

some information concerning the temperature and pressure dependence of these rates. In experiments in which the catalyst testing converters described above were used, the temperature coefficient of the synthesis rate on a cobalt catalyst was measured by determining the space velocity necessary for 70 percent contraction at several temperatures in the range of 175°-200° C. From the temperature coefficients, the energy of activation was calculated to be 24 ± 2 kilocalories per gram molecular weight of $2H_2 + 1CO$ reacting.

Synthesis of Hydrocarbons from Hydrogen and Carbon Monoxide

Fischer-Tropsch Process Development

A brief review of the Fischer-Tropsch process, including some of the information contained in captured German documents, has been published.⁸⁴

The synthesis of gasoline and Diesel oil from water-gas (a mixture of hydrogen and carbon monoxide) is accompanied by the evolution of a large amount of heat; namely, about 7,000 B.t.u. per pound of oil produced. The temperature of the reaction must be controlled within a narrow range of about 5° C. (9° F.) to avoid excessive methane production. These specifications necessitate rapid and efficient heat transfer from the catalyst surfaces to some cooling medium. The design of German converters involves the use of very narrow layers of catalyst and consequently very large amounts of steel (about 15 tons per barrel of oil per day). Recent process designs by United States oil-company engineers specify a turbulent bed of catalyst powder with heat-exchange tubes in the bed, or a heat exchanger outside the reaction zone, the catalyst suspension in the gas stream being passed from the converter through a heat exchanger and back into the converter. An even simpler process involving no internal metal heat-exchange surfaces is in process of development in the experimental plant of the Bureau of Mines. This process consists in injecting a cooling oil along with the feed gas. The boiling range of this cooling oil is so chosen that it will vaporize upon absorption of heat from the catalyst surface. Early experiments with a 12-inch catalyst bed 3 inches in diameter showed that very precise temperature control was obtained, but that the yield of oil per unit volume of catalyst per hour was erratic, and, although equal in amount to that of the German designs, the space-time yield was much lower than the American "fluid-flow" designs just described. Part of the difficulty causing the low and erratic yield has been traced to poorly reproducible catalyst-preparation procedure; but most of the trouble probably is caused by poor distribution of cooling oil and disturbance of the steady-state films of oil and gas on the catalyst surface by changes in cooling oil distribution.

⁸⁴/ Golumbic, N., Review of Fischer-Tropsch and Related Processes for Synthetic Liquid Fuel Production: Bureau of Mines Inf. Circ. 7366, 1946, 24 pp.

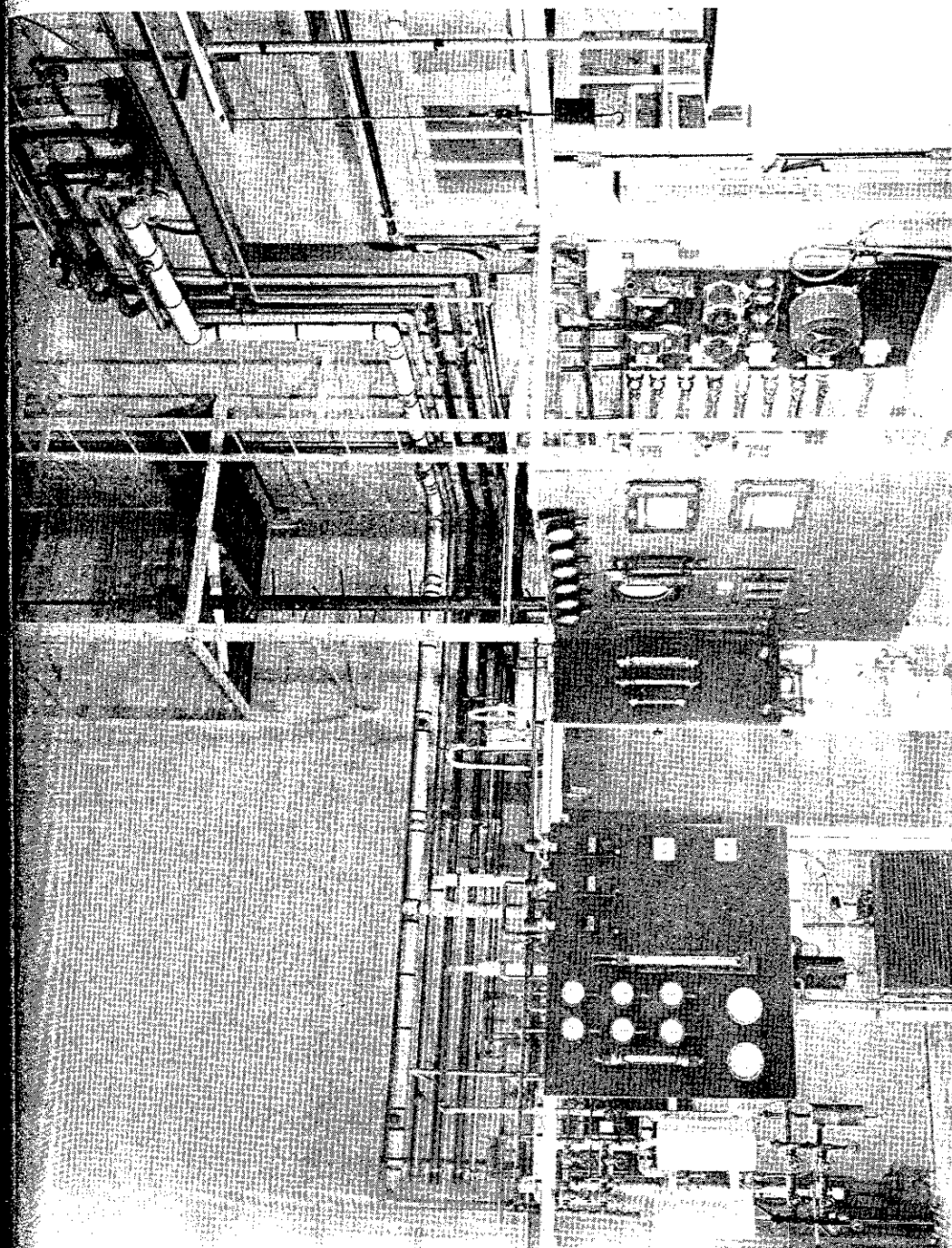


Figure 29. - Fischer-Tropsch experimental plant with internally cooled converter.

The internally cooled converter previously described^{85/} was redesigned and rebuilt to accommodate a catalyst bed 3 inches in diameter by 8 feet deep and to provide adequate control of all operating conditions, such as pressure, temperature, rate of cooling-oil circulation, space velocity, and rate of recycling of end gas. Provision was made, also, for sample withdrawal at several points in the 8-foot column. A photograph of the partly completed unit is shown in figure 29.

Experiments with counter-current flow of cooling oil and a pelleted Co-ThO₂ Filter Cel catalyst showed that the maximum space velocity (volumes of synthesis gas per volume of catalyst per hour) permissible without flooding is about 200, whereas exploratory tests with co-current flow indicated that space velocities of 600 or larger could be used without flooding. An additional advantage of co-current operation was a much lower yield of methane and carbon dioxide than in the counter-current procedure. A recent co-current run operated for 200 hours at a space velocity of 100 at 183° C. and 100 pound per square inch pressure yielded about 11 kilograms of oil plus wax per cubic meter of catalyst per hour. The weight ratios of methane to oil plus wax and carbon dioxide to oil plus wax were, respectively, 0.20 and 0.16 for this run, as compared with 0.44 and 0.34 for a counter-current operation. Experiments at higher space-velocities in co-current operation are in progress.

The process-development laboratory has been enlarged during recent months as regards personnel, space, and equipment so as to conduct exploratory "bench" or laboratory-size experiments on several processes simultaneously. Three processes are being investigated; they are:

1. The liquid-phase catalyst-suspension process in which a finely divided catalyst is dispersed in a fraction of Fischer-Tropsch oil whose boiling point at operating pressure is maintained slightly higher than the desired operating temperature. Cooling may be accomplished by evaporation of oil or by circulation of a cooling fluid through an internal heat exchanger or by a combination of both types of cooling. Detailed plant have been completed for a 3-inch-diameter converter to have a maximum capacity of 2 liters of catalyst suspension and operate at 20 atmospheres pressure. Porous disks fabricated of sintered iron powder have been found suitable for distributing the feed gas. Special methods of producing extremely finely divided catalyst powders have been developed for use in this process.

2. Fluidized fixed-bed processes are being studied chiefly to develop such a process for production of a larger fraction of Diesel oil than is possible with the fluid-flow process now used industrially. To obtain some experience in control of important factors in fluidized catalyst operation, experiments in glass equipment were made with silica gel microspheres. One of the important variables is the manner in which the gas is introduced. Thus far, the best results have been obtained using a cone containing a

^{85/} Fieldner, A. C., Fisher, P. L., and Brewer, R. E., Annual Report of Research and Technologic Work on Coal, Fiscal Year 1944: Bureau of Mines Inf. Circ. 7322, 1945, 79 pp.

fixed filter or gas distributing disk. Comparison of the quality of the fluidization is made on the basis of linear gas velocity, bed density, and bed resistance. Other variables to be studied are tube diameter, bed height, transverse baffles, and other dispersion devices, and particle size and its distribution.

3. The hot-gas recycle process, in which all of the heat of reaction is carried out of the reaction vessel by the sensible heat of the gas, involves very large recycle rates of the order of 50 to 100 parts of recycle gas to 1 part of fresh gas.

Coal Hydrogenation

Experimental Plant

The maintenance and mechanical design and assembly group of the experimental plant has been greatly improved as a result of greater availability of suitable mechanically adept personnel during the past year. Several additional automatic controls, such as high-pressure flowmeters, liquid-level controllers, and automatic alarm devices, have been installed. Reaction baskets were designed and used in most of the operations. These are fabricated of ordinary steel, and when coking occurs they are replaced by new baskets, thus avoiding the time-consuming and laborious decoking of converters. The mechanical group has been active, also, in design of special spray devices for atomizing coal-oil paste, of special paste and hydrogen preheaters, and in construction of models to study mechanical features of the coal hydrogenation process.

Further work was done on the production of a heavy ("Bunker C" type) fuel oil, using a pressure of 3,500 pounds per square inch. Under this pressure it was found possible to increase the throughput to about five times that at 1,000 pounds per square inch, using the same catalyst and temperature conditions in the converters. In the recent operations at the higher pressure, the hydrogen consumption was about the same as at 1,000 pounds per square inch. Data were obtained, also, for the increase in throughput with increasing reaction temperature. In the range of 420°-460° C., the throughput could be doubled for every 20° C. increase in reaction temperature. The effective contact times at different reaction temperatures and at 3,500 pounds per square inch pressure were as follows:

Temperature, ° C.	420	440	460
Contact times, hours	1.05	0.55	0.25
Hydrogen absorbed, percent of moisture and ash-free coal	4.6	5.3	5.1

Another objective of several runs in the experimental plant was to determine the importance of the extent of the gas to liquid interface in the first stage of coal hydrogenation. Two converters in series (see fig. 30) were packed with 1/2-inch coke, and the operation was conducted so as to produce chiefly fuel oil. The coke packing occupied about 50 percent of the converter volume. Coal-oil paste (see fig. 31 for photograph of paste-pump

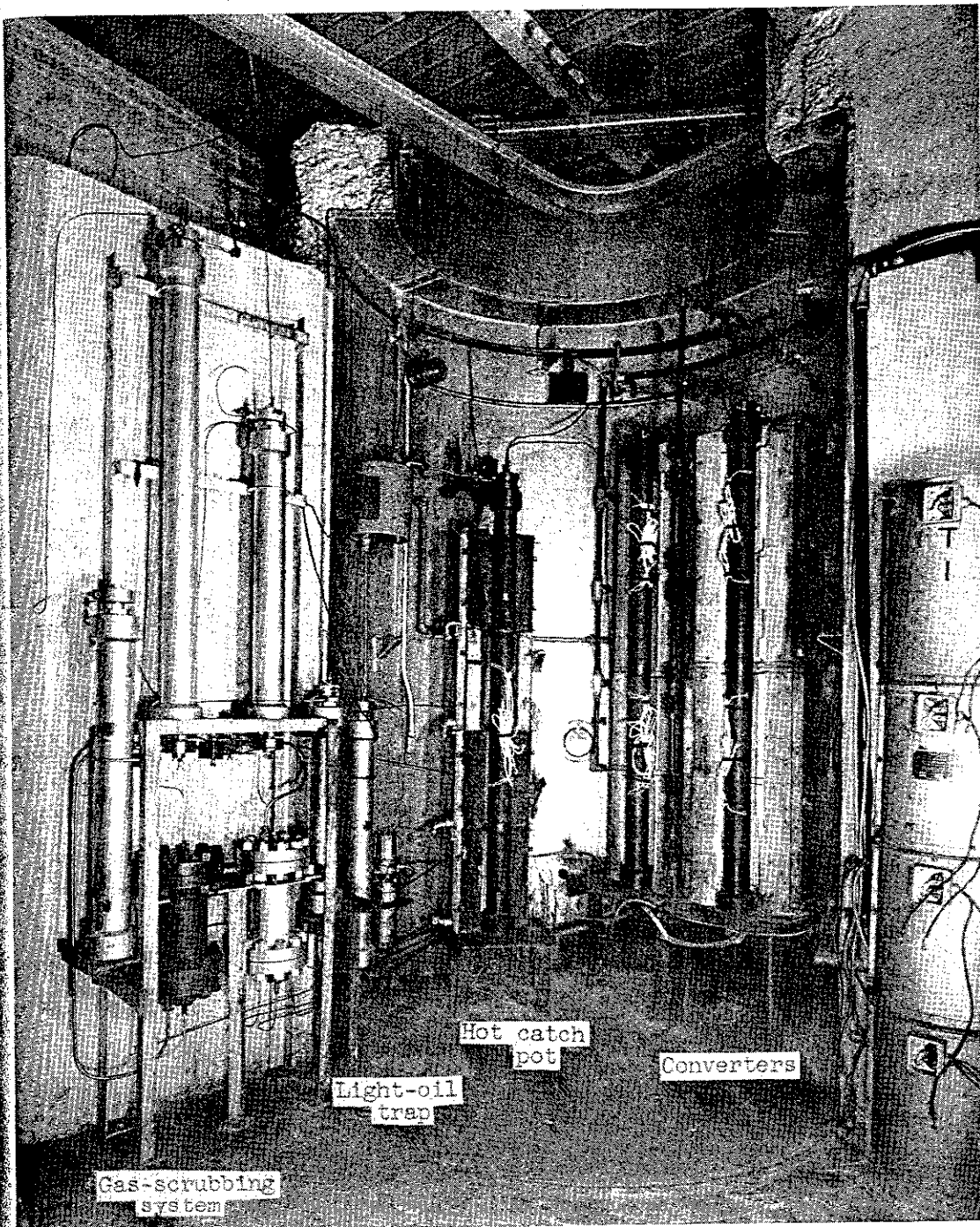


Figure 30. - Coal-hydrogenation experimental plant.

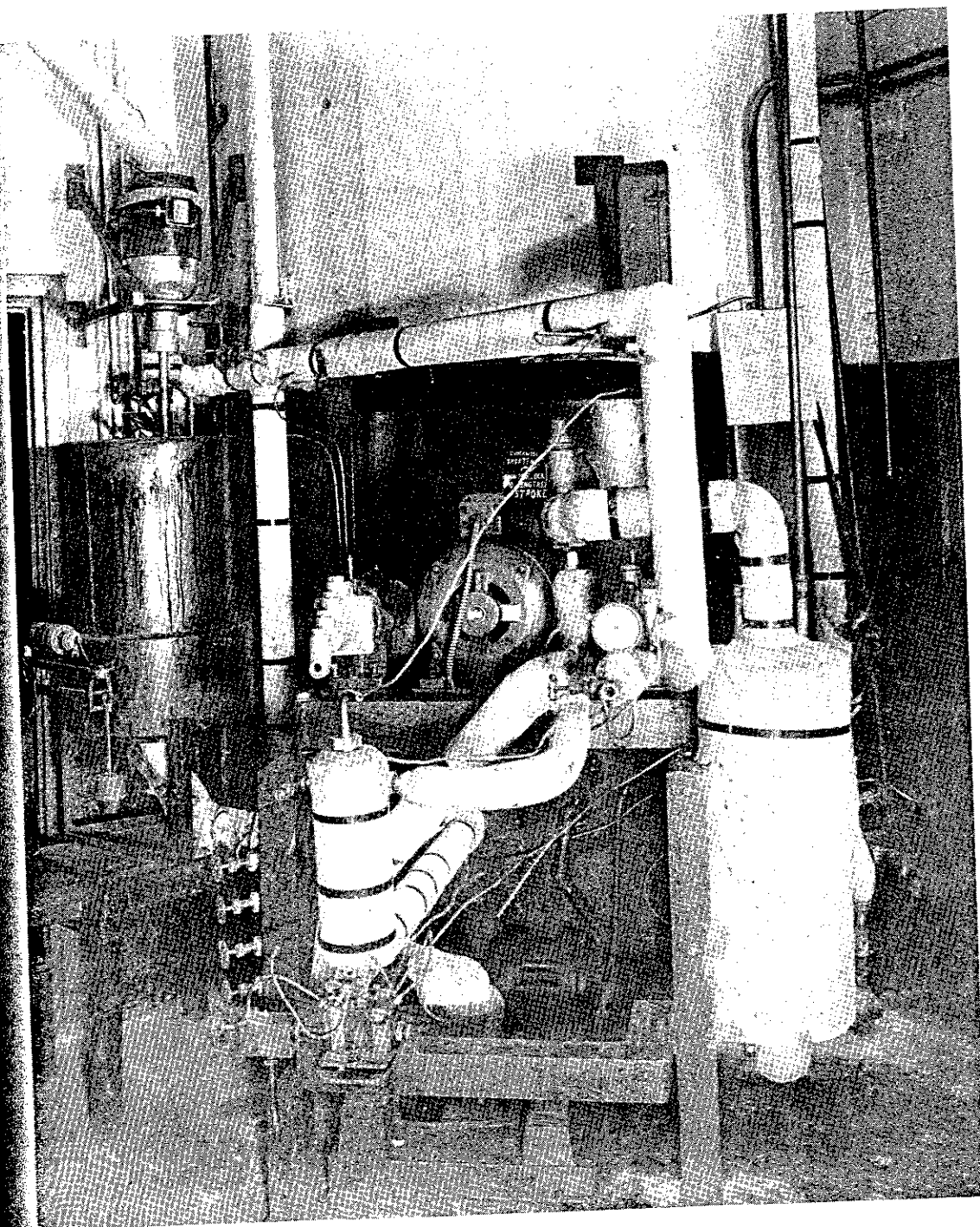


Figure 31. - Paste-pump assembly, coal-hydrogenation experimental plant.

assembly) and compressed hydrogen were introduced at the bottom of the first converter and moved upward through the column of coke. The overflow from a standpipe in the first converter was conducted to the bottom of the second converter. It was found that only about one-half as much throughput could be maintained as was possible in an operation without the coke packing but otherwise identical with the operation just described. A smaller size (4 to 8 mesh) of coke packing did not result in any observable increase in throughput. It is apparent, therefore, that breaking up the size of the hydrogen bubbles by the coke packing did not increase the rate of coal hydrogenation. An appreciable decrease in the amount of hydrocarbon gas produced was noted in the packed converter system as compared with the unpacked.

To obtain a much larger increase in gas to liquid interface than in the system described in the previous paragraph, the preheated coal-oil paste was introduced at the top of column of coke, so that it would percolate down through the packing. In this fashion the entire surface of the coke, covered with a film of coal-oil solution, was exposed to hydrogen. The contact time at reaction temperature in this mode of operation was much smaller for a given throughput than in that described in the preceding paragraph. Even at one-half of the throughput used in the normal mode of operation, very serious operating difficulties were encountered with the percolation operation. After the seventh recycle batch, the amount of solids in the crude heavy oil was so high that centrifuging was difficult. Residual solids built up in the coke packing, so that the free space was reduced to such an extent that there was insufficient contact time for efficient hydrogenation. Addition of light oil to the pasting oil failed to improve the operation. Apparently the increased gas to liquid interface did not increase the rate of coal hydrogenation sufficiently to compensate for the greatly reduced contact time at reaction temperature in this operation.

The experimental plant was operated also in some preliminary runs on the possibility of using a fixed catalyst to accelerate the conversion of heavy oil to middle oil (or "gas oil"). It was thought that if the fixed catalyst were preceded by a bed of adsorptive material on which the nonvolatile oxygenated fractions of the heavy oil would be retained, rapid catalyst deterioration could be avoided and the nonvolatile constituents periodically dissolved by flushing the purification bed with a suitable solvent oil. It was found that a molybdic acid-on-alumina catalyst could be kept active for about 10 days in such a system, and that periodic flushings would be necessary every 4 or 5 days. Continuation of this research has been postponed until more information is available on the "steady-state" concentration of nonvolatile oxygenated compounds in liquid-phase coal hydrogenation and on their solubility in various light-oil fractions.

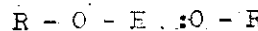
Experiments in Small Autoclaves

A series of experiments was concerned with the solvation and depolymerization of coal.^{86/} Tables 27 and 28 present data from various solvation

^{86/} Orchin, M., and Storch, H. H., Solvation and Hydrogenation of Coal: Ind. and Eng. Chem. (In preparation.)

experiments. One atmosphere of hydrogen was present in all these experiments. In the experiments presented in table 27, the autoclave contents after reaction were transferred directly to centrifuge bottles, and the insoluble material was separated by centrifugation. The residue from the centrifugation was then extracted exhaustively with benzene, and the dried insoluble material was analyzed for ash to determine the percentage of liquefaction. In the experiments presented in table 28, the autoclave contents were poured after reaction, into benzene, and the benzene mixture was centrifuged. The insoluble residue was exhaustively extracted and analyzed for ash to determine the percentage liquefaction. A comparison of experiments BK-98 and BK-99 in table 27 shows that under the same conditions o-cyclohexylphenol gives better liquefaction than tetralin. Comparison of BK-88 with G-68 indicates that tin sulfide and ammonium chloride have a deleterious effect upon the rate of liquefaction. Comparison of G-68 with BK-94 shows that the rate of liquefaction is unchanged with a small increase of the cyclohexylphenol-to-coal ratio. The results recorded in table 28 indicate that dilution of the product of the reaction with benzene causes the precipitation of additional benzene-insoluble material, resulting in lower liquefaction yields. Comparison of G-80 in table 28 with G-68 in table 27 indicates the magnitude of this difference. Comparison of G-74 of table 28 with BK-98 of table 27 indicates that the difference in working up the product affects the results with tetralin less than it does with o-cyclohexylphenol.

The results of these experiments can be correlated satisfactorily if one assumes that liquefaction in these experiments results principally from solvation of the coal by the solvent molecules. It is assumed that the coal structure is held together by secondary valence forces, which cause association of the coal polymer units. The association is assumed to be due to hydrogen bridging such as that that occurs in oxygen- and nitrogen-containing compounds. It is known that water, formic acid, acetic acid, and many other oxygen-containing compounds are associated. This association results from hydrogen bridging in which the



oxygen atom functions as an electron donor and the hydrogen as an electron acceptor to form a coordinate valence bond. Hydrogen bridging of this intramolecular type has important influence upon the physical properties of substances. Rodepush has stated in this connection that "it is remarkable that, as weak and relatively unstable a bond as the hydrogen bond is, it can affect physical strength and other important physical properties." It has been shown that natural polymers such as protein and cellulose depend for their structure to a considerable degree upon cross linkages of hydrogen bonds.

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TABLE 27. - Solvation experiments at 400° C.

Run No.	Vehicle	Catalysts	Time, hours	Ratio, vehicle coal	Percent liquefaction, m.a.f. ^{1/}
BK-87	Tetralin	2.50 percent SnS	1	4	58.4
BK-89	Tetralin	0.55 percent NH ₄ Cl	1	4	57.0
BK-98	Tetralin	2.50 percent SnS	1	4	54.7
BK-99	o-cyclohexylphenol	0.55 percent NH ₄ Cl	1	4	79.9
BK-88	o-cyclohexylphenol	2.50 percent SnS	1	4	74.5
BK-94	o-cyclohexylphenol	0.55 percent NH ₄ Cl	2	3	82.6
G-68	o-cyclohexylphenol	None	0.5	4	81.6
BK-100	o-cyclohexylphenol	None	0.5	4	82.7
BK-106	5-hydroxyl-1, 2, 3, 4-tetrahydronaphthalene	None	0.5	4	88.0

^{1/} In these experiments, the bomb contents were poured directly after the reaction into a centrifuge bottle without the addition of any benzene.

TABLE 28. - Solvation experiments at 400° C.

Run No.	Vehicle	Catalysts	Time, hours	Ratio, vehicle coal	Percent liquefaction, m.a.f. ^{1/}
BK-96	U.S.P. cresol	None	0.5	4	22.0
BK-97	U.S.P. cresol	None ^{2/}	0.5	4	13.5
G-74	Tetralin	None	0.5	4	50.2
BK-93	o-cyclohexylphenol	None	2.0	1	30.5
G-80	o-cyclohexylphenol	None	0.5	4	63.7
G-76	50 percent tetralin, 50 percent o-cyclohexylphenol	None	0.5	4	56.0
G-70	p-cyclohexylphenol	None	0.5	4	60.2

^{1/} In these experiments, the bomb contents were washed out with benzene and the benzene suspension was centrifuged.

^{2/} 1,000 p.s.i. nitrogen was used in this experiment.

The striking effectiveness of o-cyclohexylphenol as a coal solvent may well be due to its ability to form hydrogen bridges. If the coal structure is held together by hydrogen bridges, then a substance which itself can form hydrogen bridges would be expected to solvate the coal. Tetralin lacks this property of forming hydrogen bridges, and so is less effective than o-cyclohexylphenol. If compounds capable of forming hydrogen bridges are, per se, good solvents for coal, one might expect the cresol would behave as a good solvent. Experiments BK-96 and BK-97 show, however, that cresol is a very

ineffective solvent for coal. Its inferiority can, however, be satisfactorily explained on the basis that it has no hydrogen available to saturate the fragments of dissociated coal. Tetralin, which lacks a hydrogen-bonding group, is superior to cresol, probably because it can function as a hydrogen donor. That it, indeed, does this has been convincingly demonstrated by the fact that about 8 percent of the tetralin used in experiments G-74 was converted to naphthalene. Further substantiation of the necessity of hydrogen for good liquefaction is found in the experiments listed in table 29. In these experiments, high-pressure hydrogen was used. The results of experiment G-71 are particularly interesting. Though cresol is a very ineffective solvent without hydrogen (cf. BK-96, table 28), it produces excellent liquefaction in the presence of hydrogen. The hydroxyl group aids in the dissociation of the coal, and the high-pressure hydrogen saturates and stabilizes the dissociated fragments. The effect of catalysts in the hydrogenation experiments is in marked contrast to that in the solvation experiments. Experiments BK-92, GB-65, and GB-66 were run under identical conditions, except that increasing quantities of ammonium chloride were used. The increased ammonium chloride resulted in increased liquefaction and increased hydrogen consumption. The effect of tin sulfide is illustrated by comparison of G-67 with GB-66. In the former case, no tin sulfide was used, whereas in the latter the presence of 1 percent tin sulfide increased liquefaction about 12 percent.

TABLE 29. - Hydrogenation experiments at 400° C. and 1,000 p.s.i.
initial hydrogen pressure

Run No.	Vehicle	Percent SnS	Percent NH ₄ Cl	Time, hours	Ratio, vehicle coal	Percent liquefaction, m.a.f. basis
M-34	Tetralin	1.0	0.55	1	1	83.2
G-67	o-cyclohexylphenol	0.0	0.55	1	1	78.9
BK-92	o-cyclohexylphenol	1.0	0.0	1	1	80.0
GB-65	o-cyclohexylphenol	1.0	0.11	1	1	85.0
GB-66	o-cyclohexylphenol	1.0	0.55	1	1	90.7
G-69	p-cyclohexylphenol	1.0	0.55	1	1	88.4
G-75	Coal hydrogenation tar acids ^{1/}	1.0	0.55	1	1	90.6
G-82	Pasting oil ^{2/}	1.0	0.55	1	1	84.7
G-77	Petroleum ether, extract of pasting oil ^{3/}	1.0	0.55	1	1	85.1
G-78	Same as G-77	1.0	0.55	1	1	84.4
G-71	U.S.P. cresol	1.0	0.55	1	1	91.7
BK-105	1, 2, 3, 4,-tetrahydro-5-hydroxynaphthalene	1.0	0.55	1	1	86.0

^{1/} The tar acid fraction from a light oil from the hydrogenation of coal was separated and the fraction b.p. 220-290°, used as vehicle.

^{2/} A typical pasting oil from a coal-hydrogenation plant.

^{3/} A petroleum ether extract of the above.

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From a consideration of the data, it is apparent that in the coal-hydrogenation process the coal structure is held together by associative forces of the hydrogen-bonding type, and that hydrogen-bonding solvents are effective vehicles for coal hydrogenation reactions. In the absence of high-pressure hydrogen, the solvent molecule must be capable of not only dissociating the coal, but it must also serve as a source of hydrogen to saturate the dissociated fragments of the coal structure.

Some of the evidence that suggests that the coal-liquefaction process involves the breaking of hydrogen bonds in the coal is listed below.

1. The magnitude of the difference in liquefaction results when the two different methods of working up the bomb contents are used in the cases of tetralin and o-cyclohexylphenol as vehicles. This results from the greater quantity of material precipitated upon dilution with benzene of the coal solution in o-cyclohexylphenol, as compared to the precipitate obtained when the coal in tetralin solution is diluted with benzene.
2. The precipitate obtained by dilution with benzene of the coal in o-cyclohexylphenol has a higher oxygen content than the corresponding precipitate obtained from tetralin.
3. Catalysts do not improve the liquefaction when solvents are used without high-pressure hydrogen.
4. Increasing the vehicle-to-coal ratio increases the liquefaction in solvation experiments, whereas under certain conditions the increase has no effect in hydrogenation experiments.
5. U. S. P. cresol per se is a poor solvent for coal, but produces excellent liquefaction in the presence of high-pressure hydrogen.
6. The concomitance of liquefaction and oxygen elimination suggests oxygen is involved in the linking of the coal polymer.
7. Catechol has been shown to produce low molecular weight fragments from humic acid by the simple process of solution.
8. Solutions of coal in o-cyclohexylphenol are very stable and can be kept without apparent change.

Identification of Products of Coal Hydrogenation and Study of Typical Reactions Involved in the Process

Organization of the personnel and erection and standardization of equipment for the precision distillation laboratory were completed. The equipment includes a 3-inch by 20-foot, stainless-steel, Foster-Wheeler distillation column with Stedman packing and a 25-gallon boiler. This is to be used for the initial distillation of synthetic liquid-fuel oils. The fractions obtained by the use of this still will be subjected to "type-separations"