

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Pilot-Plant Operations

The data from runs in the liquid-phase pilot plant to determine the rate of liquefaction of Rock Springs, Wyo., coal suggest that in a commercial hydrogenation of Rock Springs coal, the liquefaction results obtained by the use of ferrous sulfate as a catalyst may closely approximate those obtained with SnS. Pilot-plant investigations (see Fig. 44) of the relative activity of impregnated nickel (ous) chloride for the hydrogenation of coal indicate that 0.5 percent nickel impregnated on the coal produces a liquefaction and a hydrogenation of asphalt comparable to those produced by 0.1 percent tin sulfide.

The vapor-phase hydrogenation unit, which has a normal operating pressure of 10,800 pounds per square inch, was operated to determine the activity of a German hydrogenation catalyst for the production of Diesel oil from a blend of light oils obtained by hydrogenating various coals in the Pittsburgh pilot-plant operations. This particular catalyst was shown to produce a good aromatic gasoline in a single-pass operation, but several passes would be required to produce a usable Diesel oil which requires further saturation of the aromatic constituents. The use of heavy-oil feeds at 500° C. led to rapid deterioration of this catalyst.

Additional experiments have been made on the fluidized-coal-hydrogenation process, in which a stream of hydrogen, preheated and under a pressure of 500 to 1,000 pounds per square inch, is used to fluidize a bed of powdered coal containing 0.1 to 1.0 percent of catalyst. About 25 percent of the coal substance is thus converted to hexane-soluble oil in several minutes at reaction temperature (500° C. or 932° F.). At the same time, about 20 percent of the coal substance is converted to hydrocarbon gases; and the residue - about 55 percent of the original coal - is converted to a coke containing virtually no sulfur, as 90 to 95 percent of the sulfur in the original coal is hydrogenated to hydrogen sulfide in this stage. The equipment and techniques employed in this stage of the process are quite familiar to the petroleum industry; and, because of the relatively low pressures involved, no expensive and cumbersome forgings, fittings, valves, etc., are required. In addition, the efficiency of the utilization of hydrogen is increased, because most of the available hydrogen contained in the coal feed is used in the production of oil.

The production of coke in the hydrogenation stage is not disadvantageous, because, while it is still in a dense, fluidized condition under a pressure of 500 pounds per square inch, it can be converted by steam and oxygen to a sulfur-free synthesis gas under suitable pressure for use in the Fischer-Tropsch process. The sulfur remaining after the hydrogenation stage is largely in the form of pyrites, which probably would be eliminated as sulfate in the ash of the residue from the gasification operation. Elimination of a sulfur-purification step and compression of synthesis gas represent important economical improvements in producing a suitable synthesis gas for the Fischer-Tropsch process.

Laboratory-Scale Experiments

The solution of coal by high-boiling compounds which contain both a hydroaromatic ring and an aromatic hydroxyl group (for example, orthocyclohexylphenol) has been described previously as chemical in nature. Another type of solvent for coal, as exemplified by phenanthrene, 9-methylphenanthrene, phenanthridine, carbazole,

5, 6-benzoquinoline, 5, 6-benzoquinoline, α -naphthol, and β -naphthol, has been studied. These solvents, refluxing over powdered Bruceton coal, extract as a dispersion about 85 percent of the coal, corresponding to the total anthraxylon plus the translucent-atritite coal fractions; they have, with the exception of α -naphthol, little dispersing action on Wyoming coal. α -Naphthol is unique in that it is a powerful solvent for both coals.

Little is known of the extraction mechanism of phenanthrene-type solvents, except that there appears to be both a temperature specificity (only α - and β -naphthols show appreciable extracting action below 300° C.) and a structure specificity (anthracene, which is an isomer of phenanthrene, is relatively a much less efficient solvent, and its presence in a mixture with phenanthrene or carbazole strongly depressed the extracting power of the latter materials). Increasing the oxygen content of the coal by extensive roasting in air results in a much lower degree of dispersion. Little difference was found between the molecular weights of coal extracts obtained by various combinations of phenanthrene, benzene, and cyclohexane, but comparison of the C:H ratio showed the fractions to have different degrees of aromaticity.

Knowledge of the extractibility of coal by phenanthrene and other solvents is important to a study of the function of recycle oil vehicles used in the Bergius-I.C. process. Thus, extraction could be used as a preliminary step to prepare a low-ash substratum which would decrease the difficulty of processing the "heavy-oil let-down" of the conventional process. A dispersion of Bruceton coal in phenanthrene has been shown to be as susceptible to hydrogenation as the original coal, and it was demonstrated that phenanthrene is not affected by the conditions and catalysts used for coal hydrogenation, thus permitting recovery of phenanthrene. The substitution of phenanthrene by solvents obtained directly from coal is being investigated, and a coal-hydrogenation oil-product fraction boiling above 320° C. has been found to be as effective a solvent as phenanthrene.

Basic Laboratory Research

Reaction Mechanism

Experiments to determine the reaction mechanism for the hydrogenation of coal were continued. The mechanism outlined in the 1948 Annual Report has been supported and elaborated to present the following picture.

The primary reaction in coal liquefaction by hydrogenation is the production of reactive fragments of the coal structure which are then stabilized either by polymerization to benzene-insoluble material or by the addition of hydrogen, a reaction assumed to be catalyzed by tin. The resultant benzene-soluble material is largely asphaltic. This asphalt is converted, by a noncatalytic reaction, to gaseous hydrocarbons and to reactive fragments by a reaction catalyzed by halogen-acid-producing substances (HCl, HI, NH₄Cl, etc.). These reactive fragments may (1) recombine to produce asphalt, (2) polymerize still further to produce benzene-insoluble material, or (3) be stabilized by the addition of hydrogen (catalyzed by tin) to produce an oil. The following diagram indicates this scheme of reactions:

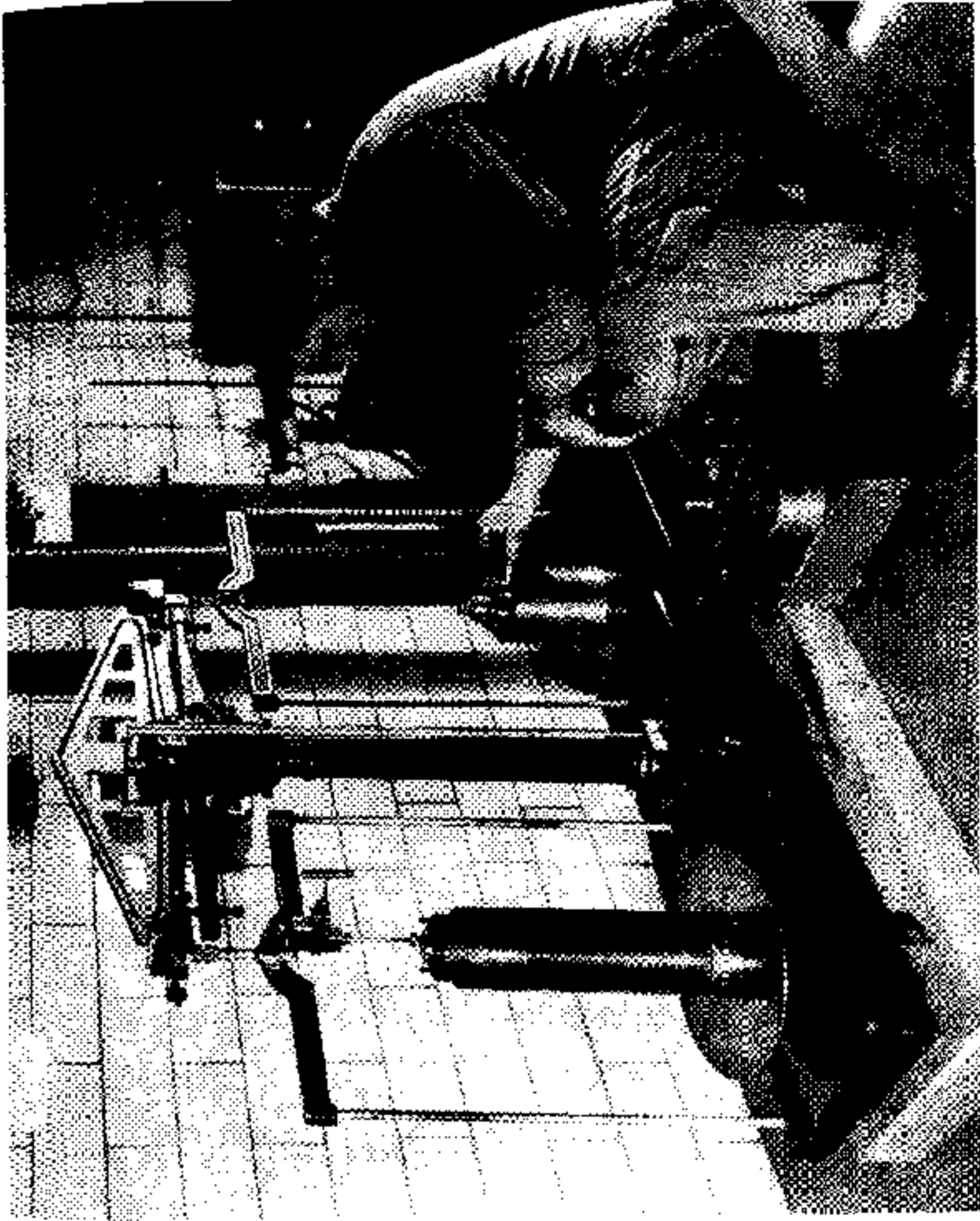
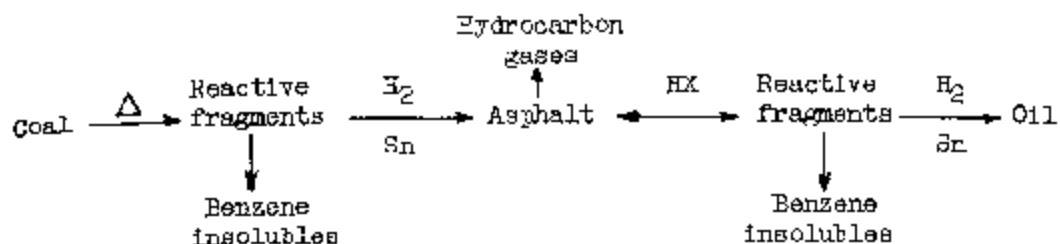


Figure 45. - Batch autoclave experiments; weighing autoclave and contents.



The primary fragmentation of coal is associated with the splitting of carbon-oxygen bonds and proceeds with very little gas production, although a large fraction of the oxygen in the coal is eliminated here, chiefly as water. The conversion of asphaltic material to oil is associated with the rupture of carbon-to-carbon bonds; and its rate increases with temperature until, at about 450° C., the rate of this reaction approximately equals the conversion of coal to asphalt.

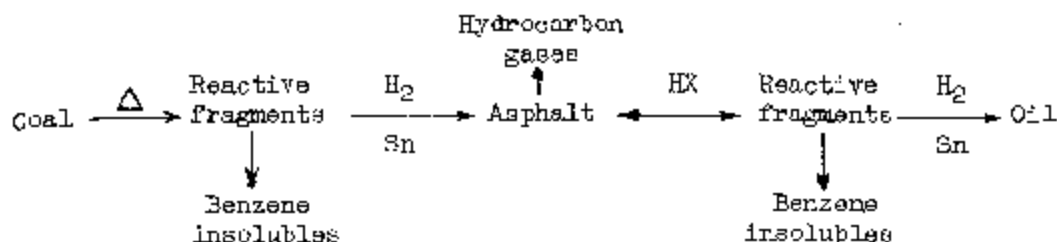
Use of this proposed mechanism makes it possible to interpret many experimental results that have been previously confusing or unexplained. It can be seen that: (1) tin used in the absence of splitting catalyst should behave like no catalyst at all because the splitting of asphalt to form fragments, which is assumed to precede hydrogenation stabilization, proceeds very slowly in the absence of halogen-producing substances; (2) hydrochloric acid used alone in an inert atmosphere would cause a large production of benzene-insoluble material, because stabilization of the fragments can then occur only by a disproportionation process; (3) polymerization catalysts, such as phosphoric acid, should produce especially large quantities of benzene insoluble; and (4) any substance that is both a splitting and a hydrogenation catalyst (perhaps hydriodic acid) should result in high conversion of asphalt and low production of benzene-insolubles. As the bulk of hydrocarbon-gas production is shown as occurring by secondary reactions, only a small amount accompanying primary liquefaction, then, to minimize hydrogen consumption and hydrocarbon-gas production, coal should be hydrogenated in two stages. The first stage should involve only primary liquefaction under conditions of minimum gas formation, and the second would involve further processing of the primary products under the same conditions for this step.

The above mechanism for the conversion of coal to oil still does not explain the unique excellence of tin as a coal-hydrogenation catalyst under a great variety of conditions of temperature and pressure and irrespective of the chemical form in which tin is used. Experiments have shown, however, that stannous sulfide may be, dynamically speaking, the "least common denominator" for all forms of tin in coal-hydrogenating conditions. Calculation of the free-energy changes involved indicates that stannic oxide can be completely converted to stannous sulfide at 700° K., provided the hydrogen sulfide pressure is kept above 0.06 atmosphere. This condition is almost certainly met in most coal hydrogenations.

The hydrogenation of Rock Springs coal at 1,000 p.s.i. hydrogen pressure and temperatures of 400° to 538° C. in a unit in which the time of contact of the coal with hydrogen at reaction conditions could be varied at will indicated that, in this case, liquefaction increased rapidly during the first 3.5 minutes at operating temperature. This period was followed by a slow increase in liquefaction with continuing time. In these experiments, some liquefaction is indicated as taking place with little or no elimination of oxygen.

Tests for Coal Hydrogenation

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Catalysts for Coal Hydrogenation

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hydrogenation of coal, but it is ever less economically desirable. Zinc bromide and lead bromide exhibited marked catalytic activity, resulting in liquefactions of 75 and 78 percent, respectively. It seems probable that the effect is due to the hydrogen bromide liberated under reaction conditions which may act as a hydrogen donor as hydrogen iodide does. Low-grade tin ores with high sulfur contents proved to be as effective for the hydrogenation of Bruceton coal as did pure tin when used at the same tin-concentration level. This may be of economic importance, as large quantities of these low-grade ores are available in Bolivia. Such low-grade ores are relatively undesirable commercially, and their use in the coal-hydrogenation process would effect a savings by eliminating catalyst refining costs. This saving will be offset, however, by an additional cost of removal from the product mixture of the inert solids added by using the low-grade ores. Any practical value of these ores must then arise from a favorable balance of these two factors.

Effect of Physical Distribution. - Recent tests have indicated that the physical state in which the catalyst is introduced into the reaction mixture may be important to its resulting activity. Catalysts usually have been added to a coal charge before hydrogenation in the form of a powder, because it had been found previously that, in the case of stannous chloride and ammonium molybdate, the same results were obtained whether the catalyst was impregnated on the coal or added as a powder. Ferrous sulfate, however, while virtually useless as a catalyst in the powdered state, produced liquefactions when it was impregnated on the coal that closely approached those obtained with tin catalysts, although the asphalt produced by the ferrous sulfate was somewhat higher. Similarly, impregnated nickel (ous) sulfate was found to be a good catalyst, while nickel (ous) chloride seems to be as effective as stannous chloride.

Analysis of Coal-Hydrogenation Products

The most valuable coproduct from the hydrogenation of coal is the alkali-soluble portion, commonly designated as the tar-acid fraction. This material is a complex mixture of acidic aromatic hydroxy compounds or phenols. Information concerning tar acids produced in the liquid-phase hydrogenation of coal is of considerable engineering and chemical interest, in that the primary reaction in the liquefaction of coal is probably the hydrogenolysis of carbon-to-oxygen bonds, and a study of the structure of the phenolic products should shed light on the constitution of coal. Knowledge of the constitution of these phenols would also serve to indicate those industrial markets in which they might be utilized as raw materials. The possibility of increasing the tar-acid yield from the hydrogenation of coal can be estimated from a study of the degradation of the primary asphaltic products to learn whether the molecular weight could be reduced without eliminating oxygen as water (see fig. 46).

The tar-acid fraction of the n-hexane-soluble portion (oil) of the liquid product obtained by mild hydrogenation of Pittsburgh-bed (Bruceton) coal (to produce fuel oil as the major product) was isolated by extraction of a benzene solution of the oil with alcoholic sodium hydroxide. The yield of tar acids was 9.4 percent by weight of the n-hexane-soluble oil, 5.2 percent of the total oil produced in the hydrogenation, or 4.0 percent based on moisture- and ash-free coal. The tar acids were subjected to distillation and 136 fractions collected. On the basis of refractive indices and boiling points, these were combined into 70 fractions. Chemical and physical investigation (see fig. 47) of selected fractions resulted in the isolation and identification, either as pure compounds or derivatives, of 16 individual phenols.

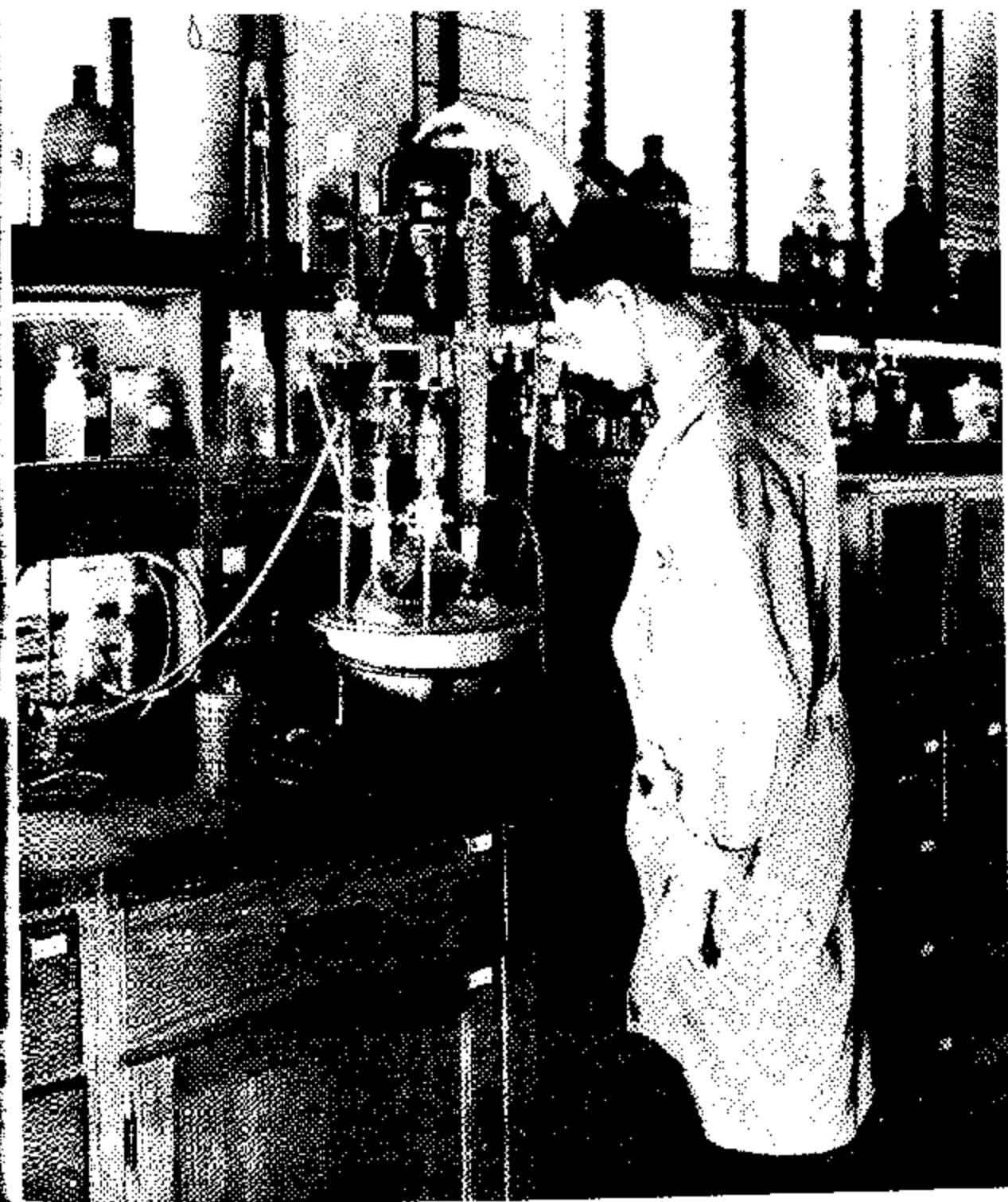


Figure 46. - Synthesizing organic compounds.

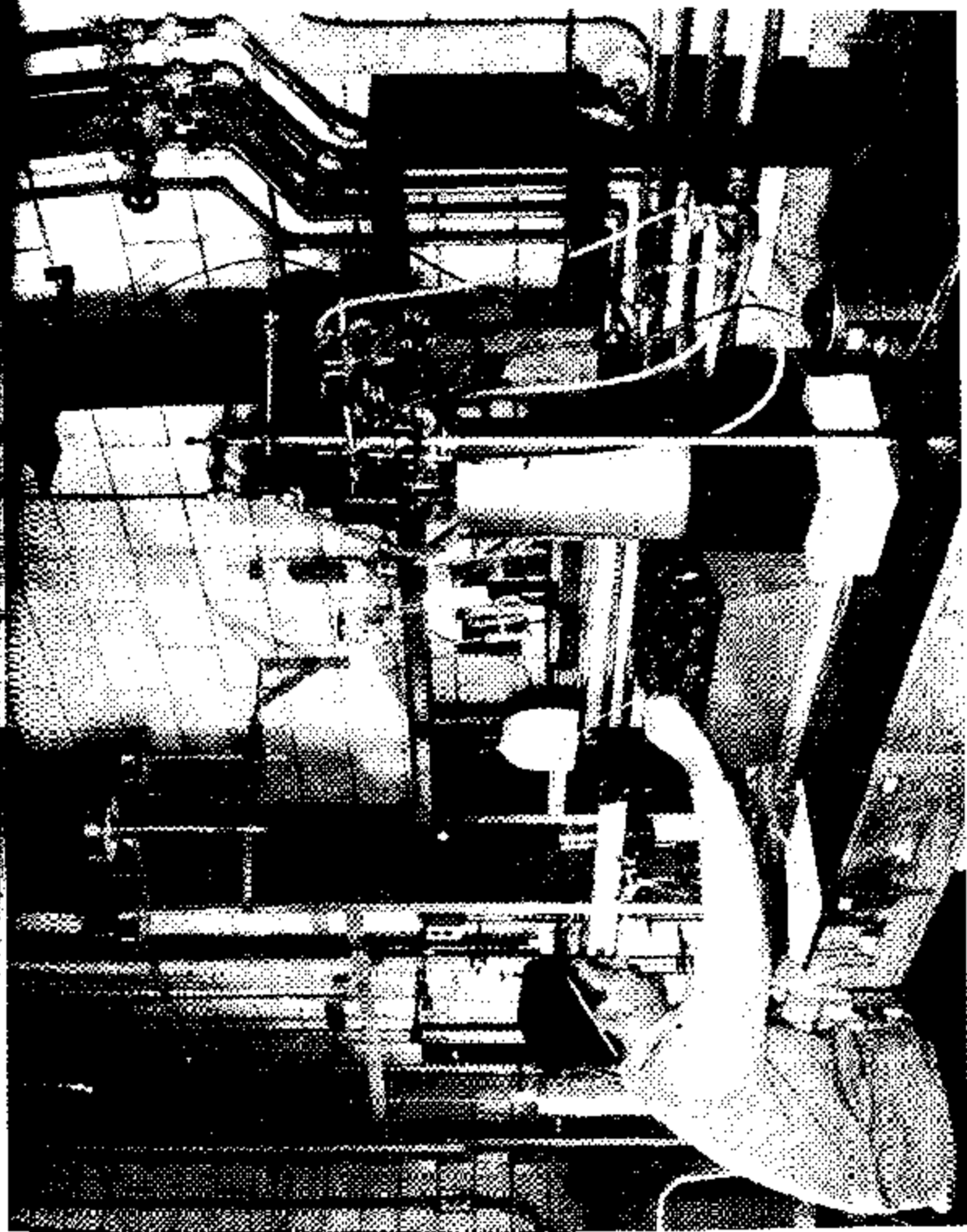


Figure 47. - Apparatus for precise determination of freezing point of organic compounds.

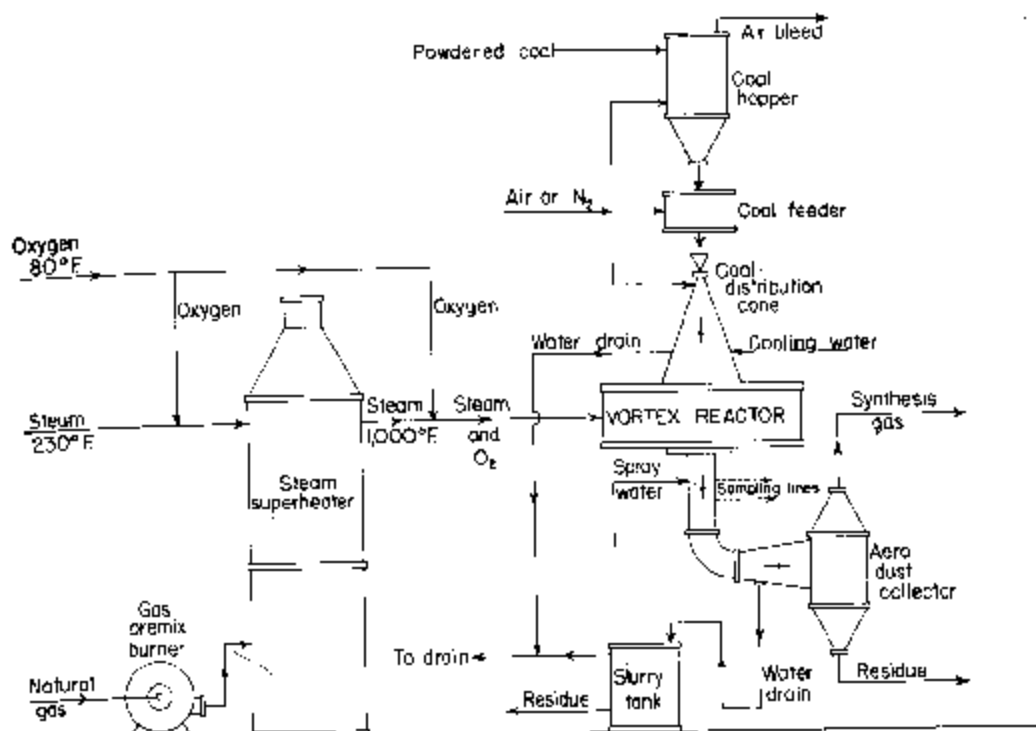


Figure 48. - Flow sheet of vortex gasifier.

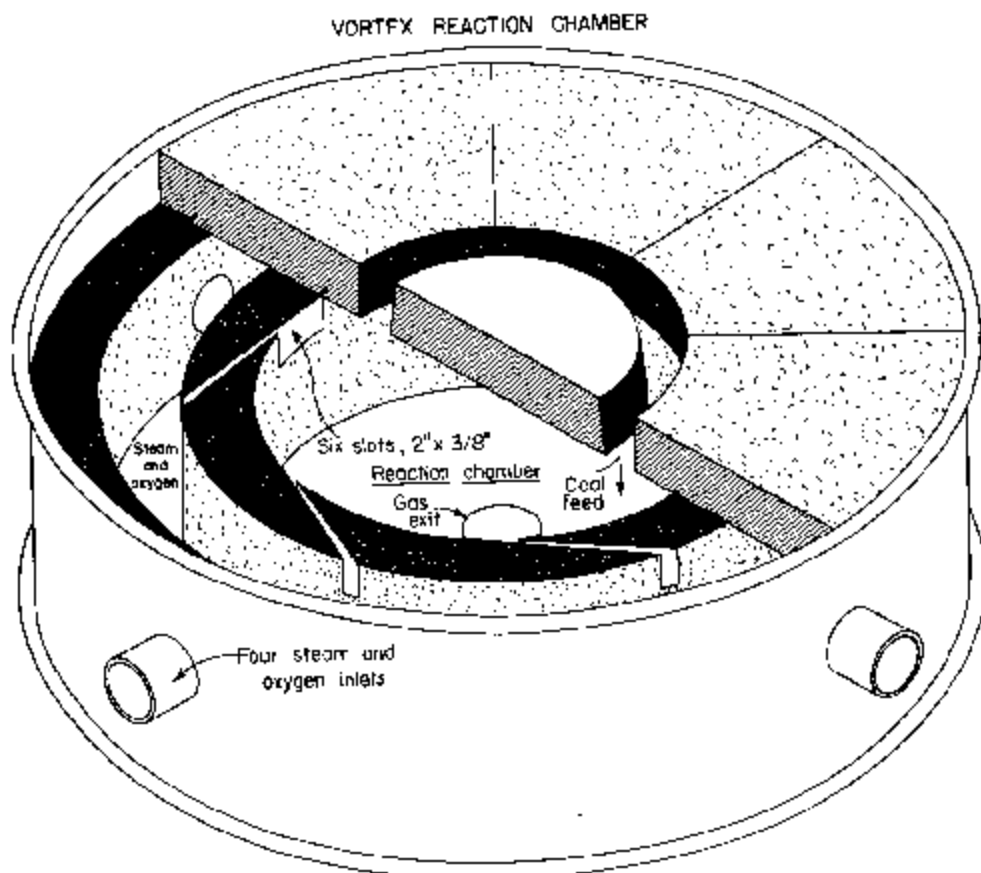


Figure 49. - Vortex reaction chamber.

In the lower-boiling fractions, phenol and o-cresol were isolated as pure compounds and m- and p-cresol as m- and p-methyl-phenoxyacetic acids. Four isomeric xylenols were found. 3,5-Xylenol and 2,5-xylenol were isolated as pure compounds. 2,4-Xylenol was identified through its N-(2-fluorenyl)-carbamate; 3,4-xylenol was not detected by chemical methods but was shown by infrared spectroscopy to be present in small quantities. Of the ethylphenols, only one, m-ethylphenol, was identified by chemical means; o- and p-ethylphenols were shown to be present by infrared spectroscopy.

Analysis of the higher-boiling fractions is considerably more difficult because of the greater complexity of the tar-acid mixtures and because no infrared reference spectra are available. However, application of the countercurrent distribution technique has resulted in the isolation and identification of 4- and 5-indanol and p-phenylphenol. 3-Methyl-5-ethylphenol and o-phenylphenol were also isolated and identified. The countercurrent distribution technique, when applied to a synthetic mixture of 3,5-xylenol, 2,5-xylenol, and 2,4-xylenol or a mixture of o-, m-, and p-ethylphenols, shows that 3,5-xylenol and o-ethylphenol can be readily separated from their respective mixtures. The shapes of the distribution curves show that each compound distributes itself essentially independently of the others, in accordance with the distribution law. This technique permits measurement of partition coefficients of the components of a mixture without isolation of the individual compounds. These coefficients should be considered in the same category as the boiling point, melting point, and refractive index of a compound.

The presence of relatively large amounts of the indanols suggests that their unsaturated analogues - the hydroxy indenenes - may constitute a significant fraction of the "reactive fragments" formed in the primary hydrogenation of coal.

Gasification of Coal

Vortex Combustion Studies for Powdered-Coal Gasification

An experimental unit of the vortex type (see figs. 48 and 49) was operated in a series of tests in which coal was gasified with oxygen and steam. Material and heat balances were calculated from the resulting data and indicate that the following correlations may be drawn:

1. The percentage of carbon gasified is almost directly proportional to the pounds of oxygen supplied per pound of coal in the feed; it is independent of the throughput, which appears to be a result of the hydrodynamics of the unit. At higher throughputs, despite the shorter residence time of the gas, higher tangential velocities occur in the vortex, thus keeping smaller coal particles in the vortex longer than in the case of lower throughputs.
2. The water-gas equilibrium is reached in the exit gases.
3. The reduction of carbon dioxide by carbon proceeds so slowly that the ratio $\frac{PCO}{PCO_2}$ is about 1/100,000 of the theoretical value at exit gas temperature.
4. The volume of carbon monoxide and hydrogen produced per pound of coal gasified is a function of the heat lost from the unit. On extrapolation of the data to zero heat loss, a production of 30 to 40 cubic feet of carbon monoxide and hydrogen per pound of coal gasified was predicted. However, the actual heat losses for this unit varied from 20 to 40 percent, and this extrapolated value must be used cautiously. Examination of the order in which the reactions occur in the vortex unit