Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Fluidized-Bed Hydrogenation

The possible advantages of hydrogenating coal in a fluidized bed (see fig. 39) instead of in the liquid phase have been mentioned in the previous annual report. This year's studies were concerned with finding conditions under which a continuous fluidized process is operable, and especially with developing a method of operation that would avoid agglomeration of the fluidized mass. Two small units were used for this purpose; in one, the coal was heated to reaction temperature in 1 to 2 hours and kept at that temperature for a certain time. In the second unit, coal was charged only after the reaction temperature and the rate of flow of hydrogen had been established. The coal was thus heated to reaction temperature in less than 10 minutes, and the temperature was permitted to rise (by as much as 100° C.) depending on the amount of energy liberated during the hydrogenation.

From the experience gained with these units, the following conclusions were drawn: Slow heating of the fluidized coal without catalyst permits removal of the liquid products by the fluidizing gas at a rate rapid enough to prevent agglomeration. Addition of a catalyst accelerates the hydrogenation under otherwise equal conditions to a point where the heavy oil acts as a binder for the coal particles, and subsequent coking of the solid results in agglomeration. Rapid heating of the coal to less than 400° C. does not lead to agglomeration because the oil can be removed as rapidly as it is formed. Rapid heating of a very reactive coal to 500° C. or higher also results in satisfactory operation. In this case, the heat of reaction raises the temperature of the coal particles so that any liquid that remains on them is carbonized and agglomeration is prevented. If the coal is not reactive enough, or if an inert diluent (ash) absorbs the heat of the reaction, agglomeration may occur.

Thus, a continuous unit should be operable below about 400° C., or at high enough temperatures to carbonize any liquid not removed from the coal particles by hydrogen. Construction of such a pilot plant has been completed. It is operable up to 700° C. and permits a contact time of 6 minutes at a rate of flow of 5 pounds of coal per hour. The reactor consists of a 1-inch pipe provided with a screw feeder at the bottom, a 3-inch pipe separator at the top, and a 1-inch external standpipe leading to pressurized receivers. Gases and vaporized liquids pass overhead from the separator through a stainless-steel filter into the product-recovery system, while the char falls by gravity through the standpipe into the receivers.

Bench-Scale Studies

Hydrogenation of Various Coals

The objectives of the study of the Bergius-I.G. coal-hydrogenation process during the past year were determination of the suitability of various coals, of the applicability and activity of a number of catalysts, and of the kinetics of the hydrogenation process.

A blend of Western Kentucky coals was found to be suitable for use by the Demonstration Plant at Louisiana, Mo. Hydrogenation with impregnated ferrous sulfate catalyst at 450° to 475° C. and 700 atmospheres gave satisfactory results. A sample of Illinois No. 6 coal, Darmstadt No. 1 mine, Marissa, St. Clair County, Ill., was hydrogenated successfully at the same pressure, after neutralization of the alkaline ash with sulfuric acid and impregnation with ammonium molybdate as catalyst. When hydrogenated at about 250 atmospheres after impregnation with 1 percent of ferrous sulfate, its product distribution was similar to that obtained from the Kentucky coal blend.

Three coals were hydrogenated in a rotary autoclave at an initial pressure of hydrogen of 1,000 p.s.i.g., for 1 hour, at 450° C., and with or without a catalyst (1 percent tin plus 0.5 percent ammonium chloride). These coals came from Lake DeSmet Reservoir, Wyo.; Butte Valley Co., Huerfano County, Colo.; and Baldy Coal Co., Las Animas County, Colo. The results obtained with these coals are compared in table 17 with those obtained with coal from the Bureau's Experimental Mine, Bruceton, Pa.; Rock Springs coal, D.O. Clark Mine, No. 9 bed, Superior, Wyo.; a blend of Western Kentucky coals, obtained from the Demonstration Plant, Louisiana, Mo.; and Beulah lignite, Beulah mine, Mercer County, N. Dak. The Lake DeSmet coal samples correspond to the 60- to 100- foot, 100- to 140- foot, and 140- to 180- foot layers in the coal vein. The DeSmet, Butte, and Baldy coals had high ash contents as received and would be more suitable for hydrogenation after removal of ash and moisture.

An extensive study was made on the Rock Springs coal to determine the effectiveness of various catalysts in the range of 425° to 485° C. and at an initial pressure of 3,700 p.s.i.g. of hydrogen. Iron, nickel, molybdenum, tin, and zinc were used in different forms and ranges of concentration. The most important criterion in the evaluation of these catalysts was the yield of hexane-soluble oil which is the most desirable product. Nickel and molybdenum, impregnated on the coal, were the best catalysts from that point of view. Economically, the use of 0.1 percent of nickel (impregnated as nickel chloride in these tests) appears preferable because it produced large amounts of oil and small amounts of gaseous hydrocarbons and is cheaper even than impregnation of 0.5 percent of iron as ferrous sulfate.

Rock Springs coal was used to determine the effect of the initial pressure of hydrogen upon the extent of liquefaction of the coal at 450° C. No effect was noticed for a contact time of up to 7 minutes. After 14.5 minutes, however, increased pressure of hydrogen (in the range of 500 to 2,000 p.s.i.g.) resulted in a reduction of the amount of benzene-insoluble material. It appears that, after 14.5 minutes, thermal cracking of the coal had proceeded to such an extent that stabilization of the unsaturated fragments had become dependent upon the partial pressure of hydrogen.

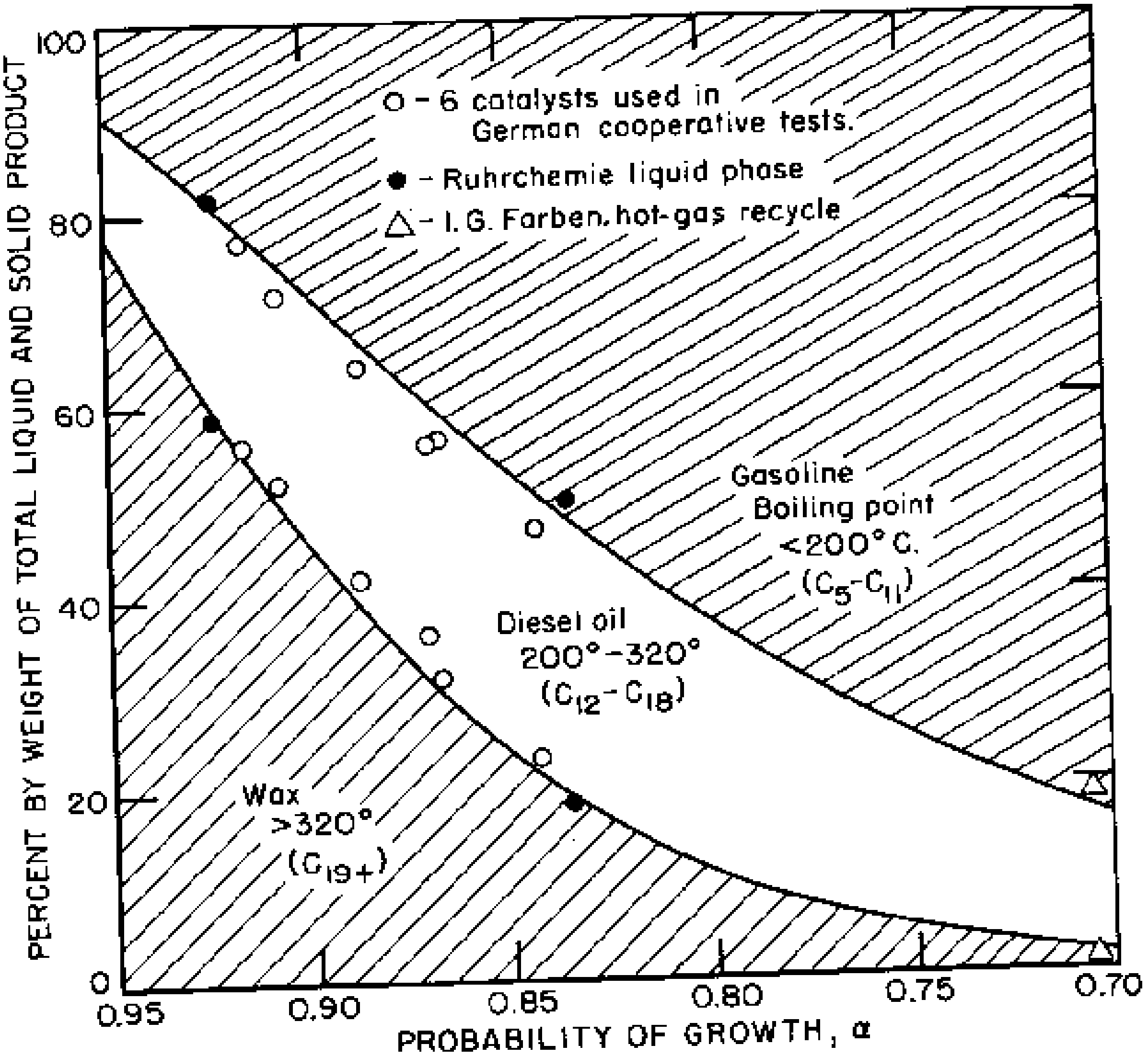

Figure 38. - Correlation of theoretical and observed product distributions of liquid and solid Fischer-Tropsch hydrocarbons obtained with iron catalysts.

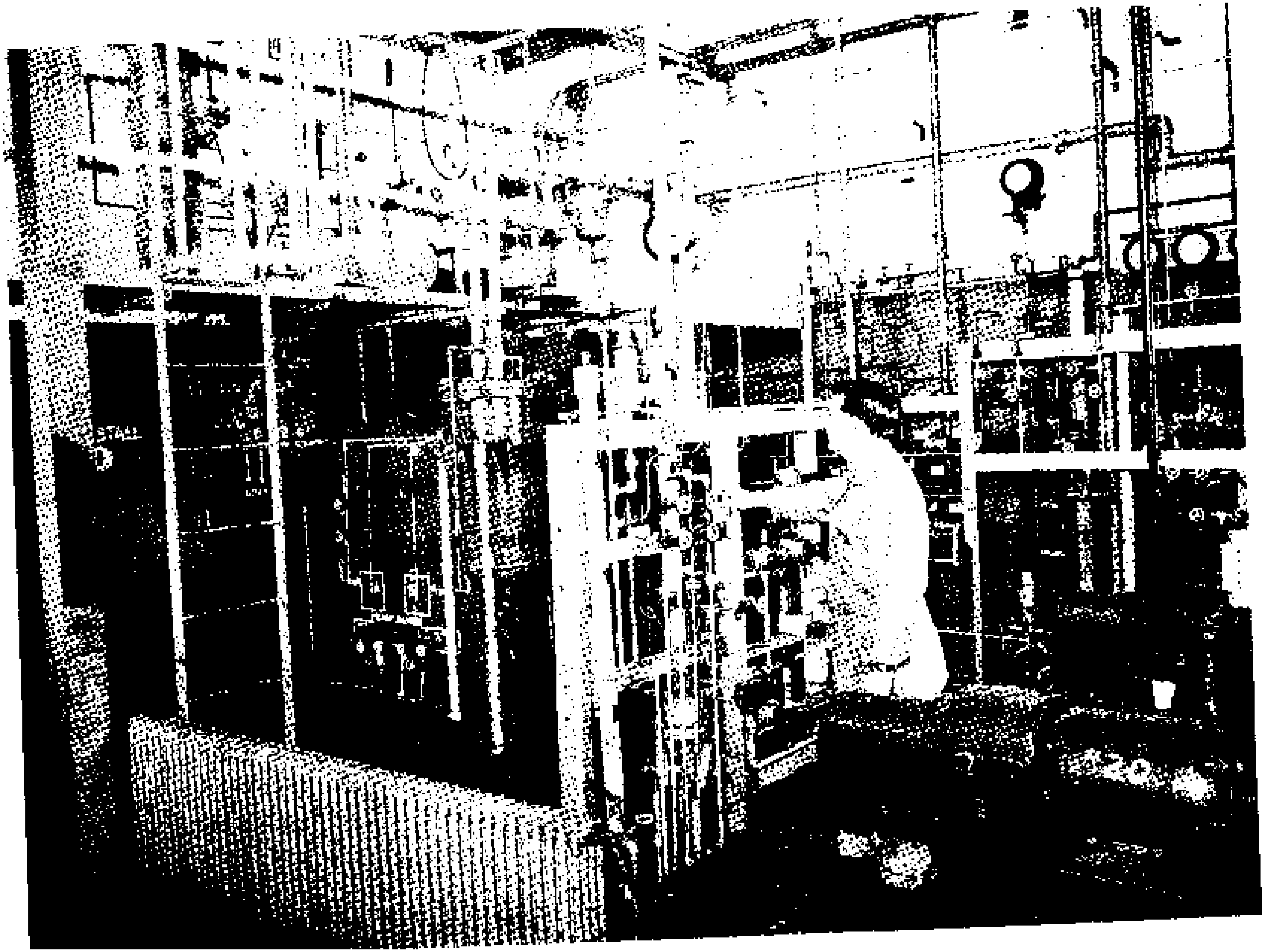

TABLE 17. - Product distribution (weight percent; m.a.f. basis) from hydrogenation of various coals (without vehicle) for 1 hr. at 450° C. and 1,000 p.s.i.g. initial hydrogen pressure.

Test No.	Coal	Catalyst	Benzene-insolubles	Asphalt	Oil	Gaseous hydro-carbons	CO_2	H_2O	H_2 consumed
986	Bruceton	1 percent Sn + 0.5 percent NH_4Cl	12.99	43.02	27.99	12.51	0.65	5.9	4.37
1230	Rock Springs	do.	12.86	32.80	26.64	17.23	2.90	11.28	4.74
1719	Kentucky	do.	9.84	46.00	23.09	14.66	.33	7.72	4.34
1218	Beulah lignite	do.	43.27	13.60	19.90	11.60	9.00	11.86	3.65
	Lake DeSmet								
1767	60-100 feet	do.	18.35	26.01	16.88	17.70	9.02	15.87	4.61
1770	100-140 feet	do.	14.18	39.82	20.04	15.35	8.77	16.52	4.58
1805	140-180 feet	do.	27.61	18.85	16.17	15.07	9.30	16.48	4.29
1778	Baldy	do.	18.96	42.21	21.41	15.29	.15	5.26	3.94
1829	Butte	do.	42.71	13.22	19.61	15.31	2.73	9.74	3.66
1623	Bruceton	None	53.08	16.47	11.36	13.13	.61	6.98	2.57
1228	Rock Springs	do.	66.64	7.70	5.90	8.44	3.48	8.44	1.48
1216	Beulah lignite	do.	51.12	8.5	11.18	11.5	10.34	10.32	2.37
	Lake DeSmet								
1765	60-100 feet	do.	47.54	9.57	9.31	12.16	9.88	12.58	2.65
1768	100-140 feet	do.	52.79	6.47	6.13	13.70	9.80	13.06	2.69
1772	140-180 feet	do.	43.5	11.72	6.26	13.84	10.27	13.54	3.12
1775	Baldy	do.	73.48	7.99	4.30	9.48	1.06	4.25	.94
1833	Butte	do.	57.27	9.05	7.34	16.52	3.12	9.48	2.91

The pressure dependence in the range of 500 to 4,000 p.s.i.g. (initial pressure of hydrogen) of the hydrogenation reaction at 400° C. was determined with Rock Springs coal in two series of tests, one with tin and the other with molybdenum catalyst. Assuming that the amount of reaction was the same with both catalysts during the heating and cooling periods and allowing for the amount of reaction that takes place during these periods, straight lines were obtained when the logarithm of the amount of remaining benzene insolubles was plotted as a function of time. While the specific reaction rate constants thus obtained differed for the two catalysts, a plot of these constants as a function of pressure yielded identical slopes for both catalysts. The specific reaction rate constants are therefore a measure of the efficacy of the catalyst, and this method may be useful for quantitative evaluations of the activity of primary hydrogenation catalysts. Furthermore, the observed correlation of hydrogenation with pressure permits prediction of the yields over a range of pressures from only one experiment with any given coal, thus saving considerable time.

Hydrogenation and Coking of Oils Obtained from Coal

The production of gasoline by hydrogenation of coal necessitates catalytic splitting and hydrogenation of the middle oil, which is a product of the liquid-phase hydrogenation process. For this purpose, the Demonstration Plant has been using a German catalyst consisting of molybdenum, chromium, zinc, and sulfur on a clay support treated with hydrofluoric acid. Work has been started at the Coal-to-Oil Laboratories to duplicate or improve this catalyst, using a middle oil derived from a blend of Western Kentucky coal and the German catalyst for the orienting experiments. Removal of the primary gasoline, amounting to about 35 weight-percent of the middle oil, was advantageous because more gasoline was produced from the stripped oil, less hydrogen was consumed, and less hydrocarbon gas was generated. Furthermore, extraction of the gasoline preserved the phenols and cresols contained in it from (at least partial) destruction by high-pressure hydrogenation. After removal of the phenolic constituents, the primary gasoline had a motor octane number of about 73 and was therefore suitable as motor-gasoline stock. The secondary gasoline, derived from the hydrogenation product of the middle oil, had a motor octane number of about 79, irrespective of prior extraction of the oil.

The residual oil from coal hydrogenation (heavy-oil let-down or H.O.L.D.) is a mixture of oil and solids containing enough oil to remove the unreacted coal, ash, and catalyst from the plant. Recovery of the liquid fraction of this material is necessary for optimum utilization of the coal. The liquid consists of "oil," soluble in n-hexane; "asphaltene," insoluble in n-hexane but soluble in benzene; and benzene-insoluble material. One method of treating H.O.L.D. is steam stripping, and a continuous steam-stripping unit is illustrated in figure 40. Distilled water is pumped by a Zenith gear pump from the water supply bucket to the steam superheater, where it is heated by a 30-foot length of No. 14 (B. & S. gage) nichrome V wire. The superheated steam flows into the mixing block. A second Zenith gear pump moves the oil from a heated feed bucket through a preheater into the mixing block. Both pumps are operated from the same drive shaft and hence give a fixed steam:oil ratio. The

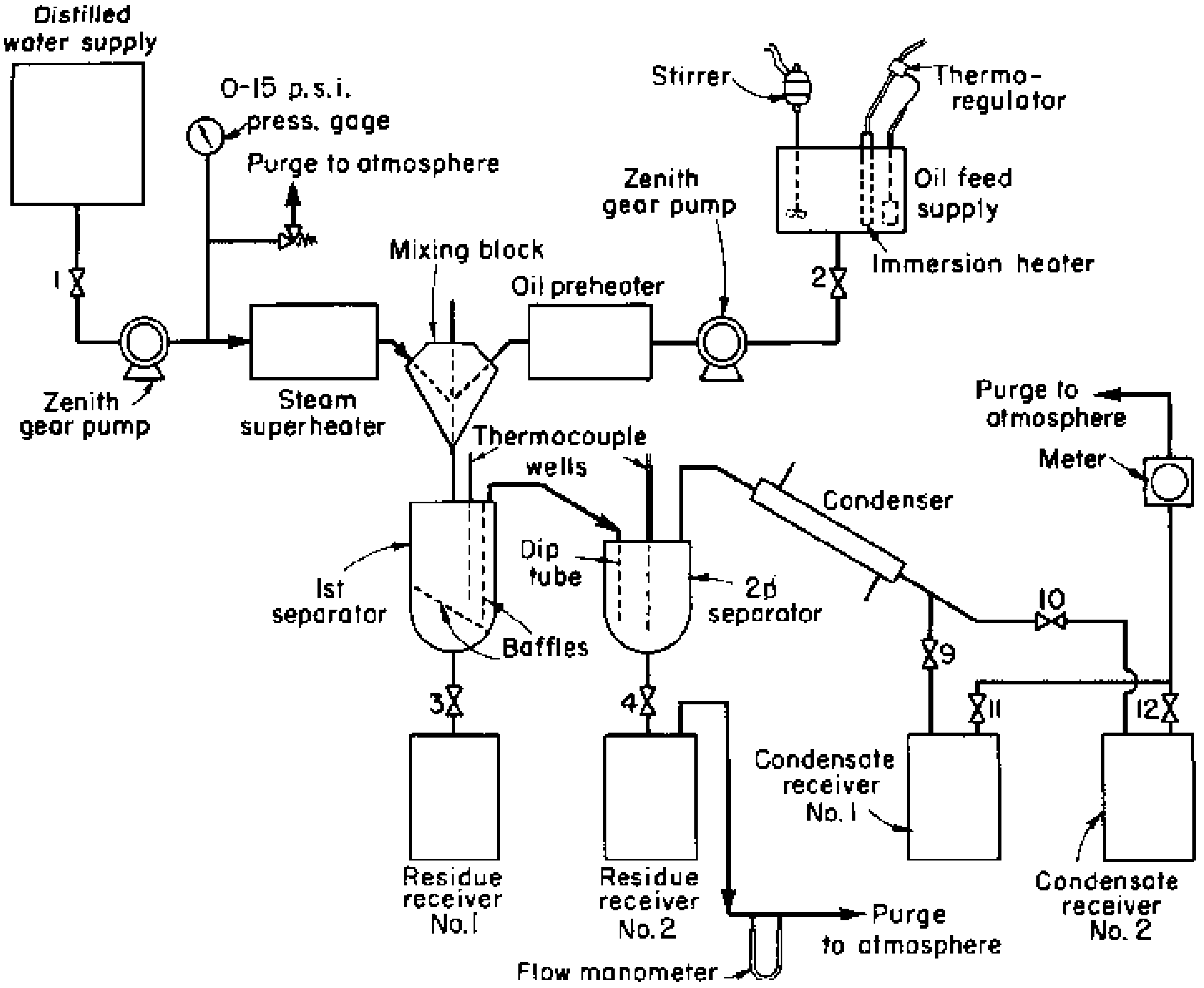

Figure 40. - Flow diagram of heavy-oil-let-down steam stripper.

mixture of oil and superheated steam enters the first separator, where benzene-insolubles and asphaltene residue are removed. The volatile materials pass into the second separator (held at a lower temperature) where heavy oils are separated. The lighter oils and steam pass overhead, then through a water-cooled condenser, and are collected in the condensate receivers. The noncondensable gases are metered and purged to the atmosphere. The condensed light oils and water in the condensate receivers are separated by decantation. The residue from the first separator and the oil from the second separator are withdrawn into receivers 1 and 2, respectively, through let-down valves. In this unit, an H.O.L.D. containing about 50 percent of n-hexane-soluble "oil" was separated into (1) a residue containing 99 percent of the benzene-insolubles and most of the ash, with an almost equal amount of "asphaltene"; and (2) a product containing 99.8 percent of the "oil," the remainder of the "asphaltene," and very little ash.

Another approach to the treatment of H.O.L.D. is coking. The effect of reaction temperature on the yield obtained during coking of H.O.L.D. was studied in the coking unit illustrated in last year's report. With unextracted H.O.L.D., the amount of distillate increased from 30 to 50 percent of the feed, while the content of benzene-insolubles in the residue rose from 60 to virtually 100 percent as the coking temperature was raised from 400° to 500° C. When the n-hexane-soluble "oil" was extracted from the H.O.L.D. and coked separately, the amount of gaseous product was smaller, and the recovery of distillate varied between 35 and 80 percent while benzene insolubles in the residue increased from 0 to 92 percent upon coking over the same temperature range. The "oil" fraction appeared to be the primary gas producer in H.O.L.D., 15 to 20 percent of the "oil" being converted to gas and benzene-insoluble material during coking. The behavior of the "asphaltene" and benzene-insoluble fractions during coking is under investigation. Knowledge of the product distribution obtained from these H.O.L.D. fractions will make possible the prediction of product distribution from coking of any H.O.L.D., provided its composition (in terms of these fractions) is known. Comparison of results obtained with the coking unit and those obtained with a commercial contact coking unit showed the results to be equivalent, so that the data obtained in this small unit will be useful for the design of a large coking unit that is to be built at the Demonstration Plant.

Characterization of Coal-Hydrogenation Products

Composition of Gasoline Obtained from Coal

A sample of gasoline produced by vapor-phase hydrogenation at the Demonstration Plant, Louisiana, Mo., was fractionated as follows:

Boiling point, °C.	Weight, percent, of gasoline
Below 50......................	8.8
50-150........................	66.3
150-185.......................	18.2
Above 185.....................	1.3
Volatiles and loss............	5.4
Total....................	100.0