ketones and/or acids, esters, and alcohols in the products of the two processes reveals that the Stanolind product is significantly richer in ketones and/or acids and esters, particularly in the higher-boiling fractions. The lower alcohol contents of the Stanolind fractions may be attributed to water-washing of the product and operation at higher temperatures.

Comparison of the weight-percent distribution of the products from the Stanolind and internally cooled converter processes is interesting. The maximum amount of the Stanolind product (26.4 percent) boils in the range 60° to 100° C., whereas the product from the internally cooled converter yields a maximum (12.4 percent) in the range 100° to 150° C. (Although a value of 15.7 percent was obtained between 0° and 60° C. for the product from the internally cooled converter, this includes the C_4 hydrocarbons obtained from the charcoal-trap liquid. The Stanolind product was stabilized to eliminate these compounds.) The amount of residue (that fraction boiling above 320° C.) was found to be much larger for the product from the internally cooled converter (36.2 percent) than for the Stanolind product (6.8 percent). Distillation equipment is shown in figure 39.

Investigation of a method for converting isobutene and isopentenes into the respective chlorides, which are separated from the remaining mixture of hydrocarbons before it is analyzed by means of the mass spectrometer, suggests that this technique may be applied to the analysis of products from the Fischer-Tropsch synthesis. Such an analysis has been complicated heretofore by the similarity of the mass spectra of the butene compounds. The role played by spectrometric techniques in the characterization of Fischer-Tropsch products has been most important (see fig. 40). Much of this analytical equipment has been shown in previous annual reports.

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Pilot-plant Operations

Fuel-oil production. - The liquid-phase coal-hydrogenation pilot plant was operated with a series of catalysts to determine their relative efficiencies for the hydrogenation of Rock Springs coal at 460° C. and 1,500 p.s.i. to produce a heavy fuel oil. Using a coal-oil paste containing 35 percent of coal, the results indicated that these catalysts, when impregnated on the coal, were decreasingly effective with respect to coal liquefaction and asphalt removal, in the following order: Ammonium molybdate, stannous chloride, nickelous chloride, and ferrous sulfate. Comparison of these results with the yields obtained in tests made at 3,500 p.s.i. show that the liquefaction of coal is increased significantly with pressure. This procedure for production of a No. 5 or 6 fuel oil at 1,500 p.s.i. is quite operable and may be important in emergencies for fuel-oil production in places like Australia or South Africa, where coal but no petroleum deposits exist.

Middle-oil production. - The liquid-phase pilot plant was then operated to produce a middle-oil product using the most efficient catalyst of the series, ammonium molybdate, and maintaining the heavy-oil trap at a temperature of 300° C. Using a molybdenum concentration of 0.5 percent impregnated on Rock Springs coal and maintaining conditions of 460° C. and 1,500 p.s.i., a "middle-oil" product was obtained that ranged from 30 to 36 percent, based on moisture- and ash-free (m.a.f.) coal. In addition, about 13 percent more centrifugal heavy oil was obtained (27 percent more based on m.a.f. coal) than was required for preparing the paste pumped into the high-pressure plant. About half this excess heavy oil was collected as excess oil or was withdrawn as samples; the rest was consumed in paste-handling losses. Actually, the ratio of middle oil to excess centrifuged heavy oil collected in this operation was about 55:45, which corresponds neither to a "fuel-oil" nor to a "middle-oil" operation, but is more nearly a compromise. With the present solids-removal system it is doubtful whether stable recycle operation to make more middle oil and less excess heavy oil is possible. The centrifugation of high-viscosity heavy oils with high solids content is considerably poorer than that of the heavy oil made in a fuel-oil operation. In the latter case, the centrifuge removes about 50 to 60 percent of the insolubles in the heavy oil fed to it, in contrast to only about 30-percent removal in the former. With low effective solids removal in the centrifuge, it becomes necessary, to prevent accumulation of solids in the plant, to take solids out of the system in the form of excess heavy oil. It will be necessary, therefore, to improve the solids-removal procedure materially before this pilot plant can be operated successfully on a true recycle basis to produce high yields of middle oil with no excess heavy oil.

Bench-scale Studies

Vapor-phase hydrogenation unit. - The hydrogenation of a coal-hydrogenation middle-oil product in the vapor-phase unit (see fig. 41) at 400° C. and 9,000 p.s.i., using tungsten sulfide catalyst demonstrated that this catalyst has excellent refining properties - that is, the hydrogenated product was essentially free from nitrogen, sulfur, and oxygen - and that the hydrogenation was largely a liquid-phase rather than vapor-phase reaction under these particular operating conditions. When tungsten sulfide catalyst was used to hydrogenate a heavy-oil product containing more than 20 percent asphalt plus benzene-insoluble material, a product containing 55 to 60 percent of material distilling below 325° C. was obtained. Smooth operation was continued at 440° C. and 9,000 p.s.i. for about a month, and the run was discontinued only because of insufficient feed-stock while the catalyst was still active.

A study was made of the efficiency of tungsten sulfide as a catalyst for the refining of shale oil produced by the "gas flow retort," a pilot-plant retort at the Oil Shale Demonstration Plant. At a constant pressure of 9,000 p.s.i. and a space velocity of 0.5 kilogram per liter of catalyst per hour, considerable hydrogenation, nitrogen elimination, and molecular weight reduction took place at 400° C. Additional refining took place at higher temperatures and was accompanied by an increase in the paraffin nature of the product. To minimize the gasoline fraction, which was of low octane number, the operation was conducted at 440° C. and a space velocity below 1.0 kilogram per liter of catalyst per hour. At these conditions, only 10 percent by weight of the feed was obtained as gasoline, and 48 percent as Diesel fuel with a cetane number of 50 to 63. Operation at lower pressure (4,000 p.s.i.) yielded an unsatisfactory product. Because of the high hydrogen content of the shale oil, the production of high-octane gasoline is not possible by simple high-pressure hydrogenation of this feedstock. An additional refining step would have to be included in this process to upgrade the gasoline to a premium product. Conversely, the direct hydrogenation of Diesel fuel from shale oil should be carried out under conditions that produce a maximum quantity of Diesel fuel and a minimum quantity of gasoline.

The use of a catalyst containing zinc, chromium, molybdenum oxides, and sulfur supported on fullers earth for the vapor-phase hydrogenation of shale oil at 9,000 p.s.i. pressure proved inferior to the use of tungsten sulfide catalyst in both quantity and quality of Diesel-oil production; it was superior, however, in gasoline production. Both catalysts consumed hydrogen equally. Similar tests with cobalt

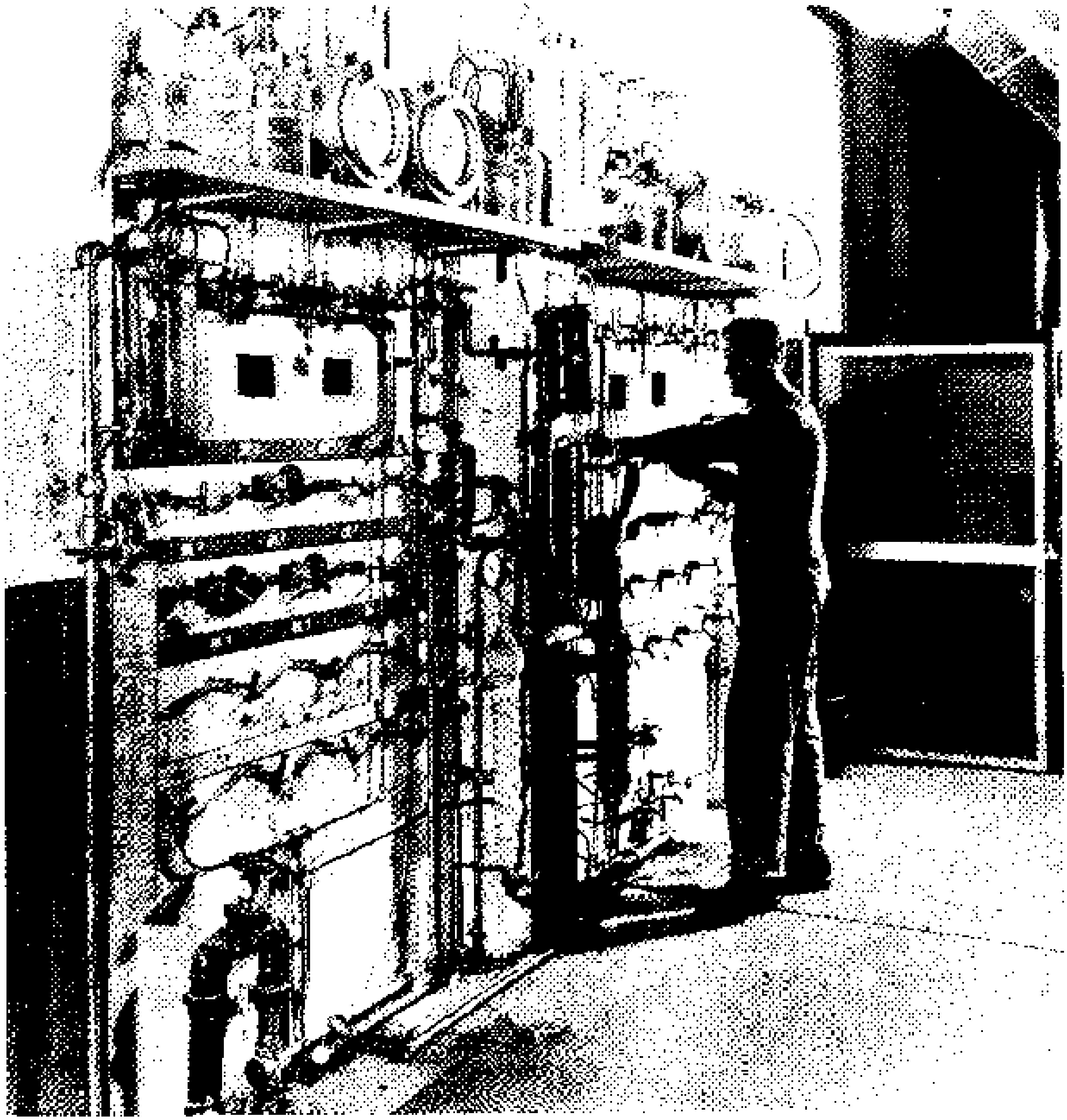

Figure 41. - Control panel for vapor-phase hydrogenation unit.

molybdate on alumina as catalyst showed that this material was comparable to tungsten sulfide for the production of Diesel fuel.

Fluidized-bed hydrogenation unit. - Many features of the usual high-pressure liquid-phase coal-hydrogenation process as carried out by the Germans indicate potential advantages in effecting a reaction between dry coal and hydrogen: The equipment required to condition heavy oil let-down for use as a pasting or injection oil with coal feed could be eliminated; reaction space used by the oil portion of the coal-oil feed mixture could be used for the reaction of additional coal; and the removal of unreacted coal as a dry material instead of a mixture with oil would materially decrease the capital and maintenance cost of the hydrogenation plant. In addition, work in batch autoclaves, where coal was hydrogenated in both the presence and absence of a heavy-oil vehicle, indicated that the heavy oil exercises a deleterious effect upon the reaction.

Accordingly, bench-scale experiments have been carried out in which hydrogen, entering the top of a unit, passes down through a dip tube and through a porous plug at the bottom of the coal bed; it then flows up through the coal bed. Excess hydrogen and volatile products leave the reactor at the top, pass through a condenser, and enter a high-pressure ice trap. The uncondensed gases are then depressurized, metered, sampled, and purged. Uncatalyzed studies have been carried out in this unit to show the effect of varying operating conditions and to study the characteristics of the products thus obtained. The results of these studies are summarized in tables 10, 11, 12, 13, and 14.

TABLE 10. - Effect of hydrogen flow rate

Charge: 100 grams Rock Springs coal; 1 hour at reaction temperature

Test No.	Pressure, p.s.i.g.	Temperature, °C.	Flow rate, SCFM	Products, grams						Total recovered, grams
				Residue	Oil	Water	CO_2	CO	Hydrocarbon gas	
42	250	600	0.25	55.9	16.8	11.5	2.7	0.9	12.4	100.2
63	250	600	1.0	54.2	16.3	11.6	3.7	-	14.9	100.7
70	500	600	0.50	47.3	22.2	11.3	3.2	1.0	17.3	102.3
51	500	600	1.0	46.3	22.5	11.2	2.7	-	17.8	100.3
58	500	600	2.0	47.2	22.5	11.8	3.7	-	17.5	102.7

TABLE 11. - Effect of temperature and pressure

Charge: 100 grams Rock Springs coal; 1 hour at reaction temperature

Test No.	Pressure, p.s.i.g.	Temperature, °C.	Flow rate, SCFM	Products, grams							Total recovered, grams
				Residue	Oil	H_2O	CO_2	CO	H_2	Hydrocarbon gas	
45	125	600	0.125	69.5	9.1	9.3	3.0	1.5	0.2	6.7	99.3
56	125	600	.125	59.6	12.1	11.9	1.8	1.5	-	13.2	100.1
55	125	500	.125	70.6	11.1	8.9	1.9	0.7	-	6.7	99.9
42	250	600	.25	55.9	16.8	11.5	2.7	.9	-	12.4	100.2
54	250	500	.25	67.6	13.6	9.5	2.4	.9	-	5.8	99.8
70	500	600	.5	47.3	22.2	11.3	3.2	1.0	-	17.3	102.3
39	500	500	.5	61.8	17.1	11.5	2.8	-	-	7.6	100.8
57	1,000	600	1.0	37.5	24.5	12.0	2.9	-	-	25.1	102.1
67	1,000	500	1.0	56.1	20.2	10.2	4.4	-	-	8.0	99.2

TABLE 12. - Effect of time of reaction

100 grams Rock Springs coal

Test No.	Time at temperature, hr.	Pressure, p.s.i.g.	Flow rate, SCFM	Temperature, °C.	Products, grams						Total recovered	H absorbed percent oil produced
					Residue	Oil	H_2O	CO_2	CO	Hydrocarbon gas		
66	0.0	500	0.5	600	51.5	20.4	12.4	3.0	-	12.5	99.8	7.3
62	.5	500	.5	600	48.5	22.9	11.5	4.0	-	14.4	101.3	10.4
70	1.0	500	.5	600	47.3	22.2	11.3	3.2	1.0	17.3	102.3	14.4

TABLE 13. - Product oil properties

Test No.	Temperature, °C.	Pressure p.s.i.g.	Ultimate composition, percent					Asphalt, percent	Light oil, percent[a]
			H	C	N	S	O		
42	600	250	9.3	84.2	0.4	0.4	5.7	-	-
70	600	500	8.0	83.9	1.3	.4	6.4	74.2	13.5
57	600	1,000	7.7	84.9	1.1	.2	6.1	55.3	[b] 43.0
54	500	250	9.3	82.6	0.7	.4	8.0	44.2	37.0
39	500	500	8.1	84.7	1.0	.4	5.5	-	14.7
67	500	1,000	8.1	83.5	0.8	.3	7.3	78.5	16.8

[a] Oil obtained by stripping product oil at 30° C. and 1-2 mm. Hg pressure.

[b] For this test product stripped to 200° C. at 1-2 mm. Hg pressure.

TABLE 14. - Ultimate analysis of residue char

Test No.	Temperature, °C.	Pressure, p.s.i.g.	Residue, grams	Analysis, percent					
				H	C	N	S	O	Ash
42	600	250	55.9	2.7	84.6	1.6	0.3	1.3	9.5
70	600	500	47.3	3.0	84.2	1.6	.1	2.1	9.0
57	600	1,000	37.5	2.6	81.9	1.3	.1	0.0	14.1
54	500	250	67.6	3.4	82.2	1.9	.6	3.9	8.0
39	500	500	61.8	3.4	83.0	1.9	.5	2.6	8.6
67	500	1,000	56.4	3.7	85.9	1.8	.3	2.8	7.5
Coal	(moisture free, tests 39, 42, 54, and 57)			5.2	73.5	1.6	.8	12.4	5.5
Coal	(moisture free, tests 70 and 67)			5.6	74.8	1.5	.7	12.9	4.5

Powdered Arkansas lignite was fluidized in a stream of hydrogen, preheated and placed under a pressure of 500 p.s.i. At 500° C., with a hydrogen linear velocity of about 0.2 foot per second and in the absence of catalyst, total oil and gas yields of 35 percent and 22 percent, respectively, were obtained. In addition, the asphalt content of the product oil was much lower than that obtained from uncatalyzed Rock Springs coal. Thus, this lignite is especially suitable for fluidized-bed hydrogenation.

Fluidized-bed hydrogenation of Rock Springs coal, using impregnated catalysts, which had been found effective in batch autoclave tests, indicated that the presence of catalyst had a negligible effect on the yield of product oil. However, in similar tests (shown in table 15) made with a coal charge diluted with ground coke, the use of impregnated ammonium molybdate as a catalyst greatly increased the potential oil production from Rock Springs coal. Where previously an oil yield of 15 to 20 percent (m.a.f. coal) could be anticipated, by using a coke:coal ratio of 3 and increasing the flow of hydrogen threefold, an oil yield of 40 percent could be obtained.

TABLE 15. - Product distribution in hydrogenation of Arkansas lignite and Rock Springs coal in fluidized bed unit

Test No.	Coal	Catalyst	Temperature, °C.	Pressure, p.s.i.g.	Time	Percent on m.a.f. coal				
						Residue	Oil	Gaseous hydrocarbons	CO_2	H_2O
66	Rock Springs	None	600	500	0	56.4	22.3	13.6	3.3	16.2
177	Rock Springs	$(NH_4)_2MoO_2$ undiluted	600	500	0	51.0	17.1	19.0	2.2	12.4
178	Rock Springs	$(NH_4)_2MoO_4$ diluted with coke	600	500	0	37.0	32.0	22.6	-	11.7
130	Arkansas lignite	None	600	500	0	24.5	34.1	22.0	10.7	14.6

Although such bench-scale experiments hardly can be considered as more than the preliminaries to the process development work needed to establish a dry-coal process, comparison of the data from the fluidized hydrogenation of coal with treatment of the same coal by the "standard" high-pressure Bergius-I.G. techniques offers a means of evaluation.

Using data presented by Hirst and coworkers, it is found that even at this early point in its development, dry-coal hydrogenation compares well with high-pressure liquid-phase hydrogenation. Hydrogen consumptions for both processes are approximately the same, using middle oil as a basis. The coal utilization or conversion in both processes is roughly equal if total coal fed to the plant is used as a basis. (This basis of "total" coal fed includes the coal used for power and gas production in the high-pressure plant on the assumption that the char residue obtained in the fluidized process would be suitable for power-plant fuel and gasification.

It is reasonable to assume that the lower-pressure fluidized plant may be less costly in spite of the higher temperature of operation; and, with comparable hydrogen usage and oil production, a decrease in product cost should be possible. It is also a reasonable expectation that future research and development will produce process improvements and solve the many foreseeable engineering problems involved in operating a fluidized bed under pressure of 250 to 1,000 pounds per square inch. Construction of a fluidized-bed coal-hydrogenation pilot plant is in progress, which will utilize the oil-recovery and gas-handling facilities already existing in the liquid-phase pilot plant.

Variable contact-time unit. - Rock Springs coal was hydrogenated in a unit designed for varying the length of time that the coal particles are exposed to reaction conditions. At a temperature of 450° C., pressures of 500, 1,000, and 2,000 p.s.i., contact times of 1.6 and 7.2 minutes, and, in the absence of catalyst, the product distribution was found to be essentially independent of hydrogen pressure. At 538° C., however, an increase in pressure increased liquefaction and gas production. These results can be interpreted on the basis of the coal-hydrogenation mechanism advanced in last year's report by assuming that, at 450° C., the rate of polymerization of reactive fragments is slow compared with the rate of hydrogenation stabilization, whereas at 538° C., the two rates are comparable. These studies are being continued in an attempt to arrive at a quantitative kinetic treatment of the data.

Bench-scale coking of heavy-oil let-down. - As part of an investigation of methods of processing heavy-oil let-down from the liquid-phase coal-hydrogenation process, tests are being made with a bench-scale coking unit (see fig. 42). The design of this unit is similar to that employed in the oil industry for approximation of the product distribution to be expected from commercial delayed coking of residual oils. Uncentrifuged heavy-oil let-down from the liquid-phase coal-hydrogenation pilot plant was subjected to a vacuum-stripping treatment and then heated slowly to 450° C. in the coking unit. Preliminary results showed that the coked residue contained 96.9 percent benzene-insoluble material.

Hydrogenation of Beulah lignite. - Because North Dakota lignites are important as a potential source of liquid fuels, a study has been made of the influence of temperature and pressure on the hydrogenation of Beulah lignite. The temperature range studied was 400° to 475° C. at an initial hydrogen pressure of 1,000 p.s.i.; similarly, at a constant reaction temperature of 450° C., the initial hydrogen pressure was varied from 500 to 2,500 p.s.i. The catalyst used in all cases was impregnated ammonium molybdate plus sulfuric acid, which has been shown in these laboratories to be superior to all other catalysts for lignite.

Over the range studied, liquefaction increased with both increasing temperature and pressure, but in no case was it possible to obtain liquefactions appreciably over 85 percent. This value is less than that obtained with Beulah lignite in pilot-plant runs in which liquefactions above 90 percent were achieved at a reaction pressure of 3,300 p.s.i. The yield of "oil" (including asphalt) observed in these early pilot-plant runs was about 50 percent, which is comparable to the maximum value of oil plus asphalt obtained in these experiments. A yield of asphalt-free oil of at least 45 percent can be obtained from Beulah lignite. Qualitatively, it appears that the primary liquefaction is influenced less by pressure than is the conversion of asphalt to oil. This is in agreement with recent data on Rock Springs coal. The data on carbon dioxide production demonstrate that the reverse water-gas shift reaction

$$CO_2 + H_2 = CO + H_2O$$

took place to some extent. This reaction is thermodynamically possible at these temperatures and hydrogen pressures, and its rate would be expected to increase on increasing the temperature or hydrogen pressure.

Coal-hydrogenation catalysts. - Extensive studies of coal-hydrogenation catalysts and of methods of applying them in liquid-phase coal-hydrogenation processes were carried out in batch autoclave experiments. The importance of catalyst distribution has been demonstrated previously for such catalysts as ferrous sulfate, ammonium molybdate, and nickelous chloride. These experiments were carried out, however, in the absence of added vehicle, and it remained to be determined whether the effect of catalyst impregnation would be as important when vehicle is present initially. Accordingly, a group of experiments was performed in which Rock Springs coal was hydrogenated in the presence of heavy-oil vehicle. The results showed that

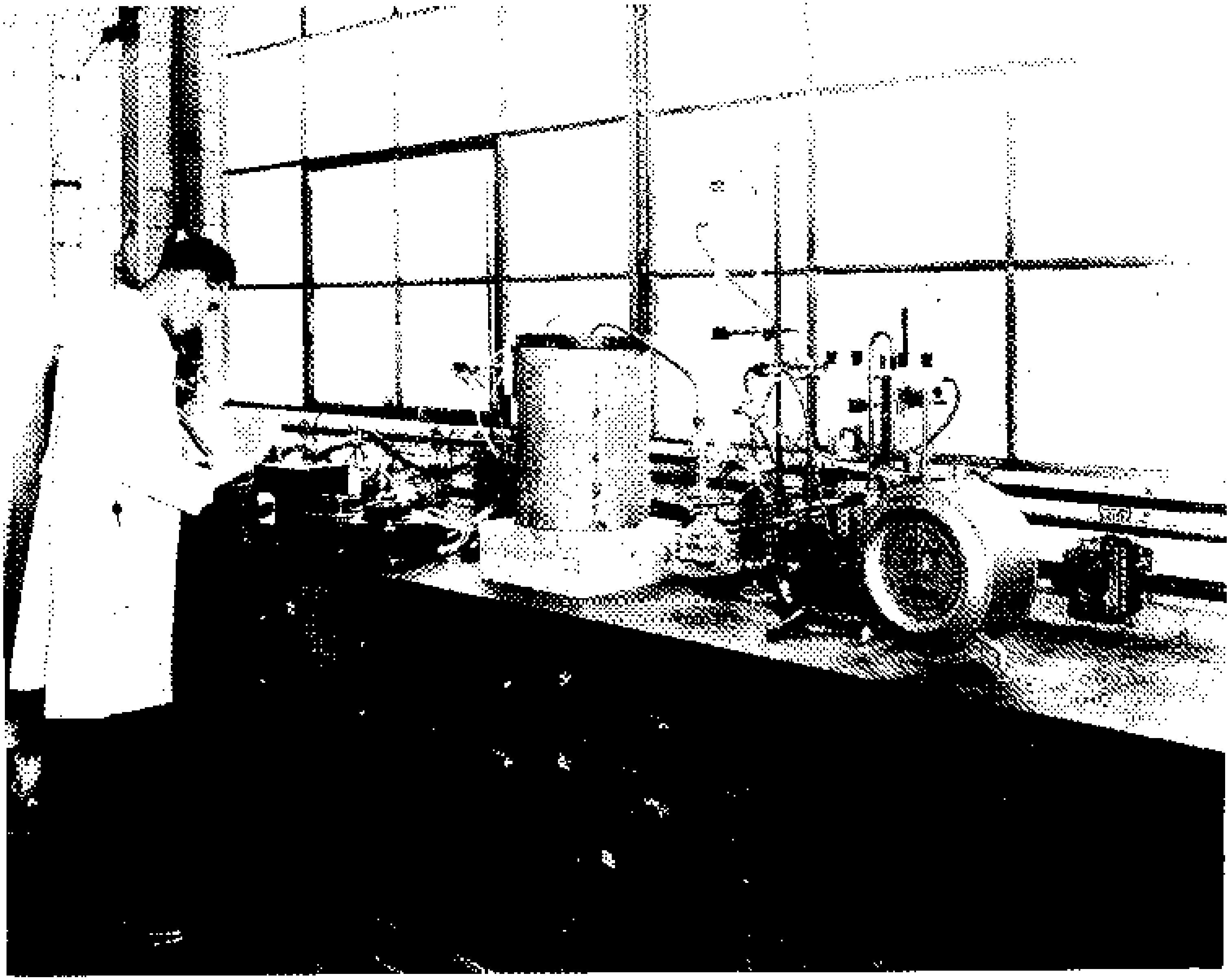

Figure 42. - Bench-scale coking unit.

the effect of catalyst impregnation is qualitatively the same whether vehicle is present or not, but that the quantitative relationships in the products obtained are somewhat different.

Previous studies of impregnated catalysts had all been made on a finely ground (less than 200-mesh) coal. On a commercial scale, it would, of course, be more convenient to impregnate larger coal particles prior to the final grinding. To determine the effectiveness of such a procedure, particles of Rock Springs coal in the 2- to 6-mesh range were impregnated with ferrous sulfate, after which the coal was ball-milled to a particle size of less than 200-mesh. Upon hydrogenation at standard conditions, 81.2 percent liquefaction was obtained, compared with 84.9 percent obtained when impregnation was carried out after the ball-milling operation. Impregnating the larger particles is thus almost as effective as impregnating the finely ground coal, and is much more desirable on a plant scale.

Hydrogenation of pure asphalt at 450° C. and 1,000 p.s.i. initial hydrogen pressure for 1 hour with various impregnated catalysts showed these materials to be decreasingly effective for the conversion of asphalt to oil, in the following order: stannous chloride, tin plus ammonium chloride, ammonium molybdate plus sulfuric acid, nickelous chloride, and ammonium molybdate. An unsuccessful attempt to hydrogenate Bruceton coal with only water as a catalyst demonstrated that the beneficial effect achieved by impregnation does not arise from the presence of water. It was found that the use of coal, 80 percent of which was uncatalyzed and 20 percent of which was neutralized and impregnated with ammonium molybdate, yielded results as good as those produced with coal uniformly impregnated with catalyst. Pickle liquor, containing ferrous sulfate and sulfuric acid and available commercially where it is used to remove scale and other surface imperfections from metals, produced results on impregnation similar to those obtained when pure ferrous sulfate was used. When samples of anthraxylon from Rock Springs coal and samples of the whole coal were hydrogenated under standard conditions, they were observed to exhibit the same behaviour toward the catalysts used. This similarity implies that the response of Rock Springs coal towards these catalysts is a property only of the coal substance and not of the ash content.

Characterization of Coal and Coal-hydrogenation Products

Progress in the development of a suitable process for synthesizing liquid fuels directly from coal has long been hampered by a lack of basic knowledge concerning the original composition of the parent coal substance. The inherently simpler chemistry involved in the synthesis of liquid fuels from carbon monoxide and hydrogen (Fischer-Tropsch process) has resulted in the rapid advance of commercial possibilities in this field. To attain this objective in the direct hydrogenation of coal, therefore, investigations on the constitution of coal are in progress in the Bruceton laboratories.

In attacking this problem, one of the most popular methods employed by previous investigators has been to examine the products obtained from some reaction involving coal and, from the results, to speculate on the structure of the parent substance. Such studies have been made in the past on halogenation, oxidation, reduction, and hydrolytic reactions. The hydrogenation or reduction of coal yields products of an aromatic nature, and the constitution of these materials has led to the postulation of an aromatic or hydro-aromatic structure for coal.

In a variation of this experimental method, a comparison was made of the products obtained by similar and separate treatment of coal (presumably aromatic in structure) and cane sugar (known to possess an aliphatic structure). This was accomplished by hydrogenating powdered Bruceton coal and commercial cane sugar separately in batch autoclaves for 1 hour at 400° or 450° C. in the presence of 1 percent tin and 0.5 percent ammonium chloride and 2,500 p.s.i. initial hydrogen pressure. The hydrogenation of sugar at both temperatures produced the same amounts of water and carbon dioxide. This indicates that elimination of oxygen is probably one of the first steps in the thermal decomposition of sugar, and that it probably occurs at temperatures below 400° C. It is of interest to note that about 80 percent of the oxygen is eliminated in the form of water, and only about 20 percent in the form of carbon dioxide. The hydrogenation of both coal and sugar at 400° C. produces an asphalt characterized by solubility in benzene and insolubility in a n-hexane. At 450° C., portions of both coal and sugar were converted to oil. Because of the apparent dissimilar structures of both parent substances, a careful comparison of these apparently similar products was most pertinent.

Asphalt. - Previously, the characterization of asphalt has depended on ultimate analyses and solubility characteristics. Recent development of a method using thin asphaltic films, however, has led to the procurement of infrared absorption data. Accordingly, infrared spectra of the asphalts obtained from both coal and sugar were compared (see fig. 43), and it was established that these products were virtually identical. The only distinct difference between these spectra was the existence of a C=O band at 5.85 microns in the sugar spectra. Nitrogen and sulfur are known to be present in the coal asphalt, but the only indication of the presence of these compounds is a weak band at 8.62 microns (indicated in fig. 43 by arrows). The most important part of these spectra for establishing identity is the region beyond the so-called functional group positions (beyond 7 microns). From 7 to 15 microns, absorption bands appear for vibrations of complete molecules or for large sections of them. It is in this region that no two molecules, except optical isomers, can have identical spectra. Molecules consisting of the same molecular species or units that differ only in molecular weight may have nearly identical spectra. This is probably the situation that exists for these two asphalts.

Heavy oils. - The infrared spectra of the heavy oils from sugar and coal compare even more closely than those of the asphalts (see fig. 44). A trace of C=O is indicated in the 400° C. sugar sample, but none whatever can be seen in the oil obtained from sugar at 450° C. The spectra of the sugar samples both exhibit slightly more hydroxyl content than the oils from coal, and the coal products indicate slightly greater concentrations of aromatics.

Light oils. - The mass spectra of the light oils from sugar and coal at 450° C. show a great profusion of mass peaks, but the two spectra have nearly identical patterns (see fig. 45). Furthermore, it is possible to pick out the mass peaks due to C_6 to C_{10} aromatics, hydro-aromatics, naphthenes, and paraffins. The infrared spectra of these products are complex, but the same bands occur in both.

The above spectral evidence establishes beyond a doubt that the products from the hydrogenation of sugar and coal are very similar. Carbonyl groups are present in the sugar products, and a weak band found in the spectra for asphalt from coal possibly indicates nitrogen or sulfur compounds; otherwise, the differences are confined to slight variations in the concentrations of the constituents. It is evident, therefore, that if products of similar structure can be obtained from such apparently different substrates as sugar and coal, considerable hazard exists in making deductions regarding the constitution of coal from a study of the products obtained by high-temperature, high-pressure hydrogenation.

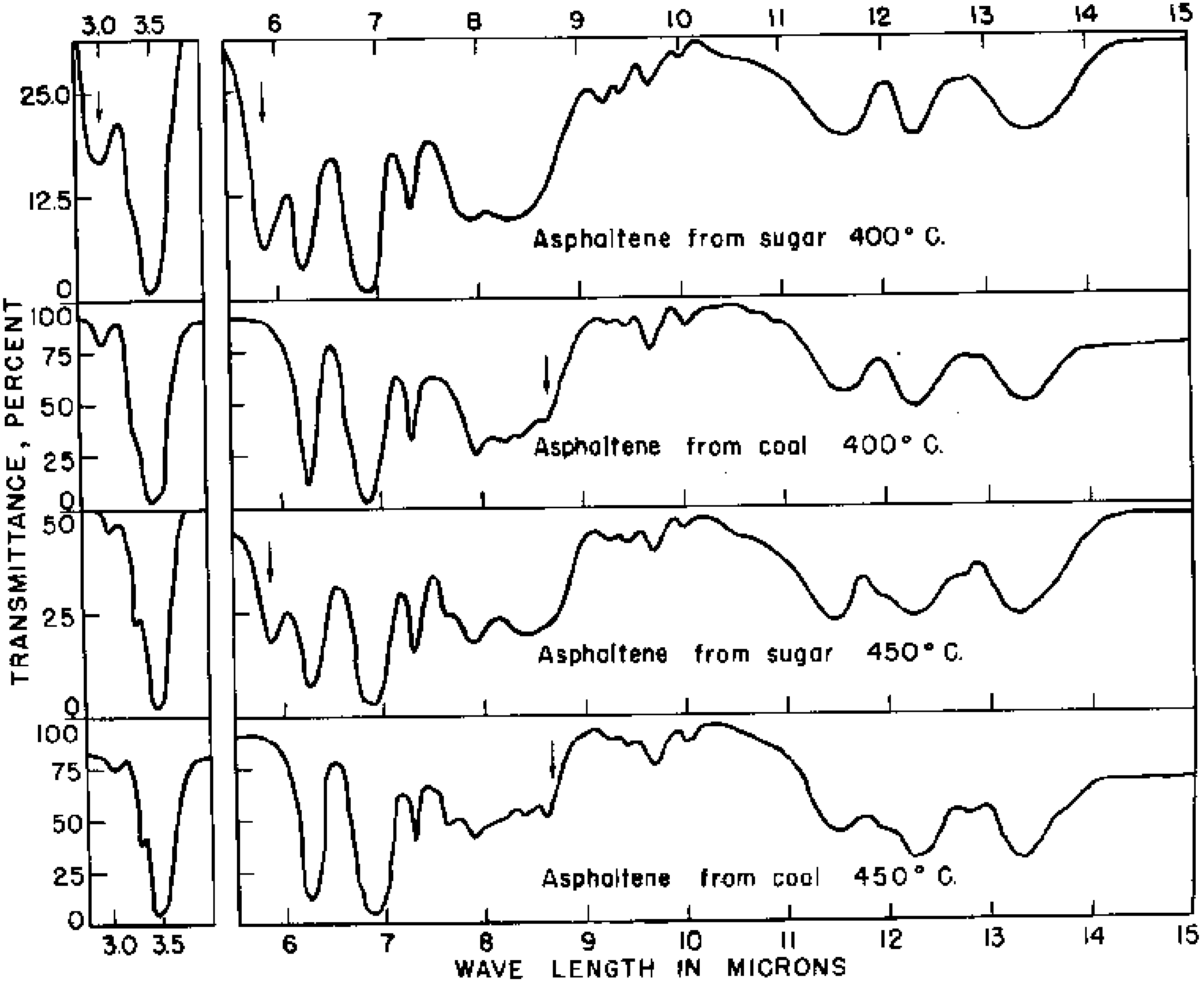

Figure 43. - Infrared spectra of asphaltene from coal and sugar.

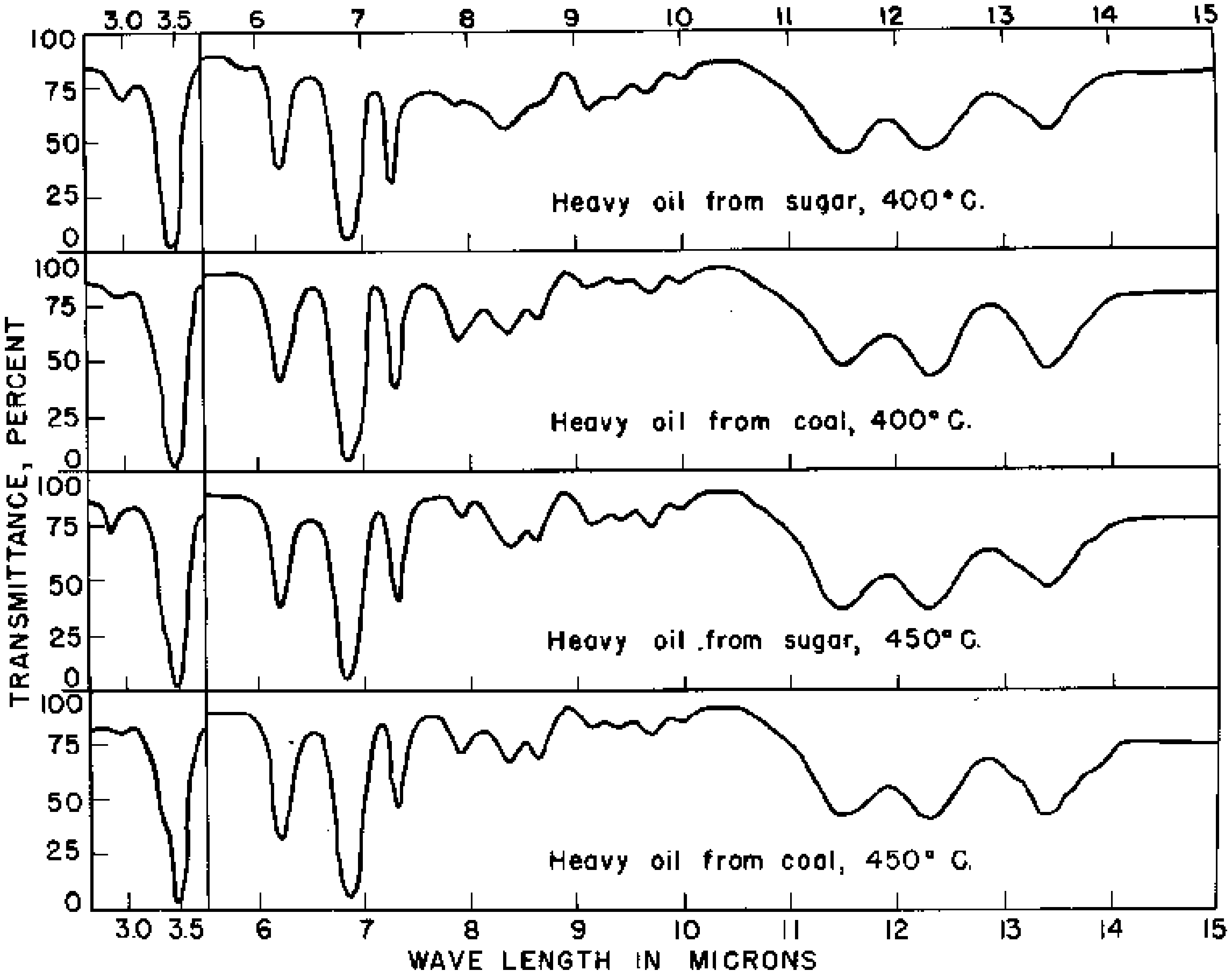

Figure 44. - Infrared spectra of heavy oil from coal and sugar.

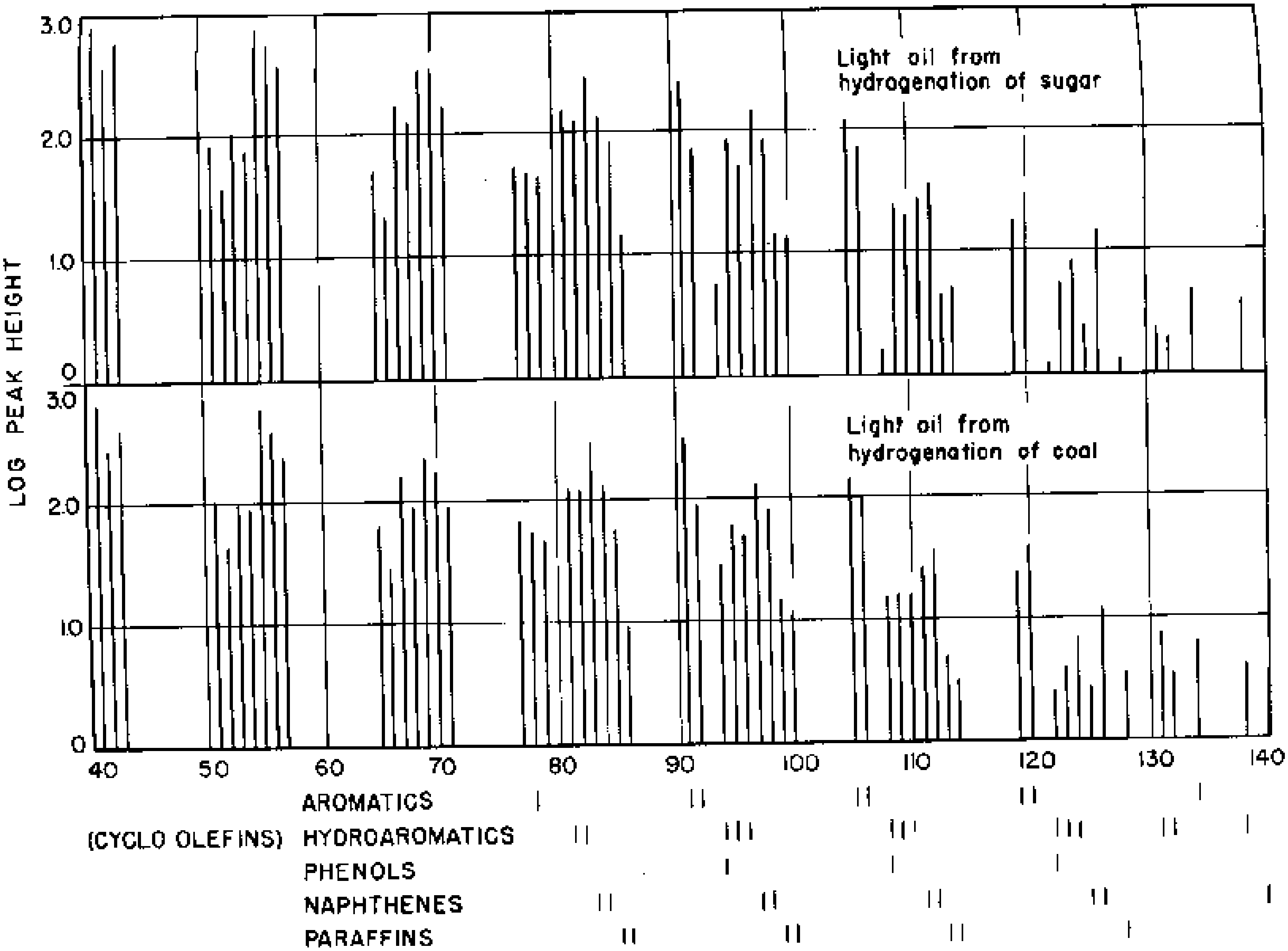

Figure 45. - Mass spectra of light oil from coal and sugar.

Study of the Oxygen Linkages in Coal

In a number of experiments, the nature of the oxygen elimination during hydrogenation of partly (air) oxidized coals was studied. The nature of the combination of atmospheric oxygen with a coal substrate is of critical importance, as it has been amply demonstrated that the addition of a small quantity of oxygen can have a profound effect upon the coal so treated. For example, a bituminous coking coal, when oxidized, no longer yields a coke, nor is it extractable with aromatic solvents. The character of the groups in the coal that react with oxygen is unknown. It was felt, therefore, that a study of the nature of the oxygenated products obtained by mild hydrogenation of oxidized coals would shed light on the types of oxygen linkages involved in the oxidized coals.

In accordance with this objective, Wyoming noncoking subbituminous coal (impregnated with 1 percent Fe as $FeSO_4$) was first hydrogenated under the conditions necessary to convert it to a coking coal. The benzene-insoluble fraction of this hydrogenated product was then divided into two portions, one of which was dried in air and the other in a vacuum. The air-dried and vacuum-dried portions were then hydrogenated for 1 hour at 450° C. under an initial hydrogen pressure of 1,000 p.s.i. From the data collected in this experiment and in one in which a sample of air-dried Bruceton (coking) coal that had lost its coking properties was hydrogenated under the requisite mild conditions for regenerating the coking action, the following conclusions were reached.

The air drying of the benzene-insoluble fraction of partly hydrogenated Wyoming coal greatly lowered its ease of liquefaction. A liquefaction of about 50 percent was obtained, compared with 70 percent when the vacuum-dried fraction was hydrogenated. This effect may parallel that which occurs when the benzene-insoluble fraction of a phenanthrene extract of Bruceton coal is hydrogenated. The air-dried fraction of this extracted coal yields a liquefaction of 47.7 percent, compared to the vacuum-dried fraction, which yields 54.5 percent liquefaction.

Despite the increased oxygen content of the air-dried Wyoming coal fraction, slightly less total oxygen was eliminated by hydrogenation than in the vacuum-dried fraction. There was also a difference in distribution of oxygen among the products. Greater relative amounts of carbon dioxide, carbon monoxide, and water were formed in hydrogenating the air-dried material. The amount of oxygen in the insoluble portion and in the soluble portion of the air-dried material was less than that in the vacuum-dried material. It would appear that the oxygen attack on the Wyoming coal material is such that some unreactive oxygenated structures were formed that are harder to break up than the oxygen-containing structures in the original material. Oxygen evidently is not added on peripheral structures alone, which would lead to easy and complete oxygen elimination by mild hydrogenation.

Air oxidation of Bruceton coal does not have the great depressing effect on liquefaction evident in Wyoming coal. Previous results on the hydrogenation of Bruceton coal and Bruceton anthraxylon showed little significant difference between liquefaction of the air-dried and untreated materials. It is of interest also to make this comparison when the oxidized Bruceton coal is hydrogenated under conditions necessary for regenerating its coking property, and here, again, oxidation does not significantly change the extent of liquefaction. There is, however, a difference in the relative distribution of oxygen among the products. Far more carbon dioxide than carbon monoxide is formed in air-dried coal, whereas a preponderance of carbon monoxide is observed in untreated coal.

From these facts it would appear that the attack of atmospheric oxygen on Bruceton coal is different from its attack on Wyoming coal. The oxygen reacts with structures in Bruceton coal to give oxygenated materials that are quite susceptible to hydrogen attack leading to easy elimination of oxygen.

Gasification of Coal

Vortex Combustion Studies for Powdered-Coal Gasification

In an experimental unit of the vortex type, the gasification of coal with oxygen and steam was studied, and a specially designed coal distributor was used, which spread the coal throughout the unit by means of a spinning plate. Despite a very great improvement in gas composition and an increase in carbon conversion of more than 15 percent at the same oxygen-to-coal ratio with the spinning-plate distributor, it was soon evident that some other means of increasing carbon conversion must be sought. The most promising method of doing so was to decrease the size of the particle to bring its equilibrium radius within the vortex, or, correspondingly, by increasing the tangential velocity. The vortex design used up to this point - that is, a vortex 2 feet in diameter, 8 inches deep, and containing nine slots each 3/8-inch by 2-inches - was selected because it gave the maximum tangential velocity for the gas throughputs required for gasification. However, if a shallower vortex were used, the tangential velocity should increase. From a theoretical standpoint, reducing the depth of the vortex by half will reduce the size of the particle, leaving the reaction zone by one-half if both the radial and tangential velocities are doubled.

Accordingly, after suitable changes in equipment design, experiments were carried out that showed that no change occurred in the carbon conversion when the vortex was reduced to 4 inches. Further reduction in depth to 2 inches decreased the carbon conversion by 9 percent. As the reduction in depth also decreased the time available for gasification and increased the coal throughput per cubic foot of reactor volume, these results possess considerable significance. Tests made with the 2-inch vortex showed that, as was the case with the 8-inch vortex, the carbon conversion remained essentially constant when the coal throughput was varied at the same oxygen-to-coal ratio.

To provide greater flexibility for determining the effect of the geometry of the reactor on carbon conversion, major design alterations were made that resulted in a vortex 24 inches in diameter, 24 inches deep, and containing an outlet diameter of 4 inches, with nine slots, each 3/8 inch by 2 inches, at the top of the reaction chamber. Contrary to the results found by previous investigators, tests made with a "forced" vortex in a reactor containing a concentric silicon carbide tube produced carbon conversions much lower than those obtained with a "free" vortex in a reactor unmodified by the center tube. In a test made to determine the effect of introducing the gases through slots at the bottom of the reactor, the carbon conversion was found to be about 10 percent lower than for the same feed conditions with slots at the top of the reactor.

Experimental work with the vortex reactor is thus being directed toward solution of the following problems:

1. To determine whether the thermodynamic method of correcting for heat losses in terms of an equivalent amount of oxygen can be experimentally verified for the vortex reactor. This problem can be attacked by (a) varying the throughput to the reactor, thereby changing the heat losses per pound of coal, (b) preheating the oxygen