

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 100**

**Prepared by**  
**BUREAU OF MINES**

**T. O. M. Reel No. 100**  
**Abstract Study of Special Reel 416**

**PATENT CLAIMS OF THE KAISER WILHELM INSTITUTE FOR THE SYNTHETIC  
PRODUCTION OF FUELS**

**Folders of documents containing correspondence and specifications of  
processes for which patent application is being made**

by

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**Item 20571** Process for the Production of Paraffin: F. Fischer and H. Pichler (to Studien u. Verwertungs G.m.b.H.) Germ. Appl. St. 56469, Cl. IV d/120, July 30, 1937; Nov. 23, 1943; Special Microfilm Reel 416.

The process in general refers to the production of solid paraffin from CO and H<sub>2</sub> in presence of a catalyst containing Co at a temperature below 250°C. and pressure from 2 to 50 atm. The preferred operating conditions are as follows: Synthesis gas CO:H<sub>2</sub> = 1:2; catalyst produced by precipitation and consisting of Co-Th-Kgühr; pressure 5-20 atm. with the gases remaining in the contact chamber for a period proportional to the increase in pressure that is, at 10 atm., it would remain 10 times as long as at one atm.; temps. from 180 to 200°C. The best yield, 150-160 g./m<sup>3</sup> of gas is obtained under the above conditions. (NOTE: In July 1938, a patent application was filed in Canada).

**Item 20572** Process for the Catalytic Production of Branched Hydrocarbons: Studien u. Verwertungs G.m.b.H. Germ. Appl. St. 62439, Cl. IVd/120, November 5, 1942; Special Microfilm Reel 416.

Production of branched hydrocarbons from a mixture of dimethylether and H<sub>2</sub> at temps. above 300°C. (preferably 400-500°C.) and at increased pressure (preferably above 100 atm.), using as catalyst oxides of the third and fourth groups of the periodic system (preferably ThO<sub>2</sub>). Example: A mixture of dimethylether and H<sub>2</sub> (1:5) is conducted at 450°C. and 30 atm. over a Th catalyst produced by precipitation from a Th nitrate solution with soda resulting in a conversion of 12 percent of the dimethylether to iso-C<sub>4</sub> HOs and 15 percent to liquid hydrocarbons; at 150 atm., the conversion was 25 percent and 20 percent respectively, and at 300 atm., 35 percent and 25 percent respectively, the liquid products having an octane number of 80.

**Item 20573** Process for the Catalytic Production of Hydrocarbons: F. Fischer, H. Pichler, and K. Ziesecke (to Studien u. Verwertungs G.m.b.H.), Germ. Appl. St. 62438, Cl. IVd/120, November 5, 1942, Addition to St. 61125; Special Microfilm Reel 416.

The method of St. 61125 for the production of branched hydrocarbons from CO and H<sub>2</sub> using ThO<sub>2</sub> as the catalyst has been improved by substituting pressures preferably above 100 atm. (200 to 500 atm.) and temperatures of 350 to 450°C. Under these conditions, liquid, branched, aliphatic, and cyclic hydrocarbons are almost entirely produced. For the production of an active catalyst basic Th(CO<sub>3</sub>)<sub>2</sub> is precipitated from a dilute Th(NO<sub>3</sub>)<sub>3</sub> solution with soda, and the precipitate thoroughly washed free from alkali with boiling water and dried at 300°C. in a stream of air.

Item 20574 Process for the Production of Antiknock Hydrocarbons: F. Fischer, H. Pichler, and K. Ziesecke (to Studien u. Verwertungs G.m.b.H.), Germ. Appl. 62589, Cl IVd/12o, December 14, 1942, Special Microfilm Reel 416.

In the production of branched aliphatic hydrocarbons from CO and H<sub>2</sub> (cf. St. 62438) with a ThO<sub>2</sub> catalyst, the Th can be replaced wholly or in part by other oxides from the third to the sixth group, that is, the oxides of Al, W, Zr, or the rare earths. At pressures between 200 and 500 atm. and temperatures above 350°C., these catalysts will produce branched, aliphatic hydrocarbons, and at still higher temperatures, cyclic hydrocarbons. The activity of the catalyst is increased by adding a small amount of ZnO (Al<sub>2</sub>O<sub>3</sub>:ZnO = 4:1). By passing synthesis gas at the rate of 400 liters/liter of catalyst/hr. at 300 atm. and 410°C., a yield of 100 g./Nm<sup>3</sup> of inert-free gas of gasol and liquid hydrocarbons is obtained. These liquid products consist almost entirely of branched, aliphatic hydrocarbons, 80 percent of which are iso-butane and iso-butene.

Item 20575 Process for the Production of Solid, Liquid, and Easily Liquefied Aliphatic Hydrocarbons from CO and H<sub>2</sub>: F. Fischer and H. Pichler (to Studien u. Verwertungs G.m.b.H.) Germ. Appl. St. 56470, Cl IVd/12o, July 30, 1937, July 20, 1944, Special Microfilm Reel 416.

A synthesis gas consisting of CO:H<sub>2</sub> = 3:2 is passed over an Fe catalyst at 2-50 atm. pressure and below 320°C. The catalyst consists of Fe and Cu in proportions of 4 to 1; it is made by dissolving iron-II-chloride and copper-II-chloride in water, precipitated with Na<sub>2</sub>CO<sub>3</sub>, washed until free from alkali, impregnated with 0.125 percent K<sub>2</sub>CO<sub>3</sub>, dried at 110°C., granulated and deposited on a carrier. Induction of the catalyst takes place at above 200°C., and a pressure below that of the succeeding synthesis (or at 240°C. and atm. pressure) with synthesis gas in the vol. ratio of CO:H<sub>2</sub> = 1:2, and until the gas contraction attains a maximum of about 30 percent in about 3 days time. The following conversion may then be carried out at 15 atm. and 260°C. with a synthesis gas of composition CO:H<sub>2</sub> = 3:2 and at a rate of 400 liters of gas/kg.Fe/hr. Contraction amounts to 50 percent, and the yield of hydrocarbons to 130-150 g./m<sup>3</sup> gas, of which 80-90 grams are solid and liquid hydrocarbons and 50 grams of easily liquefiable benzene.

(NOTE: In a letter of Dec. 14, 1940, it is stated that the Applications St. 56470 and 56856 have been combined and patents have been granted in Argentina 49042; Belgium 429337; England 518614; French 841043; Italy 363998, 367973; Hungary 122138, 123067; South Africa 908/38, 1478/38; South Rhodesia 75/38. Further applications are pending in U.S., Australia, Bohemia, Brazil, India, Canada, Chile, Holland, Japan, Manchuko, Norway, Sweden, and Spain.)

Item 20576 is a continuation of 20575 having the same application number St. 56470.

Item 20577 Process for the Production of Hydrocarbons from Carbon Monoxide and Hydrogen: F. Fischer and H. Pichler (to Studien u. Verwertungs G.m.b.H.) Germ. Appl. St. 60409, Cl IVd/12o, January 22, 1941, Special Microfilm Reel 416.

Higher hydrocarbons are produced by carrying out the process at pressures above atm. (10-30 atm.) and at temperatures of 180 to 230°C. over Fe catalysts and with a synthesis gas of composition  $\text{CO}:\text{H}_2 = 1:3$  or 4. The catalyst is prepared by precipitation from Fe nitrate and pretreated at 0.1 atm. and 325°C. with CO. By carrying out the synthesis in 2 or 3 repeated steps, the yield of liquid products can be increased from 60-70 g./m<sup>3</sup> of gas to 110 and 140 grams respectively.

Item 20578 Process for the Production of Higher Hydrocarbons from Carbon Monoxide and Hydrogen under Increased Pressure: F. Fischer and H. Pichler (to Studien u. Verwertungs-G.m.b.H.) Germ. Patent-738091, Cl-120.1.03, August 2, 1943; Appl. St. 58896, Cl IVD/120, July 7, 1939, July 1, 1943. Special Microfilm Reel 416.

Fe catalysts are used for synthesizing hydrocarbons from CO and H<sub>2</sub> at 10-30 atm. and 200-300°C. Before use, the catalyst is pretreated with CO or gases containing CO at 230-350°C. and a pressure amounting to a fraction of 1 kg./sq. cm. The catalyst is prepared by precipitation from Fe nitrate solution and contains a few 0.1 percent of alkali. The time of pretreatment is about 24 hours at a rate of 400 liters of CO/kg. of Fe/hour. The best synthesis results are obtained with a gas of composition  $\text{CO}:\text{H}_2 = 1.8:1$ , a pressure of 15 kg./sq.cm. and a temperature of 235°C. The gas contraction amounts to 55 percent with practically a complete conversion of the CO. Yields of solid, liquid, and gasol hydrocarbons are 150 g./m<sup>3</sup> of CO + H<sub>2</sub> mixture, without any lessening of catalyst activity in 3 months of operation.

Item 20579 Process for the Production of Hydrocarbons from Carbon Monoxide and Hydrogen: F. Fischer and H. Pichler (to Studien u. Verwertungs G.m.b.H.), Germ. Appl. St. 56856, Cl IVD/120, November 25, 1937, Special Microfilm Reel 416.

Higher hydrocarbons are produced by synthesis from a gas mixture containing CO and H<sub>2</sub> in at least equal proportions at temperatures of 230-320°C. and pressures of 2-100 atm. in presence of an Fe catalyst which has been pretreated at ordinary pressure or at any other pressure lower than that at which the succeeding synthesis is carried out, by CO or a gas containing it at about 250°C., and until the gas contraction has attained about 30 percent. The catalyst is prepared by thermal decomposition up to 300°C. of Fe nitrate and contains about 0.25 of K<sub>2</sub>CO<sub>3</sub> based on the Fe content.

Item 20580 A Process for the Conversion of High-boiling Hydrocarbons into Lower-boiling Hydrocarbons: F. Fischer, H. Koch, and W. Gilfert (to Studien u. Verwertungs G.m.b.H.), Germ. Appl. St. 63927, Cl IVD/120, March 8, 1944, Special Microfilm Reel 416.

As catalyst for the cracking-hydrogenation process, use is made of a mixture of water-free AlCl<sub>3</sub> and water-free HCl in the vol. proportions of one AlCl<sub>3</sub> to 0.5 or more of HCl. The process is carried out at a temperature below 200°C. (preferably at 100°C. or below) and under a partial pressure of hydrogen of at least 50 atm. Example: 25 g. of a synthesis product from CO and H<sub>2</sub> boiling between 200 and 450°C. and free from olefins were treated in a glass-lined autoclave with 17 grams AlCl<sub>3</sub> and 31 g. HCl under a H<sub>2</sub> pressure at 50°C. of 200 atm. After a 2-hour treatment and separation of the mixture, the HC had the following composition in weight percent: 38 percent isobutane, 21 percent isopentane, 19 percent isohexane, 11 percent isooctane, 4 percent iso-octane, 7 percent isononane, and higher-boiling isoparaffins. Other examples are given.

Item 20581 Process for the Production of Solid, Liquid, and Easily-liquefiable Aliphatic Hydrocarbons from Carbon Monoxide and Hydrogen: F. Fischer and H. Pichler (to Studien u. Verwertungs G.m.b.H.), Germ. Appl. St. 61859, Cl IVd/12o, May 5, 1942; Special Microfilm Reel 416.

For the production of the hydrocarbons an Fe catalyst is used which has been pretreated with CO at temperatures between 200 and 500°C. preferably between 240 and 325°C., and at atm. pressure. The catalyst is prepared by precipitation from an Fe nitrate solution by means of soda, the precipitate washed until free from alkali, alkalinized by 0.125 percent  $K_2CO_3$ , dried at 110°C. and granulated. The induction is performed at atm. pressure and 260-290°C. by passing over it, 400 liters per hour of CO until CO<sub>2</sub> formation attains a constant value, followed by conversion with 400 liters per hour of synthesis gas (CO:H<sub>2</sub> = 3:2) at 15 atm. and 240°C. The gas contraction amounts to 50 percent and a yield of 130-150 g./Nm<sup>3</sup> of synthesis gas is obtained.

Item 20582 Process for the Production of Solid Aliphatic Hydrocarbons: F. Fischer and H. Pichler (to Studien Verwertungs G.m.b.H.), Germ. Patent 705528, April 30, 1941, Cl 12o. 1.03, Appl. St. 57429, Cl IVd/12o, May 10, 1938, March 27, 1941; Special Microfilm Reel 416.

A process for the production of solid aliphatic hydrocarbons from H<sub>2</sub> and the C oxides at temperatures below 300°C., preferably between 150 and 280°C., and at increased pressure, particularly above 30 atm., using a catalyst of Ru or one containing it. The catalyst is prepared by conversion of metallic Ru with caustic-potash and K nitrate into K ruthenate, which is dissolved in water and converted at boiling temperature with MeOH into Ru dioxide which is precipitated, filtered, washed, and dried. Reduction takes place with synthesis gas (CO:H<sub>2</sub> = 1:2) at atm. pressure and about 150°C. At a temperature of 195°C. and 100 atm. pressure, one liter of CO-H<sub>2</sub> mixture per gram Ru per hour is passed over the catalyst yielding per cubic meter of gas 150-160 grams of hydrocarbons, 2/3 of which is solid, oil-free paraffin, the rest liquid hydrocarbons. The life of the catalyst is practically unlimited. The paraffin is white and melts at 118-120°C.

Item 20583 is a continuation of 20579 having the same Appl. Number St. 56856.

Item 20584 Process for Producing Iron Catalysts: F. Fischer and H. Pichler (to Studien u. Verwertungs G.m.b.H.), German Appl. St. 60795, Cl IVd/12o, May 23, 1941, Special Microfilm Reel 416.

A process for the production of precipitated Fe catalysts for the synthesis of hydrocarbons from H<sub>2</sub> and the C oxides consisting in decomposing an Fe salt solution at temperatures below 50°C. with soda to such an extent that no precipitate is formed and then heating the solution to boiling after the following precipitation step. The precipitate is then washed, alkalinized with 0.125-1 percent  $K_2CO_3$  and dried at 100-120°C. Example: 1 kg. of an acid Fe nitrate solution obtained by dissolving 900 grams of Fe shavings in 10 liters of dilute HNO<sub>3</sub> (d. 1.12) is decomposed at room temperature in 4 liters of soda solution. The Fe solution

becomes dark red without a precipitate being formed. The solution is filtered, and 10 liters of the solution are diluted with 25 liters of water and heated to boiling, made slightly alkaline, and after precipitating, heated to boiling for one minute. The precipitate is then filtered and washed until alkali-free and then alkalized with 0.25 percent of  $K_2CO_3$  and dried at  $110^\circ C$ . The completed catalyst is solid, dark-brown to black in color, and shows a lustrous fracture. Before use for the synthesis process, the catalyst is pretreated for 3 days with a 1:2 mixture of  $CO:H_2$  at  $250^\circ C$ . and 1 atm. On passing a synthesis gas of  $CO:H_2 = 3:2$  over it at 15 atm. and  $250^\circ C$ ., 150 grams of solid, liquid, and gasol hydrocarbons are obtained per cubic meter of gas. The catalyst will last for many years.

Item 20585 Process for Producing Formic Acid from Carbon Monoxide and Water: F. Fischer, H. Pichler, and H. Buffleb, (to Studien u. Verwertungs G.m.b.H.), German Appl. St. 61649, Cl IVd/120, March 14, 1942, Special Microfilm Reel 416.

A process for the production of formic acid from CO or CO-containing gases and water in the liquid phase, at high pressures preferably above 1000 atm. and at temperatures not over  $200^\circ C$ . in presence of a catalyst consisting of 1-10 N  $H_2SO_4$ , preferably about 5 N.