

Hydrogenation of Coal to Liquids on Fixed Beds
of Silica Promoted Cobalt Molybdate Catalyst

Sayed Akhtar, Sam Friedman, and R. W. Hiteshue

U.S. Bureau of Mines, 4800 Forbes Avenue
Pittsburgh, Pennsylvania 15213

INTRODUCTION

The essential steps in the conversion of coal to liquid fuels are coal liquefaction, ash removal, and processing of the de-ashed liquid for the removal of S, N, and O, conversion of asphaltenes to oil, addition of H, cracking, and if the objective is gasoline, octane improvement¹. In practice, the functions of the process steps may overlap. Thus, certain methods of coal liquefaction are accompanied by considerable conversion of asphaltenes to oil, cracking, and partial removal of the heteroatoms. The cost and complexities of processing the de-ashed liquid depend on its composition and, therefore, on the method of coal liquefaction. The present work describes the hydrogenation of slurries of coal in high-temperature tar to a liquid of low asphaltenes, S, N, and O content on fixed beds of pelleted cobalt molybdate catalyst in single pass experiments.

EXPERIMENTAL

Plant and Procedure

Figure 1 is a flow diagram of the hydrogenation plant. The combined stream of hydrogen and mixtures of coal and high-temperature tar passed through a preheater before entering the packed bed reactor which was an 11-foot long stainless steel tube of 3-inch id. The gases and liquids leaving the reactor were led through a receiver for liquid products which was fitted with a water-cooled condenser in its upper part. The heavy liquids and coal residues were collected in this vessel from where they were intermittently discharged into a secondary vessel at atmospheric pressure. The gases and vapors leaving the receiver for heavy liquids were passed through a second condenser to liquefy the lighter ends of the liquid products. The lighter liquid products were collected in a second receiver, and the gas stream was reduced to atmospheric pressure, metered, and flared.

As a precaution against runaway temperatures, the slurry was first introduced into the reactor at 350° C and the incipient hyperactivity of the catalyst was allowed to subside before the reactor was raised to higher temperatures. The heating rate was set at about 10° C per hour, and after the reactor had been heated to the desired temperature, the plant was operated for a nondata period of 2 hours to ensure steady conditions. Similarly, whenever any of the process variables was changed, the plant was allowed 2-3 hours of equilibration time.

The charge weight of catalyst was 31 pounds, and the paste feed rate was 10 lb/hr which is equivalent to a throughput of 20 lb/hr/cu ft of empty reactor. Hydrogen was introduced at a rate of 500 cu ft/hr. The liquid products were collected in batches of 50 pounds and analyzed by conventional methods. Gases were analyzed by gas-solid chromatography. The conversion of organic benzene insolubles to benzene solubles and gases was computed from the total organic benzene insolubles in the feed (maf coal + organic benzene insolubles from tar) and the organic benzene insolubles in the liquid products. To determine the conversion of maf coal, the conversion of organic benzene insolubles from tar under identical experimental conditions should be known separately. The latter information is available for only one set of temperature and pressure, namely 425° C and 4,000 psi².

Materials

Technical data for the commercial silica promoted cobalt molybdate catalyst employed in this work are presented in table 1, and the analyses for coals and high-temperature tars are given in tables 2 and 3 respectively. The three lots of coal differed chiefly in ash content: lot #1 coal had 4.7 percent ash compared to 7.0 percent ash in lot #2 coal, and 11.1 percent ash in lot #3 coal. The two lots of tar differed in ash content, oil distillable below 355° C, and viscosity. Hydrogen of better than 98.5 percent purity was prepared by catalytic reforming of natural gas.

RESULTS AND DISCUSSIONS

In view of the scale of the experiments, it was not practicable to investigate the influence of every change in each process variable with a fresh bed of catalyst. It was therefore decided to study the changes in one variable on one bed and to correct the results by empirically determined factors for catalyst de-activation before comparing them. Thus, the influence of changes in slurry composition was studied on one bed, that of changes in temperature on another bed, and the influence of changes in pressure on a third bed. The specifications for the three experiments were as follows:

1. Influence of slurry composition.

Temperature: 425° C }
Pressure: 4,000 psi } constant

Slurry composition, wt pct: a. 20 coal - 80 tar
b. 30 coal - 70 tar
c. 40 coal - 60 tar

2. Influence of temperature.

Slurry composition, wt pct: 30 coal - 70 tar }
Pressure: 4,000 psi } constant

Temperature: 450° C
460° C
470° C

3. Influence of pressure.

Slurry composition, wt pct: 30 coal - 70 tar }
Temperature: 425° C } constant

Pressure: a. 4,000 psi
b. 3,000 psi
c. 2,000 psi
d. 1,000 psi

Catalyst De-activation

Batchwise analysis of the liquid products from these experiments revealed that under fixed experimental conditions the specific gravity of the liquid products and their composition in terms of organic benzene insolubles, asphaltenes, oil, H, N, and S were approximately constant over the duration of the experiment. The rate of catalyst de-activation vis-a-vis these properties of the liquid products thus appears to be negligible and the results from successive hydrogenations under different experimental conditions may be compared without any correction for catalyst de-activation. The data for a few selected parameters are plotted against time in figures 2-4.

Table 1.- Technical data^{1/} for silica promoted cobalt molybdate catalyst

Chemical composition, wt pct

CoO	3
MoO ₃	15
SiO ₂	5
Al ₂ O ₃	support

Physical properties

Bulk density, lb/cu ft	60
Surface area, m ² /g	200
Pore volume to 10,000 Å, cc/g	0.4
Pore diameter (average), Å	100
Size and form	1/8 inch x 1/8 inch tablets

^{1/} Supplied by the manufacturers.

Table 2.- Ultimate analysis of hvab Pittsburgh coal,^{1/} weight-percent

	<u>Lot #1</u>		<u>Lot #2</u>		<u>Lot #3</u>	
	<u>As recd.</u>	<u>maf</u>	<u>As recd.</u>	<u>maf</u>	<u>As recd.</u>	<u>maf</u>
Moisture	0.6		1.3		0.8	
Ash	4.7		7.0		11.1	
Carbon	79.8	84.3	77.2	84.2	73.5	83.4
Hydrogen	5.4	5.7	5.2	5.7	4.9	5.6
Nitrogen	1.6	1.7	1.5	1.6	1.4	1.6
Sulfur	1.2	1.3	1.6	1.7	1.3	1.5
Oxygen (by diff.)	6.7	7.0	6.2	6.8	7.0	7.9

^{1/} 70 percent through U.S. Standard sieve 200.

Table 3.- Inspection data for high-temperature tar

	<u>Lot 'A'</u>	<u>Lot 'B'</u>
<u>Solvent analysis, wt pct</u>		
Benzene insolubles	13.5	14.0
Asphaltenes	34.7	39.6
Oil	51.8	46.4
<u>Ultimate analysis, wt pct</u>		
Carbon	92.2	92.3
Hydrogen	5.1	4.9
Nitrogen	1.1	1.2
Sulfur	0.8	0.6
Oxygen (by difference) ..	0.8	1.0
<u>Ash, wt pct</u>	<0.1	0.7
<u>AWPA distillation, wt pct</u>		
325° C	2.9	0.0
325° - 355° C	11.1	0.1
<u>Viscosity, ssf at 180° F</u>		
(82° C)	389	500

The hours on stream for a batch plotted in these figures are computed for the point of time midway in the batch.

An additional check on the stability of the catalyst's activity was conducted while investigating the influence of pressure. After 150 hours of experiments at the series of pressures 4,000-1,000 psi, the plant pressure was restored to 4,000 psi and the hydrogenation continued for 29 hours. The batchwise inspection data of the liquid products from this period for organic benzene insolubles, asphaltenes, and specific gravity are given in figure 4, and the average analysis of the liquid products is compared with the average analysis of the liquid products from the earlier period of hydrogenation at 4,000 psi in table 4. The agreement in the results for the two periods is within experimental error. The experiment however revealed a measurable loss in the catalyst's activity with respect to the yield of oil boiling below 355° C: the average yield decreased from 53 percent by weight of the feed to 37 percent in 139.5 hours--the time interval between the midpoints of the two periods of experiment at 4,000 psi. To allow for catalyst de-activation, the actual yields in experiments at 425° C may therefore be corrected according to the following equation before comparison:

$$\text{Corrected yield} = \text{Actual yield} (1 + 0.0031 \times \text{hours on stream}).$$

Table 4.- Average analysis of liquid products
at 4,000 psi and 425° C

	<u>1st period</u>	<u>2nd period</u>
Hour on stream	0 - 50.5	150.5 - 179
<u>Solvent analysis, wt pct</u>		
Organic benzene insolubles	7.1	7.1
Asphaltenes	12.3	14.2
Oil	77.1	75.2
Ash	3.5	3.6
<u>Ultimate analysis, wt pct (ash-free basis)</u>		
Carbon	88.5	88.3
Hydrogen	8.3	8.1
Nitrogen	0.4	0.5
Sulfur	0.3	0.3
Oxygen (by difference)	2.5	2.9

Influence of Slurry Composition

The influence of slurry composition on the parameters of interest is shown in figure 5. At 425° C and 4,000 psi, approximately 74 percent of the combined organic benzene insolubles from coal and tar was converted to benzene solubles or gases, and the conversion was independent of slurry composition in the range 20-40 wt pct coal. This corresponds to an average conversion of about 81 percent maf coal. The concentration of residual organic benzene insolubles and asphaltenes in the liquid products increased linearly with increase of coal concentration in the feed and, correspondingly, the concentration of oil decreased. As the coal concentration increased from 20 to 40 percent in the feed, the concentration both of organic benzene insolubles and asphaltenes in the liquid products increased by about 50 percent, from 8.4 percent

to 12.7 percent and from 11.0 percent to 17.2 percent respectively. The oil concentration decreased from 80 to 68 percent.

Ultimate analysis of the liquid products revealed that the residual concentration of S, 0.2 percent, was only nominally affected by increase in coal concentration, but the concentration of N increased sharply from 0.3 to 0.7 percent as the coal concentration increased from 20 to 40 percent. For the same change in coal concentration, the H content of the liquid products decreased from 8.5 to 7.8 percent.

The yield of oil boiling below 355° C was highest at 30 percent coal concentration: the corrected yield amounted to 47 percent by weight of the feed compared to 37 percent at both 20 percent and 40 percent coal concentrations. The shape of the yield curve in figure 5 is of course arbitrary in-so-far as the precise location of the maxima is concerned.

The yield of total liquid products and gaseous hydrocarbons, 95 percent and about 1.5 percent of the paste feed respectively, were independent of slurry composition.

Influence of temperature

The influence of temperature on the hydrogenation of 30 weight-percent coal slurry at 4,000 psi is shown in figure 6. The results for 425° C are from the previous experiment. The conversion of organic benzene insolubles at 450° C was the same as at 425° C--about 75 percent--but decreased to 65 percent at 460° C and 55 percent at 470° C. The solvent and ultimate analyses of the liquid products showed a similar pattern of influence of temperature. The analyses of the products at 425° C and 450° C differed only marginally, but the analyses of the products at 460° C and 470° C were markedly different. The concentration of organic benzene insolubles, asphaltenes, S, and N increased rapidly with temperature above 450° C and the concentration of oil and H decreased. The yield of oil boiling below 355° C decreased from 38 percent by weight of the feed at 425° C to 29 percent at 470° C.

Another undesirable influence of increase in reaction temperature was an inordinate increase in the yield of gaseous hydrocarbons--from about 1.5 percent of the paste feed at 425° C to 9.2 percent at 450° C. Since the objective of this program calls for maximizing the yield of liquid products, the gaseous hydrocarbons represent a wasteful consumption of H₂. The yields of gaseous hydrocarbons at 460° C and 470° C were 7.8 and 5.7 percent of the paste feed respectively. Thus, in the range of temperature 425°-470° C, the yield of gaseous hydrocarbons appears to be maximum at 450° C.

The yield of total liquid products was 95 percent by weight of the feed at 425° C, 90 percent at 450° C, and 93 percent each at 460° C and 470° C.

Influence of Pressure

The influence of pressure on the hydrogenation of 30 wt pct coal slurry at 425° C in the range of 1,000-4,000 psi is shown in figure 7. The conversion of organic benzene insolubles even at the lowest pressure of 1,000 psi was 55 percent, and increased with pressure to 74 percent at 2,000 psi, and 79 percent at 3,000 psi. The conversion at 4,000 psi, 81 percent, was only nominally different from that at 3,000 psi. Thus, insofar as the conversion of organic benzene insolubles is concerned, the advantage in operating above 2,000 psi is nominal. However, the solvent and ultimate analyses of the liquid products and the figures for the yield of oil boiling below 355° C show substantial improvement in the quality of the liquid products between 2,000 and 4,000 psi.

the concentration of asphaltenes decreased from 24.9 percent at 2,000 psi to 12.3 percent at 4,000 psi, the concentration of N decreased from 0.8 percent to 0.4 percent, the H content of the liquid products increased from 6.9 percent to 8.3 percent, and the corrected yield of oil boiling below 355° C increased from 38 percent to 57 percent. Indeed, the H content of the liquid products and the yield of oil boiling below 355° C appear to be increasing at significant enough rates near the upper limit of our pressure range that some investigation at pressures higher than 4,000 psi may be profitable.

It may be noted that the removal of S is independent of pressure: the residual concentration of S in the liquid products was essentially constant at about 0.2-0.3 percent over the range of 1,000 to 4,000 psi. The removal of N, however, is pressure dependent. The residual concentration of N in the liquid products decreased linearly with increase in pressure, from 1.0 percent at 1,000 psi to 0.4 percent at 4,000 psi. The yields of total liquid products and gaseous hydrocarbons, 95-98 percent and about 3 percent of the paste feed respectively, were independent of pressure.

Throughout the series of experiments described in the present work, the material balance was 95-98 percent, and ash recovery was essentially quantitative.

Influence of Ash

In the course of the investigations described above, the hydrogenation of 30 wt pct coal slurry at 425° C and 4,000 psi was conducted twice: first during the investigation of the influence of slurry composition, and again during the investigation of the influence of pressure. We will call the former run A and the latter run B. A comparison of the results of the two runs--for convenience brought together in table 5-- shows that the conversion of organic benzene insolubles and the yield of oil boiling below 355° C was higher in run B than in run A. We believe this difference is due to the higher ash content of the coal and tar employed in run B compared to the ash content of the coal and tar employed in run A. In run B, the coal employed came from lot #3 which had 11.1 percent ash, and the tar came from lot B which had 0.7 percent ash. For run A, the coal had come from lot #1 which had 4.7 percent ash, and tar from lot A which had <0.1 percent ash. Ash from hvab Pittsburgh coal contains 10 percent or more Fe, a conventional catalyst for the conversion of coal to liquids. In addition, the ash has been reported to contain Sn, Mn, and other transition elements known to have catalytic activity in the hydrogenation of coal (3).

CONCLUSIONS

Slurries of coal in high-temperature tar can be hydrogenated on fixed beds of pelleted cobalt molybdate catalyst. The concentration of oil in the liquid products decreased as the concentration of coal in the feed increased from 20 to 40 percent. In the range of temperature 425° C-470° C and pressure 1,000-4,000 psi, hydrogenation of 30 wt pct coal slurry proceeded most favorably at 425° C and 4,000 psi. Under these conditions, 91 percent of maf coal was converted to liquids and gases, with the yield of liquid products amounting to 96 percent of the paste feed. Approximately 77 percent of the liquid products was oil, 7 percent organic benzene insolubles, 12 percent asphaltenes, and the balance ash. The liquid products contained 8.3 percent H, 0.4 percent N, and 0.3 percent S on an ash-free basis. The initial yield of oil boiling below 355° C was 53 percent by weight of the feed.

REFERENCES

1. Mills, G. Alexander. "Conversion of Coal to Gasoline," Ind. & Eng. Chem., v. 61, No. 7, 1969, pp. 6-17.
2. Akhtar, Sayeed, et al. Unpublished results.
3. Sol Weller and Michail G. Pelipetz. Catalysts in Liquid-Phase Coal Hydrogenation. Proceedings of the third World Petroleum Congress, 1951, Sec. 4, pp. 91-97.

Table 5.- Influence of ash on the hydrogenation of coal slurry in high-temperature tar

	Run A (low ash)	Run B (high ash)
Conversion of organic benzene	74	81
insolubles, wt pct	74	81
Conversion of maf coal, wt pct	81	91
<u>Solvent analysis of liquid products, wt pct</u>		
Organic benzene insolubles	10.2	7.1
Asphaltenes	13.6	12.3
Oil	74.7	77.1
<u>Ultimate analysis of liquid products, wt pct (ash-free basis)</u>		
Carbon	88.8	88.5
Hydrogen	8.1	8.3
Nitrogen	0.5	0.4
Sulfur	0.2	0.3
<u>Yield of oil boiling below 355° C, wt pct of feed (corrected for catalyst de-activation)</u>		
	46.9	56.6

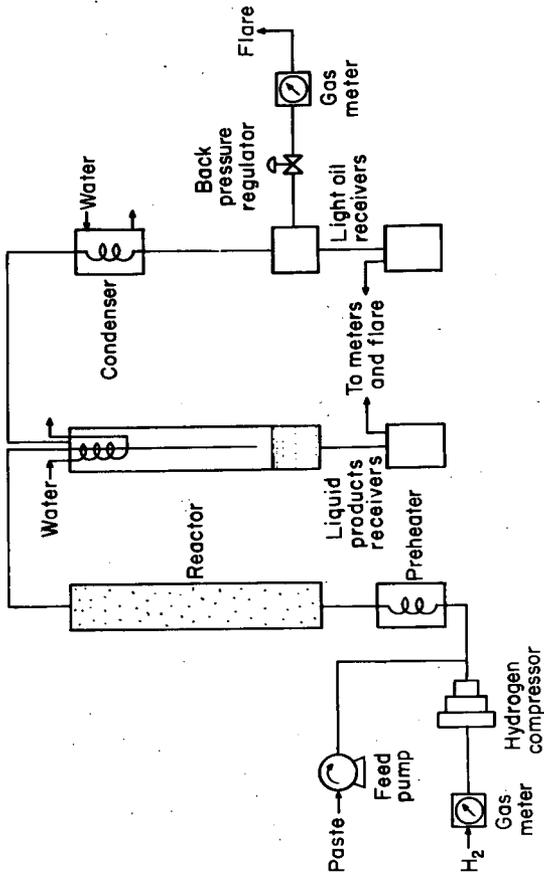


Figure 1—Hydrogenation plant.

L-11355

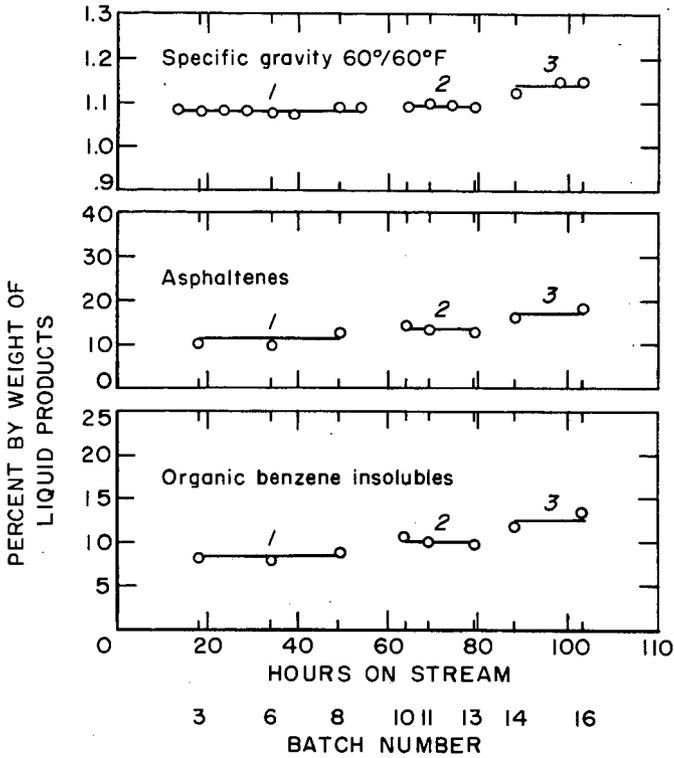


Figure 2 - Batchwise analysis of liquid products from the hydrogenation of coal slurries of different composition. 1. 20 coal-80 tar, 2. 30 coal-70 tar, 3. 40 coal-60 tar.

L-11631

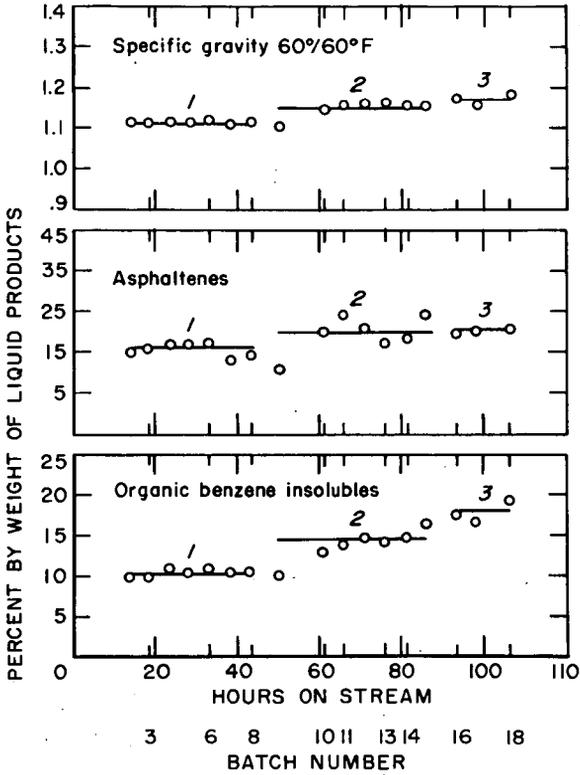


Figure 3-Batchwise analysis of liquid products from hydrogenation at different temperatures. 1. 450°C, 2. 460°C 3. 470°C

L-11632

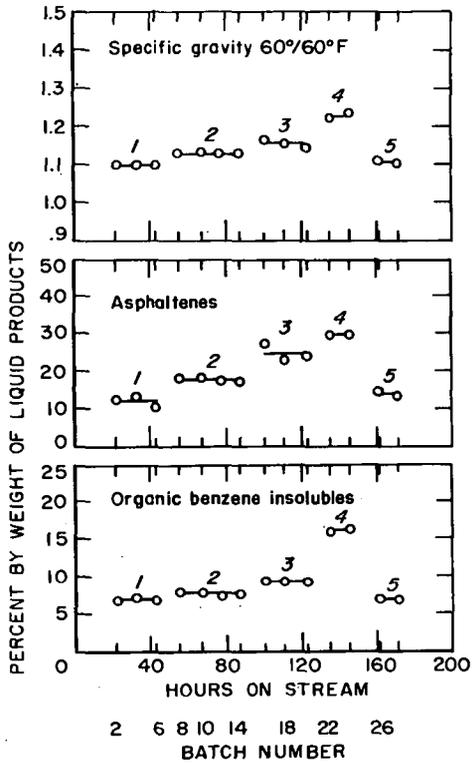


Figure 4- Batchwise analysis of liquid products from hydrogenation at different pressures.
1. 4,000 psi, 2. 3,000 psi
3. 2,000 psi, 4. 1,000 psi
5. 4,000 psi.

L-11633

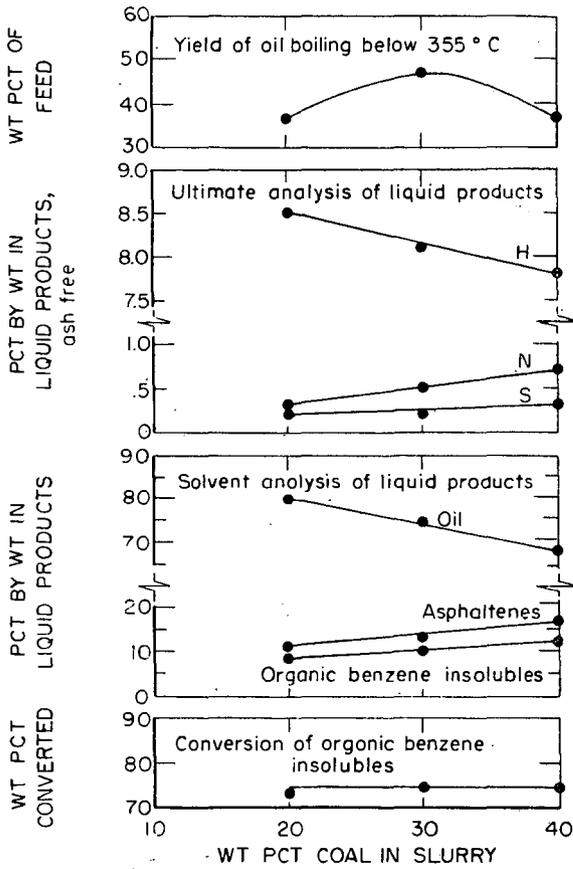


Figure 5—Influence of slurry composition on insols. conversion and composition of liquid products.

L-11634

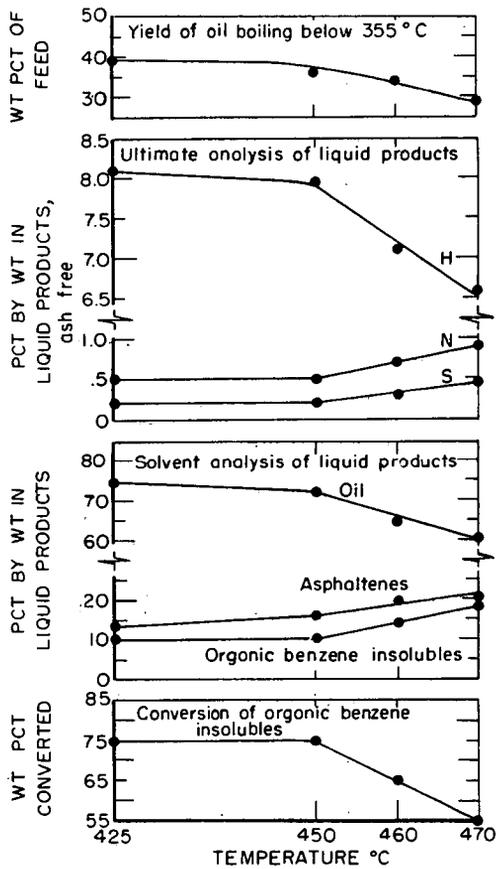


Figure 6—Influence of temperature on insols. conversion and composition of liquid products.

L-11635

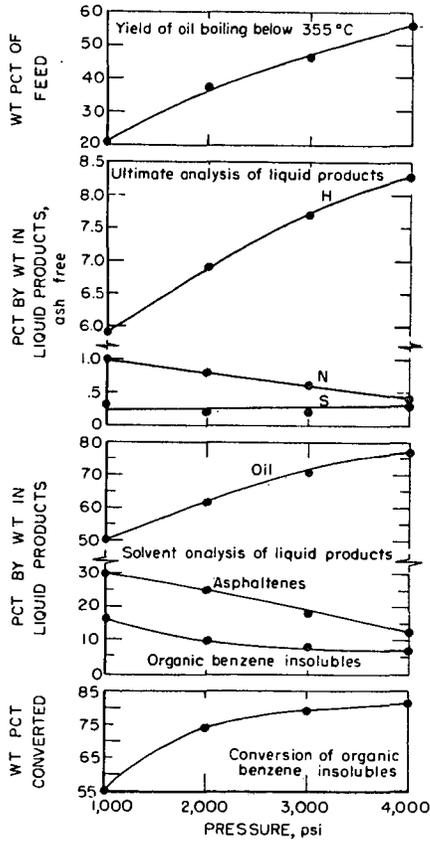


Figure 7—Influence of pressure on insols conversion and composition of liquid products.

L-11636