

Effect of Water Vapor

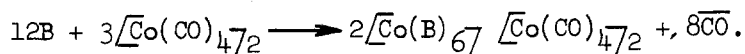
As water is a primary product of the synthesis, it was interesting to study the effect of water vapor in the synthesis gas upon the course of the synthesis. Accordingly, a reduced-iron catalyst was operated alternately with normal gas and with gas saturated with steam. During operation with steam-containing gas, the activity of the catalyst and its usage ratio of synthesis gas (volumes of hydrogen used per volume of carbon monoxide) decreased, while the production of carbon dioxide and methane increased. The volume of carbon monoxide consumed per hour was about the same in both cases. The catalyst therefore appears to have activated the same amount of carbon monoxide, but a large part of that gas was consumed in the water-gas reaction in the presence of steam. At the same time, the ratio of hydrogen to carbon monoxide was increased by the shift reaction, which resulted in greater yields of methane. The effect of water vapor on catalytic activity was not completely reversible; it decreased with increasing age of the catalyst.

Reactions of Synthesis Gas in the Presence of Metal Carbonyls

Systems containing carbon monoxide-hydrogen-metal carbonyl are being studied because certain homogeneous reactions occur that probably are related to those in the Fischer-Tropsch synthesis. Previous Annual Reports have discussed such systems wherein the substrate is an olefin (the oxo synthesis) or an alcohol (homologation of alcohols). The specific compound that may be the catalyst in such systems is cobalt hydrocarbonyl. Work was done on its preparation and properties and on the homologation reaction during this year.

Cobalt Hydrocarbonyl

A new preparation of this unusual compound stemmed from study of the reactions of dicobalt octacarbonyl and discovery that this compound undergoes internal rearrangement of electrons in the presence of a base (B) in the Lewis sense. This reaction, called homomolecular disproportionation, occurs according to the generalized equation



Acidification of the resulting salt causes liberation of cobalt hydrocarbonyl. According to the new procedure, dicobalt octacarbonyl is added to excess pyridine (5 minutes). The solution is added dropwise to excess dilute sulfuric acid, and the evolved cobalt hydrocarbonyl is condensed (45 minutes). Its ready availability by this method provided an opportunity for studying some of the properties of cobalt hydrocarbonyl. It is a strong acid that decomposes above its melting point, -26°C ., according to a second-order rate law. Comparison of its infrared spectrum with that of cobalt deuterocarbonyl did not give any information on the location of the hydrogen atom, probably because of the intense absorption of the carbonyl groups.

Homologation of Alcohols

Homologation of tertiary butanol was carried out at 200°C . and 4,000 p.s.i. pressure with $1\text{H}_2:1\text{CO}$ in a continuous reactor in the presence of 2-ethylhexanol and dicobalt octacarbonyl. About two-thirds of the reaction product consisted of isovaleraldehyde and one-third of isoamyl alcohol; about 11 percent of the starting material was recovered unreacted after the discharged material had been hydrogenated. Surprisingly, a small amount of neopentyl alcohol was found, although previous investigators had stated that no quaternary carbon atoms could be formed in this reaction. Similar conclusions regarding the absence of compounds with quaternary carbon atoms in Fischer-Tropsch products have been reported, and it appears important

to reinvestigate Fischer-Tropsch products to see whether quarternary carbon atoms are present.

Refining Synthesis Products

Two processes were used during the year for converting primary synthesis product to high-grade fuel. Thermal cracking broke down a wax fraction to liquid fuel, and bauxite treatment effectively deoxygenated two gasoline samples.

After about 2 percent of iron was removed from a Fischer-Tropsch wax, thermal cracking experiments were conducted with it at 100 to 300 p.s.i.g. pressure, 525° to 625° C., and throughputs of 100 to 1,000 cc. per hour. In a typical case (200 p.s.i., 525° C.), 88 percent of the wax was cracked; of this, 30 percent was converted to gasoline, 20 to Diesel oil, 28 to fuel oil, and 10 to gas.

Passage of the oxygen-rich oils from two nitrated-iron catalysts over bauxite at 350° C. resulted in 90+ percent removal of hydroxyl groups. Experiments with pure alcohols had shown that this elimination proceeds by both dehydration and dehydrogenation.

A debutanized gasoline from the Demonstration Plant was also subjected to bauxite treatments between 350° and 437° C. The octane numbers of the treated products improved with temperature up to about 400° C., beyond which there appeared to be little change. The motor octane number was raised from 55 to 71, and the research octane number from 55 to 79. Infrared analysis indicated that alcohols and ethers were completely destroyed and acids and ketones reduced to insignificant amounts by this treatment.

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Fluidized Hydrogenation

The pilot-plant work on this project has been severely handicapped owing to lack of manpower and funds. In addition, the problems encountered have made progress difficult. To study the mechanical, transport, and product-recovery requirements, the plant was operated as a fluidized carbonization unit. Nitrogen was used as the fluidizing medium at atmospheric pressure and temperatures of 500° to 600° C. Early results under these conditions with Rock Springs, Wyo., coal resulted in agglomeration and plugging of the reactor. Increasing the flow rate of the gas did not eliminate the agglomeration.

Dilution of the powdered coal with powdered coke eliminated agglomeration. Test runs of several days were completed without difficulty. The necessary dilution ratio was about 3:1 (coke-coal) for 30 minutes contact time; with reduced contact time, a lower dilution rate appears feasible. The oil yields were 6 to 8 percent of the coal charged. The unit is being made ready for operation with hydrogen at 500 to 1,000 p.s.i.g., and the mechanical improvements, developed during the operation with nitrogen, are being incorporated. A laboratory-scale fluidization unit is shown in figure 30.

Coal Assaying

The Bergius process for coal hydrogenation consists of an initial liquefaction step - treatment of coal (in the form of a coal-oil paste) with hydrogen at high

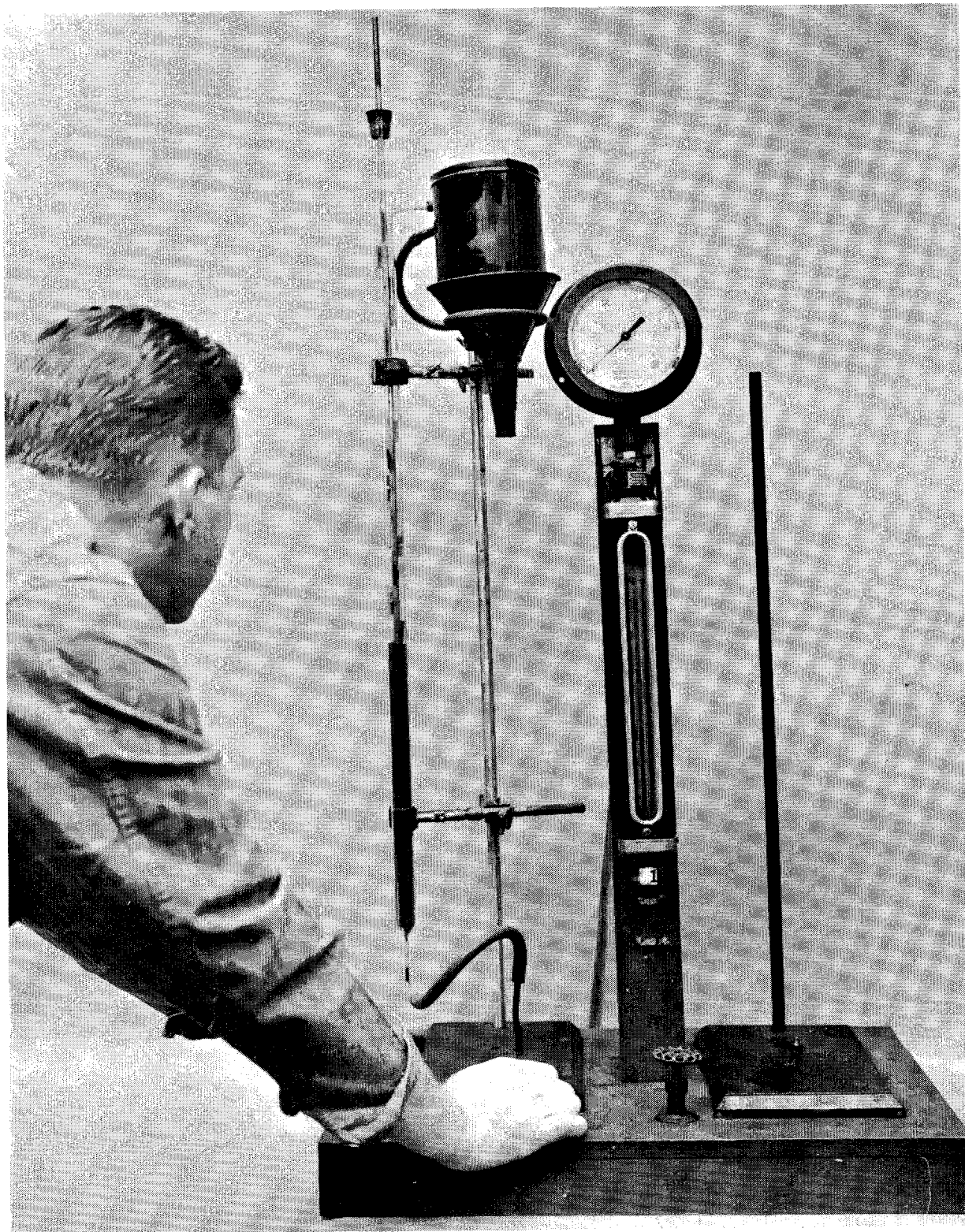


Figure 30. - Laboratory-scale fluidization unit.

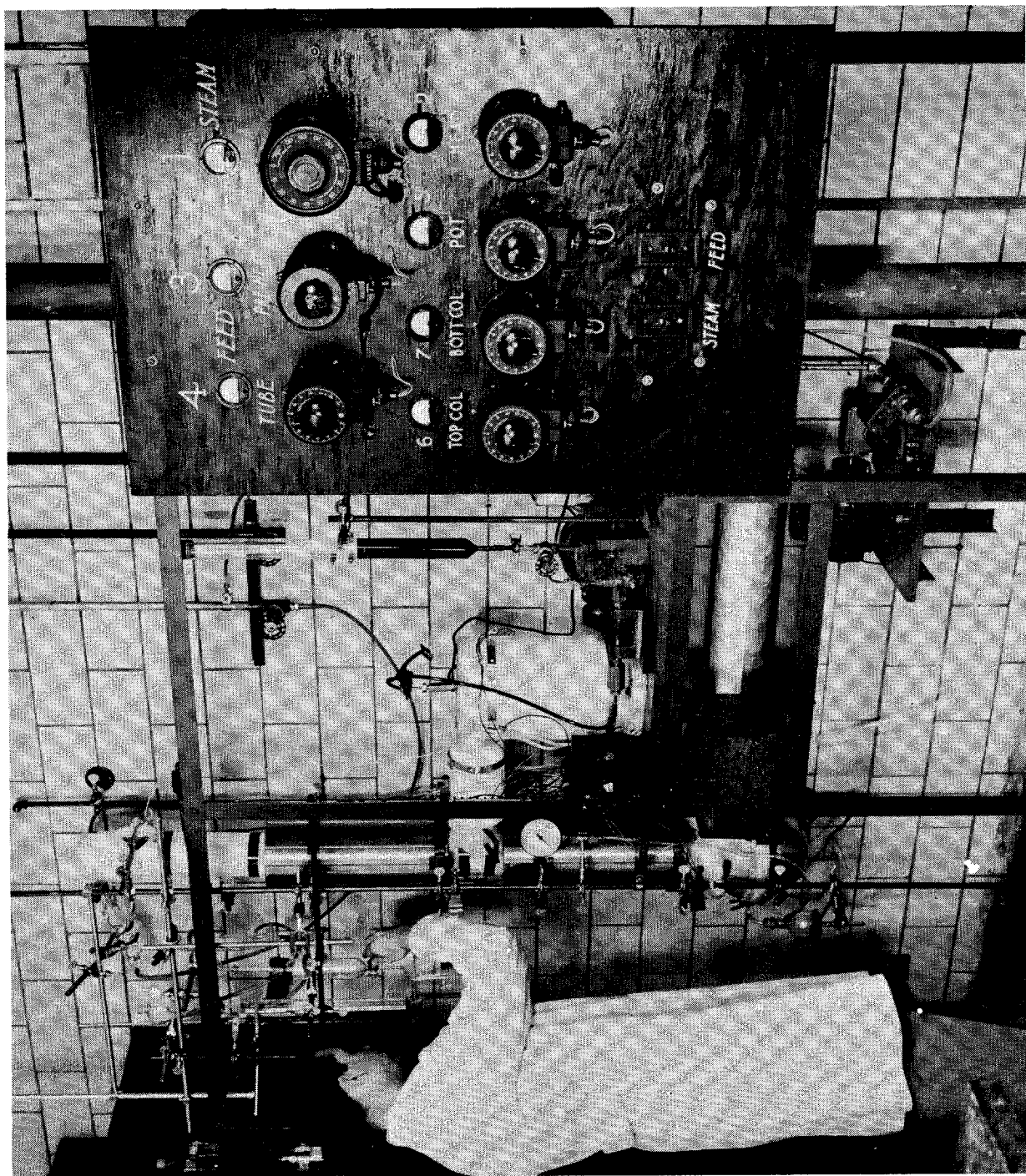


Figure 31. - Continuous distillation column for removing gasoline from coal-hydrogenation oils.

pressure and temperature in the presence of a catalyst - followed by catalytic hydrogenation of the product, the so-called middle oil, in the vapor phase. Important aspects of the research and development program are evaluation of American coals as to their amenability to the first step of this process, search for active catalysts, and establishment of optimum conditions for the process.

Compactness, flexibility, and low cost of equipment and operation make the autoclave an excellent tool for studying the liquefaction of coal. Until recently, however, the reliability of the results thus obtained was in some doubt, as no direct comparison could be made between autoclave and plant data. Evaluation of the data obtained at the Demonstration Plant with Western Kentucky and Illinois coals has now made this correlation possible. Tables 17 and 18 (see also fig. 31) show the satisfactory qualitative and quantitative agreement of the results, proving the reliability of autoclave testing as an assay method.

Autoclave assays were made for 1 hour at 450° C. and 4,000 p.s.i.g. initial hydrogen pressure in the presence of 0.5 percent of ferrous sulfate catalyst with seven Colorado coals (from Somerset, Bear, Hawk's Nest, and Oliver mines in Gunnison County, and Wise Hill, Knez, and Baker mines in Moffat County) and one Pennsylvania coal (from Waverly mine, Washington County). All of these coals are satisfactory for hydrogenation. The importance of the method of impregnating catalyst on coal was demonstrated by hydrogenating two batches of Lake DeSmet coal under identical conditions; one batch had been mixed with 1.76 percent of dry ferrous sulfate in the crusher, and the other had been impregnated with 1.18 percent of ferrous sulfate in solution. Despite its lower catalyst content, the impregnated coal yielded more hexane-soluble oil and less asphaltene.

TABLE 17. - Hydrogenation products from Kentucky coal
Basis, m.a.f. coal; FeSO₄ catalyst

	Demonstration Plant run 6 463° C., 8,300 p.s.i.	Autoclave results 465° C., 4,000 p.s.i. initial H ₂ pressure
Products, weight percent:		
Benzene insolubles.....	3.95	2.59
Total oil.....	70.69	72.83
Gaseous hydrocarbons.....	15.47	18.74
CO ₂ + CO.....	.95	.68
H ₂ O.....	9.47	8.18
N ₂ + S eliminated.....	3.85	3.23
Unaccounted for.....	1.28	-
Hydrogen consumed.....	5.66	6.25
Total oil ultimate		
C.....	86.24	87.04
H.....	9.77	9.56
N.....	.79	.48
S.....	.26	.15
O.....	2.94	2.77

TABLE 18. - Hydrogenation products from Illinois coal
Basis, m.a.f. coal; FeSO₄ catalyst

	Demonstration Plant run 7 463° C., 8,000 p.s.i.	Autoclave results 450° C., 4,000 p.s.i. initial H ₂ pressure
Products, weight percent		
Benzene insolubles.....	4.90	3.15
Total oil.....	68.42	75.25
Gaseous hydrocarbons.....	13.58	13.64
CO ₂ + CO.....	1.76	1.05
H ₂ O.....	9.05	7.94
N ₂ + S eliminated.....	4.17	4.17
Unaccounted for.....	3.43	-
Hydrogen consumed.....	5.31	5.20
Total oil ultimate		
C.....	85.55	85.78
H.....	9.95	9.10
N.....	.83	.89
S.....	.19	.30
O.....	3.47	3.93

Coking Heavy-Oil Let-Down (H.O.L.D.)

The residual oil from the liquefaction step (heavy-oil let-down or H.O.L.D.) contains unreacted coal, ash, and catalyst. Recovery of the liquid content of this material is necessary for economic reasons. In last year's Annual Report, coking of H.O.L.D. was discussed, and it was stated that knowledge of the coking properties of the liquid fractions makes it possible to predict the product distribution obtained upon coking any H.O.L.D., provided its composition is known in terms of these fractions. They are "oil," soluble in n-hexane; "asphaltene," insoluble in n-hexane but soluble in benzene; and benzene-insoluble material. This year, the coking properties of the last two fractions were determined, so that comparison between this method and direct coking of an H.O.L.D. became possible. An H.O.L.D. obtained from Western Kentucky coal at the Demonstration Plant was used for this purpose; it consisted of 48.6 percent of "oil," 28.6 percent of "asphaltene," 6.4 percent of benzene-insolubles, and 16.4 percent ash. Agreement of the data (see table 19) shows the validity of the method. Thus, the necessity for coking tests of H.O.L.D. is obviated.

TABLE 19. - Comparison of calculated and experimental yields from coking of H.O.L.D. at 550° C.

(a) Yields, fraction of total, from H.O.L.D. components

	"Oil"	"Asphaltene"	Benzene-insolubles
Distillate.....	0.78	0.40	0.10
Residue (coke).....	.17	.53	.89
Gas plus loss.....	.05	.07	.01

(b) Comparison of yields, percent of total

	Calculated	Experimental
Distillate.....	50.1	53.7
Residue (coke).....	45.6	42.6
Gas plus loss.....	4.3	3.7

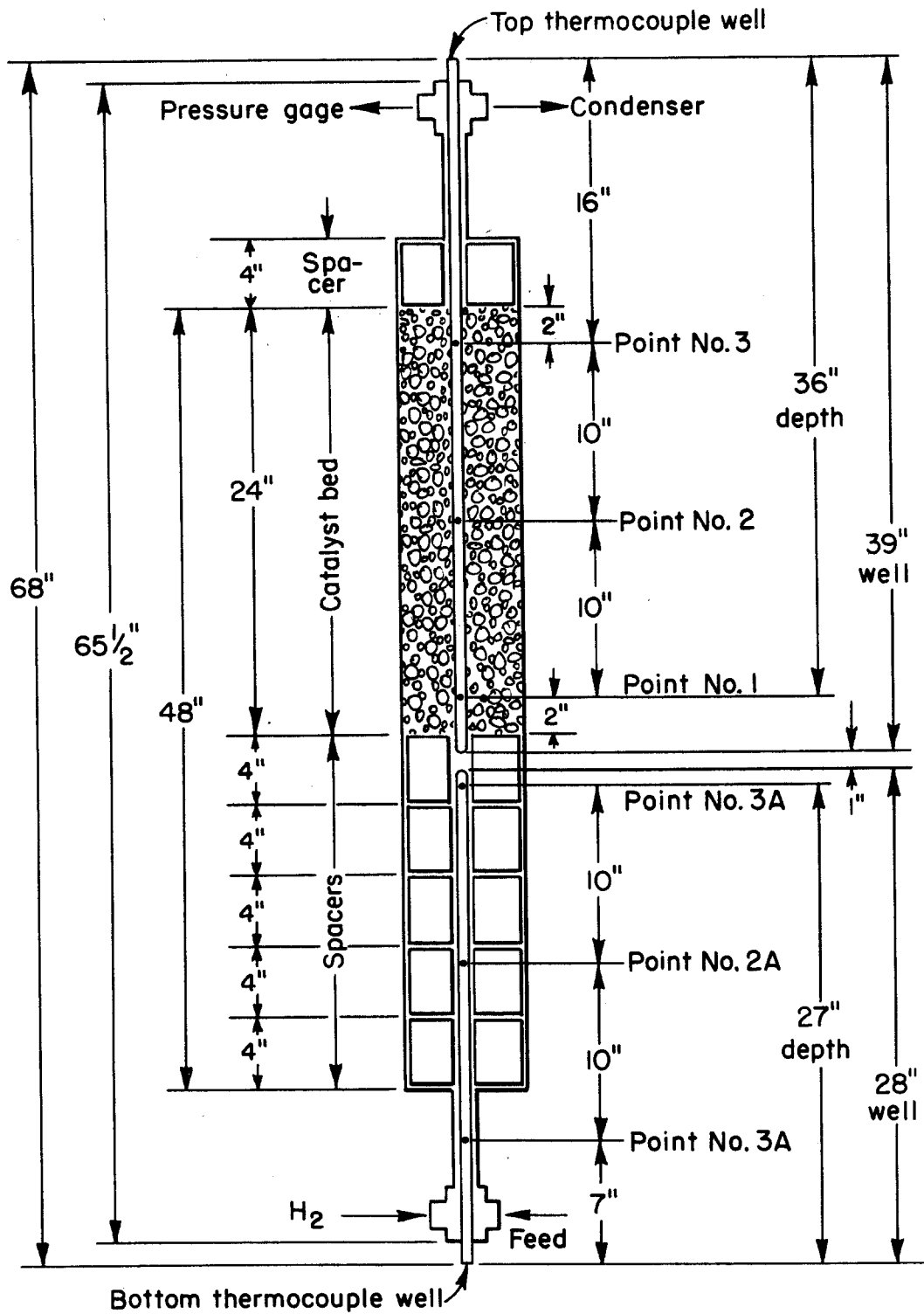


Figure 32. - Reactor for vapor-phase-hydrogenation unit.

Development of Vapor-Phase Catalyst

The hydrogenation of middle oil at the Demonstration Plant has been carried out with a German catalyst, K-536, consisting of molybdenum, chromium, zinc, and sulfur on a clay support treated with hydrofluoric acid. Initial development work on an equivalent American catalyst was mentioned in the previous Annual Report. This project, now essentially completed, involved selection of a suitable supporting material, determining optimum methods of impregnation, and obtaining adequate mechanical strength, chemical activity, and durability of the catalyst.

A pelleted catalyst, prepared for the Bureau by a commercial source according to the German specifications, was not quite as efficient a cracking catalyst as the German, although its ability to remove oxygen, sulfur, and nitrogen from the middle oil equaled that of the German product.

Further Bureau development work was carried out with a different supporting clay, using both extrusion and pelleting techniques. Extrusion resulted in a mechanically weak product. However, proper equipment may lead to better results with extruded catalyst, and this problem is still under study. The pelleted catalyst was mechanically satisfactory, especially those batches containing 1.5 percent of graphite as a pelleting lubricant.

According to German practice, ammonium sulfomolybdate was to be one of the ingredients of the catalyst. Since a commercial source of this chemical could not be found, two rather complicated and expensive procedures were tried for making the compound. During reduction of both the Bureau and the German catalysts, much of the molybdenum was volatilized, possibly as a hydrate of molybdenum oxide. A different procedure of making and adding ammonium sulfomolybdate was therefore tried: Molybdenum oxide was dissolved in ammonium sulfide in stoichiometric proportions, and the solution of ammonium sulfomolybdate was added directly to the mixer. This simpler procedure was effective in avoiding loss of molybdenum during reduction. Some molybdenum is still lost during operation.

Figure 32 shows the reactor of the vapor-phase hydrogenation unit. The bottom portion of the reactor serves as preheater. Middle oil enters at the bottom without external preheating, while hydrogen is added after external preheating to 850° F.

Considerable experimentation with preparation and testing of catalysts finally resulted in a mechanically strong and chemically active product that was used for a durability test. This test, originally scheduled to last 4 weeks, was extended for another week to run a new feed stock that had just been received from the Demonstration Plant. The results of the experiment are summarized in table 20. Gasification was low; activity remained constant during the test and was higher than that of the German catalyst. The catalyst pellets were in excellent condition after use, and their crushing strength had increased from 13 pounds before reduction to 33 pounds after use.

TABLE 20. - Hydrogenation of middle oil with pelleted catalyst BK-536-P-L4

	Operation		
	41-1-A (1st week)	41-1-D (4th week)	41-2 (New feed oil)
Temperature.....°F.	932.8	934.2	933.6
Feed rate.....gm./hr.	149.3	151.3	149.6
Oil/l. cat./hr.....Kg.	1.0	1.0	1.0
Oil/kg. cat./hr.....Do.	0.96	0.96	0.96
Product oil.....weight percent of feed	80.3	80.5	80.7
Gaseous hydrocarbons.....Do.			
C ₁ -C ₃	11.91	12.70	14.01
C ₄	5.64	5.09	4.94
C ₅ and higher.....	3.11	2.02	1.55
Hydrogen usage.....Do.	3.85	3.80	4.10
Analysis of product oil.....weight percent:			
Carbon.....	87.59	87.37	87.72
Hydrogen.....	12.28	12.18	11.58
Nitrogen.....	.07	.07	.12
Sulfur.....	.02	.02	.03
H:C atomic ratio.....	1.68	1.67	1.58
Gasoline			
Specific gravity.....	0.8067	0.8017	0.8160
Gum.....mg./100 cc.	0.90	1.65	0.73
Octane no., motor method.....	76.9	77.2	80.1
Carbon.....percent	87.42	86.99	87.30
Hydrogen.....Do.	12.68	12.38	11.94
Nitrogen.....Do.	.03	.04	.08
Sulfur.....Do.	.02	.07	.10
Distillation of product oil...weight percent			
Gasoline.....	85.92	83.78	75.50
Residue.....	13.58	14.21	21.29
Loss.....	.50	2.01	3.21
Corrected gasoline.....			
.....weight percent of product oil	86.42	85.79	78.71
Gasoline.....weight percent of feed	69.40	69.06	63.52

Refining Shale Oil

For conversion of crude shale oil to specification, petroleum fuels, nitrogen, and sulfur must be eliminated, and the average molecular weight of the oil must be lowered. Although molecular weight can be reduced by thermal cracking, hydrogenation or chemical refining methods must be used for removing nitrogen and sulfur. Results of studies of several hydrogenation catalysts were given in the 1950 Annual Report. These were utilized in a fixed catalyst bed, so that the crude oil had to be free of solids to avoid their deposition in the bed.

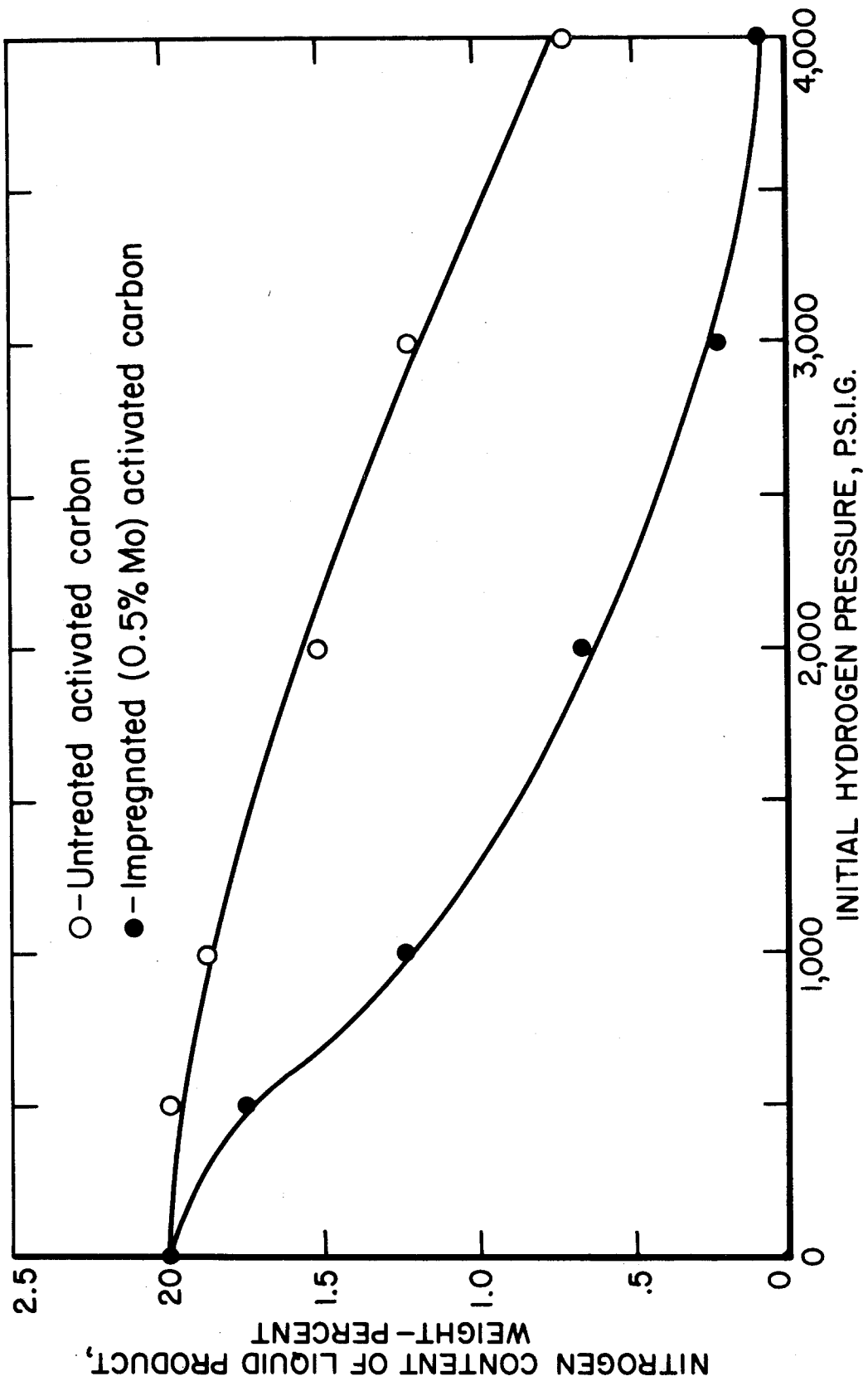


Figure 33. - Elimination of N₂ during hydrogenation of crude shale oil.

Tests in batch autoclaves, using a finely powdered catalyst added directly to the oil, indicate that activated carbon, especially when impregnated with ammonium molybdate, is a very satisfactory catalyst for hydrogenation of shale oil.

Preliminary experiments with activated carbon in an inert atmosphere indicated that it does not increase the rate of thermal cracking of crude shale oil. In the presence of hydrogen, however, activated carbon was quite effective in eliminating nitrogen and sulfur. Figure 33 compares the effects of untreated activated carbon and carbon containing 0.5 percent of molybdenum. Almost complete elimination of nitrogen was achieved with the impregnated catalyst at 4,000 p.s.i.g. initial pressure of hydrogen. Even at 2,000 p.s.i.g. initial pressure, 75 percent of the nitrogen was eliminated. The hydrogen-carbon atom ratio of the oil increased from about 1.6 to 1.9 during treatment at 4,000 p.s.i.g. These results were much better than those obtained with two commercial cracking catalysts.

Kinetics of Hydrogenation

Effect of Organic Compounds

It has been suggested that some organic compounds, especially those that have a solvent or dispersive action upon coal, might affect the yield of soluble oil obtained during hydrogenation of coal. Autoclave experiments were therefore made with coal impregnated with 10 percent of phenol, pyridine, or anthracene in methyl alcohol solutions; in addition, a sample treated with alcohol only was run. The impregnation was done in a glass vessel with constant stirring until the material was fluid. When the mixture became pasty, it was first dried at room temperature and then in a drying oven until all of the methyl alcohol was removed. The dried coal was hydrogenated at 450° C. and 1,000 p.s.i.g. initial pressure of hydrogen. The results showed that no catalytic effect was exerted by these compounds.

Pressure Dependence of Hydrogenation

Studies of the kinetics of coal hydrogenation were continued with Rock Springs, Wyo., coal at 400° C. Experiments without catalyst, with 1 percent tin plus 0.5 percent ammonium chloride, and with 1 percent molybdenum all showed that the hydrogenation is a first-order reaction with respect to remaining benzene-insoluble material. The specific reaction-rate constants are linear functions of initial hydrogen pressure, and - in units of (minutes)⁻¹ and p.s.i.g., respectively - are expressed as follows:

$$K = 3 \times 10^{-6}P \quad (\text{no catalyst})$$

$$K = 1.5 \times 10^{-5}P \quad (\text{tin plus ammonium chloride})$$

$$K = 1.5 \times 10^{-5}P + 0.0225 \quad (\text{molybdenum})$$

This means that the initial hydrogen pressure must be five times as high in the absence of catalyst as in its presence for the same extent of liquefaction of coal. For example, the rate of hydrogenation of Rock Springs coal is the same at 500 p.s.i.g. pressure with molybdenum as at 2,000 p.s.i.g. with tin or at 10,000 p.s.i.g. without catalyst. This emphasizes the importance of catalysts to the coal-hydrogenation process.

The initial part of the reaction appears to be a purely thermal degradation in which 6 percent of the coal is eliminated as carbon dioxide, water, and gaseous hydrocarbons. More carbon dioxide and gaseous hydrocarbons are formed in the absence of

catalyst than in its presence, the rate of formation of the former being constant throughout most of the reaction, while the rate of formation of the latter decreases with time. The hydrogen content of the benzene-insolubles is less than that of the original coal in the absence of catalyst, but greater in its presence. The linear dependence of the amount of benzene-solubles formed on the amount of benzene-insolubles remaining over the range of most of the reaction indicates that coal behaves like a homogeneous substance during hydrogenation. Complete, uncatalyzed hydrogenation would result in formation of less benzene-soluble oil than the corresponding catalyzed reaction. In all cases, the initial product is insoluble in benzene and gradually becomes soluble as further hydrogenation occurs.

Formation of Oxygenated Compounds

During the hydrogenation of coal, oxygen is eliminated as carbon dioxide and water. The oxygen content of coal is a function of its rank, and a classification of coals based on their ultimate composition (and hence also their oxygen content) appears to be most useful for comparing their hydrogenation properties. A study was made of the effect of the oxygen content of bituminous coals on their hydrogenation products.

In table 21 the ultimate composition of 10 bituminous coals is summarized, with other data that influence the cost of the hydrogenation process. All data were obtained by hydrogenation of these coals for 1 hour at 450° C. at an initial hydrogen pressure of 4,000 p.s.i.g. and in the presence of 0.5 percent of iron; the catalyst was introduced by impregnation of the coal with aqueous ferrous sulfate. The oxygen content of these coals ranged from 8 to 21 percent.

More hydrogen was consumed per unit of product oil as the oxygen content of the coal increased. Increased oxygen content of the coals was, of course, accompanied by a decreased carbon content. The yield of oil per unit of coal decreased in direct proportion to its oxygen content. Although higher oxygen contents corresponded to larger yields of carbon dioxide, most of the oxygen was still eliminated as water. This means that much hydrogen was wasted during hydrogenation of a coal that has a high oxygen content. The formation of gaseous hydrocarbons also increased with increasing oxygen content, so that additional hydrogen was consumed in the formation of this product. The ultimate compositions of the product oils indicated that the average composition of the benzene-soluble oil was not influenced by the oxygen content of the coal.

Additional experiments at 400° to 475° C. revealed that the oxygen content of the product, as well as its average molecular weight, decreased with increasing temperature of hydrogenation. The rate of elimination of oxygen was greatest at the beginning of the formation of soluble oil. The carbon dioxide formed during that period could be reduced to hydrocarbons and water, especially in the presence of molybdenum at 400° C.

TABLE 21. - Ultimate composition of some bituminous coals and characterization of their hydrogenation products

	(All yields calculated per 100 gm. of moisture- and ash-free coal)									
	Coal									
	Bruceton	Kentucky	Illinois	Rock Springs	Oliver	Somerset	Hawk's Nest	Knež	Baker	Lake Desmet
Ultimate analysis . . . percent										
Hydrogen	5.53	5.52	5.43	5.30	5.63	5.59	5.53	5.04	5.11	4.95
Carbon	82.98	80.57	77.51	78.45	79.42	80.40	80.81	77.38	76.99	70.95
Nitrogen	1.66	1.51	1.49	1.67	1.64	1.71	1.81	1.96	1.50	1.35
Sulfur	1.64	2.64	3.66	.90	.92	.79	.73	.70	.86	1.13
Oxygen	8.19	9.76	11.91	13.68	12.39	11.51	11.12	14.92	15.54	21.62
Total oil product gm.	77.02	78.29	72.84	72.85	73.13	74.56	74.00	69.80	68.65	63.91
Total hydrogen consumed Do.	5.28	5.21	5.32	5.30	4.98	5.12	5.35	5.81	5.58	5.71
Oxygen as CO ₂ Do.	0.11	0.52	0.77	1.89	0.96	0.68	0.60	2.43	3.10	4.65
Oxygen as water Do.	6.25	6.90	8.03	8.27	9.26	8.46	8.10	10.98	10.43	13.58
Hydrogen as water Do.	0.78	0.86	1.00	1.02	1.18	1.01	1.03	1.39	1.29	1.70
H ₂ as gaseous hydrocarbons Do.	2.75	2.44	2.83	2.96	2.81	2.90	2.92	3.03	3.10	3.00
Hydrogen in oil Do.	6.96	7.23	6.76	6.42	6.36	6.59	6.69	6.16	6.04	5.74
Carbon grams										
In oil	67.46	68.33	63.09	63.21	63.92	65.09	64.36	60.57	59.77	55.52
In gaseous hydrocarbons	10.99	9.77	12.34	11.83	11.50	11.64	11.85	12.11	12.46	11.94
Carbon percent										
In benzene-insolubles	5.41	2.82	2.34	3.45	4.60	4.27	5.40	4.88	4.65	2.42
In oil	81.30	84.81	81.40	80.57	80.77	80.96	79.85	78.28	77.63	78.25
In gaseous hydrocarbons	13.24	12.13	15.92	15.10	14.47	14.47	14.66	15.64	16.18	16.48