for many phenols of known constitution, and this information was applied to the qualitative and quantitative estimation of the composition of most of the tar-acid fractions. Ultraviolet absorption spectra were determined for all the phenols separated from coal-hydrogenation oils in this laboratory. Classical methods of organic chemistry, such as crystallization, preparation of deriva-tives, and degradative studies, were also used.

Chemical and physical investigation of certain of the fractions resulted in the isolation and identification of 16 individual phenols: Phenol; o-, m-, and p-cresol; o-, m-, and p-ethylphenol; 2,5-, 2,4-, 3,4-, and 3,5-xylenol; 3-methyl-5-ethylphenol; 4-, and 5-indanol; and o- and p-phenylphenol. Evidence was obtained for the presence of 2,3-xylenol and mesitol. The proportions in which 14 phenols were found were estimated quantitatively by infrared spectrophotometry.

A study of the phenolic constituents of coal-hydrogenation asphalt was made by the countercurrent distribution method (39). This study showed the presence of two groups of phenols: (1) A group extracted by aqueous alkali, which included alkylphenols and phenylphenols; and (2) another group soluble only in Claisen's methanolic alkali solution and probably a mixture of phenols with polynuclear structures. Close agreement between experimental and theoretical distribution curves indicated considerable homogeneity for each group with respect to partition coefficient. The asphalt fraction extracted by Claisen's alkali contained about one-third of the total oxygen in the asphalt; this oxygen was mostly in the hydroxyl form. Only about 30 percent of the oxygen in the residue could be definitely ascribed to hydroxyl oxygen.

Composition of Gasoline From Coal Hydrogenation

The Bureau of Mines operated a 200-barrel-per-day coal-hydrogenation plant at Louisiana, Mo., for several years. The oil from liquid-phase hydrogenation was used as feed in the vapor-phase hydrogenation. As the composition of the product of this plant is of theoretical and practical importance, the gasoline fraction of the vapor-phase feed and the entire vapor-phase product were examined (23).

The vapor-phase product was of greatest interest. C_6 to C_8 hydrocarbons constituted 58 percent of the product; of this, 19.0 percent was paraffins, 49.9 percent naphthenes, and 31.2 percent aromatics (all weight percents). Obviously, gasoline from coal hydrogenation can be a valuable source of benzene, toluene, and C_8 aromatics. For example, 1 ton of dry ash-free coal yields by carbonization about 2 gallons of benzene, but by hydrogenation it yields about 18 gallons.

Process Development

Pilot-Plant Studies at 3,500 and at 1,500 p.s.i.

Process variables and catalysts were investigated at 3,500 p.s.i., using a Wyoming Rock Springs and a Pittsburgh-seam coal, to determine the feasibility of producing fuel oil from coal at moderate pressures and to obtain data on the primary liquefaction step. A typical flowsheet for these experiments is shown in figure 41. The reactor system consisted of two converters fitted with 2-inch inside-diameter liners, 87 inches long. Details of the equipment have been published (22). Tests were conducted on a recycle basis, using coal
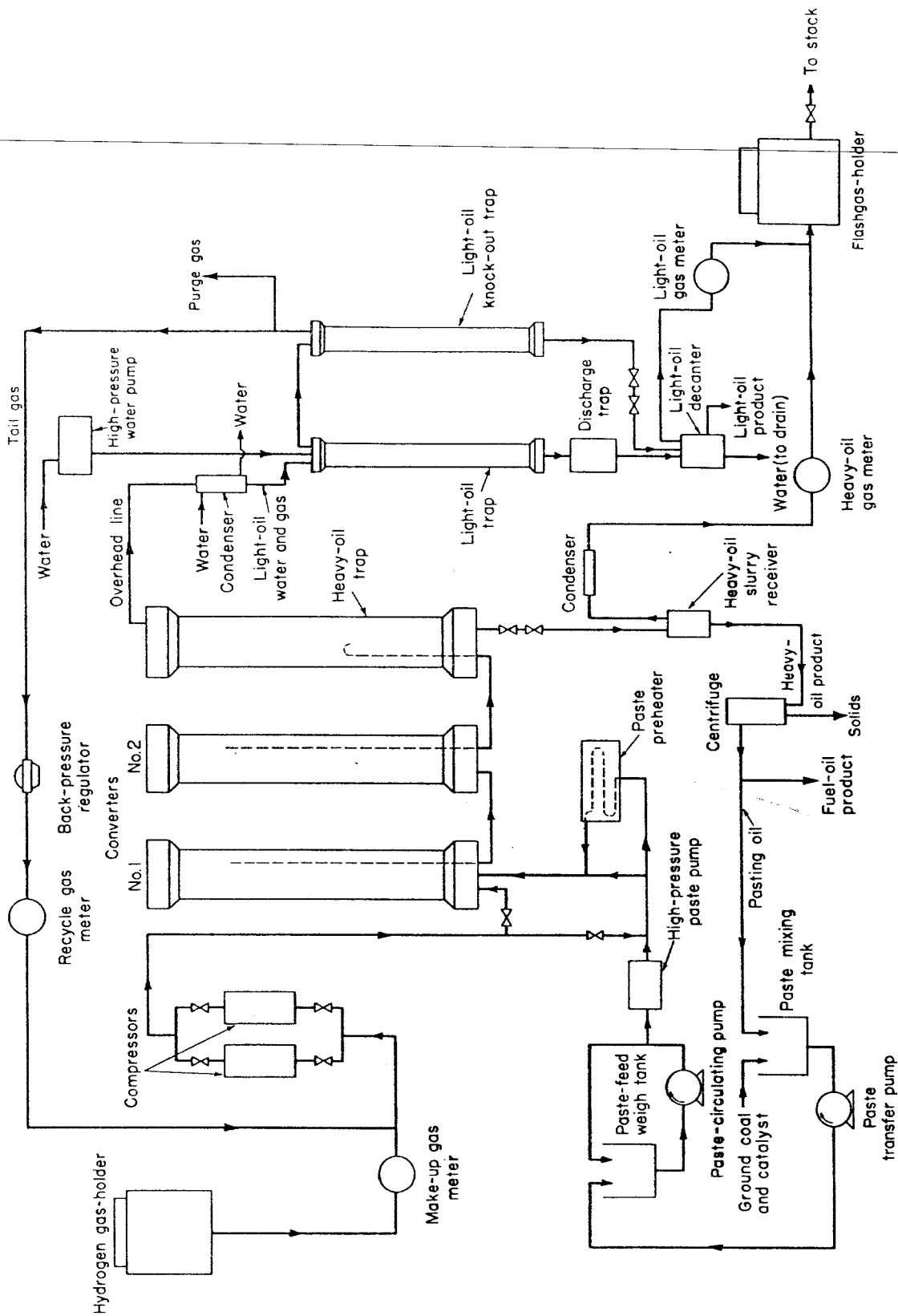
FIGURE 41. - Flowsheet of Pilot Plant for Hydrogenating Coal at 1,500 and at 3,500 p.s.i.

paste containing 35 weight-percent coal, with residence times from 0.2 to 0.9 hour, at temperatures from 440° to 480° C. (824°-896° F.).

With Rock Springs coal and 0.1 percent stannous sulfide plus 0.05 percent iodoform, a decrease in residence time (at constant temperature and pressure) resulted in a linear increase in space-time-yield of oil. At 440° C. (824° F.), 3,500 p.s.i., and 0.9 hour residence time, the yield of soluble oil per cubic foot of reaction space amounted to 15 pounds per hour. With a residence time of 0.2 hour, this increased to 70 pounds per hour. With the lower space-time-yield, the product oil contained about 10 percent asphaltenes, while with the higher space-time-yield, asphaltenes increased to 22 percent. With 0.9 hour residence time, the hydrogen absorption and hydrocarbon gas production amounted to 9 and 14 percent, respectively, based on moisture- and ash-free coal; while with 0.2 hour residence time, hydrogen absorption and hydrocarbon-gas production decreased to 4 and 7.5 percent.

At 0.2 hour reaction time, 70 pounds of soluble oil per hour per cubic foot of reaction space, with an asphaltene content of 22 percent, was obtained at 440° C. Increasing the reaction temperature to 480° C. reduced the space-time-yield to 60 pounds of oil of 12 percent asphaltene content. Hydrogen absorption increased from 4 to 9 percent and hydrocarbon gas yield from 7.5 to 8.3 percent, based on moisture- and ash-free coal.

The effects of time and temperature on the hydrogenation of a Pittsburgh-seam coal (Bruceton) were like those described for Rock Springs coal. However, the oil produced from Bruceton coal was considerably higher in average molecular weight. Fuel oil meeting Bunker C requirements was produced from Rock Springs coal at 440° C., using 0.3 hour contact time with stannous sulfide catalyst. Similar oil could be produced from Bruceton coal only by increasing residence time to 0.5 hour.

Studies were conducted at 460° C. (860° F.) and 3,500 p.s.i. to determine the efficacy of various catalysts for producing fuel oil from Rock Springs coal under recycle pasting-oil conditions. Base runs were made without a catalyst and with 0.1 percent tin (stannous sulfide) plus 0.5 percent ammonium chloride, 1.0 percent iron as ferrous sulfate, 0.5 percent nickel as nickelous chloride, and 0.1 percent metallic zinc plus 1 percent ammonium chloride, based on moisture- and ash-free coal. Except for zinc, these catalysts converted coal to liquid and gaseous hydrocarbons at essentially the same rate. With 0.4 hour residence time, about 73 percent of the moisture- and ash-free coal was converted to oil containing 16 percent asphaltenes and about 13 percent to gaseous hydrocarbons. With 0.9 hour residence time, 60 percent of the moisture- and ash-free coal was hydrogenated to oil containing 10 percent asphaltenes, and about 25 percent to gaseous hydrocarbons. No significant differences in catalyst selectivity were noted.

With zinc, conversion to oil was poor. With 0.4 hour residence time only 46 percent of the coal was converted to oil and about 21 percent to gaseous hydrocarbons. Longer contact time of 0.9 hour produced coal-to-oil conversion of 60 percent and coal-to-gas conversion of 30 percent.

It appears that iron, nickel, or tin could be used at 3,500 p.s.i. and 460° C. to produce fuel oil from Rock Springs coal. Iron would be cheaper and more available during an emergency.

Continuous coal-to-fuel-oil operation at low pressures would permit use of conventional commercial equipment and thus expedite adoption of synthetic-oil production during emergencies. Studies were carried out at 460° C. and 1,500 p.s.i. with Rock Springs coal. The efficacy of 1 percent nickel as nickelous chloride, 0.5 percent tin as stannous chloride, 0.5 percent molybdenum as ammonium molybdate, and 1.0 percent iron as ferrous sulfate, based on m.a.f. coal, was determined for residence times from 0.3 to 1.0 hour, under recycle pasting-oil conditions.

At 1,500 p.s.i. and 460° C., 87 to 92 percent of the moisture- and ash-free coal was converted to liquid and gaseous hydrocarbons. Conversion was least with iron and nickel and greatest with tin and molybdenum. About 55 to 60 percent of the m.a.f. coal was converted to oil with 7 to 17 percent asphaltene content and containing 27 to 46 weight-percent material boiling under 355° C. (635° F.). Molecular degradation was greatest with tin or molybdenum and least with iron or nickel. From 18 to 25 percent of the moisture- and ash-free coal was transformed to gaseous hydrocarbons. Gas formation was least with iron and greatest with nickel. The methane and ethane content of these gases amounted to 60 and 21 volume-percent, respectively; the total butane and propane content was 13 percent.

Coal hydrogenation at 1,500 p.s.i. would apparently be feasible for the production of fuel oil, provided active catalysts such as tin or molybdenum could be utilized. Iron did not seem desirable in view of its ineffectiveness in decreasing molecular weight; however, longer residence times might permit use of iron under these low-pressure conditions.

Hydrogenation of Coal at High Temperatures

The objective of high-temperature coal-hydrogenation studies was to determine the feasibility of converting coal into refined gasoline in a single step. Autoclave experiments at final temperatures of 500° to 525° C. (932° to 977° F.) had produced oils of relatively low molecular weight, and suggested the possibility of converting coal into gasoline in a single-step process, provided high enough temperatures, large quantities of active catalysts, and appropriate throughputs could be utilized without incurring coking.

Bench-scale experiments on the effect of flow rates of gas and coal paste upon the extent of reaction and type of products were performed in a 32-foot coil of 1/8-inch inside-diameter tubing wound in a helix of 4-inch diameter. Rock Springs coal was impregnated with 1 percent molybdenum after neutralization with sulfuric acid. Coal paste was prepared by mixing 40 percent by weight of coal with 60 percent of an oil distilling from 250° to 312° C. (482° to 594° F.). The reactants were passed through the coil, without recycling, at 535° C. (995° F.) and 8,000 p.s.i. A schematic flowsheet of the unit is shown in figure 42.

An eightfold change in paste rate at constant gas flow did not affect conversion or type of products. About 95 percent of the coal was converted to liquids and gases. Yields of gasoline, based on m.a.f. feed (coal plus pasting oil), amounted to 17 percent, residual oil (boiling above 204° C.) to approximately 73 percent, and hydrocarbon gases to 7 percent. A sixfold change in gas velocities, at constant paste rate, caused little change in the conversion of coal. However, the gasoline content of the product oil increased with decrease in gas velocities. These changes apparently were due primarily to
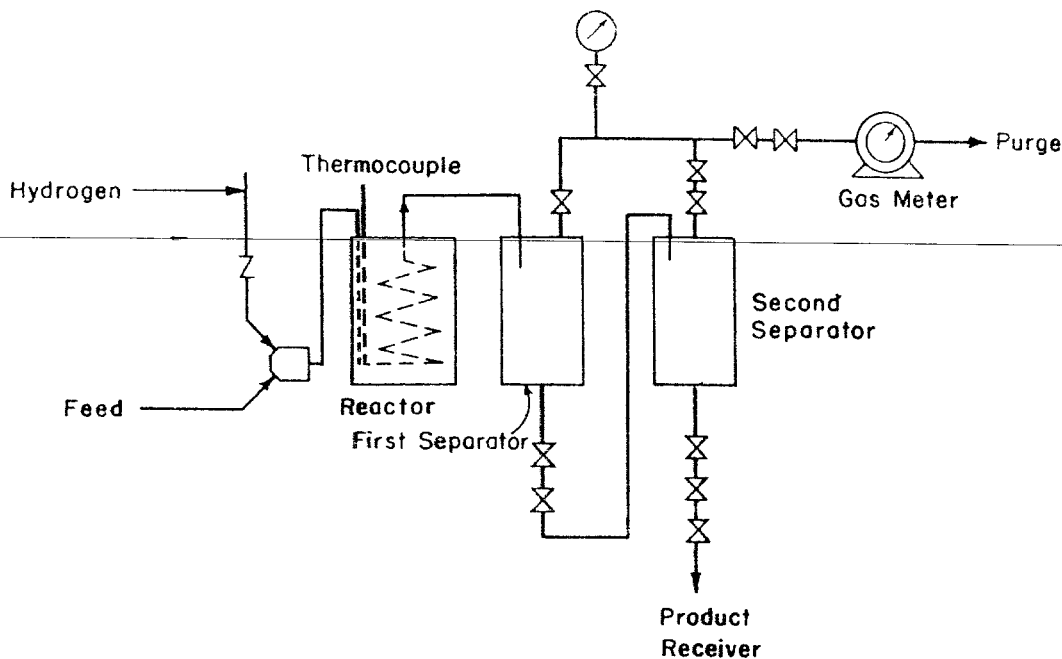
FIGURE 42. - Bench-Scale, High-Temperature Hydrogenation Unit.

hydrogenation of the vehicle oil. Hydrogenation of vehicle oil alone showed the same relationship between gasoline content of the product and gas rate.

The data suggested the following hypothesis: Slugs of coal-oil slurry entered the tubular reactor. After traversing a short distance the vehicle oil was vaporized, and the vapors hydrogenated to gasoline and higher boiling hydrocarbons. Concurrently, coal was rapidly converted to primary products, such as asphaltenes and heavy oils, which were pushed through the tube and formed a rather thin film on the walls where they hydrogenated to lighter fractions and vaporized.

This bench-scale work was complicated by plugging within the reactor. Concentrated coal masses were formed, with localized overheating and carbonization.

Pilot-plant trials were begun in the unit shown in figure 43. The reactor was a vessel 3 inches in diameter and 10 feet in length, designed for continuous operation at 8,000 p.s.i.g. and 525° C. (977° F.). In the early experiments the lower two-thirds of the reactor was used as a preheater and the upper third as a reaction zone. Temperature control was maintained by varying the external heating and the amount of cold gas fed into the reactor. The coal paste contained 60 weight-percent of a distillable (250° to 312° C.) oil and was fed directly into the reactor. With 1 percent molybdenum, on a m.a.f. coal basis, results were only moderately successful at temperatures of 480° to 510° C. (896° to 950° F.). Only the upper third of the reactor could be utilized as reaction space without incurring "runaway" temperatures. Heat was required to bring the reactants to the initial reaction temperature (425° C.), and then cooling to remove the heat of reaction. In the single converter such control was impossible because there was no clear line of demarcation between the heating and cooling zones.

In spite of these difficulties some data were obtained (tables 9 and 10). Increasing the temperature from 480° to 510° C. (896° to 950° F.) had little

effect upon conversion, gasoline yields, hydrogen consumption, or product distribution. The conversion of coal to liquid and gaseous products was about 98 percent, and the gasoline yield amounted to about 10 percent of the total feed. The residual-oil fraction, boiling above 200° C., was approximately 74 percent of the total feed and contained about 2.3 percent asphaltenes. The hydrogen content of the residual oil, slightly over 9 percent, was about the same as in the original vehicle oil. Hydrocarbon gases were 4.8 to 6.3 weight-percent of the feed.
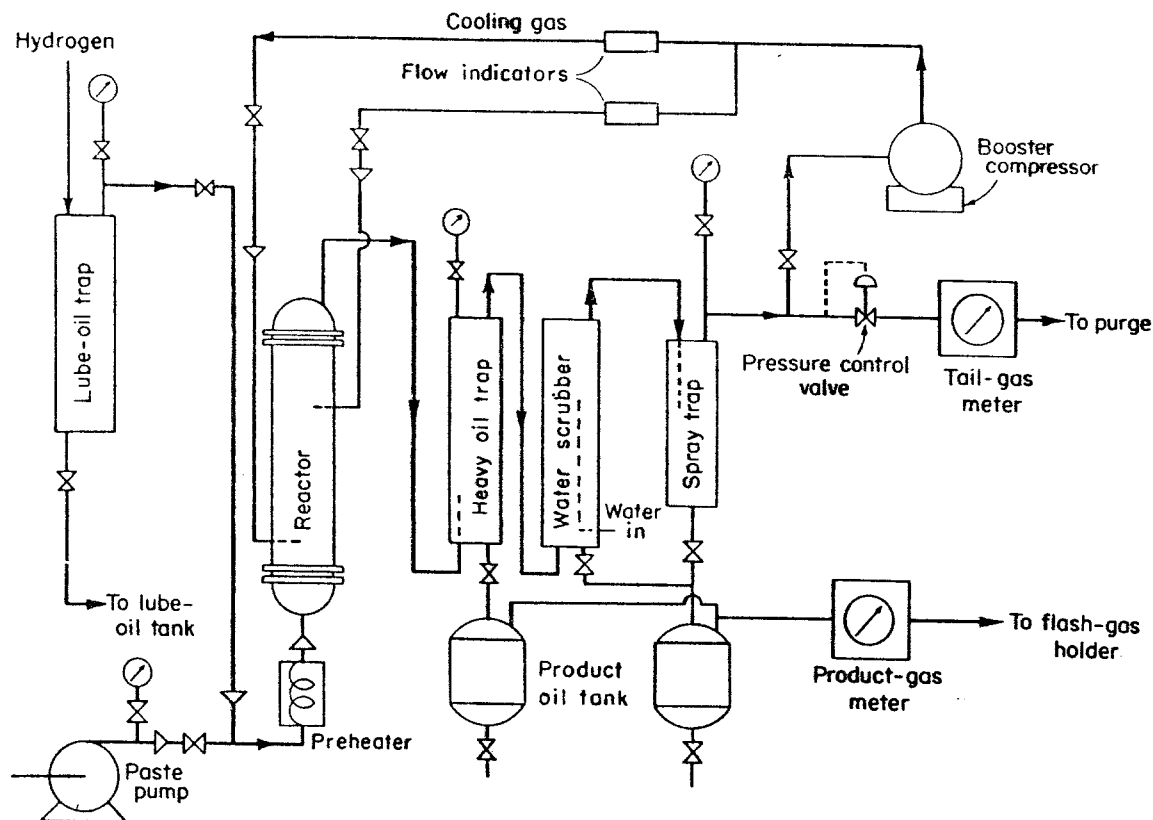

FIGURE 43. - High-Temperature-Hydrogenation Pilot Plant, Simplified Flowsheet.

As described above the system was not suited for adequate temperature control throughout the reactor. Therefore, the system was drastically redesigned. The revised plant (fig. 44) included an external preheater and an insulated reactor with two cold-gas admission points. External furnaces compensated for radiation and convection losses. The reactants were preheated rapidly to 425° C. (797° F.) and then discharged into the reactor. The heat of reaction was the sole source of additional heat, and final temperatures were maintained by admission of cold hydrogen. Many runs were made to develop necessary operating and mechanical techniques. Tests were conducted at 8,000 p.s.i., using topped high-temperature tar vehicle with 1 percent molybdenum on a m.a.f. coal basis. At reactor temperatures of 450° C. (842° F.), cold gas admitted in the bottom section provided adequate control through the reactor. At 480° C. (896° F.) control was not possible due to "runaway" temperatures. Temperature rise at 480° C. amounted to about 2.5° C. per minute, a considerable increase over that experienced at 450° C. At 500° C. the rise was about 5° C. per minute.

TABLE 9. – Material balance for coal hydrogenation in the
high-temperature pilot plant

	Materials, weight-percent based on m.a.f. coal, for the following hydrogenation temperatures:			
	480° C.	490° C.	500° C.	510° C.
Feed				
Moisture- and ash-free coal..........	100.0	100.0	100.0	100.0
Vehicle oil.........................	142.8	145.6	141.3	139.0
Ash................................	1.9	1.8	1.5	1.3
Hydrogen absorbed...................	6.6	6.8	6.6	7.0
Total............................	251.3	254.2	249.4	247.3
Product				
Oil				
Gasoline range..................	25.4	23.9	25.1	25.3
Residual........................	190.4	188.9	179.4	180.6
Hydrocarbon gases...................	11.8	13.4	14.3	14.9
Water (net)........................	13.4	14.0	11.7	11.4
Organic benzene insolubles..........	2.0	2.2	2.2	1.9
Ash................................	1.7	1.9	1.7	1.5
Total............................	244.7	244.3	234.4	235.6
Recovery, percent....................	97.4	96.1	94.0	95.3

TABLE 10. – Analysis of product streams from coal hydrogenation
in the high-temperature pilot plant

Hydrogenation temperature, °C.	Ultimate analysis, weight-percent				
	Hydrogen	Carbon	Nitrogen	Sulfur	Oxygen
			Gasoline		
480	12.30	85.54	0.55	0.04	1.57
490	11.86	85.44	.58	.06	2.06
500	11.66	85.70	.55	.07	2.02
510	11.96	85.75	.50	.04	1.75
			Residual oil		
480	9.26	88.36	.72	.12	1.54
490	9.16	88.03	.27	.08	2.46
500	9.12	88.39	.78	.08	1.63
510	9.18	88.32	.78	.12	1.60

	Hydrocarbon gases				
	Total carbon, weight-percent	Components, weight-percent			
		C_1	C_2	C_3	C_{4+}
480	79.79	27.8	24.4	23.0	24.9
490	79.24	35.6	22.8	20.6	21.0
500	79.86	28.3	22.2	22.3	27.2
510	79.31	35.1	23.6	20.0	21.3

Tail gas

Cooling gas

To product receiver

Insulation (85 percent Magnesia, 1" thick)

M

Booster compressor

Middle cooling gas outlet

Converter (10 ft. long, 3" I.D.)

Bottom cooling gas outlet

Metal cone

Furnaces

Hydrogen and coal paste

x Internal thermocouple
< External thermocouple

Lead bath preheater
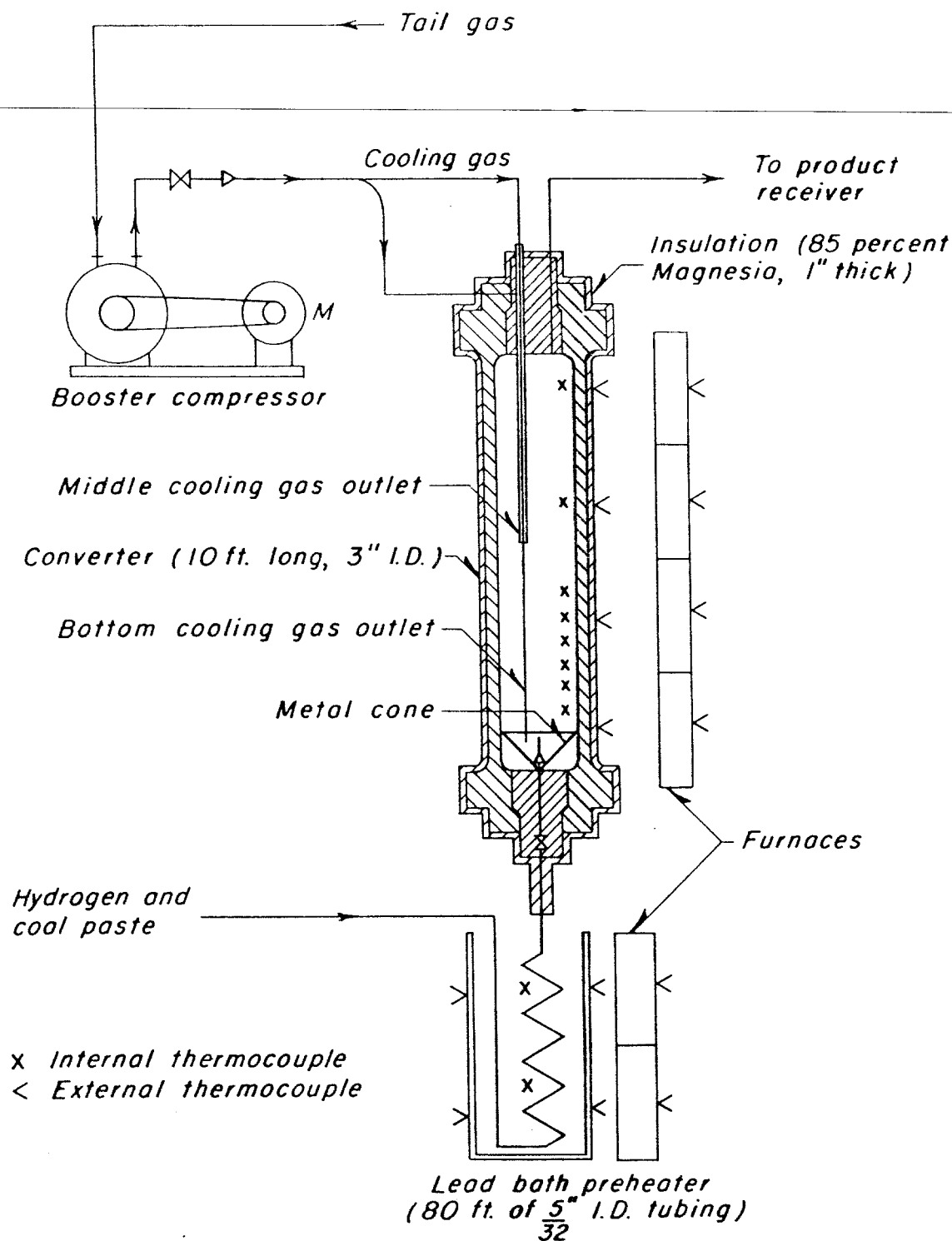(80 ft. of $\frac{5"}{32}$ I.D. tubing)

FIGURE 44. - Preheater and Reactor in High-Temperature Coal-Hydrogenation Pilot Plant.