monoxide, 14.0 percent carbon dioxide, 0.6 percent methane, 2.7 percent nitrogen, and 0.2 percent oxygen.[33] The Fischer-Tropsch process can be satisfactorily operated with the content of inerts as high as twelve percent.

The principal source of mixtures of carbon monoxide and hydrogen is the reaction between steam or carbon dioxide and carbonaceous materials such as coal, coke, oil, coke-oven gas, or natural gas.[34] The average composition of water gas is 51 percent hydrogen, 40 percent carbon monoxide, 3 percent carbon dioxide, and 5 percent nitrogen and methane.

Conversion of Coke or Coal

In the older water-gas generators coke was treated with steam in a generator. Periodic blasting with air was essential to maintain the operating temperature above 1,000° C. These air-blasting operations were conducted at relatively high pressures and high space velocities so as to decrease the air-blast time to one-sixth to one-eighth of the steam blast and thereby reduce the heat losses. About 35 to 40 pounds of coke were consumed per 1,000 cubic feet of water gas produced. It was necessary to add to this coke consumption the amount necessary to produce the steam, of which about twice the theoretical amount was employed. The yield of water gas was 60,000 cubic feet per ton of coke. At Belle, W. Va., the du Pont Co. operates the largest plant in the Western Hemisphere for the production of water gas by the classical system of alternate blasting with air and steam. Until 1936 one of the largest installations of water-gas generators was that at Billingham, England. There were 21 generators, each of which produced 172,000 to 950,000 cubic feet of water gas per 24 hours from coke and steam. These generators had an inside diameter of 8.8 to 16.3 feet.

The German firms Bamag and Didier-Werke in 1936 built generators whose unit capacity was about 22 million cubic feet a day. The Didier generators were in service at the Brabag plant at Ruhland in central Germany. The Brabag plant had six generators, each with a capacity of about 900,000 cubic feet per hour. One-quarter- to one-inch non-coking coal or lignite briquets are used to react with the steam in the Didier generator. The generator is a combination of a vertical retort and water-gas generator, both being operated continuously. The bituminous coal or lignite moves downward from the hopper, and the produced retort gas that flows up through the bed of hot coke has its methane content converted by pyrolysis and reaction with steam. The resulting gaseous product is a mixture of carbon monoxide and hydrogen suitable for the Fischer process. Only such quantity of coke is produced as suffices for operating the gas producer for heating the carbonization chambers. A part of the steam is made by means of the sensible heat in the gases produced, and the remainder is obtained by the heat of reaction in the Fischer process. The composition of the product is: 9.4 percent carbon dioxide, 30.5 percent carbon monoxide, 56.5 percent hydrogen, 1.0 percent methane, 2.2 percent nitrogen, 0.2 percent oxygen, 0.2 percent C_nH_m, in which the ratio of hydrogen to carbon monoxide is 1.95. The thermal efficiency when using lignite briquets is 75.5 percent.

33/ See footnote 8.
34/ See footnotes 4 and 8.

The Pintsch-Hillebrand generator is similar to the Didier machine in that it has both a carbonization and a gasification zone. Lignite briquets pass countercurrent to a flow of a preheated mixture of steam, carbonization gas, and a fraction of the synthesis-gas product.

The Bamag generators, which were of the Winkler model, were in service at Oppau and at Mersebourg, Germany. The Winkler generator operates continuously, using 1 volume of oxygen plus 2 volumes of steam superheated to 375° C. for continuous blasting. Lignite, coal, or semi-coke, 4- to 40-mesh in size, can be used as fuel. The fuel is kept in a stage of turbulent agitation like a boiling liquid by the ascending gases consisting of air plus steam or oxygen plus steam. In this way the fuel bed, which is about 5 feet thick, is heated rapidly and uniformly. Table 2 shows the composition of the product and the consumption of raw material. The hydrogen content of the gas is about 40 percent, the remainder being oxides of carbon and nitrogen. The ratio of carbon monoxide to dioxide depends on the operating temperature and hence on the ratio of oxygen to steam, but the carbon dioxide content is usually rather high, and the gas requires further treatment to increase the hydrogen content.

TABLE 2. - Products and raw-material consumption in Winkler generator

Gas composition	Percent by volume	
	Oxygen + steam	Oxygen + air + steam
CO_2	13 to 20	15.2
CO	47 to 36	32.9
H_2	39 to 41	29.7
CH_4	0.6 to 0.4	1.3
N_2	0.4 to 0.5	20.9
Raw-material consumption per 1,000 cubic feet of product		
Coke ... pounds	40.9	33.0
Air ... cubic feet	-	242
O_2 (98 percent) ... cubic feet	284	179
H_2O ... pounds	19	13.2

About seven large Winkler gas generators were in operation in Germany, and one employed at Leuna produced 2,648,000 cubic feet of gas an hour. The chief advantage of the Winkler machine is that it will function with a wide variety of finely divided fuels, such as semicoke and lignite. In addition, its gas-generating capacity per square foot of generator surface is 5,000 to 10,000 cubic feet as compared with 1,500 cubic feet for the old-style water-gas machines.

The Lurgi process for gasifying solid fuels, using steam and oxygen under 20 atmospheres pressure, is a continuous process for producing a mixture of water gas and methane. The capacity per square foot of generator surface of the Lurgi machine is said to be about three times that of other types of water-gas generators. The gas obtained in the Lurgi machine contains 30 percent

carbon dioxide, 15 to 20 percent carbon monoxide, 30 to 35 percent hydrogen, 15 to 20 percent methane, and 2 percent nitrogen. The high operating pressure of the Lurgi generator favors the production of methane and carbon dioxide. For Fischer-Tropsch synthesis, neither of these constituents is desirable; but it is reported that conditions can be so adjusted, particularly by adding carbon dioxide in appreciable amounts to the steam-oxygen mixture, as to minimize the production of methane and to produce a gas containing 62 percent hydrogen and 31 percent carbon monoxide.

The gasification of low-temperature coke with steam seems to have been extensively practiced in Germany during 1932-9.

Anthracite and low-volatile bituminous coals can be directly gasified.[35] Using a Welsh steam coal (14.5 percent volatile matter, 7.6 percent ash, and 7.6 percent potential tar) experiments at the Fuel Research Station showed that it is possible to obtain a yield of 65,800 cubic feet of gas per ton of coal charged. A typical analysis of water gas obtained by direct gasification of Welsh steam coal showed it to contain 3.8 percent carbon dioxide, 0.2 percent C_nH_m, 39.7 percent carbon monoxide, 54.1 percent hydrogen, 0.7 percent methane, and 1.5 percent nitrogen.

Conversion of Coke-Oven and Natural Gas

The average coke-oven gas has the following composition: Carbon dioxide 3.0 percent, C_nH_m 2.0 percent, carbon monoxide 7.0 percent, hydrogen 55 percent, methane 27.0 percent, nitrogen 6.0 percent. Methane and unsaturated hydrocarbons (mainly ethylene) can be converted with steam, either at high temperature in a generator or at somewhat lower temperature in the presence of a catalyst. From 100 volumes of gas of the above composition it is possible to obtain 190 volumes of converted gas with the following composition: Carbon dioxide 4.2 percent, carbon monoxide 16.3 percent, hydrogen 75.3 percent, methane 1.0 percent, nitrogen 3.2 percent.

Natural gas, methane from coal seams, oil-refinery waste gases, low-temperature carbonization retort gas, or any other gas rich in methane can be made to react with steam, oxygen, or carbon dioxide, or any combination of these oxygenated raw materials.[36] Equilibrium relations involved in the methane-steam reaction show that above 850° C., the reaction is almost entirely confined to $CH_4 + H_2O \rightarrow CO + 3H_2$, and with an excess of steam present at a temperature of about 750° C. the reaction is mainly $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$. In the absence of catalysts, the rate of reaction of methane with steam is slow, becoming appreciable only at temperatures higher than 1,300° C. By passing methane plus steam plus carbon dioxide over a nickel catalyst at 750° C., the following reaction may be realized: $3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H_2$. Catalysts consisting of nickel deposited on a refractory mixture of alumina and clay are of satisfactory activity and durability. In the temperature range of 900° to 1,000° C., nearly theoretical conversions are obtained. For lower temperatures (750° to 850° C.) nickel-magnesia-china clay catalysts are used.

35/ See footnote 4.
36/ See footnotes 4 and 8.

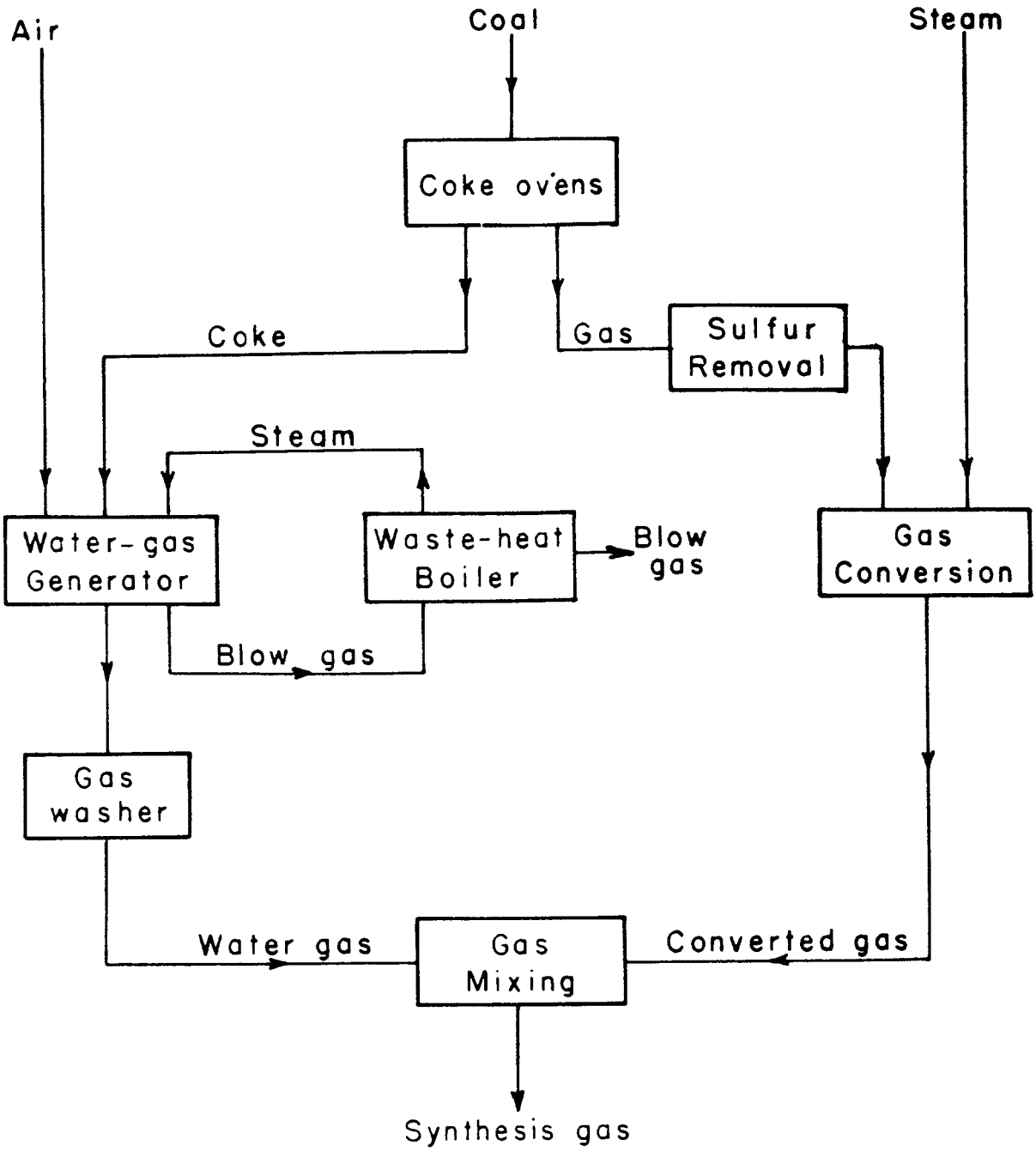

Figure 3. - Gas-production flow sheet.

Conversion to Synthesis Gas

Water gas may be converted to synthesis gas by treatment with steam. This may be carried out by passing a portion of the gas over an iron oxide catalyst at a temperature of 400° C. The carbon dioxide produced is scrubbed out with water or by reaction with ethanolamines, which are subsequently regenerated. If one-third of the water gas is converted with steam and mixed with unconverted gas, the mixed gas would have the following composition: Carbon dioxide 5.1 percent, carbon monoxide 30.0 percent, hydrogen 61.0 percent, methane 0.4 percent, and nitrogen 3.5 percent. Assuming that 1,000 cubic feet of water gas are produced from 37.3 pounds of coke, the synthesis gas would have a volume of 60,000 cubic feet per ton of coke. As the gas contains 91 percent of hydrogen plus carbon monoxide, the equivalent volume of ideal gas would be 54,600 cubic feet per ton of coke.37/

By treating 25 percent of the gas obtained by direct gasification of low-volatile coal with steam in the presence of a catalyst and mixing with the untreated gas, a synthesis gas of the following composition may be obtained: Carbon dioxide 11.5 percent, C_nH_m 0.1 percent, carbon monoxide 28.5 percent, hydrogen 58.0 percent, methane 0.5 percent, and nitrogen 1.4 percent. This gas is equivalent to 62,000 cubic feet of ideal gas a ton of Welsh steam coal.38/

In converted coke-oven gas, the hydrogen content is too high. However, if 190 volumes of converted gas are mixed with 250 volumes of water gas, 440 volumes of synthesis gas with the following composition would be obtained: Carbon dioxide 4.6 percent, carbon monoxide 30.4 percent, hydrogen 60.9 percent, methane 0.7 percent, and nitrogen 3.4 percent.39/

Carbonization of 1 ton of coal in coke ovens may be assumed to yield 14 cwt. of coke and 6,000 cubic feet of surplus coke-oven gas. All the surplus gas could be utilized if 15,000 cubic feet of water gas were added, which would require 5 cwt. of coke. The products from 1 ton of coal would then be 9 cwt. of coke in addition to 26,000 cubic feet of synthesis gas (24,090 cubic feet of ideal gas). If it were desired to utilize all the coke and coke-oven gas for the manufacture of synthesis gas, it would be best to heat the ovens with producer gas (made from coke). If 2 cwt. of coke were used for this purpose, 12 cwt. of coke and 12,000 cubic feet of coke-oven gas would remain.40/ This method of operation may be followed by referring to the diagram (figure 3).

The coke would yield 36,000 cubic feet of water gas and the coke-oven gas, on treatment with excess steam, would give 23,500 cubic feet of converted gas. The total volume of synthesis gas would be 59,500 cubic feet, with the following composition: Carbon dioxide 5.8 percent, carbon monoxide 29.9 percent, hydrogen 60.3 percent, methane 0.7 percent, and nitrogen 3.3 percent. The equivalent volume of ideal gas would be 53,640 cubic feet.41/

37/ See footnote 4.
38/ See footnote 4.
39/ See footnote 4.
40/ See footnote 4.
41/ See footnote 4.

An alternative method of operation would be to blow the water-gas generator with a mixture of steam and coke-oven gas, using 10 cubic feet of coke-oven gas per pound of steam, whereby synthesis gas is produced in one stage.[42]

Purification of Synthesis Gas

If the synthesis gas contains more than 1 grain of sulfur per 1,000 cubic fee (0.2 gram per 100 cubic meters) the catalyst deteriorates very rapidly. Sulfur is usually removed in a multistage process,[43] in which the initial step is removal of hydrogen sulfide by moist iron oxide. If four oxide boxes are employed, the gas leaving the last stage should not contain more than 0.01 grain per 1,000 cubic feet.

The second step in the desulfurizing process is the removal of organic sulfur. Part of the organic sulfur compounds may be decomposed by passing the gas over a mixture of sulfurized iron and alkal metal carbonate at 300° to 450° C., the resulting hydrogen sulfide being removed by moist iron oxide. Alternatively, the organic sulfur compounds may be removed by catalytic oxidation. A small quantity of oxygen (0.6 percent) may be mixed with the gas and the mixture passed over a nickel catalyst prepared by the deposition of nickel hydroxide on china clay. After sulfur dioxide and hydrogen sulfide have been removed the product contains about 10 grains of organic sulfur per 1,000 cubic feet. Although this sulfur content is too high for the Fischer-Tropsch process, the method may be improved by the discovery of a more efficient catalyst. Organic sulfur compounds may be catalytically reduced to hydrogen sulfide, which may then be removed by moist iron oxide in the usual manner.

The third stage is the passage of the partly desulfurized gas at 150° to 300° C., over a mixture of iron oxide and a relatively large percentage of an alkali metal carbonate.

The influence of various promoters for the iron oxide catalysts has been studied.[44] The addition of 10 percent each of sodium hydroxide and thoria greatly improved the iron oxide catalyst. A 7:3 mixture of Luxmasse (technical iron oxide) and diatomaceous earth with 30 percent sodium hydroxide at 350° C. reduced the sulfur to 0.07 gram per 100 cubic meters (after subsequent hydrogen sulfide removal). Some investigators claim to have developed satisfactory catalysts for sulfur removal by the addition of 10 percent of copper or nickel hydroxides to Luxmasse containing 10 percent of sodium hydroxide. This catalyst when used at 200° to 250° C. and at a space velocity per hour of about 250 is reported to reduce the sulfur content of synthesis gas to less than 0.2 gram per 100 cubic meters.

MANUFACTURE OF CATALYST

Catalysts containing cobalt, nickel, and iron are active for the synthesis of liquid and solid hydrocarbons from hydrogen and carbon monoxide.

42/ See footnote 4.
43/ See footnote 8.
44/ See footnote 8.

Nickel Catalysts

Mixtures of nickel, cobalt, or both, with activating materials such as alumina, thoria, or other difficulty reducible metal oxides can be used. Nickel plus 20 percent of manganese oxide and 4 to 8 percent of thoria, alumina, tungsten oxide, or uranium oxide, mixed with 1.25 times its weight of kieselguhr, yields 100 to 160 cc. of liquid hydrocarbons per cubic meter of synthesis gas per pass at a space velocity (volumes of gas per volume of catalyst per hour) of about 150 and at optimum temperatures in the range 185° to 210° C.[45] The first pilot plant operated in Germany in 1932 employed a nickel-manganese-aluminum oxide catalyst supported on kieselguhr. Nickel catalysts are best prepared by the addition of alkali carbonates to solutions of the metal nitrates in which the kieselguhr is kept in suspension by mechanical agitation; the mixture is then filtered, washed, and dried. The presence of ammonia during the precipitation of nickel-manganese-alumina catalysts increases the yield in subsequent benzine synthesis and lowers the optimum reduction temperature from 450° to 300° to 350° C.

Another method of preparing active nickel and cobalt catalysts was invented by Raney.[46] Alloys of nickel or cobalt or both with silicon or aluminum are prepared by fusion of the constituents in an induction furnace. The silicon or aluminum is subsequently dissolved by aqueous caustic soda solution, leaving a "skeleton" of nickel or cobalt, which is a highly porous, catalytically active material. The use of silicon yielded catalysts of higher activity than those obtained from aluminum alloys, according to Fischer and Meyer.[47] These investigators also reported that the optimum ratio of nickel to cobalt is 1:1 and that the presence of small amounts of copper or manganese is undesirable. The catalyst prepared from nickel, cobalt, and silicon in the ratio of 1:1:2 is very dense, with an apparent specific gravity of about 4.5, and yields about 20 percent less liquid product in the hydrocarbon synthesis than is obtained from the same weight of nickel plus cobalt in the form of the precipitated catalysts. The precipitated catalysts deteriorate more slowly than the "skeleton" alloy catalysts, which, however, are better heat conductors. Since the reaction is markedly exothermic, the improved heat conductivity would result in lower plant-installation cost with alloy catalysts.

Cobalt Catalysts

One undesirable feature of nickel catalysts is that, at operating pressures higher than 1 atmosphere, the catalyst deteriorates rapidly because of the formation of volatile nickel carbonyl. For this and other reasons, such as higher production of methane from nickel catalysts, cobalt catalysts have been used more extensively.

Cobalt catalysts containing 5 to 10 percent copper, 4 to 12 percent manganese oxide, and 4 to 12 percent thoria, alumina, or uranium oxide mixed with 1.25 times their weight of kieselguhr, yield 120 to 170 cc. of liquid

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45/ See footnote 8.
46/ See footnote 8.
47/ See footnote 8.

hydrocarbons per cubic meter of synthesis gas per pass under the same conditions of space velocity and temperature as given above for the nickel catalysts.[48] The maximum theoretical yield is about 208 grams per cubic meter of gas containing hydrogen and carbon monoxide in a 2:1 ratio. The use of cobalt catalysts generally results in a lower yield of methane and in a higher proportion of olefins in the liquid hydrocarbon product. Fischer and his coworkers have used a cobalt-copper-thoria-kieselguhr catalyst in most of their experiments. Tsutsumi[49] reported that a precipitated catalyst containing equal parts of cobalt and nickel without the addition of promoters such as thoria or alumina is a very poor one for the hydrocarbon synthesis. He stated that his most active catalyst is a mixture of equal parts of nickel and cobalt plus 20 percent manganese oxide, 20 percent uranium oxide, and 125 percent of kieselguhr (the percentages are based on the amount of nickel plus cobalt present). Tsutsumi also found that the best ratio of catalyst to kieselguhr is in the range 1:1 to 2:1. Katayama and his coworkers[50] reported that the activity of a cobalt-nickel (1:1)-manganese-uranium-thorium oxides catalyst is increased by approximately 10 percent if it was oxidized at about 20° C. by a slow stream (space velocity per hour of about 150) of air before its final reduction.

In Fischer's early experiments a cobalt-thoria-kieselguhr catalyst, 100:18:100, was used. Recent reports[51] of the Technical Oil Mission investigators reveal that the cobalt catalyst used in the large plants in Germany also contained magnesium oxide (cobalt-thoria-magnesia-kieselguhr, 100:5:8:180 to 200). Cobalt is best for the normal (atmospheric) pressure synthesis, iron having been found unsuitable. Cobalt and iron can be used in the middle (up to 10 atmospheres) pressure synthesis. Nickel cannot be used at pressures higher than atmospheric, as the volatile nickel carbonyl which is formed is lost by the system.[52] The synthesis gas usually consists of $2H_2 + 1CO$ for cobalt catalysts and $1H_2 + 1CO$ for iron catalysts. The primary product of normal- and middle-pressure synthesis is Kogasin, which is composed largely of straight-chain paraffin and olefin hydrocarbons. The percentage of olefins decreases in the order iron, cobalt, nickel (60, 40, and 5 percent, respectively). Increase in the H_2:CO ratio increases the degree of saturation of the product, and a large increase leads to the formation of large quantities of methane. The yield of olefins is inversely proportional to the hydrogen content of the synthesis gas. The effect of increasing the carbon monoxide:hydrogen ratio is to produce more olefins and carbon dioxide.

The catalyst used at the Currieres-Kuhlmann plant at Harnes, France, contained 18 percent cobalt, 1.8 magnesia, 0.9 thoria, and 79.3 kieselguhr. This analysis is for the catalyst in the unreduced form before hydrogenation; after the catalyst is hydrogenated, it is extremely pyrophoric.

48/ See footnote 8.
49/ See footnote 8.
50/ See footnote 8.
51/ National Petroleum News, Fischer-Tropsch Process, TIIC, Index 373: Vol. 37, No. 45, 1945, sec. 2, pp. R922-R924.
52/ See footnote 6.

The raw materials used in preparing the cobalt catalyst must be pure. Small traces of impurities, such as calcium oxide and iron, are deleterious. The cobalt must be at least 99 percent pure. The remaining 1 percent is either copper or nickel. The thorium oxide must not contain even traces of lead or phosphorus. The calcium oxide content must be less than 0.2 percent by weight. The kieselguhr used must not contain iron or lime, and the silicon dioxide content must exceed 92 percent. All organic matter must be removed by roasting. At the Harnes plant the German kieselguhr from Kieselguhr-Industrie-Hannover No. 120 was preferred. Johns-Manville Filtracel was acceptable; it was chemically purer than the German material, but its size was not controlled as accurately. Finally, the nitric acid used must be made from distilled water in order to avoid all traces of calcium oxide.

The Technical Oil Mission investigators obtained a description of the catalyst manufacture at the Harnes plant.53/ The raw materials, cobalt metal and magnesium and thorium oxides, were placed in one of a series of three mixing tanks, along with the required quantity of 36° B. nitric acid and up to 1,000 liters of distilled water. Approximately 40 to 50 kilograms of nitric acid per 100 kilograms of finished catalyst were used. The acid quantity was 20 percent in excess of that required theoretically to convert the cobalt, magnesium, and thorium oxides to nitrates.

The second tank contained 10 percent sodium carbonate solution and up to 1,000 liters of distilled water. The contents of this tank and the nitrated products of the first one were quickly and simultaneously run into the third tank, which was fitted with a mechanical agitator and heated to 100° C. The resulting mixture had a pH of 7.2, slightly on the alkaline side.

Regulation of the pH was most important, as the formation of bicarbonates was undesirable. The boiling temperature also aided in releasing carbon dioxide. The kieselguhr was added to the mixture in the third tank with vigorous stirring.

The precipitate was first washed with distilled water in a plate-type filter press and then repulped with distilled water in a horizontal mixing tank with a screw-type agitator. After suitable stirring the slurry was filtered on an Oliver rotary-type suction filter. The filter cake was then put into an extruding-type press (called "Strangpresse" by the Germans), where the water content was reduced to 6 to 8 percent. The catalyst was then dried on moving belts passing through the steam-heated drier at 120° C. The time of passage was 2 hours.

The catalyst was then crushed into granules about the size of a pea in a unit with a screen bottom, 4 millimeters mesh size, where a sweeping broom device forced the catalyst through the mesh. Dust and fines were removed in a vibrating inclined screen.

The sized catalyst particles were placed in a special type of container having conical ends piped up to a closed hydrogen circuit, so that the pellets

53/ See footnote 51.

resting on a screen tray could be easily exposed to the hot gas. The hydrogen was heated in a furnace to 350° C. before entering the container. Since reduction of the oxides and carbonates produced water, the exit gas was dried by passage successively through water-cooled coils, ammonia-cooled coils, and finally silica gel, returning to the hydrogen heater for recirculation. This step took approximately 15 minutes. The catalyst was not completely reduced to cobalt metal.

After the reduction, the reactor was cooled and filled with carbon dioxide. The contents were transferred to a closed bucket container, still in a carbon dioxide atmosphere, this precaution being necessary to prevent the reduced catalyst from catching fire. The carbon dioxide was purged from the system as soon as the hydrocarbon feed entered the reactor.

Regeneration of spent catalyst was an important phase of the Harnes-plant operation.[54] The spent catalyst, containing cobalt, cobalt oxide, magnesium oxide, thorium oxide, and kieselguhr, was treated with nitric acid which dissolved the cobalt, thoria, and magnesia. After filtration the kieselguhr residue was discarded. The filtrate was neutralized with sodium carbonate solution to a pH of 4.2. This precipitated thorium and magnesium carbonates, which were separated from the cobalt and calcium nitrates by filtration. The filtrate was treated with sodium fluoride, precipitating CaF_2, which was separated from the cobalt nitrate mother liquor by filtration. The latter was then sent to the catalyst preparation plant.

The thorium-magnesium carbonate precipitate was dissolved in sulfuric acid, and upon addition of a controlled quantity of sodium hydroxide, ferric and magnesium hydroxides were precipitated. These were separated from the thorium solution by filtration. The thorium solution contained a double salt, which upon heating to 80° C. was hydrolyzed, precipitating thorium hydroxide. The latter after washing was dissolved in nitric acid and the solution sent to the catalyst preparation plant.

Cobalt catalysts may be prepared by impregnating kieselguhr with the metal nitrates and subsequent decomposing by roasting; their activity when thus prepared is about the same as when they are produced by precipitation from aqueous solutions. It appears, however, that the precipitation method is preferable for the preparation of nickel catalysts.

Iron Catalysts

The relatively high cost of cobalt and nickel has prompted continuous research on the development of iron catalysts for the Fischer-Tropsch synthesis. During the Second World War, German investigators[55] developed an iron catalyst to be used in the Fischer-Tropsch plant which they were planning to build in Italy. The catalyst contained 100 parts of iron, 2.5 to 4 parts copper, 10 parts calcium oxide, and 15 parts kieselguhr. The catalyst was prepared from the nitrates by precipitation with sodium carbonate. Other developments

54/ See footnote 51.
55/ See footnote 24.

included synthetic ammonia-type ($Fe-Al_2O_3-K_2O$) and sintered-iron catalysts. The latter was prepared by making a paste of iron powder (obtained by decomposition of iron carbonyl) with a dilute solution of sodium borate. The extruded and dried granules were heated in a hydrogen atmosphere at 850° C. for several hours. The products obtained from iron catalysts contain large amounts of alcohols when the operating temperature is 200° to 240° C. and when extensive recycle of end gas (50 parts to 1 of fresh gas) is used. When little or no recycling is done the product is largely an olefinic oil plus large amounts (up to 50 percent of the total product) of a hard wax. At higher temperatures in the range 300° to 325° C. the product is chiefly an olefinic gasoline. Iron catalysts operated at 235° C. and 15 atmospheres pressure produce increasing amounts of paraffin wax with increased (¼ to 5 percent) alkali content. In the middle-pressure synthesis with iron catalysts the ideal synthesis-gas mixture is reported to be 60 percent CO and 40 percent H_2 ($CO:H_2=1.5:1$).[56] With such a gas mixture 150-160 grams of solids, liquids, and gasol per cubic meter of synthesis gas can be obtained.

Ruthenium Catalysts

Ruthenium catalysts operating at 100 atmospheres pressure produce a mixture of solid waxes with a melting point up to 134° C.

PROPERTIES OF THE PRIMARY FISCHER-TROPSCH SYNTHESIS PRODUCTS

The product obtained by passing a gas mixture containing hydrogen and carbon monoxide over a suitable catalyst consists of gaseous, liquid, and solid portions. The gaseous portion consists of permanent gases, such as methane and carbon dioxide, in addition to unreacted carbon monoxide and inerts initially present in the synthesis gas; there are also condensable hydrocarbons, consisting mainly of propane, butane, and C_3 and C_4 olefins. These product gases may be separated from the permanent gases by adsorption on active charcoal (atmospheric pressure) or oil scrubbing (medium pressure).

The primary product of the Fischer-Tropsch synthesis, labeled "Kogasin" by Fischer, has been shown to contain largely straight-chain paraffinic and olefinic hydrocarbons, with only very minor amounts of aromatic hydrocarbons, naphthenes, and oxygenated organic compounds. Table 3 contains data on the boiling ranges and olefin contents of the various fractions of the primary product obtained in Fischer's laboratory from a cobalt catalyst.[57] The gasoline fraction boiling from 30° to 200° C., sometimes called Kogasin I, constituted 60 percent of the total product.[58] The gasoline fraction boiling to 150° C. was collected by adsorption on active charcoal. Its density was 0.680 at 20° C.; and, in despite an olefin content of 45 percent, the octane rating was only about 55. Fischer claimed that this rating might be increased to 72 by the addition of 0.5 cc. of tetraethyl lead per liter of gasoline. The only refining necessary was a wash with alkali to remove traces of fatty acids. Typical properties of Kogasin gasoline are shown in table 4.

56/ See footnote 6.
57/ See footnote 8.
58/ See footnote 4.

TABLE 3. - Composition of Kogasin

Constituents	Percent by weight	Olefin content, percent by volume
Gasol ($C_3 + C_4$).....	8	55
Gasoline to 150° C.....	46	45
Gasoline 150° to 200° C.....	14	25
Diesel oil.....	22	10
Paraffin wax from oil (melting point 50° C.).....	7	-
Paraffin wax from catalyst (melting point 90° C.)....	3	-

TABLE 4. - Properties of Kogasin motor spirit

Tests	Results, percent
Engler distillation:.....	
To 60° C.....	7
80 C.....	24
100 C.....	43
120 C.....	52.5
140 C.....	65
160 C.....	76
180 C.....	87
Specific gravity at 15° C.	0.70
Octane number.....	45

The rest of the liquid portion comprised a Diesel oil fraction Kogasin II[59] boiling between 200° and 320° C., together with a certain amount of soft paraffin wax. The solid portion consisted of hard wax, recovered from the catalyst by means of solvents.

The desirability of operating the Fischer-Tropsch synthesis in two or more stages has been generally recognized. By this procedure production is increased by about 20 percent over the single-stage operation, and the life of the catalyst is increased. Tables 5 and 6 show the data obtained by the Ruhrchemie A. G. in Germany on a two-stage operation, the first being at atmospheric pressure and the second at several atmospheres. Little paraffin wax was produced in the first stage, but the second stage yields twice as much as was reported by Fischer.[60] The second stage produced 43 percent of oil boiling above 300° C., whereas only 15 percent of the first-stage oil boiled above that temperature. The second-stage gasoline from the charcoal scrubbers had a lower olefin content than did that of the first stage. The octane rating of the 30° to 140° C. gasoline was 62; that of the 30° to 110° C. was 67.

59/ See footnote 4.
60/ See footnote 8.

TABLE 5. - Properties of products from two-stage operation

Constituent	Boiling range, °C.	Specific gravity	Olefins, volume percent		Percent by weight of total product	
			First stage	Second stage	First stage	Second stage
Gasol ($C_3 + C_4$) ...	-	-	50	25-30	5	2
Gasoline to 150° C.	30-150	0.66	35-40	20	26.5	8
Oil over 150° C. ..	100-300	.74	12	12	26.5	11
Paraffin wax	-	.85	-	-	-	21

TABLE 6. - Distillation of Kogasin from two-stage operation

Temperature, °C.	Percent by volume	
	First stage	Second stage
30	0	0
50	8	3
100	29	14
150	47	24
200	60	35
250	75	48
300	85	57

Diesel oil can be isolated from Kogasin by simple distillation. The Diesel oil obtained has a boiling range of about 200° to 360° C., a specific gravity (at 20° C.) of 0.769, a cetene value of over 100, and a heat of combustion of 10,470 to 11,300 calories per gram (18,900 to 20,300 B.t.u. per pound). This material, because of its high heat of combustion and high cetene number, is suitable for mixing with and improving oils of lower ignitibility, such as tar oils and heavy petroleum oils. An addition of 30 to 40 percent of Fischer-Tropsch Diesel oil generally suffices.

Paraffin wax with melting points ranging from 50° to 100° C. and with molecular weights up to 2,000 are produced by the hydrocarbon synthesis on cobalt, nickel, or iron catalyst. Ruthenium is far more effective than any of these in producing solid hydrocarbons. By a single pass of synthesis gas at 1 liter per gram of ruthenium per hour over the catalyst at 195° C. and 100 atmospheres pressure, 100 grams of solid paraffin and 50 grams of oil were obtained per cubic meter of gas. The solid paraffin was snow white in the crude state and melted to a clear liquid at 118° to 119° C. Hitherto unknown solvent paraffin hydrocarbons were isolated from the crude paraffin with melting points up to 132° C. and molecular weights of 7,000 to 9,000. The highest melting point reported was in the range 132° to 134° C., corresponding to an average molecular weight of 23,000.

FURTHER TREATMENT OF FISCHER-TROPSCH PRODUCTS

The gasol fraction ($C_3 + C_4$) can be liquefied by compression and sold for heating and lighting where coal gas or electricity is not available. Alternatively, it may be subjected to isomerization to convert butane to isobutane, followed by alkylation, whereby isobutane and butylene unite to form iso-octane.

Cracking the primary product fraction boiling above 200° C by means of techniques well-known to the petroleum industry and mixing the cracked gasoline with the primary Kogasin boiling up to 200° C. will produce, in about 80-percent yield, a finished gasoline with approximately 195° C. distillation end point, 68 octane number, and 0.728 density at 15° C.

The primary product of the Fischer-Tropsch synthesis does not contain any lubricating-oil fractions, but it does contain large amounts of olefins, which can be readily polymerized to yield good lubricating oil. The following possible procedures for producing lubricating oil from the hydrocarbon-synthesis products have been tested: (1) Chlorination of the gas-oil fraction (boiling point > 200° C.) and mixing the products with aromatic hydrocarbons in the presence of aluminum chloride; (2) chlorination of the gas-oil fraction and polymerization without addition of aromatic hydrocarbons; (3) direct catalytic polymerization of the olefins produced in the synthesis; and (4) chlorination of the paraffin wax, followed by elimination of hydrochloric acid and polymerization of the resulting olefins.

The lubricating oils are as stable toward air and light as mineral lubricating oils; their stability is increased by hydrogenation. Subjected to the British Air Ministry oxidation test, the oils show a greater increase in viscosity but a smaller increase in Conradson carbon than mineral lubricating oils. The properties of the lubricating oil obtained depend largely on the boiling range and olefin content of the Kogasin fraction used. The higher-boiling Kogasin fractions yield lubricating oils of the highest viscosity index. Unfortunately, the yield is small because of the low olefin content of the high-boiling Kogasin fractions. Oils made by polymerization of Kogasin fractions produced from $CO:2H_2$ are inferior to those from $CO:H_2$ Kogasin, not because of a lower olefin content of the raw material but because of difference in constitution of the olefins. The mean molecular weight of the lubricating oils ranged from 550 to 1240.

The paraffin wax produced by the Fischer-Tropsch reaction is of good quality. It can be used for the manufacture of candles or for electrical insulation, or it can be oxidized to fatty acids and hence converted into soap. By esterification with glycerol, it is possible to convert the fatty acids into edible fats.

Figure 4 represents schematically the approximate yield of products from coal by the Fischer-Tropsch synthesis, using the Ruhrchemie process.

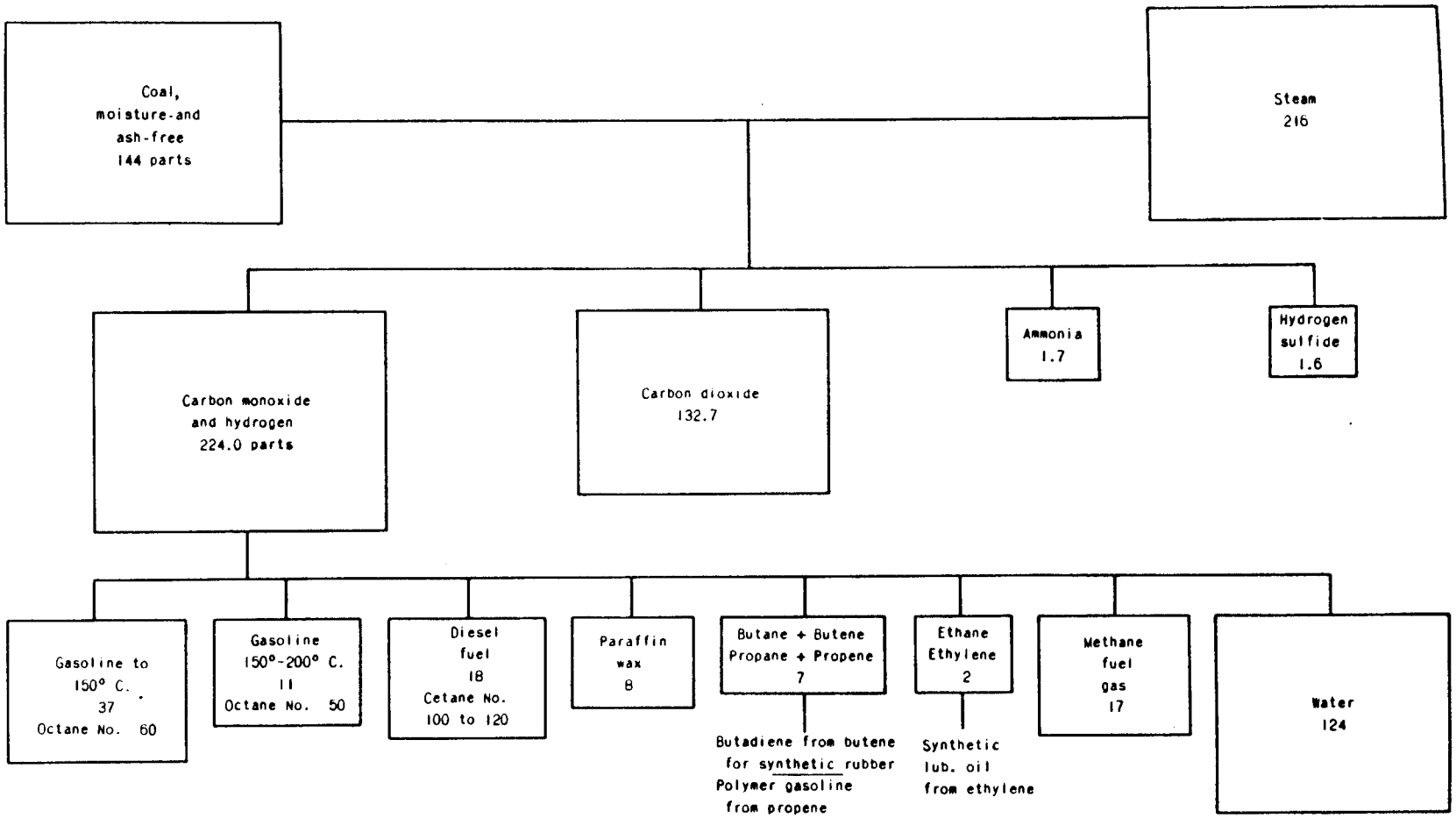

Figure 4. - Approximate yield of products from coal by Fischer-Tropsch synthesis, Ruhrchemie process.