

Ultraviolet spectrometry has been of indispensable assistance also in the aromatic cyclodehydrogenation studies. These studies<sup>124, 125, 126/</sup> were made to assist in identifying polynuclear hydrocarbons present in coal-hydrogenation oils and to provide an understanding of their mode of formation.

An experimental unit for gasifying powdered coal with oxygen and steam has been designed and erected. A general view of the unit is shown in figure 44. The essential components include an oxygen-supply system, a steam superheater, coal-feeding mechanism, reactor, and dust separator. The reactor is of the vortex type and has a design capacity of approximately 100 pounds of coal per hour. Arrangements have been provided to supply up to 2,000 cubic feet of oxygen per hour and to supply 250 pounds of steam per hour, superheated to approximately 1,500° F. The heat loss from the unit is estimated to be less than 5 percent of the heat in the coal feed at the design conditions. Mechanics of starting the unit involved several short trial operations. Recent operations have been free of any major difficulties and it is expected that the utility of the vortex for powdered coal gasification will be determined within the next year.

#### Process Development - Pilot-Plant Operations

Operation of the internally cooled (by oil circulation) process using a completely flooded bed of granular iron catalyst has been found feasible if the physical structure of the catalyst is such as to avoid disintegration by hydraulic action of the oil. Precipitated and pelleted iron catalysts are not sufficiently robust; but the sintered, or fused, iron oxides are satisfactory. Using a doubly promoted (with potassium and aluminum oxides) synthetic ammonia-type catalyst, several runs were made in the pilot plant after moving it from its Pittsburgh location to Bruce- ton, Pa. These operations varied in duration from several weeks to several months and were planned to ascertain the optimum operating conditions. Although not yet completely determined, these conditions now are reasonably well known, and the present operation will yield durability as well as product quality and product distribution data. A photograph of the plant is shown in figure 45.

The internally cooled process, as now visualized, will operate with largely conductive (by oil circulation) rather than evaporative cooling. For production of maximum amount of Diesel oil, the temperature will be in the range 230°-260° C., the pressure 300 to 450 p.s.i., and the product about 30 percent wax, 35 percent Diesel oil, and 35 percent gasoline. The wax will be subjected to noncatalytic cracking for additional Diesel oil production. For maximum gasoline production, the temperature will be in the range 300°-325° C., pressure 300 to 450 p.s.i., and the product chiefly gasoline with about 15 percent of Diesel oil and 2 to 5 percent of wax. The space-time yield under optimum operating conditions for Diesel-oil production is about half of that expected of the process when producing chiefly gasoline. The latter space-time yield is expected to be about the same as that of the fluidized iron catalyst process developed by the United States oil industry.

The slurry or liquid-phase catalyst, suspension pilot plant is shown in figure 46. Only a few preliminary operations have been made.

124/ Orchin, M., Aromatic Cyclodehydrogenation VI. Synthesis of Ring-Oxygen Compounds: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 495-497.

125/ Orchin, M., and Reggel, L., Aromatic Cyclodehydrogenation VII. Rearrangements in the Phenyl-naphthalene Series: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 1245-1247.

126/ Orchin, M., Reggel, L., Friedel, R. A., and Woolfolk, E. O., Aromatic Cyclo- dehydrogenation: Bureau of Mines Tech. Paper 708, 1948, 40 pp.

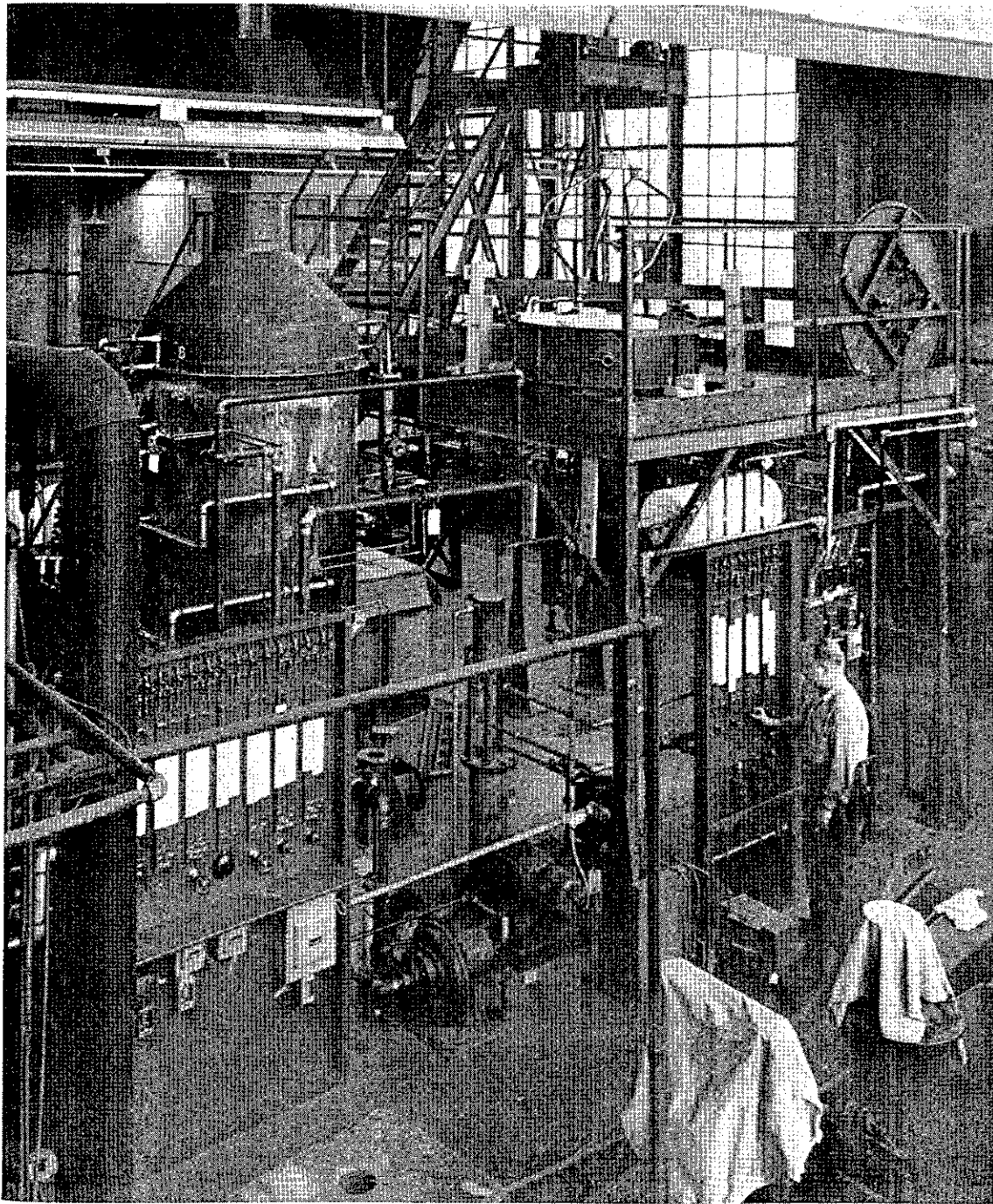


Figure 44. - Vortex powdered-coal gasification pilot plant.

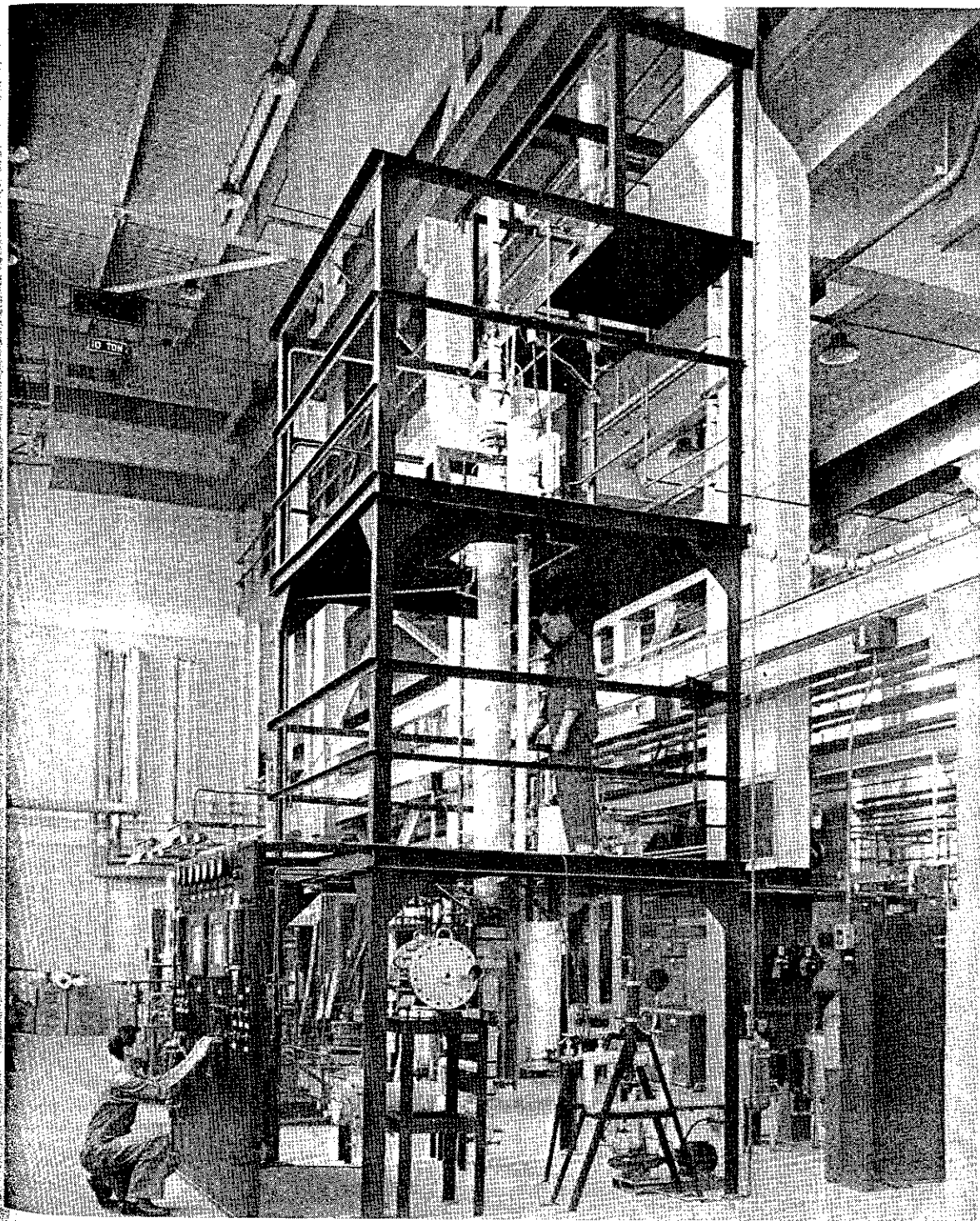


Figure 45. - Internally cooled Fischer-Tropsch pilot plant.

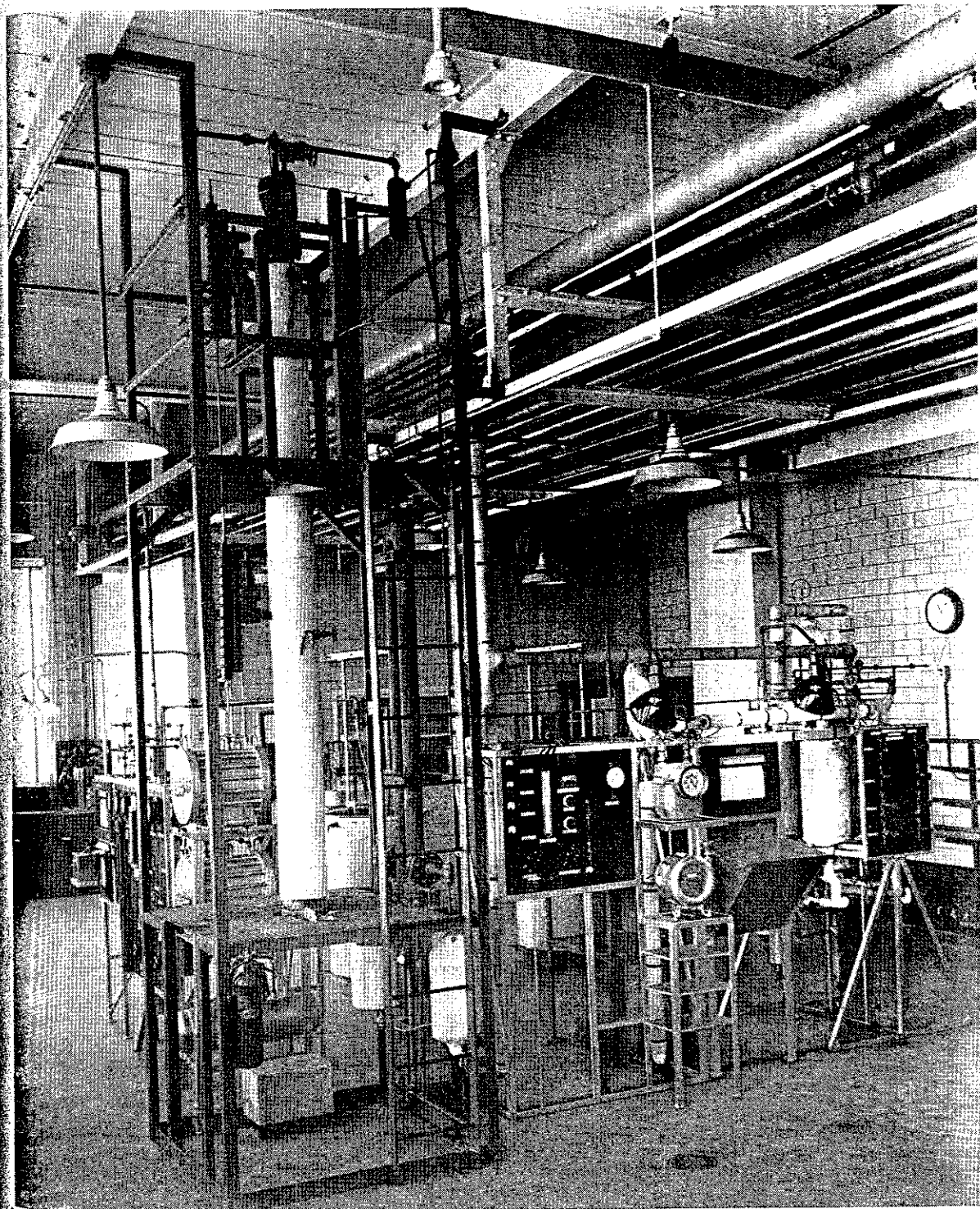


Figure 46. - Slurry-process pilot plant.

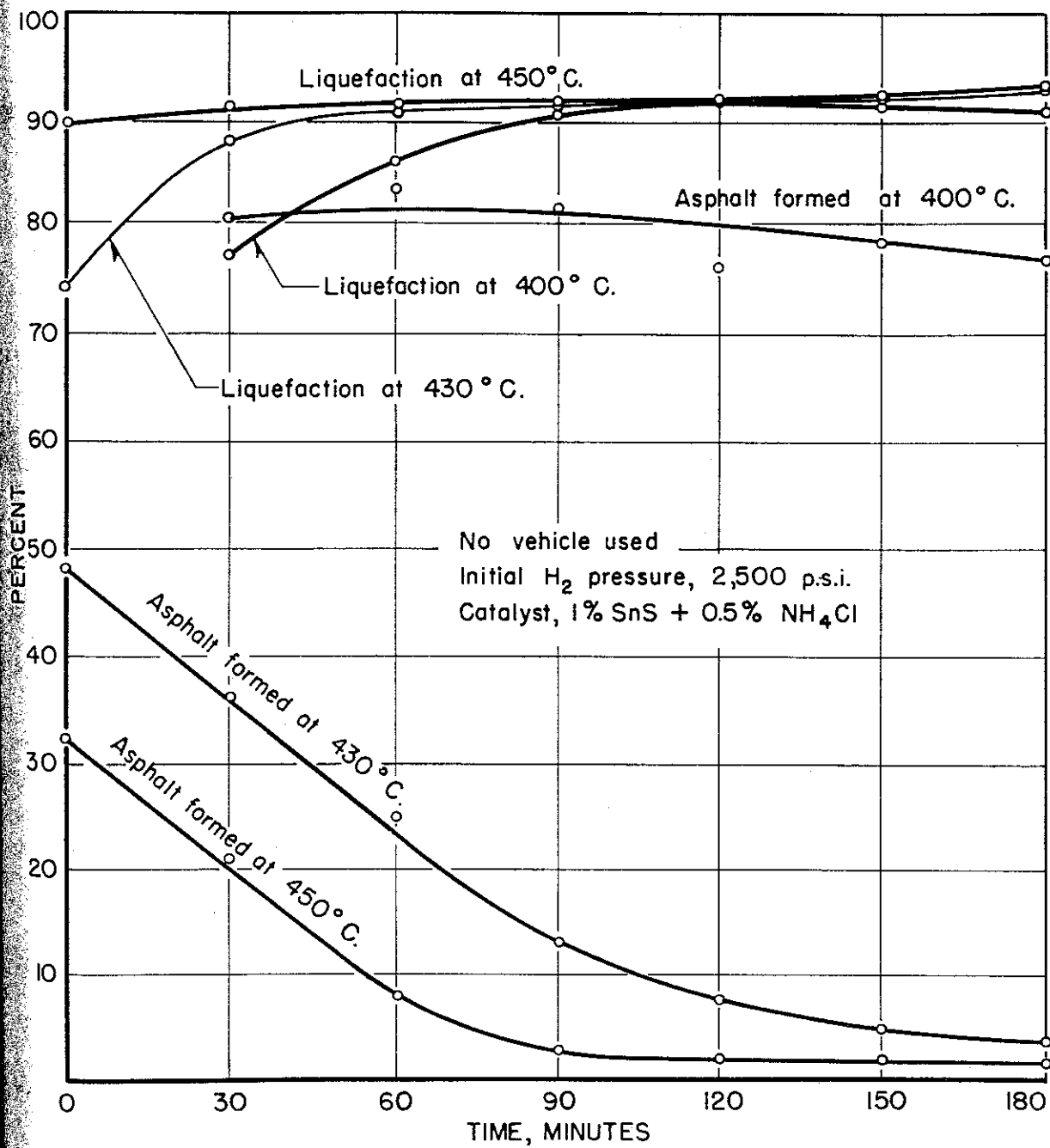


Figure 47. - Liquefaction of coal and asphalt formation.

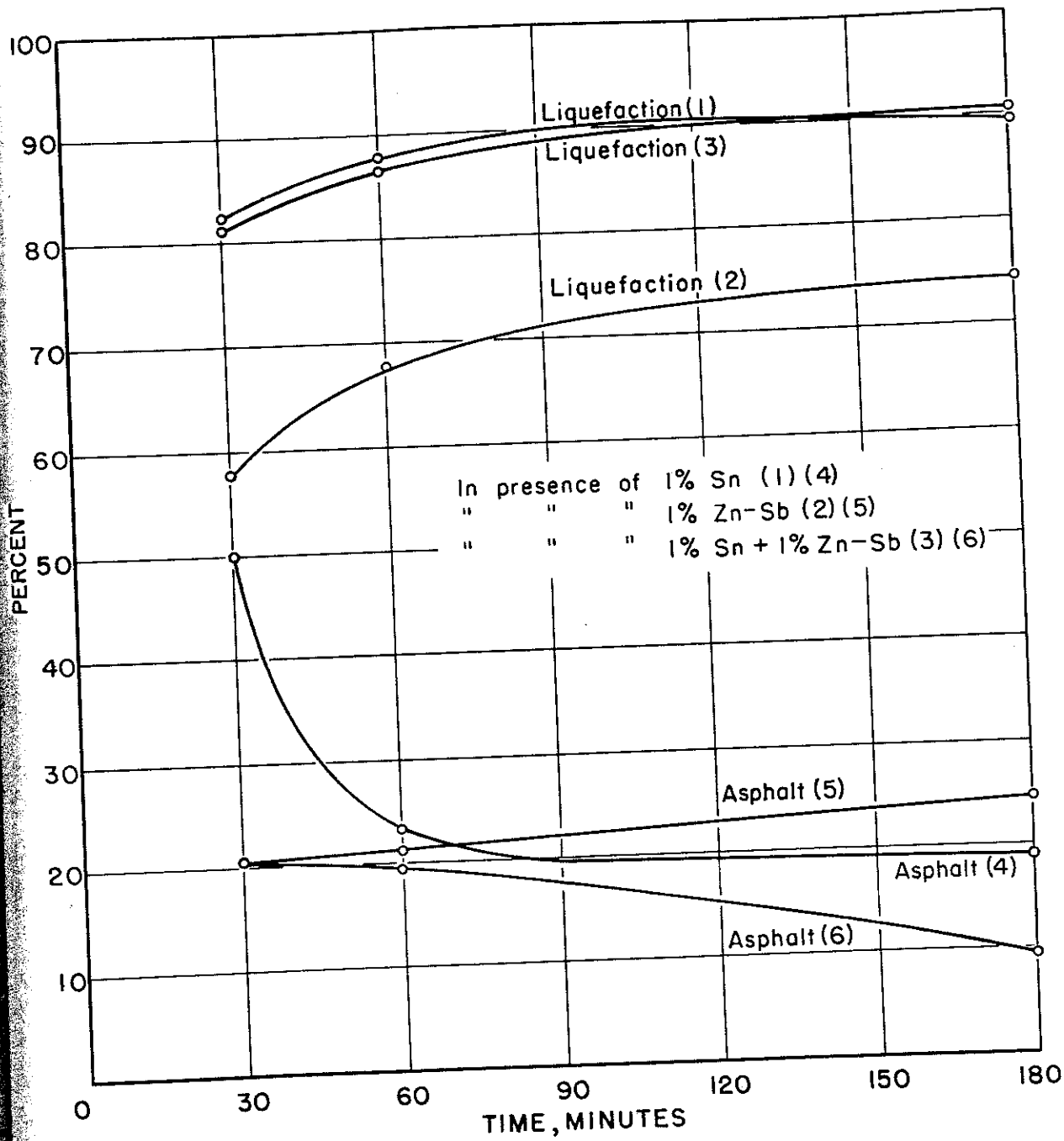


Figure 48. - Liquefaction of coal and asphalt formation at 415° C.

## Hydrogenation of Coal

### Function of Solvents and Catalysts in Early Stages of Coal Hydrogenation

The absence of a vehicle or solvent does not affect the rate of liquefaction of bituminous coal, but the quantity of asphaltic material (insoluble in n-hexane but soluble in benzol) produced is much less in the absence of solvents. This observation is of importance in that the capacity of a coal-hydrogenation plant can be increased appreciably by a decrease in the amount of asphaltic material per unit of n-hexane soluble oil produced. Because of the severe engineering difficulties and high costs involved in continuous feeding of dry coal into a high-pressure plant, the immediate application of this information concerning the reduced asphalt production in dry coal hydrogenation will be made by pumping a slurry of coal and a very low boiling oil or water. Either of these vehicles can be "flashed" out of the reactor in a stream of superheated hydrogen.

In hydrogenation of coal in absence of a vehicle, the quantity of asphaltic material per unit of liquefaction decreases rapidly with increasing hydrogen pressure in the range 1,000 to 10,000 pounds per square inch, from 0.3 to 0.1. The effects of contact time and temperature<sup>127</sup> at 2,500 pounds per square inch initial pressure (about 5,500 pounds at reaction temperature) is shown in figure 47. At 400° C., the rate of hydrogenolysis of the asphaltic material is very low, but it increases rapidly with increasing temperature so that at 430° C. the rate is high enough for a practical coal hydrogenation process.

At low temperatures (400°-415° C.) and when a hydroaromatic compound such as tetralin is employed as a vehicle, the yield of asphaltic materials can be greatly reduced by the use of powdered zinc-antimony alloy as catalyst. This effect is illustrated in figure 48. At higher temperatures, or when either no vehicle or an aromatic hydroxylated vehicle is employed, the specificity of zinc-antimony for low asphalt production is so much less pronounced that its use in a practical coal-hydrogenation process is of little or no advantage. Similar differences have been observed in studying the relative efficiencies of tin and molybdic acid as catalysts. Thus, molybdic acid is almost as highly efficient as tin for coal hydrogenation when tetralin is used as a vehicle. When no vehicle is used, molybdic acid is markedly inferior to tin.

The outstanding efficiency of tin as a catalyst for the first stages of coal hydrogenation persists under a great variety of conditions. Whatever type of vehicle is employed, in the absence of any vehicle, and in a wide range of temperatures and pressures, tin is outstandingly more efficient than other catalysts. This is also true for a wide range in rank of coal, provided an adequate adjustment is made in the proportion of ammonium chloride used to neutralize the alkaline inorganic constituents of the coal. An excess of ammonium chloride of about 0.5 percent (of the coal) beyond the neutralization point is essential in all cases for maximum efficiency of tin. No satisfactory explanation of the unique character of tin has yet been found. Laboratory experiments designed to furnish such information are in progress.

Because of the scarcity of tin, it is necessary to employ more readily available and cheaper catalysts in practical coal hydrogenation operations. As may be seen

<sup>127</sup> Pelipetz, M., Kuhn, E. M., Friedman, S., and Storch, H. H., Effect of Catalysts on Hydrogenolysis of Coal: Ind. Eng. Chem., vol. 40, 1948, pp. 1259-1264.

from table 19, when a high pressure of about 9,000 pounds per square inch of hydrogen is used, the cheaper and more readily available iron compounds approach the high efficiency of tin.

TABLE 19. - Hydrogenation of Rock Springs, Wyo., high-volatile C bituminous coal

(In laboratory autoclaves at 450° C., 3,700 pounds per square inch initial (cold) hydrogen pressure (about 9,000 pounds at reaction temperature), in absence of any vehicle. Pyrex glass liner used to avoid catalysts by metal walls.)

Run No.	Catalyst	Percent of liquefaction	Asphalt per unit of liquefaction	Percent of coal gasified
859	-	70.9	0.43	17.8
861	1 percent Sn + 0.5 percent NH <sub>4</sub> Cl ....	97.7	.07	11.6
855	0.1 percent Sn as SnCl <sub>2</sub> .2H <sub>2</sub> O .....	87.8	.50	17.8
878	0.1 percent Sn (powdered) .....	82.4	.57	13.8
849	0.1 percent MoO <sub>3</sub> .....	70.0	.43	16.6
881	0.1 percent Zn + 0.2 percent NH <sub>4</sub> Cl ..	75.6	-	-
857	0.1 percent Fe as FeSO <sub>4</sub> .7H <sub>2</sub> O .....	70.6	.51	15.6
866	1 percent Fe as FeSO <sub>4</sub> .7H <sub>2</sub> O .....	84.7	.55	13.5
872	1 percent Fe (powdered) .....	64.7	.61	11.6
875	1 percent Fe as pyrite .....	83.1	.43	13.5
845	1 percent dried "red mud" <sup>1/</sup> .....	83.5	.49	19.1

<sup>1/</sup> Obtained through the courtesy of the Aluminum Co. of America. This material is the equivalent of Bayermasse, used extensively in German coal-hydrogenation plants.

The uncatalyzed hydrogenation resulted in a liquefaction of 71 percent. As usual, Sn (in the presence of Cl) proved to be outstanding. The "Standard" catalyst, 1 percent Sn + 0.5 percent NH<sub>4</sub>Cl, produced a liquefaction of 98 percent. 0.1 percent Sn, added as SnCl<sub>2</sub>, resulted in 88 percent liquefaction, while 0.1 percent Sn powder was somewhat less effective. At a concentration of 0.1 percent, all other catalysts tried were relatively poor. Since it is desired to use an iron catalyst in the demonstration plant if possible, several iron catalysts were tested at a higher concentration level. Of these, dried "red mud"<sup>128/</sup> seems most promising. At a total concentration of 1 percent, it is as effective as 1 percent iron in the form of FeSO<sub>4</sub> (that is, 2.7 percent FeSO<sub>4</sub>), and it is probably considerably cheaper.

The extent of gasification varied in a random manner in these experiments, and it did not seem to be associated with the extent of liquefaction. The asphalt production was high in all cases except that in which 1 percent Sn was used.

#### Laboratory-Scale Process Development

A reactor for studying the hydrogenation of dry coal has been built. Experiments will be made in a wide range of temperatures, pressures, and catalysts. The apparatus, which is shown in figure 49, is arranged so that a continuous feed of powdered coal is supplied from a pressurized hopper, and a continuous stream of preheated hydrogen keeps the powdered coal in suspension. The volatile reaction products are carried out in the stream of hydrogen gas and the nonvolatiles discharged as a heavy pitch or slurry of unreacted coal and ash in a heavy oil.

Early experiments indicate that valuable process design information can be obtained from this unit.

<sup>128/</sup> See footnote 1, table 19.



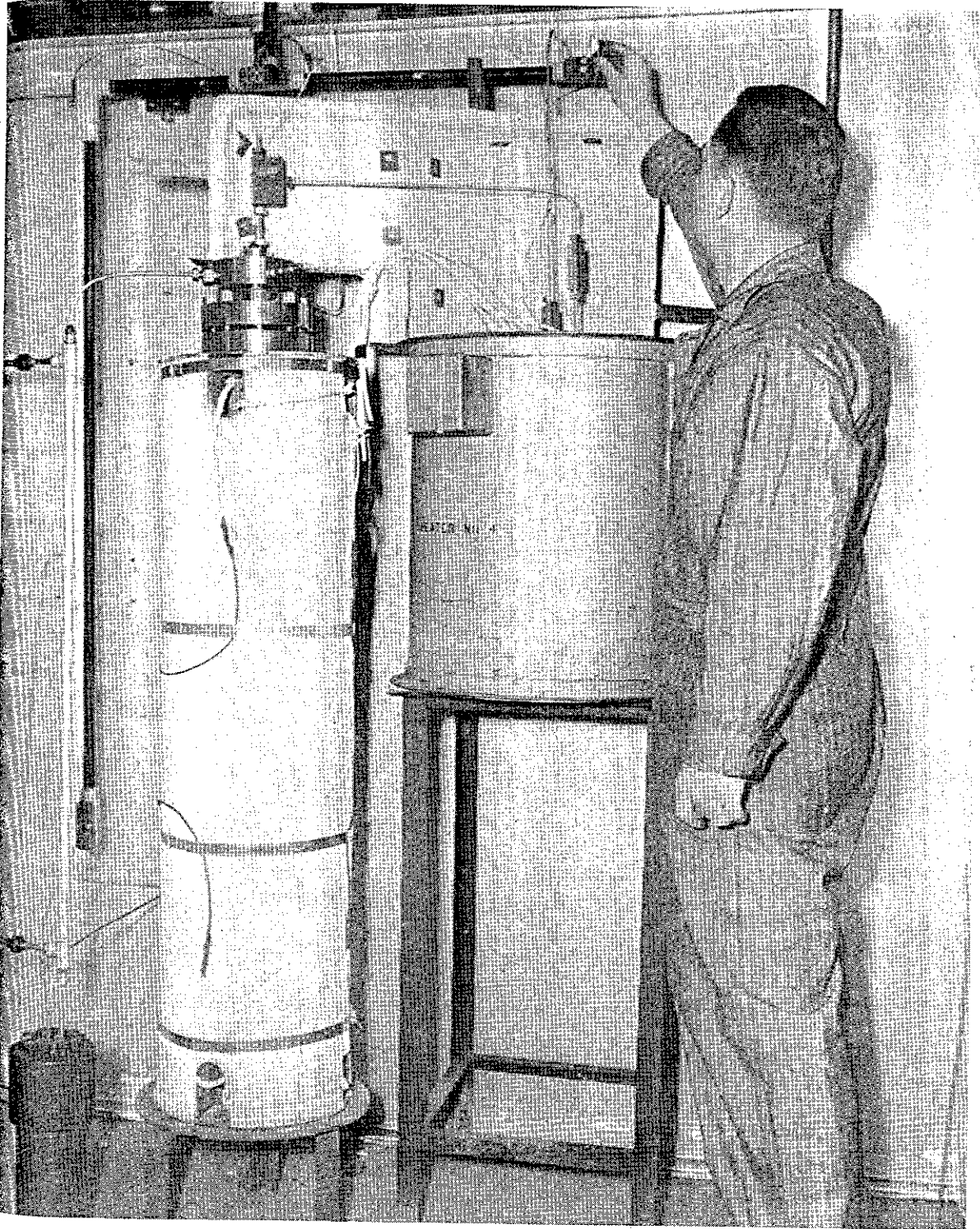


Figure 49. - Laboratory reactor for coal hydrogenation in absence of vehicle.

Because of widespread interest, a description of the bench-scale coal-hydrogenation equipment and procedures has been published.<sup>129/</sup>

Interest was expressed in determining the susceptibility to hydrogenation of gilsonite, a naturally occurring asphalt. A sample of gilsonite from the Uinta Basin, Utah, was found to contain 2.0 percent benzene-insoluble material, 79.0 percent asphalt (soluble in benzene, insoluble in n-hexane), and 19.0 percent oil (soluble in n-hexane). It had the following ultimate analysis:

Element	Weight, percent
H	10.13
C	85.16
N	3.18
O	1.18
S	0.26
ash	0.09

Several batch autoclave runs were made to determine the ease with which gilsonite is hydrogenated under our standard conditions. The results are summarized in tables 20 and 21. The density of hexane-soluble material produced was 0.911 gram per cc. at 25.6° C.

TABLE 20. - Hydrogenation of gilsonite

50 g. gilsonite, 450° C., 1 hr.

Run No.	Sn added, percent	NH <sub>4</sub> Cl added, percent	Initial pH <sub>2</sub> , p.s.i.g.	Asphalt, <sup>1/</sup> percent	Oil, <sup>1/</sup> percent	Gasification, <sup>1/</sup> percent	Benzene insolubles, <sup>1/</sup> percent
762	-	-	1,000	14.2	61.0	14.2	11.4
749	1	-	1,000	17.6	56.8	17.4	9.2
750	-	0.55	1,000	16.8	51.8	19.8	13.6
726	1	.55	1,000	4.0	79.2	15.2	4.7
739	1	.55	1,500	2.2	79.8	17.6	2.9

<sup>1/</sup> Based on weight of gilsonite only.

TABLE 21. - Production of volatile oil

Run No.	Percent converted to product distillable below 85° C., 1 atmos.	Percent converted to product distillable below 200° C., 2 mm. Hg
726	28.6	60.6
739	32.0	65.2

It is evident that the hydrogenation of gilsonite proceeds with ease, even in the absence of a catalyst. Unless both Sn and NH<sub>4</sub>Cl are present, however, there is an appreciable production of benzene-insoluble material and a decrease in the quantity of asphalt converted to oil. Gas production was about the same in all the experiments. As may be seen from table 21, about 30 percent of the gilsonite is

<sup>129/</sup> Clark, E. L., Golden, P. L., Whitehouse, A. M., and Storch, H. H., Bench-Scale Equipment and Techniques - High-Pressure Reactions: Ind. Eng. Chem., vol. 39, 1947, pp. 1555-1564.