyst on sulfur removal, H/C ratio, and conversion of asphaltenes to oils is seen from comparison of Run 9 (no catalyst) with any of the catalytic runs on Table 1. However, removal of nitrogen heteroatoms from the coal appears to be nearly as difficult with a catalyst as without.

Comparison of Runs 24 and 27 (Table 2) shows the effect of catalyst on tetralin in the absence of coal. Much more decalin was made in the presence of a catalyst: 1.4% in Run 24, but 48% in Run 27.

In three instances run time was varied with the same catalyst. Runs 19, 20, and 18, with the reference CoMo catalyst, had catalytic run times of 0.4, 2.0, and 2.5 hrs. Without exception, as run time increases, H/C and oil/asphaltene ratios increase and % pre-asphaltenes and % S decrease.

In the tetralin series, Run 43 had 0.5 hr more thermal exposure than Run 42, other things being equal, and showed more reaction in each of the variables tabulated. Similarly, Run 36 (1 hr thermal, 2 hr catalytic) shows more reaction than Run 35 (2 hr thermal, 1 hr catalytic) with the same catalyst.

Comparison of Catalysts

In general, the data indicate that all the measures of catalytic activity are interrelated. Inspection of Tables 1 and 2 shows that the following properties coincide:

- high oil/asphaltene and H/C ratios, both measuring the extent of hydrogen addition to the coal,

- low S and N in the product (the latter less definitely) and lower % pre-asphaltenes, all measures of catalytic action on the liquefied coal,

- high decalin/naphthalene ratio in both distillate and separator products, showing activity in solvent hydrogenation.

The correlation between H/C and oil/asphaltene ratios is shown graphically in Figures 5 and 6. With respect to the heavy oil runs (Fig. 5), all the points except Run 19 (0.4 hrs) appear to fit a correlation. It is concluded that some kind of thermal equilibration between coal, solvent, and hydrogen has been reached in the standard length runs, and more hydrogen addition is achieved either by longer contact time or a better catalyst. The activity differences among catalysts in the heavy oil runs are relatively small in spite of the variety of compositions employed. It is believed that the uniformity of

results is due, in part, to the fact that the vehicle is not separated from the coal and plays a major role in the observed results. Another reason may be the use of tablets in this series. Tablets tend to have similar pore structures at their external surfaces which may mask chemical differences.

Table 2 and Figure 6 show a wider range of results with tetralin and extruded catalysts. Certain NiMo catalysts have demonstrated very good relative performance in this test. However, the six NiMo catalysts tested in Runs 37 - 43, differing primarily in pore structure, show little difference in performance. It is premature to draw firm conclusions regarding the key factors that affect catalyst activity, and more work is required before relating performance to properties.

NiW catalysts have not shown up well vs. NiMo in the few tests completed. Regarding CoMo, the best comparison so far between similar NiMo and CoMo catalysts is in Runs 32 and 50 vs. 33; the NiMo catalyst appears to be somewhat more active in each category. It is interesting, however, that the CoMo causes less saturation of the solvent than expected from its position on the table. The same thing may be said of the tabletted version (Run 31). This may be an advantage.

The four tablets tested on tetralin gave similar results (Table 2). As expected, they are less active than corresponding 1/16 in. extrudates. The similarity of tablet results parallels the same finding on the heavy oil feed.

Principal Conclusions

Conversion of coal to benzene soluble liquids is primarily a thermal reaction dependent on temperature and time, only secondarily on catalyst. Addition of hydrogen to the coal liquids and solvent and removal of heteroatoms are greatly influenced by the catalyst, and these characteristics tend to correlate with each other. This suggests that one mechanism such as rehydrogenation of the solvent may be the dominating process which separates good from bad catalysts.

If this picture of the process is valid, the catalysts selected by this screening test are likely to be effective not only in direct liquefaction processes, but also in processes where catalytic upgrading of the coal liquids is separated from the liquefaction step.

Several catalysts have been identified which show better short-term performance than the reference CoMo tablet. The properties which lead to better catalyst performance have not yet been clarified, nor have aging tests been carried out.

The falling basket reactor solves a number of experimental problems in batch screening of catalysts for continuous processes, especially in separating thermal from catalytic effects and in providing a well defined reaction period. Reproducibility of results is excellent.

TABLE 1 RUNS WITH HEAVY OIL VEHICLE - RANKED BY OIL/ASPHALTENE RATIO

Run	Catalyst (1)	Conversion %	Pre-asphaltenes %	Benzene Solubles (2)			
				%S	%N	H/C(At.)	Oil/Asphaltene
22 (3)	CoMo-0402	-	-	0.04	0.42	1.02	124
18 (4)	CoMo-0402	77.0	0.6	0.11	0.79	0.99	7.0
16	HT-400 CoMo/Al	75.6	0.2	0.18	0.81	0.96	5.6
21	CoMo-0402 + 0.1% Re	75.0	0.4	0.17	0.82	0.96	5.3
20	CoMo-0402	69.3	1.4	0.14	0.80	0.96	5.2
17	NiW/Al	74.1	0.8	0.10	0.94	0.94	5.0
12	NiMo/Si-Al	73.7	0.3	0.10	0.83	0.94	4.7
11 (6)	NiW/Al	74.7	0.2	0.11	0.95	0.98	4.4
15	CoMo/Al	75.1	0.6	0.14	0.79	0.95	4.3
14	CoMo/Al-Si	72.9	0.4	0.16	0.94	0.93	3.9
23	CoMo/SiMg-Al	65.6	1.0	0.23	1.01	0.90	3.9
19 (5)	CoMo-0402	52.9	2.1	0.30	1.00	0.83	3.6
9	No Catalyst	72.8	0.6	0.37	0.94	0.87	1.3

(1) All 1/8 in. tablets. Al = Al_2O_3 and Si = SiO_2
(2) Bz sols. = vehicle + liquefied coal.
(3) No coal.
(4) 2.5 hr. catalytic reaction time instead of 2.0 hr.
(5) 0.4 hr. catalytic reaction time.
(6) Carbonaceous material left in catalyst. Sample of same was used in Run 17 after complete calcination.

TABLE 2 RUNS WITH TETRALIN VEHICLE - RANKED BY OIL/ASPHALTENE RATIO

Run	Catalyst[1]	Conversion %	Pre-asphaltenes %	COAL LIQUEFACTION PRODUCT				decalin/naphthalene	
				%S	%N	H/C (At.)	Oil/Asph.	Distillate	Separator Product
32	HT-500 NiMo/Al E	77.9	0.0	0.02	0.96	1.10	2.6	2.7	-
34	HT-115 NiMo/Al E	79.4	0.1	0.06	1.04	1.07	2.3	1.6	3.0
50	HT-500 NiMo/Al E	77.8	0.2	0.02		1.06	2.1	2.7	5.6
37	NiMo/Al E A-1	78.6	0.1	0.05	1.15	1.06	1.9	1.6	2.1
43	NiMo/Al E B-2	78.8	0.0	0.02		1.08	1.9	1.6	2.1
33	HT-400 CoMo/Al E	75.7	0.0	0.04	1.19	1.05	1.8	0.8	1.3
38	NiMo/Al E B-1	78.1	0.2	0.06		1.05	1.8	1.7	2.0
40	NiMo/Al E B-3	78.0	0.0	0.02		1.08	1.7	1.4	1.8
41	NiMo/Al E A-2	78.9	0.0	0.05		1.05	1.7	2.0	2.2
42[2]	NiMo/Al E B-2	78.1	0.0	0.04		1.06	1.7	1.2	2.2
31	HT-400 CoMo/Al T	76.1	0.4	0.09	1.21	1.06	1.6	0.8	1.0
26	NiMo/Al T	77.5	0.3	0.07	1.10	1.05	1.5	2.1	2.9
30	NiW/Al T	73.6	0.5	0.12	1.28	1.04	1.4	0.9	1.4
39	NiMo/Al E A-3	78.6	0.1	0.04		1.04	1.3	0.7	2.0
29	CoMo-0402 T Ref.	78.0	0.2	0.09	1.24	1.03	1.1	0.8	1.3
52	CoMo-0402 T Ref.	77.7	0.3	0.10		1.01	1.1	0.9	1.7
36	NiW/Al E C-1	77.9	0.2	0.07	1.28	1.01	1.1	0.4	1.1
35[3]	NiW/Al E C-1	75.5	0.6	0.09	1.37	1.01	0.9	0.2	0.7
45	NiW/Al E C-2	74.6	0.9	0.18		1.01	0.8	0.8	1.4
28	No Catalyst	71.9	2.4	0.46	1.66	0.94	0.4	0.1	0.9
44	Alumina E	70.8	1.5	0.53		0.93	0.4	0.1	0.7
24[4]	No Catalyst	-	-	-	-	-	-	5.0	5.0
27[4]	CoMo-0402 T Ref.	-	-	-	-	-	-	206.0	12.3

(1) Al = Al_2O_3. E = 1/16 in. extrudate. T = 1/8 in. tablet.

(2) 0.5 hr. thermal reaction time instead of 1.0 hr. as in Run 43.

(3) 2.0 hr. thermal and 1.0 hr. catalytic instead of 1.0 and 2.0 as in Run 36.

(4) No coal.

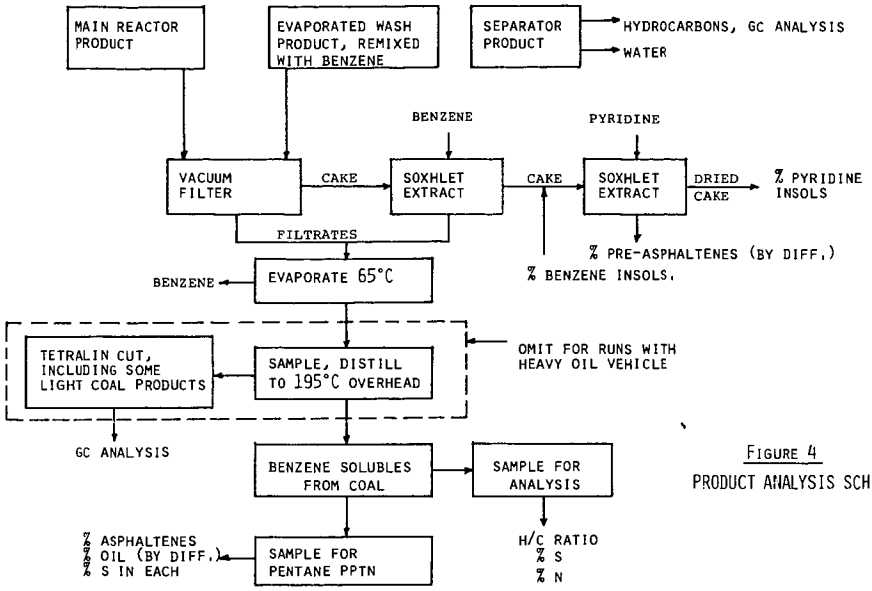


FIGURE 4

PRODUCT ANALYSIS SCHEME

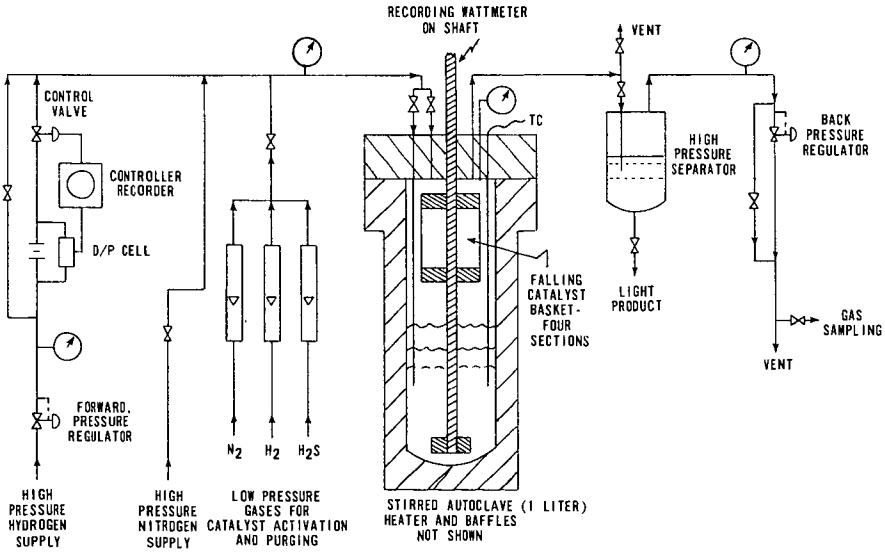


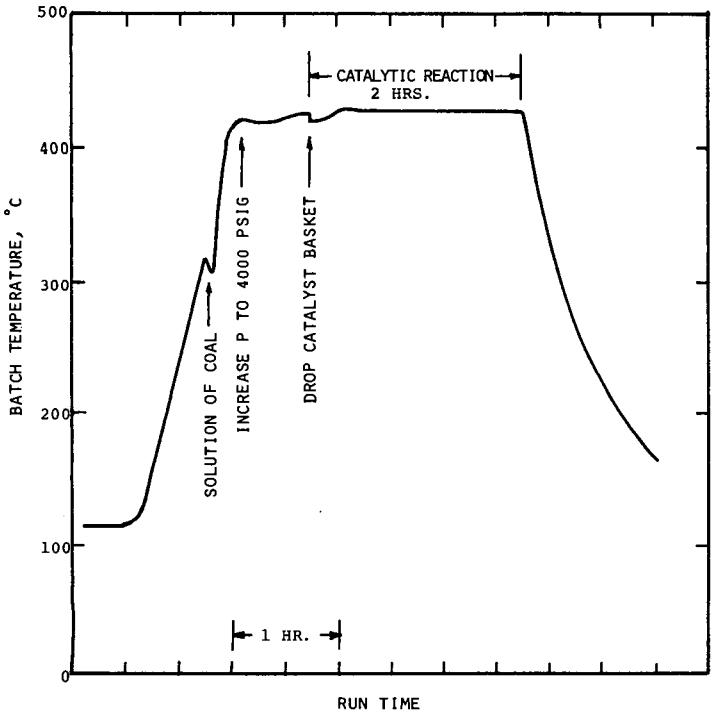
FIGURE 1

HARSHAW CATALYST SCREENING UNIT

SIMPLIFIED SCHEMATIC DIAGRAM

FIGURE 3

TEMPERATURE-TIME HISTORY
OF TYPICAL RUN
(HEAVY OIL VEHICLE)



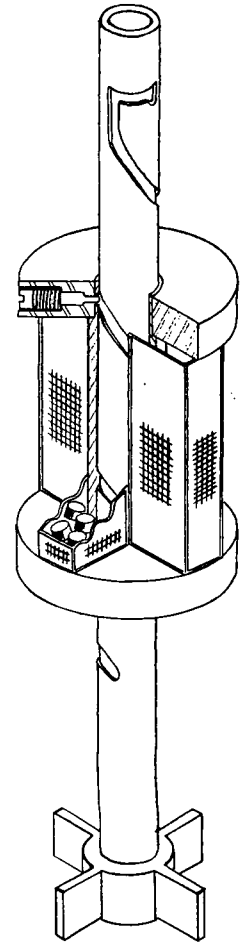
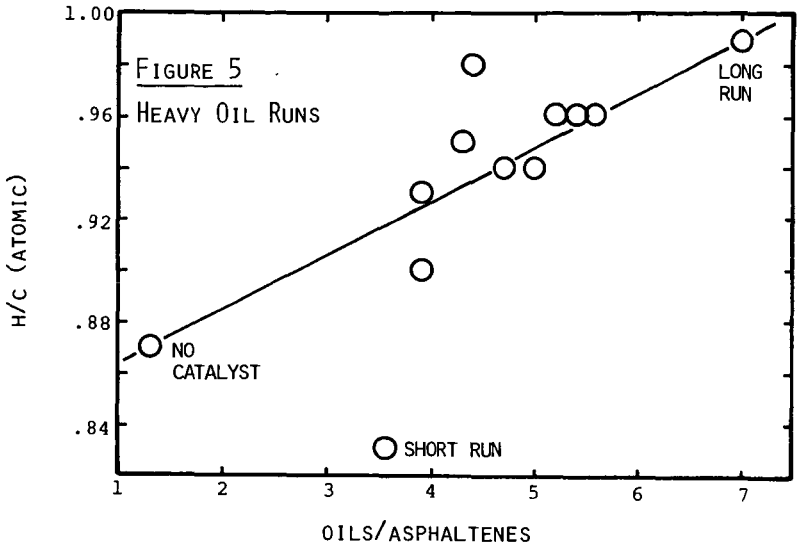
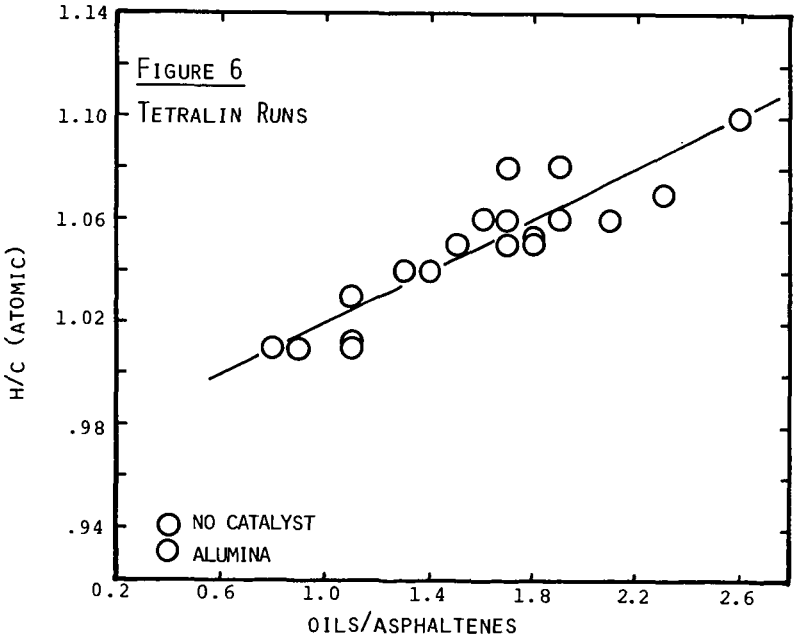


FIGURE 2
FALLING BASKET ASSEMBLY

CORRELATION OF H/C AND OIL/ASPHALTENE RATIOS
IN LIQUEFACTION PRODUCTS