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 The residue from the first separator and the oil from the second separator are withdrawn into receivers 1 and 2, respectively, through let-down valves.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 60 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

A major portion of the loss may be accounted for by dissolved gas, which was evolved during distillation. The fraction boiling at 50° to 150° C. was separated further into a paraffin-naphthene fraction; an olefin fraction, an aromatic fraction; and a fraction containing oxygen, sulfur, and nitrogenous compounds. The composition of this 50° to 150° C. cut is shown in table 18; and a further characterization by carbon number is given in table 19. This analysis was achieved by a long series of distillations, chromatographic separations, determinations of physical constants, and spectrometric analyses.

TABLE 18. - Composition of gasoline from Louisiana, Mo.

Component	Liquid-phase product, weight percent		Vapor-phase product, weight percent	
	50°-150° cut	Total product charged to v.p. unit	50°-150° cut	Total gasoline
Paraffins	17.42	-	18.92	66.31
Naphthenes - total	44.87	-	50.60	
Cyclopentane	.21	-	.34	-
Methylcyclopentane	[1]2.26	[1]0.271	[1]8.51	[1]5.65
Cyclohexane	[1]6.80	[1] .814	[1]3.51	[1]2.33
Dimethylcyclopentanes	2.83	.339	7.00	4.64
Methylcyclohexane	8.00	.958	6.95	4.61
Ethylcyclopentane	3.01	.361	5.12	3.40
C_8-naphthenes	11.01	1.319	10.30	6.83
C_9-naphthenes	6.63	-	8.86	-
Aromatics - total	21.06	-	27.50	24.74
Benzene	[1]1.60	[1]0.192	[1]6.08	[1]4.03
Toluene	6.93	.830	10.98	7.28
Ethylbenzene	7.31	.875	3.12	2.07
m.p. xylene	3.33	.399	6.16	4.09
o-xylene	1.81	.217	1.16	.77
150°	0	-	-	6.52
Olefins	9.57	-	1.1	1.4
Nonhydrocarbons	7.08	-	1.4	2.2
Unaccounted for	-	-	-	5.9
Benzene + potential benzene	10.66	1.277	18.10	12.01

[1] Benzene plus potential benzene.

TABLE 19. - Composition of 50° to 150° C. cut of vapor-phase gasoline1/

	Total	C_5	C_6	C_7	C_8	C_9
Paraffins....................	20.62	-	7.80	6.14	4.37	2.31
Cyclopentanes................	28.31	0.49	8.58	10.87	6.62	1.75
Cyclohexanes.................	20.08	-	3.57	6.15	6.56	3.80
Hydrindane...................	.13	-	-	-	-	.13
Aromatics....................	27.53	-	5.92	11.20	10.41	-
	96.67	0.49	25.87	34.36	27.96	7.99

1/ To put on basis of total gasoline, multiply by 0.6631.

Determination of Tar Acids and Bases

A blend of 21 percent gasoline, 11 percent naphtha, and 68 percent middle oil (the charging stock used for vapor-phase hydrogenation at the Demonstration Plant, Louisiana, Mo.) was examined for its tar-acid content. Half of this blend boiled below 250° C., and the tar acids were extracted with alkali from this fraction. Infrared spectrophotometric analysis showed the following percentages, based on the total amount of oil: 1.686 percent phenol, 0.724 percent o-cresol, 1.596 percent m-cresol, and 0.482 percent p-cresol.

Adaptation of a potentiometric titration method with antimony electrodes and ethylenediamine as the solvent has made possible direct determination of total tar acids in complex oils obtained by the hydrogenation of coal. This determination can be expressed in terms of the oxygen content, assuming that the oxygenates in the oils are monohydric phenols. The validity of this assumption was borne out by comparison of titrimetric data with ultimate analyses of an oil obtained by hydrogenation of Rock Springs coal.

A corresponding potentiometric titration method has been developed for estimating total tar bases in coal-hydrogenation oils. Glass and silver-chloride electrodes are used as indicator and reference electrodes, respectively, and perchloric acid in glacial acetic acid is the titrant. Phenols do not interfere with the analysis. Application of the method to oil obtained from Rock Springs coal showed about 70 percent of the nitrogen in the light and middle oils to be basic, while about 92 percent of the nitrogen in the naphtha fraction and about 30 percent of the nitrogen in the gasoline fraction were basic. Despite its high content of titrable nitrogen, only 40 percent of the nitrogen compounds of the light oil could be extracted with sulfuric acid, indicating the presence of high-molecular-weight and/or sterically hindered basic compounds.

Identification of individual tar bases up to quinoline was made for the tar-base fraction of the light oil obtained by hydrogenation of Rock Springs coal. A combination of analysis of the distillation curve of this fraction, ultraviolet and infrared absorption measurements, countercurrent distribution, neutralization equivalent determination, and formation of derivatives disclosed the presence of the following compounds: Beta- and gamma-picolines; 2,6-lutidine; aniline; o-, m-, and p-toluidine; 2,6-, 2,5-, 3,5-, and/or 2,4-xylidines; and quinoline. Although pyridine was not found, it was probably present originally but lost in the plant by washing with water and during subsequent processing.

Countercurrent Distribution

The complex phenolic mixtures (tar acid) produced by hydrogenation of coal are composed largely of homologous and isomeric phenols, separation and identification of which are difficult or impossible by fractional crystallization and distillation. Because of their potential commercial value and the importance of oxygenated compounds in the study of the mechanism of the liquefaction of coal, characterization of these tar acids has practical as well as theoretical importance. By means of the countercurrent distribution technique, a mixture of closely related compounds is distributed between two immiscible solvents in successive countercurrent stages until separation of the components is achieved. The method is particularly useful for high-boiling compounds. Besides providing a means for separating such components, it may be used to check their purity, to calculate approximate ionization constants, and to obtain information on molecular structure (steric hindrance) and hydrogen-bonding.

Further development of the countercurrent-distribution method has led to a technique for measuring large (or small) partition coefficients. It consists of increasing the concentration of solute in the denser (or lighter) phase until measurable values are obtained. This method of "interchange extraction" was subjected to precise mathematical analysis, leading to an equation that related the partition coefficient to the number of extraction stages. The accuracy of the method was tested by determining the partition coefficients of o-phenylphenol in two systems.

The possibility of utilizing silver complexes of tar acids to aid in the countercurrent separation was studied with the three isomers of cresol. This method was found to be applicable only to a mixture of m- and p-cresol. Complex formation with cineole or with cineole and silver simultaneously was unsuitable for separation of the cresol isomers.

X-ray and Spectral Analyses

T.N.F. (2,4,7-trinitrofluorenone) forms brightly colored complexes of high and sharp melting points with polynuclear compounds. These complexes are easily purified by crystallization and readily decomposed into their original components, providing another tool for the separation of isomers. Furthermore, the crystalline complexes can be identified by their x-ray powder-diffraction pattern. Of 45 T.N.F. complexes thus examined, each had its characteristic pattern, completely different from those of its isomers and from the pure polynuclear hydrocarbons.

An infrared spectrometric (fig. 41) method for analyzing tar acids through the C_8 group has been extended to include analysis of more complex mixtures of isomers. The method is applicable to determination of phenol plus the cresol isomers and to the cresols plus 2,4- and 2,5-xylenols; and only a crude separation of coal-hydrogenation oil into three fractions is now required.

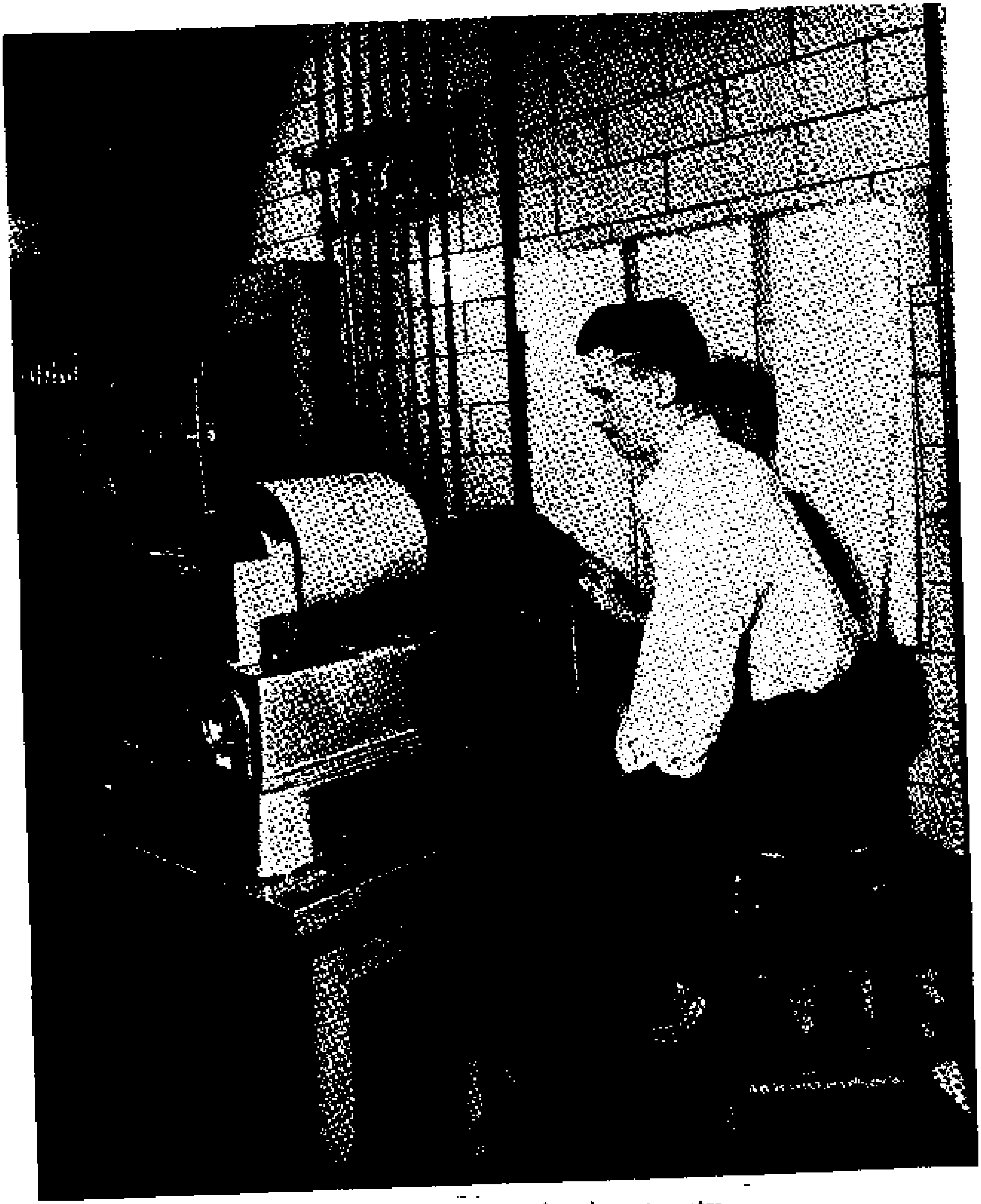

Figure 41. - Double-beam infrared spectrometer.

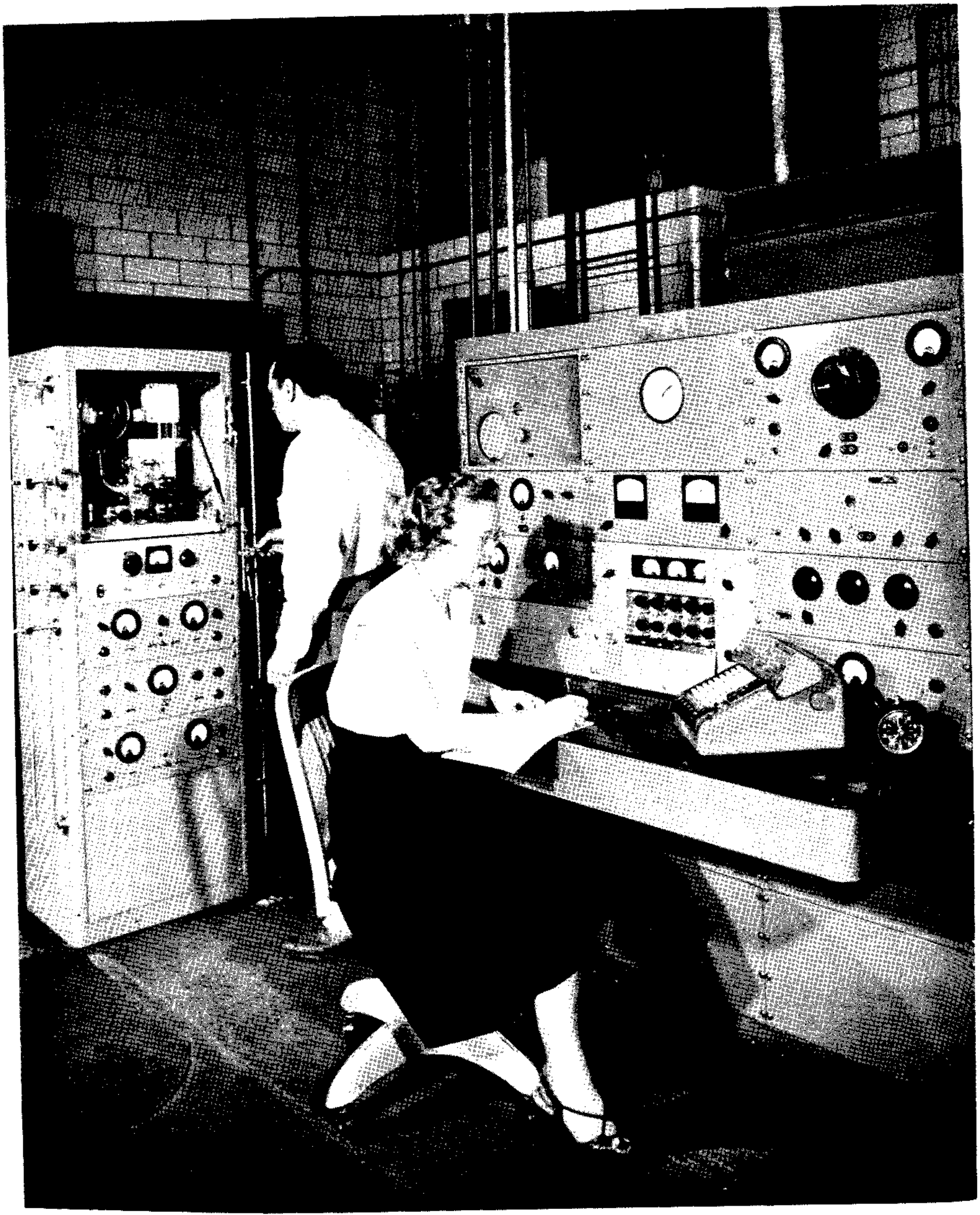

Figure 42. - Revised mass spectrometer.

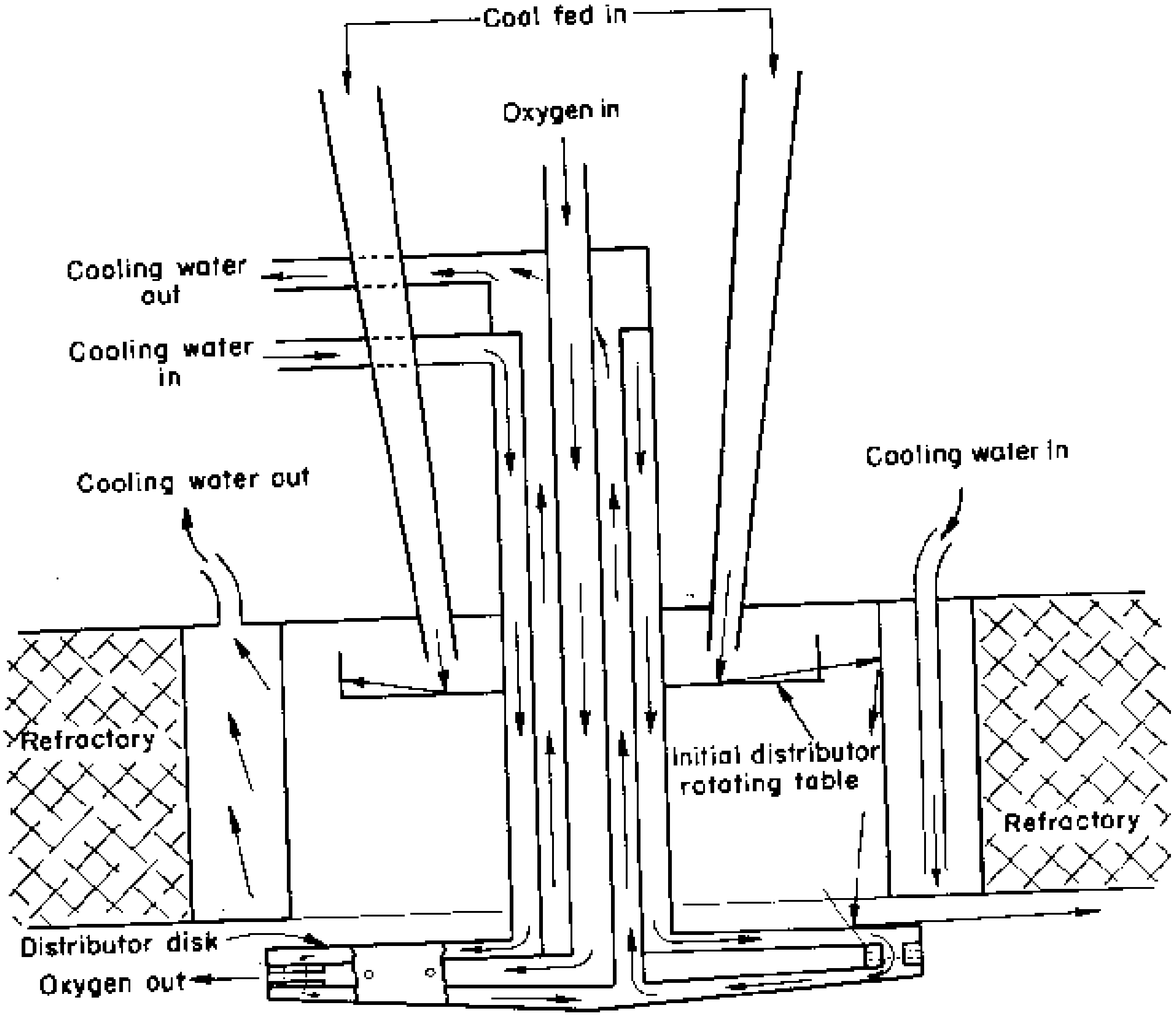

Figure 43. - Coal feeder for vortex gasifier.

A mass spectral method (fig. 42) has been developed for analyzing paraffin-naphthene fractions of gasoline obtained from coal hydrogenation. By this technique, cyclopentanes and cyclohexanes with single and with multiple alkyl side chains can be distinguished from each other and from paraffins. As yet, the method is not easily extended to C_9 and higher hydrocarbons because of the scarcity of reference compounds. However, appreciable concentrations of a C_9 (hydrindane) and a C_{10} dicyclic compound (methylhydrindane, decalin, or a terpane) have been identified in vapor-phase gasoline. The results of this analysis are incorporated in tables 18 and 19 (see Composition of Gasoline Obtained from Coal).

Gasification of Coal in the Vortex Reactor

Gasification of pulverized coal with oxygen and steam may be used for the production of synthesis gas (carbon monoxide plus hydrogen) for the Fischer-Tropsch process or of hydrogen for the hydrogenation of coal. This process has been studied in a vortex reactor to gain an insight into the operating variables and the performance characteristics of such a system and as a means of predicting the optimum conditions for adiabatic gasification of coal. The construction of the reactor and the flow diagram of the unit have been shown in the 1949 Annual Report (Bureau of Mines Report of Investigations 4651); a diagrammatic sketch of the coal feeder (fig. 43) shows the path of the coal into the reactor, as well as the oxygen outlet that permitted introduction into the reaction zone of part of the oxygen with the coal. The vortex reactor had a diameter of 2 feet, and its depth was varied from 2 to 36 inches. The unit was preheated to 2,000° F. with a mixture of natural gas, air, steam, and oxygen. After the reaction temperature was reached, the gas and air were shut off, and coal was admitted at the rate of 100 pounds per hour. Oxygen and steam were preheated to 1,300° F. and added in such amounts that the oxygen:coal ratio ranged from 7 to 11 cubic feet per pound, while the ratio of steam to coal was maintained at 0.55 pound per pound.

By introducing some of the oxygen with the coal (instead of introducing all of it through the tangential slots of the reactor), the production of synthesis gas was increased considerably under otherwise equal conditions. Increasing the oxygen:coal ratio resulted in higher reaction temperatures. Because the unit was not an adiabatic reactor, more heat was lost at the higher temperatures by radiation and convection; such losses can be reduced substantially in larger installations. The gasification reaction,

$$C + H_2O \longrightarrow CO + H_2$$

$$C + CO_2 \longrightarrow 2CO$$

did not begin until most of the oxygen had been consumed. Steam and oxygen also reacted with the volatile matter distilled from the coal; but the amount of carbon monoxide and hydrogen produced in this manner was small, so that residual char (after devolatilization of the coal) was the principal source of synthesis gas. The rate of gasification of coal was approximately of first order with respect to the amount of carbon available, at least up to space velocities of 33 pounds of coal per cubic foot of reactor space per hour. By changing the depth of the vortex reactor, the space velocity of the coal was