[Second Edition.]

PATENT SPECIFICATION

Application Date: Feb. 5, 1936. No. 3525/36.

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons and their Derivatives Containing Oxygen from Carbon Monoxide and Hydrogen.

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:—

The specification No. 16823 A.D. 1935 (Serial No. 458,035) describes a process according to which in the preparation of hydrocarbons and, if desired, their derivatives containing oxygen, from carbon monoxide and hydrogen, apparatus parts consisting of metal, in particular of iron, and etched on one surface are used as catalysts, the etched surface of the apparatus parts being swept by the reaction gases and the other side by a gaseous or liquid heating or cooling agent for the purpose of supplying or withdrawing the heat of reaction. In this manner especially good yields may be obtained with large conversions without a further addition of catalyst to the reaction chamber being necessary.

The said catalysts consisting of etched surfaces suffer, however, a marked diminution in their activity, in the same way as many other catalysts, after a greater or less time and finally become quite exhausted. This renders an interruption of the conversion necessary and a reactivation of the catalyst.

My foreign correspondents have now found that the exhausted catalysts consisting of etched apparatus parts can be very readily activated again by decomposing on them small amounts of volatile metal compounds which are capable of decomposing at elevated temperatures, in particular at temperatures up to 500° Centigrade, if desired in a reducing atmosphere, with the formation of metals. For this purpose the carbonyls of iron, nickel, cobalt and molybdenum have proved especially advantageous, of these iron carbonyl being the most suitable. The decomposition of the volatile metal compounds may be effected for example by vaporising a small amount of the compound in the reaction gas and decomposing the same during the conversion of the reaction gas at the usual reaction temperature. The volatile metal compounds, in particular the carbonyls, may naturally also be vaporised as such in an atmosphere of inert or reducing gas, in particular of hydrogen, and decomposed at a suitable temperature. It has been found to be especially advantageous to add very small amounts of the said volatile metal compounds continuously to the reaction gas whereby the catalyst consisting of etched surfaces is continuously regenerated. In this case it has been found to be preferable to add from about 0.01 to 10 cubic centimetres of volatile metal compound, in particular iron carbonyl, per day per litre of reaction space. The amount of metal compound to be added depends to a great extent on the reaction temperature because most volatile metal compounds, as for example iron carbonyl, leave the reaction chamber partially undecomposed. When the volatile metal compound is added not continuously but at intervals, as for example after some hours or days, amounts of from 0.1 to 1 cubic centimetre per litre of reaction space may, for example, be employed. The vaporisation of the volatile metal compounds may be effected merely by leading the gas current over the metal compound for example at from about 0° to 20° Centigrade or, naturally, it may be heated to higher temperatures when necessary. The metal compound may be vaporised as such or a solution of the compound in a solvent, as for example in alcohols, hydrocarbons, organic acids or esters, may be used for vaporisation.

It has further been found that the process according to this invention is not restricted to the use of etched apparatus parts but that good results are also obtained in the absence of catalysts not consisting of apparatus parts, i.e. for example of chips, pieces or the like filling the chamber, by adding the said volatile metal compounds, in particular carbonyls and especially iron carbonyl, continuously or also after certain intervals of time in

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small amounts when working in apparatus with unetched apparatus parts during the carrying out or temporary interruption of the conversion of carbon monoxide. For example simple cleaned tubes onto which the carbonyl is then decomposed and which may consist of any material, as for example iron, copper, aluminium or also ceramic materials, such as glass, porcelain, quartz materials or enamelled metals; or may be coated with the same, are sufficient.

The yields of hydrocarbons and their derivatives containing oxygen when using non-etched apparatus parts for the conversion are, indeed, not as high as those obtained with etched apparatus parts but the metals formed by the decomposition of the volatile metal compounds and deposited on the surfaces of the apparatus parts obviously exert a catalytic action on the conversion in the case of unetched apparatus parts, the said action leading to a good yield of the desired products.

It is advantageous to carry out the process at increased pressures, especially at pressures of more than 20 atmospheres. The temperatures to be used are those usual for the conversion, namely between 150° and 500°, advantageously between 250° and 400° Centigrade. The concentrations of hydrogen and carbon monoxide in the initial gas are also as usual.

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

EXAMPLE.

Within an autoclave of 1.7 litres capacity there is arranged a spiral 6 metres long of 40 windings of iron pipe having an internal diameter of 5 millimetres and an external diameter of 8 millimetres. Superheated steam at a temperature of about 330° Centigrade is led through the interior of the iron pipe. The iron pipe has been pretreated by etching the outside with a solution of 200 grams of magnesium nitrate, 50 grams of potassium nitrate and 5 grams of uranyl nitrate in 100 cubic centimetres of water and 1000 cubic centimetres of glacial acetic acid (the tube being suspended in the solution for 24 hours) and then dried.

Hydrogen is led through the autoclave at 400° Centigrade under a pressure of 100 atmospheres for 10 hours. Then, at 100 atmospheres pressure and at temperatures between 330° and 400° Centigrade, a mixture of 40 per cent of carbon monoxide and 60 per cent of hydrogen is led through for 8 weeks in such an amount that 1 cubic metre of final gas is obtained per hour. The daily yield is from about 1.6 to 2.4 kilograms of hydrocarbons, alcohols, esters, acids and the like having more than 2 carbon atoms. In the last 7 days the yield rapidly decreases almost to nil. By one addition of 25 cubic centimetres of iron carbonyl in a small autoclave arranged before the reaction autoclave and through which the reaction gas flows, the yield can again be increased to 1.8 kilograms of hydrocarbons and their oxygen derivatives per day for a period of 14 days while maintaining otherwise identical conditions. After a further vaporisation of 70 cubic centimetres of iron carbonyl within a period of 6 days, the daily yield remains at the same value; thereupon about every 8 to 14 days 10 cubic centimetres of iron carbonyl are vaporised in order to maintain the same yield. By vaporising 100 cubic centimetres of a solution of 50 cubic centimetres of iron carbonyl in 1000 cubic centimetres of the oil obtained by the reaction, the yield may be increased to from 2.3 to 27 kilograms of hydrocarbons containing more than one carbon atom per day. Up to that time the repeatedly regenerated catalyst has been continuously in operation for 140 days. A deposit of carbon in the autoclave which may occur about every 8 weeks may be readily removed by scraping without the catalyst tube being rendered useless. The temperature in the chamber fluctuates between 338° and 354° Centigrade and the pressure between 100 and 120 atmospheres. In addition to the hydrocarbons, an about equal amount of an aqueous product is obtained which contains from about 5 to 20 per cent by volume of alcohols.

The products referred to as hydrocarbons contain from 1 to 3 per cent of oxygen (combined in the form of alcohols, acids, esters and the like).

Dated this 5th day of February, 1936.

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 Containing Oxygen from Carbon Monoxide and Hydrogen.

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:—

The specification No. 458,035 describes a process according to which in the preparation of hydrocarbons and, if desired, their derivatives containing oxygen, from carbon monoxide and hydrogen, apparatus parts consisting of metal, in particular of iron, and etched on one surface are used as catalysts, the etched surface of the apparatus parts being swept by the reaction gases and the other side by a gaseous or liquid heating or cooling agent for the purpose of supplying or withdrawing the heat of reaction. In this manner especially good yields may be obtained with large conversions without a further addition of catalyst to the reaction chamber being necessary.

The said catalysts consisting of etched surfaces suffer, however, after a certain time of operation some diminution in their activity, in the same way as many other catalysts. This renders an interruption of the conversion necessary and a reactivation of the catalyst.

My foreign correspondents have now found that the catalysts consisting of etched apparatus parts can be readily activated after diminution of their activity by decomposing on them small amounts of volatile metal compounds which are capable of decomposing at elevated temperatures, in particular at temperatures up to 500° Centigrade, if desired in a reducing atmosphere, with the formation of metals. For this purpose the carbonyls of iron, nickel, cobalt, and molybdenum have proved especially advantageous, of these iron carbonyl being the most suitable. The decomposition of the volatile metal compounds may be effected for example by vaporising a small amount of the compounds in the reaction gas and decomposing the same during the conversion of the reaction gas at the usual reaction temperature. The volatile metal compounds, in particular the carbonyls, may naturally also be vaporised as such in an atmosphere of inert or reducing gas, in particular of hydrogen, and decomposed at a suitable temperature. It has been found to be especially advantageous to add very small amounts of the said volatile metal compounds continuously to the reaction gas whereby the catalyst consisting of etched surfaces is continuously regenerated. In this case it has been found to be preferable to add from about 0.01 to 10 cubic centimetres of volatile metal compounds, in particular iron carbonyl, per day per litre of reaction space. The amount of metal compound to be added depends to a great extent on the reaction temperature because most volatile metal compounds, as for example iron carbonyl, leave the reaction chamber partially undecomposed. When the volatile metal compound is added not continuously but at intervals, as for example after some hours or days, amounts of from 0.1 to 1 cubic centimetre per litre of reaction space may, for example, be employed. The vaporisation of the volatile metal compounds may be effected merely by leading the gas current over the metal compound for example at from about 0° to 20° Centigrade, or naturally, it may be heated to higher temperatures when necessary. The metal compound may be vaporised as such or a solution of the compound in a solvent, as for example in alcohols, hydrocarbons, organic acids or esters, may be used for vaporisation.

It has further been found that the process according to this invention is not restricted to the use of etched apparatus parts but that good results are also obtained in the absence of catalysts not consisting of apparatus parts, i.e. for example of chips, pieces or the like filling the chamber, by adding the said volatile metal compounds, in particular carbonyls and especially iron carbonyl, continuously or also after certain intervals of time in small amounts when working in apparatus with unetched apparatus parts during the carrying out or temporary interruption of the conversion of carbon monoxide. For example simple cleaned tubes onto which the carbonyl is then decomposed and which may consist of any material, as for example iron, copper, aluminium or also ceramic materials, such as glass, porcelain, quartz materials or enamelled metals, or may be coated with the same, are sufficient.

The yields of hydrocarbons, in particular gaseous liquid and solid hydrocarbons containing more than one carbon atom and their derivatives containing oxygen (such as methanol or other alcohols, aldehydes, ketones or carboxylic acids) are, indeed, not as high when using non-etched apparatus parts for the conversion as those obtained with etched apparatus parts but the metals formed by the decomposition of the volatile metal compounds and deposited on the surfaces of the apparatus parts obviously exert a catalytic action on the conversion in the case of unetched apparatus parts, the said action leading to a good yield of the desired products.

It is advantageous to carry out the process at increased pressures, especially at pressures of more than 20 atmospheres. The temperatures to be used are those usual for the conversion, namely between 150° and 500°, advantageously between 250° and 400° Centigrade. The concentrations of hydrogen and carbon monoxide in the initial gas are also as usual, namely between 10 and 0.3 parts and preferably between 2 and 0.5 parts of hydrogen for each part of carbon monoxide.

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

EXAMPLE.

Within an autoclave of 1.7 litres capacity there is arranged a spiral 6 metres long of 40 windings of iron pipe having an internal diameter of 5 millimetres and an external diameter of 8 millimetres. Superheated steam at a temperature of about 330° Centigrade is led through the interior of the iron pipe. The iron pipe has been pretreated by etching the outside with a solution of 200 grams of magnesium nitrate, 50 grams of potassium nitrate and 5 grams of uranyl nitrate in 100 cubic centimetres of water and 1000 cubic centimetres of glacial acetic acid (the tube being suspended in the solution for 24 hours) and then dried.

Hydrogen is led through the autoclave at 400° Centigrade under a pressure of 100 atmospheres for 10 hours. Then, at 100 atmospheres pressure and at temperatures between 330° and 400° Centigrade, a mixture of 40 per cent of carbon monoxide and 60 per cent of hydrogen is led through for 8 weeks in such an amount that 1 cubic metre of final gas is obtained per hour. The daily yield is from about 1.6 to 2.4 kilograms of hydrocarbons, alcohols, esters, acids and the like having more than 2 carbon atoms. In the last 7 days the yield rapidly decreases almost to nil. By one addition of 25 cubic centimetres of iron carbonyl in a small autoclave arranged before the reaction autoclave and through which the reaction gas flows, the yield can again be increased to 1.8 kilograms of hydrocarbons and their oxygen derivatives per day for a period of 14 days while maintaining otherwise identical conditions. After a further vaporisation of 70 cubic centimetres of iron carbonyl within a period of 6 days, the daily yield remains at the same value; thereupon about every 8 to 14 days 10 cubic centimetres of iron carbonyl are vaporised in order to maintain the same yield. By vaporising 100 cubic centimetres of a solution of 50 cubic centimetres of iron carbonyl in 1000 cubic centimetres of the oil obtained by the reaction, the yield may be increased to from 2.3 to 2.7 kilograms of hydrocarbons containing more than one carbon atom per day. Up to that time the repeatedly regenerated catalyst has been continuously in operation for 140 days. A deposit of carbon in the autoclave which may occur about every 8 weeks may be readily removed by scraping without the catalyst tube being rendered useless. The temperature in the chamber fluctuates between 338° and 354° Centigrade and the pressure between 100 and 120 atmospheres. In addition to the hydrocarbons, an about equal amount of an aqueous product is obtained which contains from about 5 to 20 per cent by volume of alcohols.

The products referred to as hydrocarbons contain from 1 to 3 per cent of oxygen (combined in the form of alcohols, acids, esters and the like).

I am aware that it has already been proposed to produce liquid hydrocarbons by interaction of metal carbonyls with smaller amounts of hydrogen than is theoretically required for the production of methane and that in this operation the hydrogen may be replaced by gases containing the same, especially those containing carbon monoxide, such as water gas. In this process the carbonyls, therefore, are not added in small amounts and for the purpose of catalytically promoting the interaction of carbon monoxide with hydrogen but as a reaction component to be reacted with the hydrogen.

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 manufacture and production of hydrocarbons or their derivatives containing oxygen by thermal conversion of carbon monoxide with hydrogen which comprises passing mixtures of these gases through spaces, heated to a reacting temperature, in which at the most the apparatus surfaces confining the same have a catalytic activity and into which small amounts of volatile metal compounds capable of being decomposed at elevated temperatures preferably up to 500° Centigrade, are introduced continuously or at intervals while continuing or after discontinuing the conversion.

2. In the process as claimed in claim 1, introducing into the reaction space carbonyls of iron, nickel, cobalt or

molybdenum or of two or more of these metals.

3. In the process as claimed in claim 1 or 2, operating in spaces confined by apparatus surfaces of which at least part consists of an etched metal, preferably etched iron.

4. In the process as claimed in any of claims 1 to 3; continuously introducing into the reaction space from 0.1 to 10 cubic centimetres of volatile metal compounds per day per litre of the said space.

5. In the process as claimed in any of claims 1 to 4, adding the volatile metal compounds while diluted by a solvent.

6. The process for the manufacture and production of hydrocarbons and their derivatives containing oxygen substantially as described in the foregoing Example.

7. Hydrocarbons and their derivatives containing oxygen when obtained by the process particularly described and ascertained.

Dated this 30th day of December, 1936.

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