

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
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PYROLYSIS OF OILS DERIVED FROM COAL AND OIL SHALE
IN A FLUIDIZED BED OF CATALYSTS

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INTRODUCTION

For the past several years new reserves of petroleum oil were found at a rate about equal to consumption. Eventually, the supply of good petroleum crude oil may decrease to a point where other sources of oil will be needed to keep up with the demand for gasoline and other oil products. Also, if oil imports were deterred for some reason, other sources of oil would be investigated quite quickly. Some of the other sources of oil which have been investigated, but not used commercially because of the economics of processing are oil shales, tar sands, and coals. Recently, processes have been developed for extracting oil from tar sands in Canada. These processes appear to be competitive locally with the present oil supplies. More recently the government had requested the reopening of the oil shale pilot plant in Rifle, Colorado. This plant is operated by the Research Foundation at the Colorado Schools of Mines and already oil companies are associated with its development. Also, private ventures are under way towards the development of oil shale. In accord with this trend towards developing commercial means for obtaining oil from sources other than petroleum, the newly established Office of Coal Research has let several contracts for investigating processes for converting coal to oil and high Btu gas.

The yield of oil from subbituminous coals varies from 10 to 30 gallons per ton which is similar to yields from oil shale. The higher ranked bituminous coals can yield as much as 50 to 60 gallons per ton. Moreover, coal has an advantage over oil shale in that it is more easily mined and crushed and it is more widely distributed. Also, the spent coal or char from the retorting process is a useful fuel while the spent shale creates a disposal problem.

Oils from coal and oil shale differ in composition from petroleum oils. In addition to the sulfur problem, which is shared also by petroleum crudes, more oxygen and nitrogen are contained in oils from coal and oil shale. Oxygen can be eliminated as water and nitrogen as ammonia by catalytic hydrogenation. (1) However, hydrogen is needed and catalyst life may be short. These are additional costs for the process. Another possible process for removing oxygen from the oil derived from coal is catalytic cracking. Here the oxygen will hopefully be removed as carbon monoxide or carbon dioxide rather than as water. This is desirable since these oils are deficient in hydrogen compared with petroleum. Therefore, the purpose of this investigation was to study the catalytic cracking of low-temperature oils derived from coal with operating conditions similar to those of commercial practice and to compare the results with those obtained with shale oil and petroleum. Successful processing of these new oils would lead to the opening of reserves estimated by many at over a trillion barrels.

EXPERIMENTAL WORK

The catalytic cracking of oils from coal and oil shale was studied by processing the condensed oils in a laboratory, regenerative fluidized-bed reactor. Investigation concentrated on the condensed oils rather than the vapors, because oils from coal and shale would probably first be used in a commercial oil refinery at a distance from the mines. Thus the oils would be transported in the liquid state and then processed. Shale oil and petroleum oil were also catalytically cracked to compare their behavior with that of oils from coal, and to compare the results of the laboratory equipment with those from a commercial plant that uses petroleum.

Sample Preparation

Petroleum oil from Continental Oil Company's refinery in Denver, shale oil from Denver Research Institute, and oil from the pyrolysis of subbituminous coal in a bench-scale fluidized

TABLE I

Cracking of Oil from Coal

Feed Catalyst	Composite		Residuum	
	Silica-Alumina	Filtrol	Filtrol	Silica-Alumina
Temperature, °F.	860	860	950	860
Yield of Liquid Products, wt. %	86.0	69.2	62.8	55.5
Naphtha, wt. %				
In Feed	11.2	11.2	11.2	0
In Product	26.1	36.0	40.8	18
Total Yield	22.4	24.9	29.9	10
Net Yield	11.2	13.7	18.7	10

TABLE II

Cracking of Oil from Shale Oil

Feed Catalyst	Composite			Residuum	
	Silica-Alumina	Filtrol	Filtrol	Silica-Alumina	Silica-Alumina
Temperature, °F.	860	860	950	950	950
Yield of Liquid Products, wt. %	69	69.2	70	70.4	54.0
Naphtha, wt. %					
In Feed	7.5	7.5	7.5	0	0
In Product	17.9	12.4	26.0	21.7	30.0
Total Yield	12.4	8.6	19.2	15.2	16.0
Net Yield	4.9	1.1	11.7	15.2	16.0
Viscosity at 100°F., Saybolt sec.					
Feed			110	184	184
Naphtha Product			40	41	39
Residuum Product			62	53	151

TABLE III

The Performance of the Laboratory Cracking Unit
Compared with that of a Commercial Unit

Unit	Commercial*		Laboratory	
	Petroleum Crude			
Feed Catalyst	Filtrol		Silica-Alumina	
Temperature, °F.	860	860	860	860
Feed Rate, w/hr/w	2.0	1.4	1.0	1.7
Yield of Liquid Product, wt. %	75	73	82	73
Yield of Naphtha, wt. %	44	6	10	15

* Refinery of Continental Oil Company at Denver, Colorado.

bed reactor were used as the feeds for the cracking unit. The shale oil and oil from coal were fed both as composite mixtures (containing the original light ends) and as residuums without the light ends. The light ends were considered as all liquids distilling below 410°F. in an atmospheric distillation and were designated as naphtha. Liquids boiling above 410°F. were designated as residuum. The petroleum oil had been previously distilled and contained no light ends.

The laboratory unit for the fluidized bed pyrolysis of coal (Figure 1) consisted of a chamber 2-1/4 inches in diameter and 4 feet long with an enlarged section on top. The bottom was conically shaped for gas distribution. The unit was electrically heated to 1000°F. and wrapped with insulation. The coal was crushed to a size consist of minus 28 to plus 100 mesh and was fed at a rate of about 5 lb./hr. by means of a hopper under a pressure of 15 psig of nitrogen. This pressurized hopper caused the crushed coal to flow in a dense phase through a 3/8-inch tube into the reactor. Natural gas from a laboratory supply line was used to fluidize the coal. This gas was used in lieu of nitrogen or other inert gas. The vapors and gases leaving the retort passed through several condensers. The uncondensable gas was metered and then vented. The spent coal or char was continuously removed through an orifice at the bottom of the reactor.

Fluidized Bed Cracking Unit

The catalytic cracking unit consisted of a regeneration chamber and a reaction chamber as shown in Figure 2. This unit was used previously (2) in cracking studies with shale oil. Each chamber was 2-1/4 inches in diameter and 20 inches long with an enlarged section at the top to prevent catalyst fines from blowing out of the unit and a conical section at the bottom for gas distribution. Heat was supplied electrically and the unit was wrapped with asbestos insulation. Catalyst was circulated by being blown with nitrogen or air through transfer lines as shown in Figure 2. The feed was preheated to about 300°F. and pumped as liquid into the bottom third of the catalyst bed. The catalyst was fluidized with nitrogen, entering at the bottom. The cracked products left the reactor and passed through a series of condensers for oil recovery. The uncondensable gas was metered and then vented. The flue gases from the regenerator were also cooled and then vented. All cracking runs were made at constant feed rate and a constant temperature with either a natural clay catalyst (referred to as Filtrol) or a silica-alumina catalyst. The temperature range studied in the different runs was from 860 to 1000°F. Most of the runs were fed at a space velocity of 1 lb. of feed per hour per pound of catalyst (w/hr/w) which amounted to 8 to 10 cc of feed per minute. Space velocities are on a nitrogen-free basis. The nitrogen added as fluidizing gas and as purge gas amounted to about 0.5 w/hr/w giving an over-all space velocity of 1.5 w/hr/w.

Analytical Procedures

Standard procedures were used for measuring the physical properties of viscosity, specific gravity, and pour point of all liquid products. An ASTM atmospheric distillation to a 410°F. end point determined the light ends. The end point of 410°F. was used because cracking in the distillation flask occurred above this temperature. The gas samples were analyzed with an Orsat apparatus.

RESULTS AND DISCUSSION

Catalytic Cracking of Oil from Coal

Oil from the low temperature pyrolysis of coal is not as aromatic as the high temperature tar from normal coking processes. It contains considerable tar acids and a multitude of various chemicals for which markets are either non-existent or the cost of obtaining pure products is prohibitive. However, low temperature pyrolysis processes can yield over twice the oil than that from high temperature pyrolysis. Thus, it has been suggested (3) that it may be economical to convert the oil from coal to petroleum refinery feedstock or directly to salable petroleum products by catalytic cracking. This investigation studied the feasibility of catalytic cracking oil from coal to obtain a gasoline fraction comparable with that from petroleum oil and shale oil.

The yield versus temperature curves for catalytic cracking a composited oil from coal are shown in Figures 3 to 5. All yields reported in the tables and on the graphs are on a solids- and water-free basis.

The yield of liquid products decreased with temperature from 69 weight percent to 46.5 weight percent between 860 and 1000°F. The naphtha yields (light ends boiling below 410°F.) increased slightly with temperature between 860 and 950°F. and then decreased rapidly. This indicated severe cracking of the light products between 950 and 1000°F. The products showed

TABLE IV

Typical Material Balances for the Cracking Unit

Feed	Residuum from Oil Shale	Residuum from Coal
Temperature, °F.	950	1000
Yields, wt. % of Input		
Oil	70.3	56.0
Gas	4.0	6.3
Carbon Deposited on Catalyst	21.0	30.0
Losses	4.7	7.7
Material Balance	95.3	92.3

TABLE V

Oxygen Balance for Catalytic Cracking of Oil from Coal

Feed	Composite Oil from Coal	Residuum Oil from Coal
Temperature, °F.	1000	1000
Oxygen Content, wt. %		
Feed	9.8	9.8
Liquid Product	5.1	6.9
Amount of Oxygen in Feed Appearing in Liquid Product, wt. %	45	41

TABLE VI

Analyses and Yields of Products from
Pyrolyzing Elkol Coal at 1000°F.

Material	<u>Elkol Coal</u>	<u>Char</u>	<u>Oil</u>	<u>Gas</u>	<u>Liquor</u>
Yield, dry basis, wt. %	-	58.7	14.1	18.0	9.2
Proximate Analysis, dry basis, wt. %					
Volatile Matter	42.2	6.6	-		
Fixed Carbon	54.5	88.2	-		
Ash	3.3	5.2	-		
Ultimate Analysis, dry basis, wt. %					
Carbon	72.0	84.9	80.7		0.2
Hydrogen	5.3	1.7	8.2		-
Nitrogen	1.0	1.2	0.8		0.1
Sulfur	0.8	0.7	0.5		0.02
Oxygen	17.6	6.3	9.8		-
Ash	3.3	5.2	-		-
Gas Composition, Volume Percent					
CO ₂				12.1	
CO				24.9	
H ₂				32.3	
CH ₄				21.9	
C ₂ ⁺				8.8	

a 2- to 4-fold increase in naphtha content over that in the feed (see Figure 5). However, the actual naphtha yield (subtracting the naphtha in the feed) varied from 5 to 15 weight percent based on feed.

A residuum from which the naphtha had been distilled was run to determine the amount of the heavier components of the feed converted to naphtha. The residuum was very viscous and had a pour point of about 200°F. A lower yield of product and naphtha resulted from processing the residuum as shown in Table I. This was probably caused by faster deactivation of the catalyst by more carbon formation with this feed.

A comparison of silica-alumina catalyst with Filtrol catalyst for cracking oil from coal is also shown in Table I. At 860°F. liquid yield was 16.8 weight percent higher with the silica-alumina catalyst than with the Filtrol catalyst. The product obtained with the Filtrol catalyst contained 10 weight percent more naphtha than that from the silica-alumina catalyst, but the naphtha yields were comparable because of the high total yield with the silica-alumina catalyst.

The viscosity of the product from cracking the oil from coal decreased from 81 Saybolt seconds at 100°F. to 45 seconds by increasing the cracking temperature from 860 to 1000°F. as shown in Figure 6. The product and residuum with the naphtha removed were both liquid at 60°F. while the feed had a pour point of 150°F.

Catalytic Cracking of a Shale Oil

Shale oil was cracked in the same laboratory unit to compare its behavior with results from cracking oil from coal.

The yields of naphtha and liquid products as a function of temperature are also shown in Figures 3 to 5 and in Table II for the catalytic cracking of a composite shale oil with a Filtrol catalyst. Both the naphtha content of the product and the naphtha yield based on feed increased to a maximum around 950°F. The curve showing the net yield of naphtha based on feed was obtained by subtracting the amount of naphtha in the feed (7.5 weight percent) from the total naphtha in the product. This left a very small quantity (1 to 10 weight percent) of naphtha that was presumably formed by cracking. However, these calculated values assumed that the naphtha in the feed went through unchanged when actually some of it was probably cracked to uncondensable gases. There was little effect of temperature on the total yield of liquid product between 860 and 950°F., but a decrease of 17 weight percent from the yield at 950°F. was caused by increasing the temperature to 1000°F. (see Figure 3). Based on these data, 950°F. appeared best for the catalytic cracking of shale oil in the laboratory unit.

The yield of naphtha from cracking residuum from shale oil was 15.2 weight percent. This was 3.5 weight percent higher than the yields from cracking the composite feed. This indicated that almost half of the 7.5 weight percent naphtha content of the composite feed was cracked to uncondensable gas and carbon. Thus, the naphtha should be removed from the shale oil before it is cracked to obtain the highest quantity of gasoline-like products. This is commonly done in petroleum oil processing. One run was made with a silica-alumina catalyst at 860°F. Data in Table II show that operating with the silica-alumina catalyst gave about five times more naphtha than that from the Filtrol catalyst. This higher yield with the silica-alumina catalyst was attributed to an inherently greater activity.

The effect of temperature on the viscosity of the products and residues for the catalytic cracking of composite shale oil is shown in Figure 6 and Table II. The viscosity of the feed was 110 Saybolt seconds at 100°F. whereas the viscosities of the products and residues ranged from 35 to 75 seconds. The viscosity of the products decreased about 30 percent as the cracking temperature was increased from 860 to 950°F. This decrease in viscosity was caused by the cracking of the feed to the less viscous naphtha. The viscosity of the products also decreased with increasing naphtha content as shown in Figure 7. An increase in the naphtha content from 7.5 weight percent to 12 weight percent lowered the viscosity by 100 percent, but the effect became less pronounced at higher naphtha concentrations. Also, the residues of the product from which the naphtha had been removed were less viscous than the feed. This indicated that even the more viscous components of the feed were cracked to less viscous products.

Comparison of Data with Catalytic Cracking of a Petroleum Oil

The yield versus temperature curves for the catalytic cracking of a petroleum oil, oil from coal, and a shale oil are compared in Figures 3 and 4. The lowest total yield of liquid products was obtained with the oil from coal. It varied between 63 and 69 weight percent over the temperature range of 860 to 950°F. whereas the yield from petroleum oil and shale oil ranged from 67 to 74 weight percent. The lower yields obtained with the oil from coal may be partly caused by its higher naphtha content which was susceptible to cracking to uncondensable gases and carbon. Also, the oxygen content of the oil from coal was lowered by catalytic cracking as

FIGURE 1
DIAGRAM OF RETORT

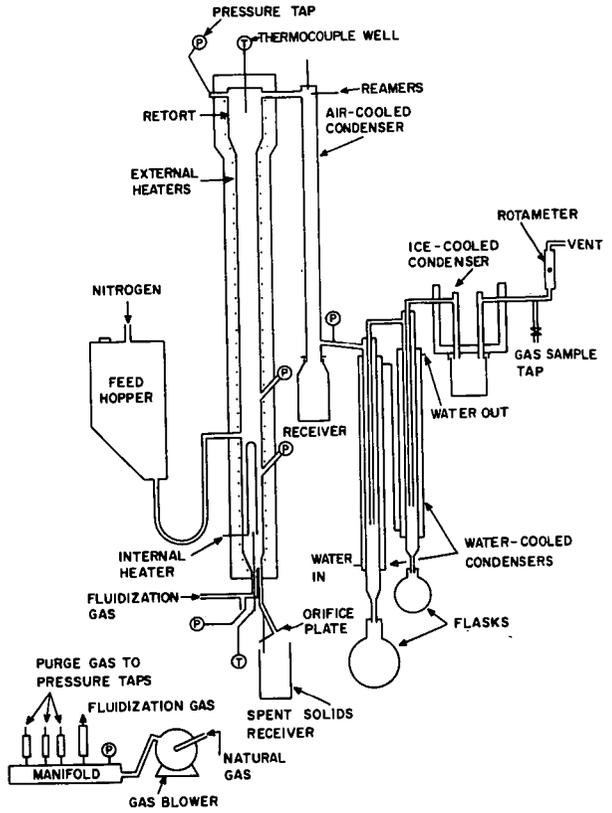
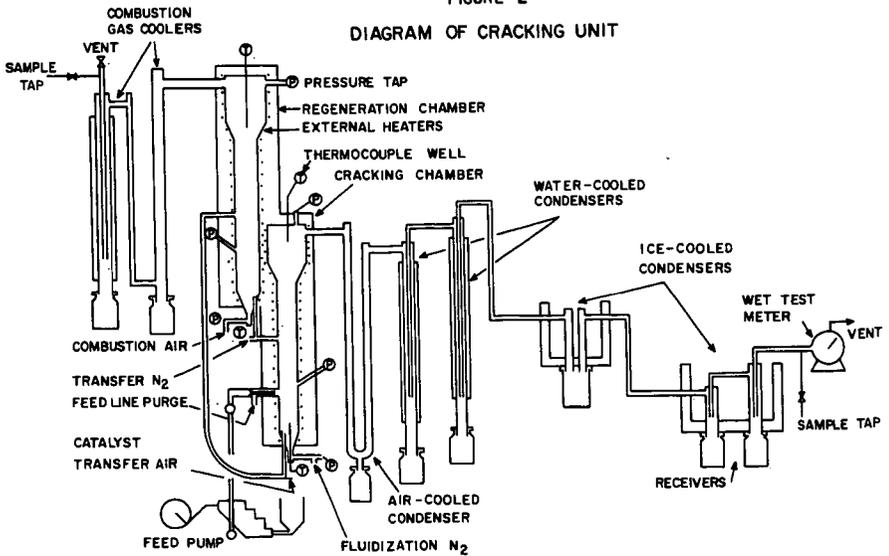


FIGURE 2
DIAGRAM OF CRACKING UNIT



discussed later. The removal of the oxygen would tend to make the yields of product less with the oil from coal than with the petroleum oil and the shale oil which do not contain as much oxygen. At 1000°F., the yields from both the oil from coal and the shale oil decreased about 15 weight percent. Thus, a temperature of 950°F. was the most suitable for cracking in the laboratory unit. This is 90° higher than the temperature used to crack the sample of petroleum oil supplied by a commercial refinery, but is within the range of cracking temperatures used in the petroleum industry. The actual naphtha yields for the petroleum oil fell between those for the shale oil and oil from coal. However, the petroleum oil has no naphtha content and thus the curve curves do not show a direct comparison between the feedstocks.

If the residuum feeds are compared with the petroleum oil, the naphtha yields were 10 weight percent for the oil from coal, 15.2 weight percent for the shale oil, and 14 weight percent for the petroleum oil. Thus, they all fell within a similar range. Therefore, all three feedstocks were cracked with comparable vigor in the laboratory unit, and both shale oil and oil from coal could be used as suitable cracking feedstocks similar to a petroleum oil residuum.

Comparison with a Commercial Refinery

A comparison of the performance of the laboratory unit with that of a commercial unit is shown in Table III, and it is evident that the laboratory unit did not perform efficiently. If the yield of naphtha is taken as a basis of efficiency, then at best the laboratory unit was only about 30 percent as efficient as the large scale unit. The main reason for the lower efficiency was less circulation of catalyst between the reactor and regenerator in the laboratory unit. This rate was difficult to control in the small apparatus. The average carbon level on the catalyst in the reactor was about 10 weight percent compared with about 2 weight percent in the commercial operation. Thus, the recirculation rate of regenerated catalyst was too low in the laboratory and contributed to lower activity of the catalyst. Nevertheless, the laboratory unit proved effective for determining the susceptibility of oils to this refining technique.

Composition of Gas from the Cracking Unit

The gas produced by cracking oil from coal contained about 20 volume percent of carbon oxides, hydrogen from 10 to 20 percent, methane from 40 to 50 percent and 20 to 25 percent C₂⁺ hydrocarbons. The average molecular weight of the gases was 20 to 25. Gas composition changed little over the temperature range of 860 to 1000°F. Gas from cracking shale oil had little carbon dioxide or monoxide, and it contained more methane.

Material Balance for the Catalytic Cracking Unit

The material balances for two catalytic cracking runs are shown in Table IV. Balances ranged from 92 to 95 percent. The carbon on the catalyst was 8.4 weight percent with the run with shale oil and 9.7 weight percent for the run with oil from coal. The carbon yield was defined as the total carbon produced during a run divided by the weight of feed. The carbon formed during a run in this investigation was determined from the carbon on the catalyst left in the reactor at the end of the run and from the amount of catalyst circulated during the run. The circulation rate was about 1 pound of catalyst circulated per pound of feed. The carbon yield as calculated in this manner ranged from 20 to 35 weight percent. This is high and hopefully could be decreased by higher rates of catalyst recirculation.

The purpose of cracking the oil from coal was partially to form useful oil products and to determine if oxygen was removed by this technique. Therefore, an oxygen balance was made to determine the effectiveness of the laboratory cracking unit in removing it. Table V shows oxygen balances for two runs. The composited oil had an oxygen content of 9.8 weight percent. This value was also used to calculate the balance for the residuum oil. The data showed that the oxygen content of the liquid product was less than that of the feed and ranged from 5 to 7 weight percent. Over half of the oxygen in the tar was removed as gas and water. Therefore, even though the laboratory unit operated at the low catalyst circulation ratio of 1 pound of catalyst per pound of feed, 50 to 60 percent of the oxygen was removed from the oil. At a higher circulation rate where more active catalyst is present in the reactor, it is likely that more of the oxygen would be removed.

Pyrolysis of Elkol Coal

The oil from coal used in this work was obtained by the pyrolysis of Elkol coal in a fluidized bed. Feed rate was approximately 5 lb. per hour which gave a residence time for the coal in the reactor of about 20 minutes. The average temperature was 1000°F. but momentary upsets could cause a fluctuation of plus or minus 50°F. Elkol coal is a subbituminous coal and does not agglomerate upon heating. Therefore, it required no special pretreatment before

FIGURE 3

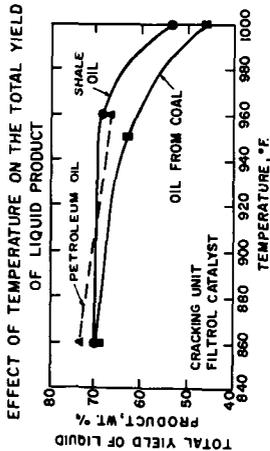


FIGURE 6

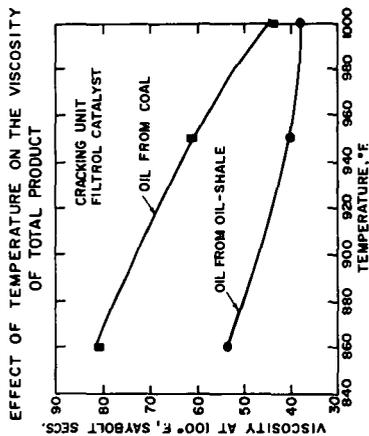


FIGURE 4

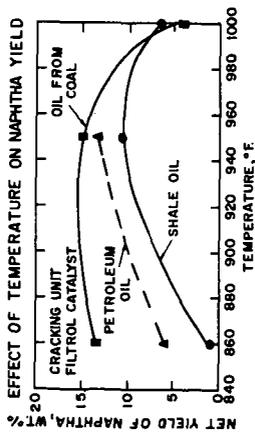


FIGURE 5

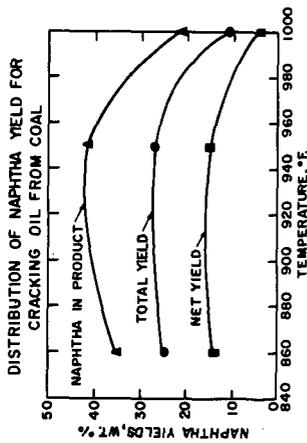
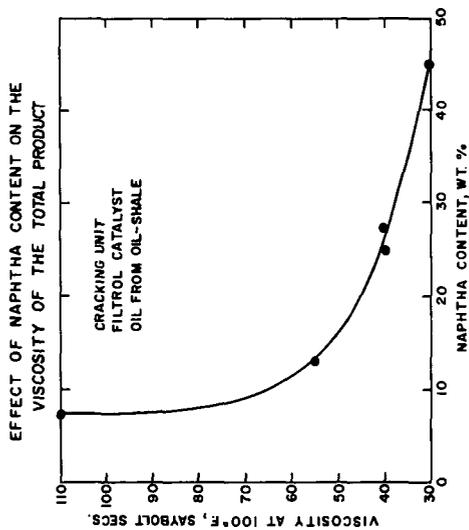


FIGURE 7



pyrolysis. Yield and analyses of Elkol coal, and products of pyrolysis at 1000°F. are given in Table VI. A typical material balance for the retorting of Elkol coal at 1000°F. is shown in Table VII. Oil yield was about 14 weight percent.

CONCLUSIONS

1. Oil from coal, shale oil, and petroleum oil were all catalytically cracked with comparable vigor in a fluidized bed.
2. A catalytic cracking temperature of about 950°F. gave the highest naphtha yields with oil from coal and shale oil.
3. Synthetic silica-alumina catalyst promoted the cracking reaction at a lower temperature than a Filtrol catalyst (natural clay) and was considered a more active cracking catalyst.
4. The pour point of oil from coal was decreased from about 150°F. to less than 60°F. by catalytic cracking.
5. The viscosities and gravities of all feeds were reduced by catalytic cracking.
6. Catalytic cracking removed over half of the oxygen from the oil obtained from coal.

ACKNOWLEDGMENT

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