Vortex Combustion Studies for Powdered-Coal Gasification

Considerable progress was made in the operation of an experimental unit for gasifying coal with oxygen and steam. The reactor is of the vortex type, and the hydrodynamics are such that as a coal particle reacts and becomes smaller, it moves toward the center. This affords a means for operating at slagging temperatures in a portion of the unit without deposition of slag on the walls.

Material and heat balances were calculated by using the data obtained from tests made in this unit. Correlation of the results indicates that, for the conditions tested, the following correlations may be drawn: 1. The percent carbon gasified is almost directly proportional to the pounds of oxygen supplies 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 calculated equilibrium constant is about 1/100,000 of the theoretical value at exit-gas temperatures. 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. As, however, the actual heat losses for this unit ranged from 20 to 40 percent, this extrapolated value must be used cautiously.

Experience gained in the initial stages of operation of the vortex has shown that it is desirable to introduce the coal horizontally, so that it is traveling with the rotating gas stream. In the initial design, the rotating gas streams must change the direction of motion of a coal particle from vertically downward to horizontal. In providing conditions to accomplish this, undesirable limitations are placed upon both design and operating variables. To overcome this difficulty, a new coal distributor has been constructed, which consists of a spinning water-cooled plate inserted into the center of the vortex. The metered coal falls onto this plate and is thrown from it uniformly around the vortex in an umbrellalike pattern. Preliminary tests are under way utilizing this new method of coal feed.

Production of Synthesis Gas

Gas Treating and Testing

The Gas Treating and Testing Laboratory continued to develop new analytical methods as well as to improve old ones. These include the turbidimetric determination of small amounts of sulfate by means of the spectrophotometer; the colorimetric determination of thiophene in gas, whereby as little as 0.0001 grain of sulfur as thiophene can be detected; and the improved platinum spiral method for determining total organic sulfur. Investigation of a number of catalysts for converting organic sulfur compounds to hydrogen sulfide without first removing the hydrogen sulfide present in the raw synthesis gas disclosed one that reduced the organic sulfur content, excluding thiophene sulfur, of a gas containing as much as 700 grains of hydrogen sulfide per 100 cubic feet to an equilibrium value of two grains per 100 cubic feet, regardless of the organic sulfur concentration in the unpurified gas.

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Another type of catalyst being investigated is one that removes hydrogen sulfide and organic sulfur simultaneously by means of catalyst absorption. Whenever the catalyst becomes fouled with sulfur, it is revivified by means of air and steam. Such a catalytic process would eliminate the usual hydrogen sulfide removal system. One catalyst studied removed 99.5 to 100 percent of the hydrogen sulfide and 99.8 to 100 percent of the organic sulfur compounds in the gas.

Oxygen Production by Multistage Fractional Permeation

An important factor in the cost of coal gasification is the cost of oxygen used in the process. At present, oxygen is produced commercially almost exclusively by the Linde process. The fact that many organic membranes are appreciably more permeable to oxygen than they are to nitrogen is the basis for experimental work on a possible process for oxygen production.

Major improvements in the economy of a permeation process could be made by (1) increasing the magnitude of the film permeabilities or (2) increasing the selectivity of the films toward oxygen. Improvements in (1) would permit a decrease in the area of the film required to achieve a given throughput; this might be achieved by finding more permeable films or by making thinner films. Improvements in (2) would not only decrease the size of the plant required but would also decrease the power requirements necessary for a given oxygen production. Such improvements might be achieved by finding films more selective than rubber latex or by incorporating into films specific oxygen carriers (possibly cobalt chelate complexes).

An apparatus was assembled to investigate the selective permeability of organic films, and eight different commercial materials were studied (table 16). Natural rubber is outstanding for its high permeability and its selectivity; however, it is subject to oxidation. Ethyl cellulose and polyethylene are promising. Additional work with ethyl cellulose films cast in the Bruceton Laboratories and with pure gases showed (table 17) that these films had an O_2/N_2 permeability ratio of about 3. Argon is enriched in almost the same proportion as is oxygen, whereas carbon dioxide becomes enriched to a much greater extent. For any commercial application it will probably prove desirable to remove carbon dioxide prior to or just after the first permeation stage. The removal of argon will be impractical, and it will be enriched along with the oxygen.

LIQUEFACTION OF COAL BY DIRECT HYDROGENATION
RESEARCH AND DEVELOPMENT

Operation of two coal-hydrogenation pilot plants, one for the first or liquid-phase stage and one for the second or vapor-phase stage, was begun. These plants are concerned with tests on raw materials, catalysts, and procedures to be used in the larger demonstration plant at Louisiana, Mo. New approaches to the problem of direct hydrogenation of coal are being made and are based on the rapid conversion of coal to distillable oil, gas, and coke at moderate pressures, short reaction periods, and relatively high temperatures. The conversion of as much as 50 percent of the coal to coke is not disadvantageous, because about as much coal is needed for fuel as is liquefied in coal-hydrogenation processes. The results of laboratory-scale tests have been encouraging, but the engineering problems are very difficult, and much pilot-plant development work must be done. The chemistry of the primary liquefaction of coal is being studied in extensive laboratory experiments in small high-pressure vessels; some very critical information has thus been obtained.

TABLE 16. - Film permeabilities to oxygen and nitrogen at 30° C.

Film	Film thickness, mils	Permeability coefficient[1] Q, cm.^{2} min.$^{-1}$ atm.$^{-1}$ x 10^6		$\dfrac{Q_{O_2}}{Q_{N_2}}$
		Q_{O_2}	Q_{N_2}	
Ethyl cellulose[2]	0.7	3.25	1.36	2.4
Polyvinyl chloride-acetate	2.0	1.75	1.17	1.5
Vinyl resin - Buna-N rubber	2.0	.70	.58	1.2
Natural rubber latex[3]	7.3	18.1	8.6	2.1
Polyethylene (Plax)	1.5	2.20	.88	2.5
Polyethylene (Bakelite)	.9	2.10	.79	2.7
Polystyrene	1.0	1.31	.44	3.0
Resproid 1404	4.3	3.01	1.08	2.8

1/ Permeability coefficient = (film permeability) (film thickness).
2/ Average of three determinations.
3/ Average of two determinations.

TABLE 17. - Permeabilities of gases through film EC-12

Gas	Permeability (P),[1] mols x 10^6 cm.$^{-2}$min.$^{-1}$ atm.$^{-1}$	P_{gas}/P_{N_2}	
		Pure gas studies	Mass spectrometer
N_2 ..	0.075	(1.0)	(1.0)
O_2 ..	.231	3.1	3.2
CO_2 .	1.07	14.3	2/32
A ...	.170	2.3	3.1

1/ Rate of permeation of gas per unit time per unit film area per unit pressure differential.
2/ A blank determination on normal air gave a high CO_2 value.

A study of the composition of synthetic liquid fuels has shown that industrially valuable byproducts of the direct hydrogenation of coal are phenolic compounds used in plastics manufacture. Quantitative analysis of mixtures of these phenols and procedures for separating the components by means of infrared spectroscopic analysis and a counter-current distribution between two immiscible solvents have been developed. The products from the hydrogenation of carbon monoxide consist chiefly of straight-chain, normal hydrocarbons with a minor amount of branded hydrocarbons, the exact isomeric composition of which was determined by infrared and mass spectrometry. This information is of critical scientific importance in ascertaining the mechanism of the synthesis; it is also of industrial significance, because the octane number of the gasoline fraction is markedly dependent on the isomeric composition.

The program for research on coal hydrogenation is indicated in the following outline:

(A) Function of solvents and catalysts in early stages of coal hydrogenation.

    (1) Action of solvents.

(B) Bench-scale process development.

    (1) Coal hydrogenation in the absence of solvents.

    (2) Substitution of water gas for hydrogen.

(C) Pilot-plant operations.

    (1) Liquid-phase hydrogenation.

    (2) Vapor-phase hydrogenation.

(D) Separation and identification of products of coal hydrogenation.

Function of Solvents and Catalysts in Early Stages of Coal Hydrogenation

Action of Solvents

The solution of coal by high-boiling compounds that contain both a hydroaromatic ring and an aromatic hydroxyl group (for example, orthocyclohexylphenol) has been described[73] as chemical in nature.

Another type of solvent for coal, as exemplified by phenanthrene, 9-methyl-phenanthrene, phenanthridine, carbazole, 5,6-benzoquinoline, 5,6-benzoquinaldine, 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 attritus 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 a relatively much less efficient solvent, and its presence in a mixture with phenanthrene or carbazole strongly depresses the extracting power of the latter materials). Increasing the oxygen content of the coal by extensive heating in air results in a much lower degree of dispersion.

Knowledge of the extractability of coal by phenanthrene and other solvents is important to a study of the function of recycle oil vehicles used in the Bergius - I. G. process, in that a two-stage coal-hydrogenation process could be set up using extraction as a preliminary step to prepare a low-ash substrate that would decrease the difficulty of processing the "heavy-oil let-down" of the conventional process[74]

73/ Orchin, M., and Storch, H. H., Solvation and Hydrogenation of Coal: Ind. Eng. Chem., vol. 40, 1948, pp. 1385-1389.
74/ Savich, T. R., Pelipetz, M. G., Budy, W. A., Clark, E. L., and Storch, H. H., Stripping of Coal Hydrogenation Heavy-Oil Slurry: Ind. Eng. Chem., vol. 41, 1949, pp. 968-971.
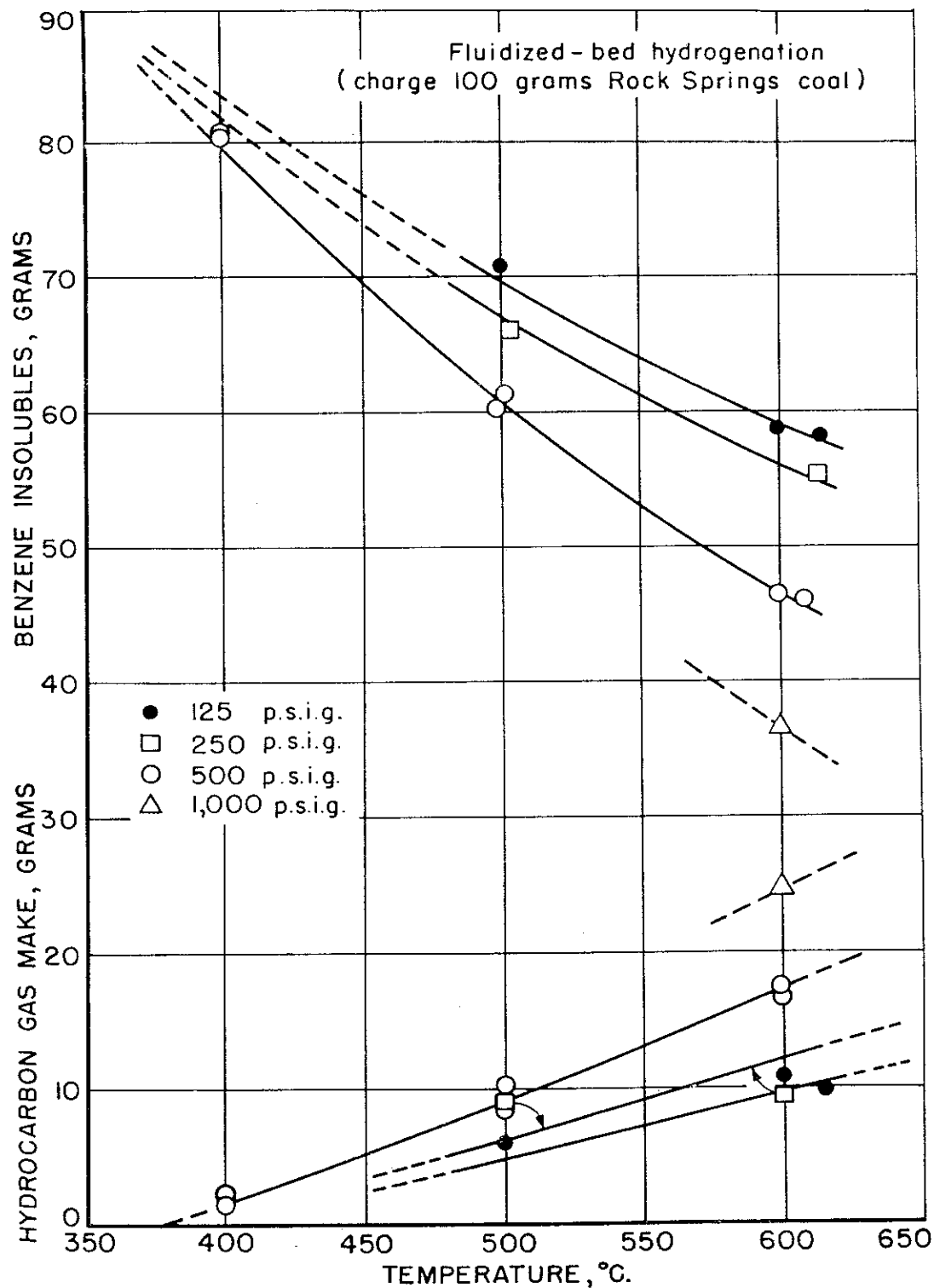
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Figure 31. – Effect of pressure and temperature on benzene-insoluble
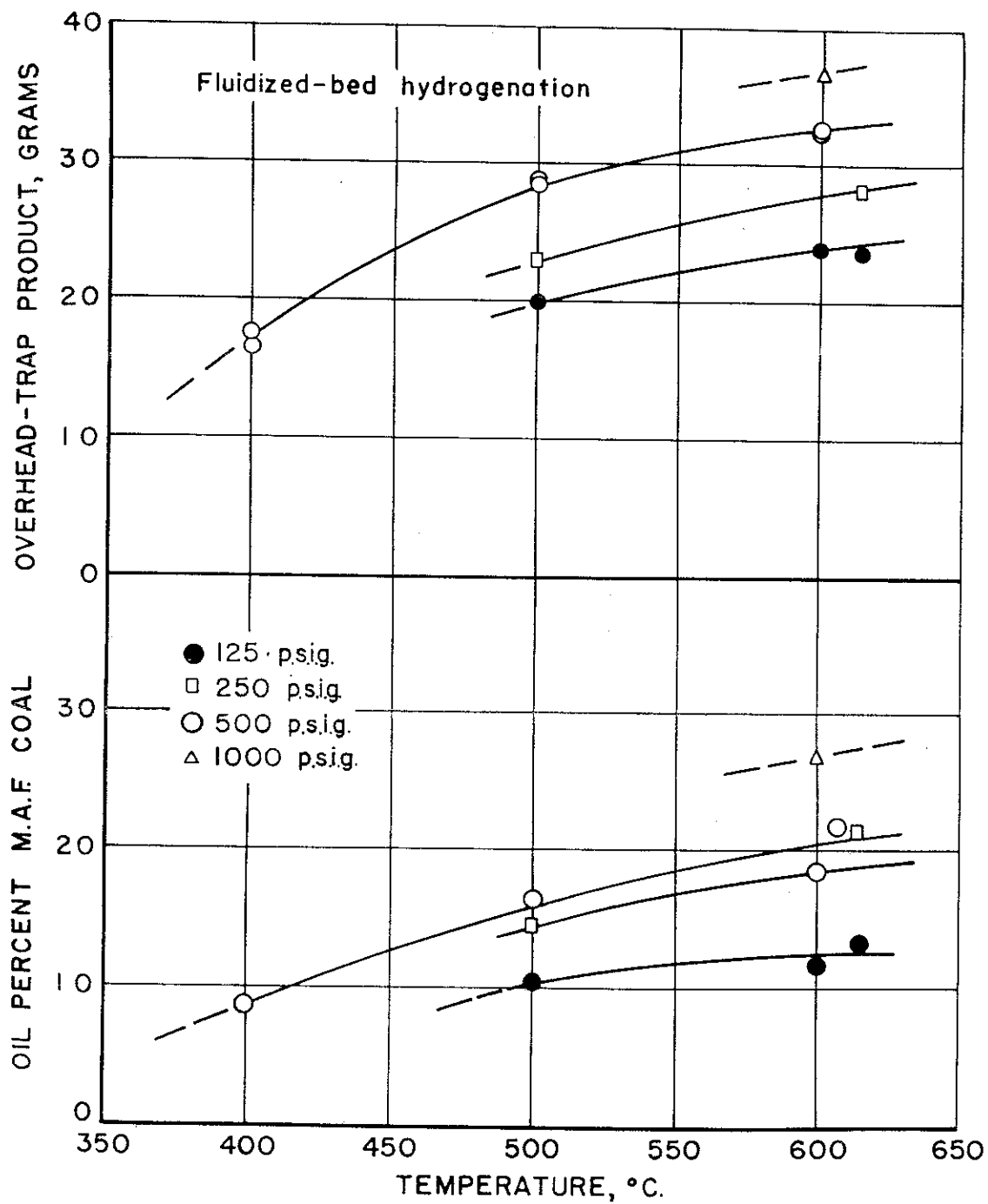residue and hydrocarbon gas production.

The figure contains:
- Title: Fluidized-bed hydrogenation (charge 100 grams Rock Springs coal)
- Y-axis (upper): BENZENE INSOLUBLES, GRAMS
- Y-axis (lower): HYDROCARBON GAS MAKE, GRAMS
- X-axis: TEMPERATURE, °C.
- Legend:
  - ● 125 p.s.i.g.
  - □ 250 p.s.i.g.
  - ○ 500 p.s.i.g.
  - △ 1,000 p.s.i.g.

Figure 32. - Effect of pressure and temperature on overhead-trap product and oil production.
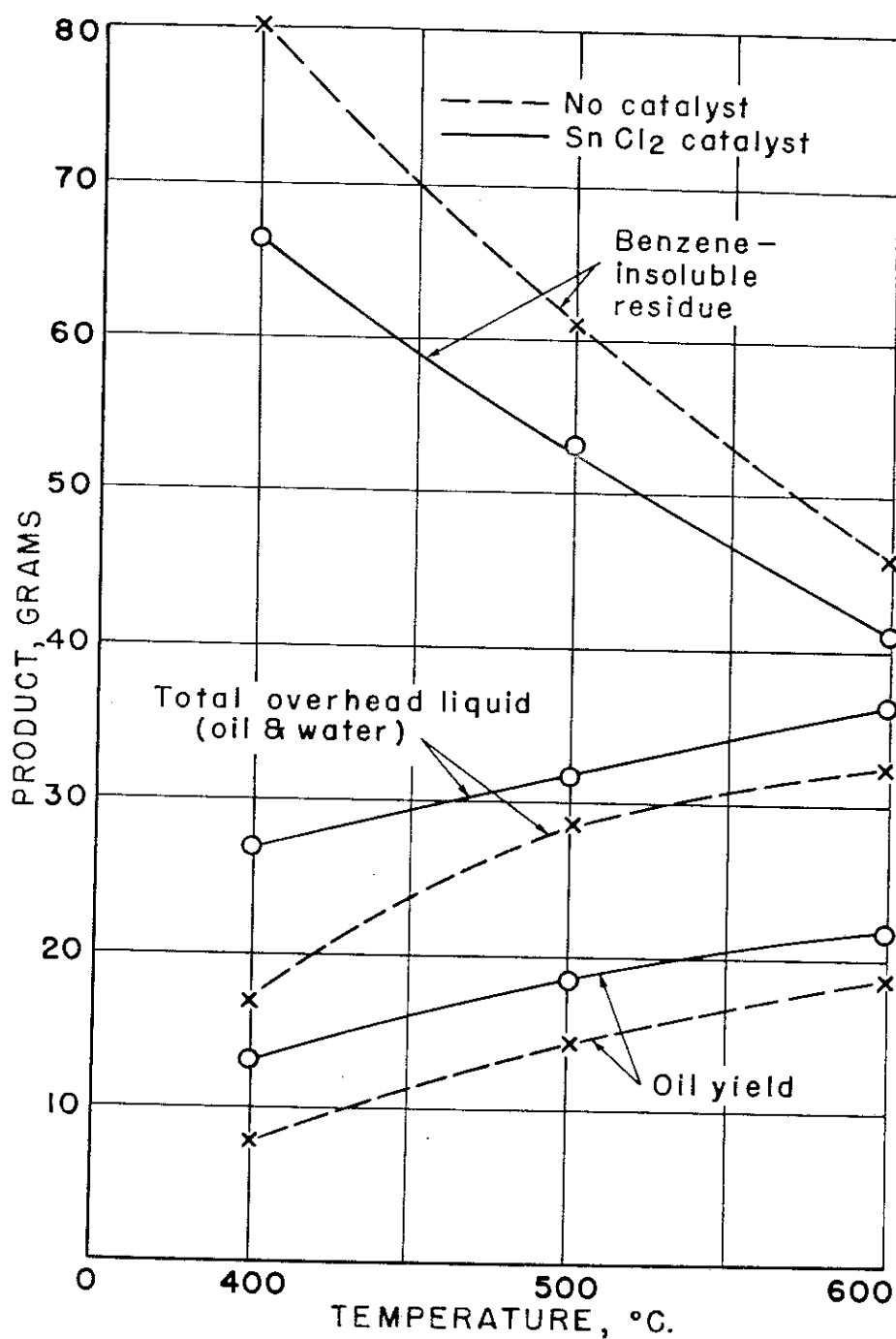
Figure 33. - Products of fluidized-bed hydrogenation in presence or absence of catalyst.

or permit the hydrogenation to be carried out over a fixed-bed catalyst. 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 phenanthrene recovery. 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.

Bench-Scale Process Development

Coal Hydrogenation in the Absence of Solvents

The hydrogenation of bituminous coal in the absence of vehicle is accomplished by suspending the coal particles, which are impregnated with catalyst in a stream of hydrogen in the reactor (fluidized bed). Such a process is of interest because of the considerable economies that may be achieved (1) by operating at a pressure of 50 to 70 atmospheres (in contrast to the 300 to 700 atmospheres employed in the conventional process) and (2) by utilizing the hydrogen that is available from the conversion of excess coal to coke in the reactor for the production of oil and gas.

Earlier studies[75] of the effects of contact time and temperature at initial hydrogen pressures of 1,000 to 10,000 pounds per square inch have been extended to include lower initial pressures (125 to 1,000 pounds per square inch) and higher temperatures (400°-600° C.) and indicate the lower limits for appreciable conversion to be 400 to 500 pounds per square inch and 500° C. Figures 31 and 32 show that operations can be so adjusted to convert from 15 to 27 percent of the moisture- and ash-free coal to oil and 12 to 27 percent to hydrocarbon gases. The omission of the usual catalyst (1 percent tin as $SnCl_2$ impregnated on the coal) results in decreased oil yields and increased benzene-insolubles as shown in figure 33. No advantages are to be gained by operation at high gas-flow rates. At decreased reaction times, however, although the production of oil is somewhat depressed, an improved utilization of hydrogen is obtained by virtue of the decrease in gasification that occurs simultaneously (see table 18).

TABLE 18. - Effect of reduction in reaction time on the
hydrogenation of coal in a fluidized bed

(100 g. Rock Springs coal, 100- to 200-mesh, 500 p.s.i. initial
H_2 pressure, reaction temp. = 600° C., rate of gas flow = 0.5 SCFM)

Test No.	Time at temp., hours	H_2 absorbed		Oil, percent m.a.f. coal	Asphalt, percent oil	Percent H_2 in oil	Percent O_2 in oil
		Percent m.a.f. coal	Percent oil				
70 ..	1	3.5	14.3	24.1	74	8.0	6.4
62 ..	.5	2.3	9.5	24.8	72	8.0	6.7
66 ..	a/0	1.6	7.8	22.1	68	8.0	6.5

a/ Heated to reaction temperature and cooling started immediately.

[75] Pelipetz, M. G., Kuhn, E. M., Friedman, S., and Storch, H. H., Effect of Catalysts on the Hydrogenolysis of Coal: Ind. Eng. Chem., vol. 40, 1948, pp. 1259-1264.

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Substitution of Water Gas for Hydrogen

It has been suggested that water gas might be substituted for the almost pure hydrogen now used industrially in the preparation of liquid fuels by the hydrogenation of coal. This would be an economic improvement, as the cost of compressed hydrogen constitutes about 50 percent of the total cost of liquid fuels prepared by the coal-hydrogenation process. Laboratory experiments at Bruceton have shown that it is indeed possible to replace hydrogen by water-gas under appropriate operating conditions. Because the water-gas shift reaction, viz., $CO + H_2O = CO_2 + H_2$, is quite fast under the conditions of coal hydrogenation, carbon monoxide is equivalent to hydrogen. However, no net decrease in cost is expected from this discovery because of the cost of the additional operation involved in removing carbon dioxide from the recycle hydrogen gas. The use of coke-oven gas as a source of hydrogen also is possible.[76]

Another procedure for reducing the cost of hydrogen consists in using byproduct hydrocarbon gases. These may be obtained under pressures of 500 to 600 pounds per square inch, reacted with steam at that pressure, and the resulting mixture of hydrogen and carbon dioxide washed with water under pressure. In this way, the initial compression of hydrogen can be avoided, and, with a relatively small sacrifice in oil yield, enough byproduct hydrocarbons can be formed to supply all the hydrogen necessary for the process. An estimate of the reduction in cost of plant installation and operating cost to be expected from the use of byproduct hydrocarbon gas for hydrogen production is being made by the demonstration-plant staff.

Pilot-plant Operations

The installation of two pilot plants, one for the first or liquid-phase stage and one for catalyst testing in the second or vapor-phase stage has been completed. The liquid-phase plant has a capacity of about 10 gallons and the vapor-phase unit about 3 gallons of liquid product per day. Operation of both plants was begun in connection with tests on raw materials, catalysts, and procedures to be used in the larger demonstration plant at Louisiana, Mo.

Liquid-phase Hydrogenation

Operations in the liquid-phase hydrogenation pilot plant were begun in February 1949 and consisted of studies of a preliminary and orienting nature. During these operations, a pasting oil-catalyst mixture, a Rock Springs coal-pasting oil mixture, and Rock Springs coal-pasting oil-catalyst mixture were passed through the pilot plant under reaction conditions; minor changes in design were made as a result of these runs. The pilot-plant is now being operated with Rock Springs coal in a run for production of light oil.

Vapor-phase Hydrogenation

Figure 34 is a photograph of a high-pressure, fixed-bed, continuous catalytic unit that is being used to test catalysts for the demonstration plant at Louisiana, Mo., and to perform hydrogenation experiments on extracts or solutions of coal. Normal operating pressure for this unit is 10,800 pounds per square inch.

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[76] Weller, S., Pelipetz, M. G., Kuhn, M., Friedman, S., and Clark, E. L., Hydrogenation of Coal in Batch Autoclaves with Coke-Oven Gas: Ind. Eng. Chem., vol. 41, 1949, pp. 972-973.

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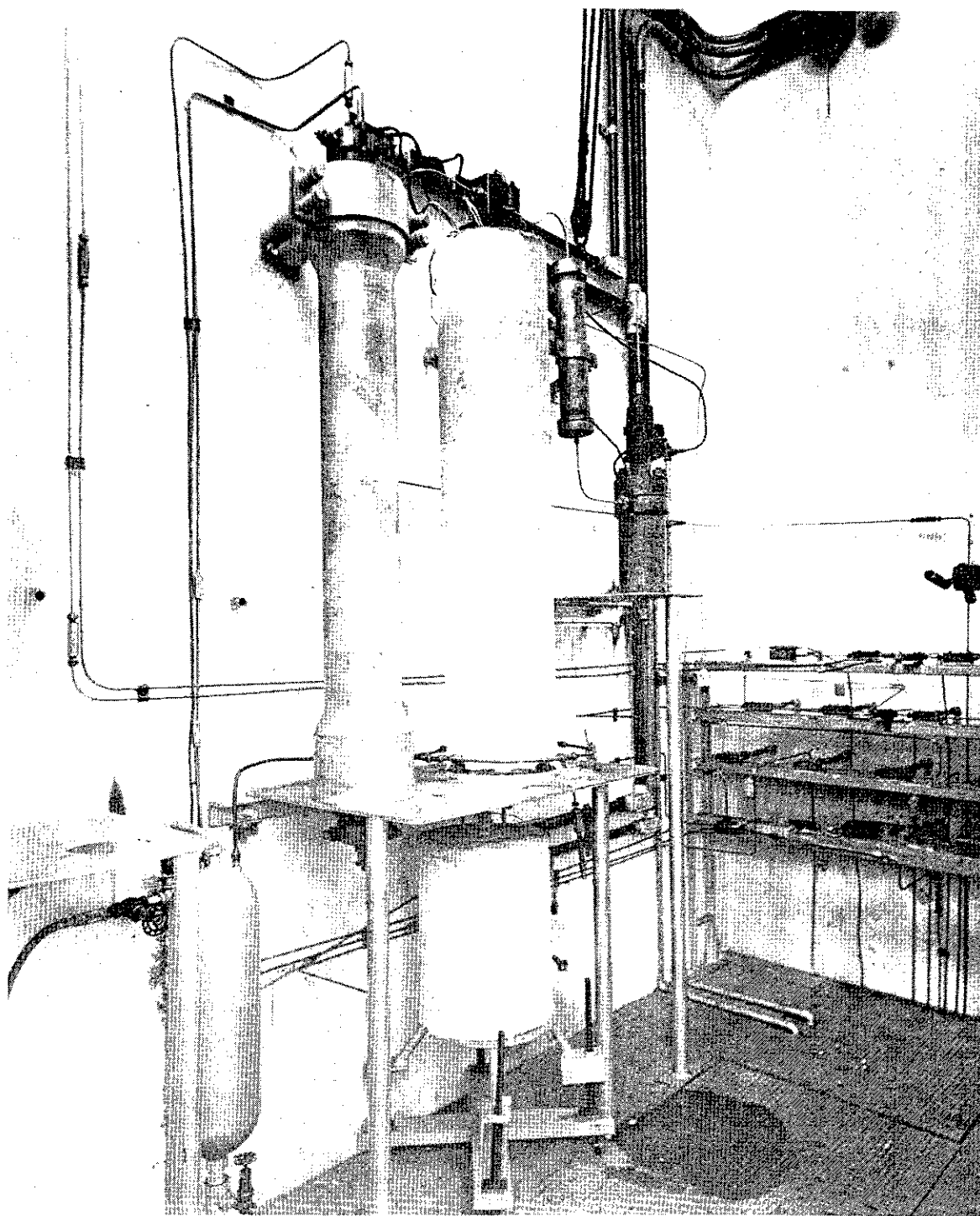the

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Figure 34. - Coal-hydrogenation vapor-phase catalyst testing unit.