

bed contained less than 4.2 percent refuse (sinks in 1.6 specific gravity). Specially developed techniques for controlling combustion in beehive-coke ovens by analysis of exit gases showed that properly operated ovens operate with a deficiency, rather than an excess of air. Measurements with optical pyrometers and thermocouples indicated that constant oven temperatures of 2,200° F. produced good coke. When the coking process nears completion, these tests show that there is a well-marked trend toward an excess of air which results in combustion of the coke and thus decreases the coke yield, unless special precautions are taken. The need of the beehive-coke industry for aid in meeting wartime demands is illustrated by the following data:

Range in properties of beehive coke received at one
blast-furnace plant

	Percent
Sulfur	0.65 to 2.50
Ash	11.00 to 22.00
1/4-inch tumbler	53 to 64

Beehive ovens in many ways provide ideal standby capacity for coke production. (1) They are simple to operate, requiring very little skill, except that developed by experience; (2) they are low in first cost, approximately \$1,000 to \$1,500 with an annual capacity of 700 tons compared with a rectangular oven of the modern type, \$2,000 to \$3,500, with an annual capacity of 1,000 tons of coke; (3) unless deliberately destroyed to avoid taxation, beehive ovens deteriorate very slowly when not in use; and (4) beehive coke manufactured from good coal is as good as any other coke made.

Figures 9 and 10 show beehive ovens before and after rehabilitation. Figure 11 shows a coke-drawing machine improvised by one operator to help meet wartime demands.

Effect on Compression of Coal Charge on Coke Properties

Practices with Saar coals in Germany and to some extent on a small-scale in England have been to compress the charges before placing them in the coke ovens. By this means a higher-density charge is obtained; and, for the Saar coals, coke of better physical properties is said to be produced. The effect of compressing charges (increased charge density) of two weakly coking American coals - the Willow Creek bed coal from Gomer mine, Lincoln County, Wyo., and the Lower Sunnyside bed coal from Columbia mine, Carbon County, Utah - on the yield and physical properties of their cokes is shown in table 15. The table makes it clear that compression of the charges of these two coals makes no significant difference in the yields but does increase the apparent specific gravity. The shatter and tumbler data show that compression weakens the cokes.

87/ Scott, G. S., Kelley, J. A., Fish, E. L., and Schmidt, L. D., Modern Beehive Coke-Oven Practice. I. Preliminary Report: Bureau of Mines Rept. of Investigations 3738, 1943, 14 pp.

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FIGURE 9.- Beehive-coke ovens before rehabilitation.

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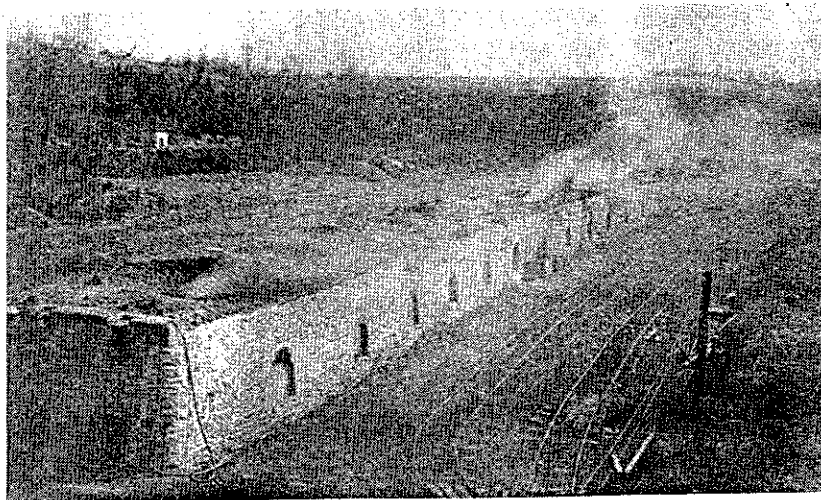


FIGURE 10.- Beehive-coke ovens after rehabilitation.

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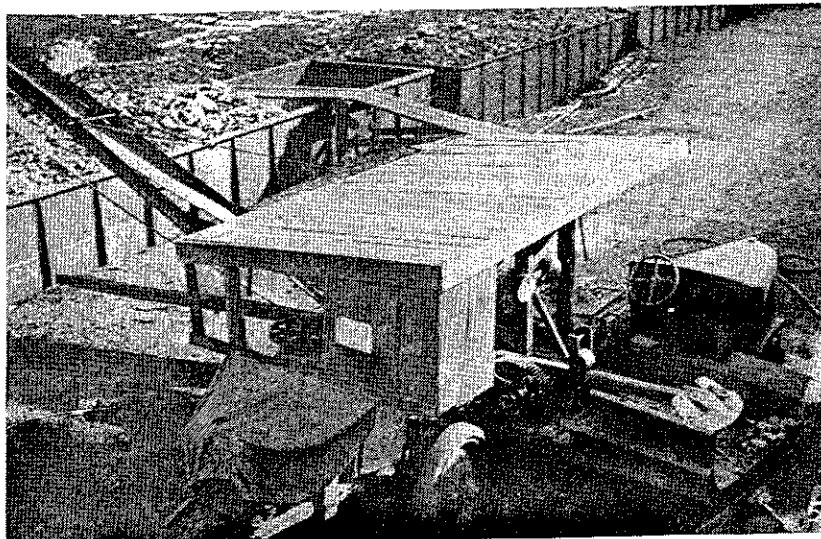


FIGURE 11.- Improvised coke-drawing machine.

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TABLE 15. - Yield and physical properties of cokes from Willow Creek (135) and Lower Sunnyside (e19) coals carbonized at 9000 C.

Coal No.	Charge density, lb. per cu. ft.	Yield of coke, percent	Apparent specific gravity	Shatter test, cumulative percent upon-				Tumbler test, cumulative percent upon-			
				1-1/2-in. screen	1-inch screen	3/4-inch screen	1/2-inch screen	1-1/2-in. screen	1-inch screen	3/4-inch screen	1/2-inch screen
135	49.2	64.2	0.80	48	76	83	89	10	41	52	62
135	55.1	64.8	.85	30	65	77	87	3	32	47	61
135	58.9	64.8	.88	25	63	76	86	2	29	47	62
e19	50.9	63.0	.78	29	67	80	92	6	44	62	76
e19	52.6	62.8	.79	23	63	79	92	5	42	62	77
e19	56.1	62.8	.81	19	63	79	91	3	41	62	77
e19	59.3	62.9	.84	18	59	77	91	3	32	56	76

Producer-Gas Investigations

Despite the inconvenience and decreased power availability of producer gas, the fuel economy of this country may yet provide an impetus for its use as fuel in fleets of trucks or buses.^{88/} Recent tests based on the operation of an updraft-type producer, fired with charcoal and installed on a 2 1/2-ton truck loaded to rated capacity, indicated a fuel consumption of 0.57 pound per gross ton-mile, which, though high, would still result in an appreciable saving in cost of fuel, as compared with gasoline. Equipment for determining the suitability of typical American solid fuels for use in portable gas producers on automotive vehicles as a substitute for gasoline is being installed at the Central Experiment Station in Pittsburgh, Pa.

LiquefactionBureau of Mines Research

Bureau of Mines interest in the production of liquid fuels from coal and lignite began in 1924 when particular attention was given to low-temperature carbonization and liquefaction of coal. The Bergius commercial scale pilot plant for the hydrogenation of coal at Mannheim, Germany, and a number of low-temperature carbonization plants in England, France, and Germany were studied. Further reports on the development of petroleum substitutes from coal stimulated activity in the United States in obtaining fundamental information relative to the effect of temperature, pressure, and nature of catalyst and to the quantity and composition of the products obtained. The Bureau undertook laboratory experiments of the Fisher-Tropsch catalytic method for making liquid hydrocarbons from water gas. Although interest waned for a time, experimental work on the liquefaction of coal was resumed in 1936 when it became evident that a forward-looking policy from the national point of view should include preparation for the time when gradual exhaustion of petroleum resources would require supplementing with gasoline and Diesel oil produced from coal the growing demand for motor fuel. Reviews of Bureau of Mines research have been presented.^{89/} A small, continuously operating unit capable of hydrogenating 100 pounds of coal in 24 hours was installed at the Central Experiment Station of the Bureau of Mines at Pittsburgh, Pa. The Bureau is now undertaking the construction and operation of a pilot plant in which the converter units are nearer commercial size, so that data may be obtained for designing commercial

^{88/} Schroeder, W. C., Fuels and Fuel Research in Great Britain: Mech. Eng. vol. 65, December 1943, pp. 881-884, 892; discussion by W. T. Reid, Mech. Eng., vol. 66, May 1944, pp. 332-333

^{89/} Fieldner, A. C., Storch, H. H., and Hirst, L. L., Bureau of Mines Research on the Hydrogenation and Liquefaction of Coal and Lignite: Bureau of Mines Tech. Paper 666, 1944, 69 pp.; Am. Inst. Min. and Met. Eng. Tech. Pub. 1750, Class F. Coal Division, No. 156, 1944, 19 pp.; Trans. Am. Inst. Min. and Met. Eng., Coal Div., vol. 157, 1944, pp. 341-362.

Fieldner, A. C., and Schroeder, W. C., Oil and Gasoline from Oil Shale and Coal: Fuel in Sci. and Practice, vol. 23, 1944, pp. 34-36.

plants.^{90/} Investigations have demonstrated that the major part of the American reserves of coals is suitable for liquefaction. Coals low in ash and nearly free of fusain and opaque attritus can be almost completely liquefied. The yields, physical characteristics, and chemical composition of the resulting oils are influenced principally by operating conditions that vary with different coals. These operating conditions may be modified to produce either fuel oil or Diesel oil, and gasoline. The yield of tar acids is sufficiently large to be important commercially in the plastics industry. The yields of benzene, toluene, and xylene are of value for explosive manufacture and solvents. The high content of aromatic compounds in the neutral oil makes it a desirable blending base for high-octane aviation gasoline. The degree of liquefaction is roughly inversely proportional to its opacity. The yield of unliquefiable organic matter can be estimated approximately from the carbon content and petrographic composition of coals.

Mechanism of Coal-Hydrogenation Processes

The reactions in which hydrogen is "transferred" from one organic molecule to another during the hydrogenation of coal to produce liquid fuels have been studied and reported in a series of four publications, the latest of which appeared during the period covered by this report.^{91/ 92/ 93/ 94/}

^{90/} Synthetic Liquid Fuels: Hearings before a Subcommittee on Public Lands and Surveys, U. S. Senate, 78th Congress; 1st Session on May 12, 1943, Washington, D. C., August 3 and 4, 1943, pp. 1-178; Pittsburgh, Pa., August 6, 1943, pp. 179-273; Salt Lake City, Utah, August 9, 1943, pp. 275-407; Sheridan, Wyo., August 11, 1943, pp. 409-469, U. S. Government Printing Office, Washington, D. C., 1943, 469 pp.

Public Law 290, 78th Congress, Chapter 172 - 2d Session, An act authorizing the construction and operation of demonstration plants to produce synthetic liquid fuels from coal, oil shales, agricultural and forestry products, and other substances, in order to aid the prosecution of the war, to conserve and increase the oil resources of the Nation, and for other purposes, April 5, 1944.

^{91/} Storch, H. H., Hirst, L. L., Fisher, C. H., and Sprunk, G. C., Hydrogenation and Liquefaction of Coal, Part I. - Review of Literature, Description of Experimental Plant, and Liquid-Phase Assays of Some Typical Bituminous, Subbituminous, and Lignitic Coals: Bureau of Mines Tech. Paper 622, 1941, 110 pp.

^{92/} Fisher, C. H., Sprunk, G. C., Eisner, A., O'Donnell, H. J., Clarke, L., and Storch, H. H., Hydrogenation and Liquefaction of Coal, Part 2. - Effect of Petrographic Composition and Rank of Coal: Bureau of Mines Tech. Paper 642, 1942, 162 pp.

^{93/} Hirst, L. L., Eisner, A., Field, J. H., Cooper, H. M., Abernethy, R. F., and Storch, H. H., Hydrogenation and Liquefaction of Coal, Part III. - Characterization of Assay Oils: Bureau of Mines Tech. Paper 646, 1942, 27 pp.

^{94/} Storch, H. H., Fisher, C. H., Hawk, C. C., and Eisner, A., Hydrogenation and Liquefaction of Coal, Part IV. - Effect of Temperature, Catalyst, and Rank of Coal on Rates of Coal-Hydrogenation Reactions: Bureau of Mines Tech. Paper 654, 1943, 50 pp.

Experiments were made in small autoclaves on the effect of temperature, catalyst, and rank of coal on the rates of primary liquefaction, and of related processes, including the absorption of hydrogen and elimination of oxygen. The results show that the rate-determining step for the absorption of hydrogen varies with temperature. Between 300° and 370° C., diffusion of hydrogen through a liquid film on the surface of the coal and catalyst is the slowest step; above 370° C. the rate-determining step is a chemical reaction between a hydroaromatic and the oxygen and unsaturated groups in the primary decomposition of the coal. The chief function of the catalyst and of hydrogen at high pressure is to increase the rate of regeneration of hydrogen carriers which are hydromatic compounds, such as tetrahydronaphthalene. The reactions of the hydrogen carrier with oxygen groups and double bonds in the primary decomposition products of the coal appear to be largely noncatalytic. The accelerating effects of the catalyst on the rates of oxygen elimination and on that of liquefaction are similar, and both processes probably are intimately associated in one reaction or group of reactions.

No direct or simple relationship was found between the hydrogen-consumption rate and the rates of oxygen removal and of coal liquefaction. The presence of a reservoir of reactive hydroaromatic compounds that will transfer hydrogen to the products of the thermal decomposition of the coal substance seems to be largely responsible for this apparent lack of direct dependence of the liquefaction and oxygen removal rates on the rate of hydrogen consumption. For maintenance of this reservoir of reactive hydroaromatics, active catalysts and high pressures of hydrogen are essential.

To ascertain the nature of these hydrogen-transfer reactions a study was made of the mixture of anthracene plus tetrahydronaphthalene in the presence of an active hydrogenation catalyst.^{95/} A 30-percent yield of 1, 2, 3, 4-tetrahydroanthracene can be obtained by heating anthracene and tetralin at one atmosphere pressure in the presence of a palladium catalyst. When these two compounds are heated together in a sealed tube in the presence of this catalyst, the reaction resembles a catalytic hydrogenation of anthracene, and a 61-percent yield of 1, 2, 3, 4-tetrahydroanthracene is obtained, along with small amount of 9, 10-dihydroanthracene and 1, 2, 3, 4, 5, 6, 7, 8-octahydroanthracene. Other hydrogen carriers, such as 2-cyclohexenone, also bring about this type of hydrogenation of anthracene. The dehydrogenation of 9, 10-dihydroanthracene in the liquid phase results in the expulsion of less than the theoretical quantity of hydrogen and the formation of some 1, 2, 3, 4-tetrahydroanthracene. To determine those constituents of the recycle oil that are most active in primary liquefaction of coal and to devise methods for increasing the concentration of these constituents in the vehicle used to carry the coal, the effect of typical coal-hydrogenation catalysts on the rate of transfer of hydrogen from tetrahydronaphthalene to anthracene is being studied.

^{95/} Orchin, M., Hydrogenation of Anthracene by Tetralin: Jour. Am. Chem. Soc. vol. 66, 1944, pp. 535-538.

Catalysts for Primary Liquefaction of Coal by Hydrogenation

Despite considerable work on testing catalysts for primary liquefaction of coal by hydrogenation, the high activity of the combination of tin and iodine has not been duplicated by any other catalyst or group of catalysts. The activity of tin may be due, in part, to its versatility in distributing itself throughout the solid, liquid, and gas phases of the hydrogenation system. It therefore alloys with the steel of the pressure vessel; it is found absorbed on the particles of fusain and durain and dissolved in the heavy oil; and there is some evidence that it enters the gas phase as volatile tin compounds.

A freshly machined stainless steel (18Cr-8Ni) surface enhances the activity of tin, but it is fouled after a short time by the adsorption of organic polymers of high molecular weight. In the Bureau of Mines continuously operating experimental plant a 3-inch I.D. by 96-inch-high converter was packed with stainless steel turnings. This packing increased the capacity of the plant by 50 to 100 percent for about 10 days, after which the enhanced activity due to the packing decreased for several days until the maximum throughput was about the same as with an unpacked converter. On the other hand, pumping hydrogen at 3,500 pounds per square inch and coal-oil paste plus 0.1 percent of the weight of coal of tin sulfide or tin hydroxide, through an unpacked converter, may be continued for months without any observable change in yield. It is probable, therefore, that alloying the tin with the steel of the converter wall does not contribute to the catalysis under conditions of long runs in which the steel walls are covered with a shellac-like layer of organic material of high molecular weight.

The catalysis by tin or tin alloys is not clearly understood. British investigations indicate no deterioration in the catalytic activity of acid-treated, tin-iron alloys when used for 13 consecutive small-autoclave tests, each of about 0.5 hour duration. The Bureau of Mines laboratory noted rapid deterioration of the enhanced activity of small amounts of tin in the presence of a large, alloy-steel surface after 10 days of continuous operation. Tin hydride is formed by the action of dilute solutions of organic acids on metallic tin in the presence of iron, the action being accelerated by the presence of minute amounts of halogens, such as iodine. The combination of tin and iodine is more active than either component alone. A possible mechanism that can explain most of the observed phenomena is that tin hydride reacts with cyclic olefins to form $R-SnH_2$, which decomposes to give $RH_2 + Sn$. The reaction is probably facilitated by prior saturation of the olefin bond with iodine or hydrogen iodide: $RI_2 + SnH_4 \rightarrow (RH)HSnI_2 + H_2 \rightarrow RH_2 + Sn + 2HI$.

Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide - Catalysts and Reaction Mechanism

The main components of catalysts (namely, iron, cobalt, nickel, and ruthenium) that are active in the synthesis of normally liquid hydrocarbons from hydrogen and carbon monoxide form relatively unstable carbides of nonionic crystal structures upon exposure to carbon monoxide in the temperature range of the synthesis. A critical review of literature on the

preparation and properties of metal carbides has been published.^{97/} In the formation of carbides from finely divided metals and carbon monoxide three principal reactions can be distinguished: (1) A rapid reaction proceeding on the surface before it has been converted with carbide and reaction products, (2) a slow reaction that may take weeks for completion, and (3) the formation of carbon, in addition to the carbide, if the temperature is above a characteristic value for each metal. The carbon formation continues until the iron is diluted to 1 percent of the total iron-carbon mass. All of the carbides of Fischer-Tropsch catalysts are more unstable than the true refractory carbides, such as calcium carbides. For all known Fischer-Tropsch catalysts the ratio of carbon-atom radius to metal-atom radius is equal to or greater than 0.58. The carbides of metals used as Fischer-Tropsch catalysts are more or less distorted interstitial compounds, with the carbon inserted into the interstices of the distorted metal lattice. It is almost inconceivable that carbide formation in the body of the catalyst will not profoundly modify the properties of the catalyst. The metal-to-metal distances will change. The electrical and magnetic properties will not remain the same. Hydrogen dissolved in the lattice probably will not behave the same, partly because many of the interstices in the metallic lattice are filled. The adsorption of the reagents and desorption of the products probably are modified by the carbides. Carbon formation, by carrying away active centers and producing irreducible residues on the catalyst, would tend to poison it. Whether this is really important in the Fischer-Tropsch synthesis is difficult to say at present.

The reaction between carbon monoxide and cobalt or iron or their oxides to form carbides is much too slow to account for the rate of the synthesis of hydrocarbons by reduction of the carbides with hydrogen when a mixture of hydrogen and carbon monoxide is used. It is known that the presence of hydrogen with carbon monoxide markedly accelerates the formation of carbon, which appears to proceed by way of the metal carbide. The following reaction is believed to be the main source of carbide: $2Co + CO + H_2 \rightarrow Co_2C + H_2O$. This mechanism is difficult to apply to iron catalysts, however, where the main oxygenated product is carbon dioxide rather than water, as on cobalt catalysts. Since cobalt is a much more active catalyst than iron for the water-gas reaction and because the most active iron catalysts catalyze this reaction to only a slight degree at temperatures below 300° C., it appears probably that water and carbon dioxide are primary products on cobalt and iron catalysts, respectively. Although metal carbides are formed on both cobalt and iron, there is evidence that the mechanism of the synthesis on cobalt catalysts differs from that on iron catalysts. The ratio of the partial pressures of methane to ethane plus ethylene in the off-gases from the synthesis is markedly different for different catalysts, as shown in table 17. The ratio for cobalt is almost 20 times larger than that for iron-copper. This fact should be correlated with the previous discovery that on cobalt catalysts, ethylene mixed with synthesis gas participates in the synthesis to form normally liquid hydrocarbons, whereas on an iron-copper catalyst the added ethylene appears

^{97/} Hofer, L. J. E., The Preparation and Properties of Metal Carbides with Critical Comment as to Their Significance in the Fischer-Tropsch Synthesis: Bureau of Mines Rept. of Investigations 3770, 1944, 39 pp.

largely as ethane. An investigation has been made on the correlation of the physical properties, particularly X-ray diffraction pattern and ferromagnetism, of iron catalysts with their mode of preparation and activity.

Effect of Pressure and Dilution of Synthesis Gas with Nitrogen

Under a total pressure of about 1 atmosphere, dilution of synthesis gas with nitrogen decreases the yield of liquid hydrocarbons per unit volume of gas but does not decrease the percentage of conversion. In fact, such dilution results in a conversion somewhat greater than would be calculated on the basis of a first order reaction. This is shown in table 18 which contains results of recent work in the Bureau of Mines. As the reaction is approximately first order in the absence of diluents and the reaction rate in the presence of nitrogen is somewhat greater than corresponds to the partial pressure of the synthesis gas, it appears probable that the slow step in the reaction is the desorption of the products.

TABLE 17. - Bureau of Mines analyses of residual gas from Fischer-Tropsch Synthesis after one pass through catalysts

Catalyst	Co-ThO ₂ -kieselguhr	Fe	Fe-Cu
	Percent by volume		
Methane	45.7	38.3	14.8
Ethane	3.6	4.3	24.8
Ethylene	1.1	4.4	7.3
Propane	3.6	4.1	9.7
Propylene	5.4	6.6	16.4
Butanes	.4		1.2
Butenes	.8	.9	3.0
Carbon monoxide	32.2	37.5	4.7
Hydrogen ^{a/}	1.1	1.0	3.3
Carbon dioxide ^{a/}	.3	.4	.3
Nitrogen ^{a/}	5.8	2.5	15.0
Ratio C ₁ /C ₂	9.8	4.4	.5

a/ Most of the carbon dioxide was removed by absorption in caustic before condensing the gas, and most of the hydrogen and nitrogen were separated by the condensation.

TABLE 18. - Bureau of Mines Results on Diluent effect of nitrogen using a cobalt catalyst

Nitrogen, percent	Yields in grams of oil per cubic meter	
	Observed	Calculated
1.0	101	-
16.3	88	84.5
28.8	90	72.3

An analysis of published data shows that the reaction rate is directly proportional to the partial pressure of the synthesis gas and inversely proportional to that of the products. The retardation of the rate by the