[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons and their Derivatives from Mixtures of Hydrogen and Oxides of Carbon.

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

It has already been proposed to react carbon monoxide with hydrogen at elevated temperature and under ordinary pressure in the presence of iron or substances containing iron as catalysts, whereby paraffin hydrocarbons are mainly formed. According to another process in which the said initial materials are reacted under increased pressure, products containing oxygen are mainly obtained. The catalysts employed for this process are generally speaking readily friable and greatly sensitive to mechanical strain.

My foreign correspondents have now found that the formation of hydrocarbons or their derivatives from mixtures of carbon monoxide and hydrogen proceeds with very good yields not only at atmospheric pressure but also, contrary to expectation, at increased pressure by carrying out the reaction at elevated temperature in the presence of catalysts which have been obtained by the treatment of fused ferrosoferric oxide with reducing gases, advantageously with hydrogen or gases containing hydrogen, at temperatures above 300° Centigrade. The catalysts thus prepared are very hard and solid and have a very good activity. The fused ferrosoferric oxide used for their preparation is preferably obtained by fusing metallic iron (which is advantageously in a comminuted state, as for example in the form of chips) in a current of oxygen. The products obtained with these catalysts consist mainly of hydrocarbons, especially those of an unsaturated nature, and contain only small amounts of substances containing oxygen.

The said catalysts have a specially high activity when they are prepared while using activating additions. It has been found that in particular titanium and silicon or their compounds, as for example titanium dioxide or silicon dioxide, have a very strong activating action for the present purpose. Other good activators are uranium, manganese, tungsten, chromium and molybdenum and their compounds, as well as copper and silver and their compounds, or potassium, calcium, magnesium and barium and their compounds. These additions may all be used in an amount of up to 20 per cent. with reference to the iron. Small amounts, up to about 6 per cent., of nickel and cobalt and compounds of these metals are also advantageous.

Catalysts which contain as additions two or more of the said metals or their compounds have a specially favourable action. Of these, those are advantageous which contain titanium or silicon or their compounds or both of the said elements or their compounds together. Generally speaking the catalysts contain besides iron a suitable amount, up to 20 per cent., of silicon or titanium or both elements, if desired in the form of their compounds, also a heavy metal other than iron and an alkali metal, in particular potassium; they advantageously also contain an alkaline earth metal and, if desired, a small amount of cobalt or nickel as a further addition. A small addition of tin or lead counteracts very well the deposition of carbon in the catalysts. The said elements to be added can naturally also all be used in the form of their compounds. A moistening of the mass before fusion effects an increase in the activity in many cases.

The method of preparing the catalysts is simple and is preferably effected by mixing the iron powder or chips with the activating additions, transferring the mixture to a suitable crucible, preferably into a double-walled water-cooled iron crucible, igniting a piece of paper or wood therein and then immediately blowing thereon a strong current of oxygen. By reason of the great heat of reaction of the combustion of the iron with oxygen, the

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mass becomes incandescent until almost all the iron has been converted into the ferrosoferric oxide.

The fused ferrosoferric oxide containing the said activating additions is treated with reducing gases before use, either in the furnace in which the reaction with the gases containing carbon monoxide is to be carried out or in a special apparatus. In many cases it is advantageous to add ammonia to the reducing gas. The treatment with the reducing gases may be carried out at ordinary or increased pressure. At ordinary pressure the temperature is comparatively high, usually between 450° and 850° Centigrade, while at increased pressure it usually lies above 400° Centigrade.

The products obtained according to this invention by the treatment of the mixtures of hydrogen and carbon monoxide contain, in addition to carbon dioxide, a little water and small amounts of oxygen-containing hydrocarbon derivatives, mainly hydrocarbons which are for the greater part unsaturated and for the lesser part saturated.

It is preferable during the reaction of the hydrogen with the carbon monoxide in the presence of the said catalysts to lead away the heat of reaction rapidly because otherwise the catalysts may be over-heated to the point at which they sinter together. The reaction temperature is advantageously at from about 300° to 420° Centigrade and the pressure is preferably above 50 atmospheres, advantageously between 100 and 250 atmospheres. Atmospheric pressure may, however, also be used as already described.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples.

EXAMPLE 1.

1000 grams of iron powder obtained by the decomposition of iron carbonyl, 50 grams of uranyl nitrate and 50 grams of titanium dioxide are fused in a water-cooled iron crucible by means of oxygen. After cooling the melt constitutes a solid and hard mass. It is broken up into grains having a size of from 5 to 10 millimetres and treated at 460° Centigrade with hydrogen.

330 cubic centimetres of the catalyst thus obtained are spread out in a layer of from about 1 to 2 centimetres in thickness between two flat heating spirals of copper tube in a high-pressure furnace and a gas mixture containing about 50 per cent. of carbon monoxide and 50 per cent. of hydrogen is led through the catalyst downwards. The superheated steam for the heating and for the withdrawal of the heat of reaction is led through the heating spirals. In the catalyst chamber, a pressure of from 75 to 80 atmospheres and a temperature of from 370° to 410° Centigrade is maintained; the gas flows through the chamber at a speed of 300 litres per hour (calculated with reference to the final gas). The final gas contains per litre on an average 73 cubic centimetres of liquid oil and 157 cubic centimetres of hydrocarbons capable of condensation at atmospheric pressure at 80° below zero Centigrade and being, similarly to the oil, mainly of an olefinic nature. The oil obtained still contains 2.3 per cent. of oxygen; it has an iodine value of 110. The composition of the final gas after the condensation of the fraction which liquefies at ordinary temperature is:

38.3 per cent. by volume of CO_2
5.1 ,, ,, ,, ,, ,, C_nH_{2n} (n being more than 2)
18.4 ,, ,, ,, ,, ,, CO
24.0 ,, ,, ,, ,, ,, H_2
10.2 ,, ,, ,, ,, ,, $C_nH_{2n}+2$ ($n=1.3$) and
3.7 ,, ,, ,, ,, ,, N_2.

About 5 per cent. of alcohols are contained in the aqueous fraction of the liquid product which amounts to 71 cubic centimetres per cubic metre of final gas.

EXAMPLE 2.

1000 grams of iron powder, 5 grams of titanium dioxide, 5 grams of uranyl nitrate and 10 grams of calcium oxide are fused in a current of oxygen in a water-cooled iron crucible. After cooling, the resulting melt is comminuted, treated at 460° Centigrade with hydrogen, oxidised with air at the same temperature and then again treated with hydrogen at the same temperature.

1075 cubic centimetres of the resulting catalyst are placed in eight layers, each of 4 centimetres thickness, within a high-pressure furnace of 100 millimetres internal diameter on a heating coil through which superheated steam is forced. A mixed gas containing from 47 to 50 per cent. of carbon monoxide and from 53 to 50 per cent. of hydrogen is led in such an amount at from 380° to 410° Centigrade under a pressure of from 50 to 100 atmospheres through the furnace that 500 litres of final gas per hour are obtained. There are thus obtained from 50 to 70 grams of oil, 60 to 90 grams of hydrocarbons of low boiling point and 100 grams of water per cubic metre of final gas. The oil contains from 0.11 to 0.5 per cent. of oxygen and has a saponification value of from 1.9 to 4.5 and an iodine value of 155. The hydrocarbons of low boiling point consist mainly of olefines containing from 3 to 5 carbon atoms.

EXAMPLE 3.

1000 grams of iron powder are mixed with 50 grams of silicon powder, 50 grams of tungstic acid, 1 gram of nickel oxide, 50 grams of potassium hydroxide and 50 grams of water, the mixture then being fused in a current of oxygen. The melt is cooled and comminuted and then treated at 650° Centigrade with a mixture of 2 parts of hydrogen and 1 part of ammonia.

The catalyst thus obtained is charged as a layer 250 millimetres in length into a high-pressure tube 500 millimetres long and 16 millimetres in internal diameter. A gas mixture containing 34 per cent. of carbon monoxide and 66 per cent. of hydrogen is then led through at a temperature of from 350° to 400° Centigrade under a pressure of from 110 to 150 atmospheres. The final gas obtained is obtained in an amount of 10 litres per hour. It has the following composition :—

23.0 per cent. by volume of CO_2
4.4 ,, ,, ,, ,, ,, C_nH_{2n} (n being more than 2)
2.6 ,, ,, ,, ,, ,, CO
47.0 ,, ,, ,, ,, ,, H_2
19.0 ,, ,, ,, ,, ,, CH_4 and
4.0 ,, ,, ,, ,, ,, N_2

I cubic metre of final gas contains 360 cubic centimetres of oil and hydrocarbons of low boiling point and 54 cubic centimetres of water.

Dated this 22nd day of November, 1935.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons and their Derivatives from Mixtures of Hydrogen and Oxides of Carbon.

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement :—

It has already been proposed to cause carbon monoxide to react with hydrogen at elevated temperature and under ordinary pressure in the presence of iron or substances containing iron as catalysts, mainly paraffin hydrocarbons being thereby formed. According to another process in which the said initial materials are brought into reaction under increased pressure, hydrocarbon derivatives containing oxygen, in particular alcohols, or also aldehydes, ketones, organic acids and the like are mainly obtained. The catalysts employed for this process are generally speaking readily friable and greatly sensitive to mechanical strain.

My foreign correspondents have now found that the formation of gaseous and in particular of liquid hydrocarbons contingently together with their derivatives containing oxygen, from mixtures of carbon monoxide and hydrogen proceeds with very good yields not only at atmospheric pressure but also, contrary to expectation, at increased pressure by carrying out the reaction at elevated temperature in the presence of catalysts which have been obtained by the treatment of fused ferrosoferric oxide with reducing gases, advantageously with hydrogen or gases containing hydrogen, at temperatures above 300° Centigrade and which preferably contain activating additions. It has been found that titanium and silicon are particularly suitable as activating additions. The catalysts thus prepared are very hard and solid and have a very good activity. The fused ferrosoferric oxide used for their preparation is preferably obtained by fusing metallic iron (which should be advantageously in a comminuted state, as for example in the form of powder or of chips) in a current of oxygen. But the said oxide may also be prepared from any desired iron compound which is capable of yielding by fusing or subsequent cooling a melt consisting of or containing ferrosoferric oxide; as such compounds there may be mentioned in particular ferrosoferric oxide itself or ordinary iron oxide from which at the melting temperatures oxygen is set free, or the substance often called ferrous oxide which is not existent as an individual compound under ordinary conditions but represents a mixture of ferrosoferric oxide and metallic iron (see Handbuch der Anorganischen Chemie by Gmelin, Volume on Iron, part B, page 26). The products obtained with these catalysts consist mainly of hydrocarbons, especially those of an unsaturated nature, and usually contain only small amounts of substances containing oxygen.

The said catalysts have a specially high activity when they are prepared while using activating additions. As already stated, titanium and silicon or their compounds, as for example titanium dioxide or silicon dioxide, have a particularly strong activating action for the present purpose. Other good activators are uranium, manganese, tungsten, chromium and molybdenum and their compounds, as well as copper and silver and their compounds, or alkali metals or alkaline earth metal, such as potassium, calcium, magnesium and barium, and their compounds. These additions may all be used in an amount of up to 20 per cent. with reference to the iron. Small amounts, up to about 6 per cent. of nickel and cobalt and compounds of these metals are also advantageous.

Catalysts which contain as additions two or more of the said metals or their compounds have an especially favourable action. Of these, those are advantageous which contain titanium or silicon or their compounds or both of the said elements or their compounds together. Generally speaking the catalysts contain besides iron a suitable amount, up to 20 per cent., of silicon or titanium or both elements, if desired in the form of their compounds, also a heavy metal other than iron and an alkali metal, in particular potassium; they advantageously also contain an alkaline earth metal and, if desired, a small amount of cobalt or nickel as a further addition. A small addition of tin or lead counteracts very well the deposition of carbon in the catalysts. The said elements to be added can naturally also all be used in the form of their compounds. A moistening of the mass before fusion effects an increase in the activity in many cases.

The method of preparing the catalysts is simple and is preferably effected by mixing the iron powder or chips with the activating additions, transferring the mixture to a suitable crucible, preferably into a double-walled water-cooled iron crucible, igniting a piece of paper or wood therein and then immediately blowing thereon a strong current of oxygen. By reason of the great heat of reaction of the combustion of the iron with oxygen, the mass becomes incandescent until almost all the iron has been converted into the ferrosoferric oxide.

The fused ferrosoferric oxide containing the said activating additions is treated with reducing gases before use, in particular with hydrogen or with gaseous hydrocarbons, such as methane or ethane either in the furnace in which the reaction with the gases containing carbon monoxide is to be carried out or in a special apparatus. In many cases it is advantageous to add ammonia to the reducing gas. The treatment with the reducing gases may be carried out at ordinary or increased pressure (for example 5 or 20 or 50 atmospheres, and preferably of the range of 100 or 200 atmospheres or still higher). At ordinary pressure the temperature is comparatively high, usually between 450° and 850° Centigrade, while at increased pressure it usually lies above 400° Centigrade.

The products obtained according to this invention by the treatment of the mixtures of hydrogen and carbon monoxide contain, in addition to carbon dioxide, a little water and small amounts of oxygen-containing hydrocarbon derivatives, mainly hydrocarbons which are for the greater part unsaturated and for the lesser part saturated.

It is preferable during the reaction of the hydrogen with the carbon monoxide in the presence of the said catalysts to lead away the heat of reaction rapidly because otherwise the catalysts may be overheated to the point at which they sinter together. The reaction temperature ranges between 150° and 500° Centigrade and advantageously between about 275° or 300° and 425° Centigrade, and the pressure is preferably above 50 atmospheres, advantageously between 100 and 250 atmospheres. Atmospheric pressure may, however, also be used as already described. The ratio of the amounts of carbon monoxide and hydrogen in the initial gases may vary greatly. Suitable ratios are for example from 1 to 3 parts of hydrogen with from 3 to 1 parts respectively of carbon monoxide. The preferred ratios are from 4 to 6 parts of hydrogen with from 6 to 4 parts respectively of carbon monoxide.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples.

EXAMPLE 1.

1000 grams of iron powder obtained by the decomposition of iron carbonyl, 50 grams of uranyl nitrate and 50 grams of titanium dioxide are fused in a water-cooled iron crucible by means of oxygen. After cooling, the melt constitutes a solid and hard mass. It is broken up into grains having a size of from 5 to 10 millimetres and treated at 460° Centigrade with hydrogen.

330 cubic centimetres of the catalyst thus obtained are spread out in a layer of from about 1 to 2 centimetres in thickness between two flat heating spirals of copper tube in a high-pressure furnace and a gas mixture containing about 50 per cent. of carbon monoxide and 50 per cent. of hydrogen is led through the catalyst downwards. The superheated steam for the heating and for the withdrawal of the heat of reaction is led through the heating spirals. In the catalyst chamber, a pressure of from 75 to 80 atmospheres and a temperature of from 370° to 410° Centigrade is maintained; the gas flows through the chamber at a speed of 300 litres per hour (calculated with reference to the final gas). The final gas contains per litre on an average 73 cubic centimetres of liquid oil and 157 cubic centimetres of hydrocarbons capable of condensation at atmospheric pressure at 80° below zero Centigrade and being, similarly to the oil, mainly of an olefinic nature. The oil obtained still contains 2.3 per cent. of oxygen; it has an iodine value of 110. The composition of the final gas after the condensation of the fraction which liquefies at ordinary temperature is :—

38.3 per cent. by volume of CO_2
5.1 ,, ,, ,, ,, ,, C_nH_{2n} (n being more than 2)
18.4 ,, ,, ,, ,, ,, CO
24.0 ,, ,, ,, ,, ,, H_2
10.2 ,, ,, ,, ,, ,, $C_nH_{2n}+2$ (average value of n being 1.3)
and 3.7 ,, ,, ,, ,, ,, N_2.

About 5 per cent. of alcohols are contained in the aqueous fraction of the liquid product which amounts to 71 cubic centimetres per cubic metre of final gas.

EXAMPLE 2.

1000 grams of iron powder, 5 grams of titanium dioxide, 5 grams of uranyl nitrate and 10 grams of calcium oxide are fused in a current of oxygen in a water-cooled iron crucible. After cooling, the resulting melt is comminuted, treated at 460° Centigrade with hydrogen, oxidised with air at the same temperature and then again treated with hydrogen at the same temperature.

1075 cubic centimetres of the resulting catalyst are placed in eight layers, each of 4 centimetres thickness, within a high-pressure furnace of 100 millimetres internal diameter on a heating coil through which super-heated steam is forced. A mixed gas containing from 47 to 50 per cent. of carbon monoxide and from 53 to 50 per cent. of hydrogen is led in such an amount at from 380° to 410° Centigrade under a pressure of from 50 to 100 atmospheres through the furnace that 500 litres of final gas per hour are obtained. There are thus obtained from 50 to 70 grams of oil, 60 to 90 grams of hydrocarbons of low boiling point and 100 grams of water per cubic metre of final gas. The oil contains from 0.11 to 0.5 per cent. of oxygen and has a saponification value of from 1.9 to 4.5 and an iodine value of 155. The hydrocarbons of low boiling point consist mainly of olefines containing from 3 to 5 carbon atoms.

EXAMPLE 3.

1000 grams of iron powder are mixed with 50 grams of silicon powder, 50 grams of tungstic acid, 1 gram of nickel oxide, 50 grams of potassium hydroxide and 50 grams of water, the mixture then being fused in a current of oxygen. The melt is cooled and comminuted and then treated at 650° Centigrade with a mixture of 2 parts of hydrogen and 1 part of ammonia.

The catalyst thus obtained is charged as a layer 250 millimetres of length into a high-pressure tube 500 millimetres long and 16 millimetres in internal diameter. A gas mixture containing 34 per cent. of carbon monoxide and 66 per cent. of hydrogen is then led through at a temperature of from 350° to 400° Centigrade under a pressure of from 110 to 150 atmospheres. The resulting final gas is obtained in an amount of 10 litres per hour. It has the following composition :—

23.0	per cent. by volume of	CO_2
4.4	,, ,, ,, ,, ,,	C_nH_{2n} (n being more than 2)
2.6	,, ,, ,, ,, ,,	CO
47.0	,, ,, ,, ,, ,,	H_2
19.0	,, ,, ,, ,, ,,	CH_4 and
4.0	,, ,, ,, ,, ,,	N_2

1 cubic metre of final gas contains 360 cubic centimetres of oil and hydrocarbons of low boiling point and 54 cubic centimetres of water.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the conversion of mixtures of carbon monoxide and hydrogen into gaseous and/or liquid hydrocarbons, contingently together with their oxygen derivatives, which comprises contacting such a mixture at a reacting temperature with a catalyst obtained by treating previously fused ferrosoferric oxide with a reducing gas at a temperature above 300° Centigrade.

2. A process as claimed in claim 1, in which the ferrosoferric oxide contains titanium or silicon or their compounds.

3. In the process as claimed in claim 2, operating with a catalyst which, besides titanium, silicon or their compounds, contains a substance comprising a heavy metal other than titanium, preferably uranium, manganese, tungsten, chromium, molybdenum, copper or silver, or their compounds.

4. In the process as claimed in claim 2 or 3, operating in the presence of a catalyst which besides titanium, silicon or their compounds and contingently a substance comprising a heavy metal other than titanium contains a small amount of a substance comprising nickel or cobalt or their compounds.

5. In the process as claimed in any of claims 2 to 4, operating in the presence of a catalyst containing an addition of a compound of an alkali or alkaline earth metal.

6. In the process as claimed in claim 5 using potassium as the alkali metal.

7. In the process as claimed in any of claims 1 to 6, contacting the mixture of carbon monoxide and hydrogen with the catalyst under a pressure above 50 atmospheres and at a temperature between 150 and 500° Centigrade.

8. In the process as claimed in any of the claims 1 to 7, contacting the mixture of carbon monoxide and hydrogen with the catalyst under a pressure above 50 atmospheres and at a temperature between 275° and 425° Centigrade.

9. In the process as claimed in any of the claims 1 to 7 contacting the mixture of carbon monoxide and hydrogen at a reacting temperature with a catalyst obtained by treating previously fused ferrosoferric oxide with hydrogen at a temperature between 400° and 850° Centigrade.

10. The process for the manufacture and production of gaseous or liquid hydrocarbons contingently together with their oxygen derivatives, from mixtures of carbon monoxide and hydrogen substantially as described in each of the foregoing Examples.

11. Gaseous or liquid hydrocarbons contingently together with their oxygen derivatives, when obtained by the process particularly described and ascertained.

Dated this 17th day of November, 1936.
J. Y. & G. W. JOHNSON,
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