# PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

## Improvements in the Preparation of Hydrocarbons 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:—

It has already been proposed to carry out the catalytic conversion of carbon monoxide and hydrogen to hydrocarbons having more than one carbon atom in the molecule in the presence of a liquid medium, in particular a proper oil (as defined in Specification No. 468,434, page 3, lines 47—52) containing a considerable amount of constituents which are gaseous or vaporous under the temperature and pressure conditions employed.

The liquid may be led in the same direction as or in counter-current to the gases to be reacted. When carrying out the process on an industrial scale, the difficulty is encountered when working in counter-current that when using the proper oil containing constituents of low boiling point, the large amount of hot gases flowing through readily entrains the said constituents from the reaction vessel so that they are not present in the desired amounts for the reaction; in the higher boiling fractions which remain liquid, the reaction proceeds much more slowly and this considerably reduced the yields per unit of space and time of the desired products.

If the liquid be led in the same direction as the gases to be reacted, the said entraining of the low boiling constituents of the liquid by the gases takes place to a considerably smaller extent. The maintenance of a uniform temperature throughout the whole reaction chamber is, however, rendered difficult because by reason of the exothermic nature of the reaction the products become increasingly hotter during their passage through the catalytic chamber and thus towards the end of the reaction vessel the lower boiling constituents are vaporised to an undesirably great extent without it being possible to return them to the reaction vessel, for example by reflux cooling, against the strong gas current.

My foreign correspondents have now found that the said reaction in the presence of a liquid medium, in particular a proper oil of the above-mentioned kind, can be carried out in a very advantageous manner by leading the liquid medium into different zones of the reaction chamber.

The liquid medium is preferably led through the reaction chamber in a cycle. The supply of the same to the different zones may be effected in various ways. For example the circulating medium may all be led through the reaction chamber and fresh medium supplied at one or more other places; the circulating medium may, however, also be divided into a number of parts and then led into the reaction chamber at different places, fresh liquid medium then being added at one or more of these places or also at one or more other places.

When working in this way, the gases to be reacted may be led either in the same direction as or in counter-current to the liquid medium. It is advantageous to work in the same direction.

The said process renders it possible, in spite of the great evolution of heat, to maintain a practically uniform temperature throughout the whole reaction chamber. A very high yield per unit of time and space may therefore be obtained, especially when working at higher pressures, without side reactions, such as formation of methane and deposition of carbon, occasioned by increases in temperature taking place.

The nature of the invention will be further described with reference to the accompanying drawings in which are shewn diagrammatically plant suitable for carrying out the process according to this invention, but the invention is not restricted to the particular plant shown.

Referring to Figure 1, the circulating liquid medium is led by the circulatory pump *f* through the heat-exchanger *b* and the preheater *i* into the reaction vessel *a*. The gas to be reacted is introduced at

[Price 1/-]

$g$. The liquid leaves the vessel $a$ together with the residual gas at $k$ and is led through the heat-exchanger $b$, into the cooler $c$ and then into the separator $d$ in which is effected the separation of the liquid constituents (including the water formed which separates at the bottom) from the gas. Fresh liquid medium is introduced through the pipes $h$ into various zones of the reaction chamber. The part of the liquid medium which is not returned from the separator $d$ through $f$ is withdrawn together with the water at l.

The temperature and pressure conditions to be used are those usual for the said reaction; it is preferable to work at temperatures between 200° and 420° Centigrade and at pressures above 10 atmospheres, as for example at 50 to 700 atmospheres; lower pressures down to atmospheric pressure may, however, be used. The relative proportions of the initial gas may be varied within wide limits; the ratio of the amounts of carbon monoxide to hydrogen generally speaking lies between 4:1 and 1:4 (measured volumetrically) and it is advantageous to work with an excess of carbon monoxide. Accompanying gases, such as carbon dioxide, nitrogen and/or methane may also be present. The liquid medium is usually added in an amount of from 0.2 to 5 parts by volume to 100 parts by volume of initial gas (measured at atmospheric pressure and room temperature).

As the final products of the reaction there are obtained, in addition to gaseous and solid hydrocarbons, mainly liquid hydrocarbons. The proportions of the single products (benzine, middle oil, lubricating oil, paraffin wax) in the total product vary according to the reaction conditions used.

The following Example, given with reference to Figure 2, will further illustrate the nature of this invention, but the invention is not restricted to this Example.

EXAMPLE.

As the synthesis chamber K there is used a high pressure tube of 150 millimetres internal width and 5.8 metres height which is filled with a catalyst in the form of pieces of from 8 to 12 millimetres in grain size. The catalyst is prepared by fusing iron with small additions of titanium oxide, manganous oxide and potassium hydroxide in a current of oxygen and is treated at 650° Centigrade with hydrogen before being charged into the tube. Into the reaction chamber K there are introduced per hour at G 87 cubic metres of gas of the following composition:—

| | | |
|---|---|---|
| 6.0 | per cent. of | $CO_2$ |
| 0.4 | ,, | $C_nH_{2n}$ |
| 44.8 | ,, | CO |
| 40.0 | ,, | $H_2$ |
| 4.4 | ,, | $C_nH_{2n+2}$ |
| 4.4 | ,, | $N_2$. |

At the same time as the gas, there are introduced per hour at H about 0.6 cubic metre of oil which has been preheated to about 290° Centigrade in the preheater W. The oil and gas flow through the chamber K in the same direction, leave the chamber together at E, flow in counter-current to colder circulating oil through the heat-exchanger A and the cooler D in which they are cooled to about 70° to 80° Centigrade. In the separator S, the condensed oil together with the greater part of the water containing alcohol formed during the reaction is separated from the gas. The excess of oil and the water are withdrawn at B, while the remaining oil is returned as circulating oil to the chamber K through the circulatory pump P through the heat exchanger A and the oil preheater W.

Of the circulating oil,
18 per cent. by volume boil up to 150° Centigrade,
21 per cent. by volume boil from 150° to 200° Centigrade,
33 per cent. by volume boil from 200° to 300° Centigrade, and
28 per cent. by volume boil above 300° Centigrade.

When, after the commencement of the reaction, the temperature in the upper part of the chamber K rises to more than 295° to 300° Centigrade, a part of the circulating oil is branched off at V and led without preheating through a tube R which is insulated up to its outlet end and which projects 1.5 metres into the reaction chamber K. By the additional supply of oil, a uniform temperature of from 280° to 300° Centigrade can be maintained in the reaction chamber.

The mixture of final gas and benzine vapour leaving the separator S is further cooled, whereby a large part of the benzine hydrocarbons is separated in the liquid state. The residual final gas obtained in an amount of 50 cubic metres per hour has the following composition:

| | | |
|---|---|---|
| 33.4 | per cent. of | $CO_2$ |
| 3.0 | ,, | $C_nH_{2n}$ |
| 21.0 | ,, | CO |
| 21.8 | ,, | $H_2$ |
| 13.0 | ,, | $C_nH_{2n+2}$ |
| 7.8 | ,, | $N_2$. |

By leading it over active carbon, further amounts of gas oil (hydrocarbons having 3, 4 or more carbon atoms) and light benzine are recovered; the remaining gas may, after removal of carbon dioxide and

if desired replenishment with fresh gas, be brought into further reactions in a second stage or returned to the same reaction chamber.

The products formed in a yield of 8.2 kilograms per hour consist of

25.0 per cent. by volume of gas oil,
69.0 per cent. by volume of benzine, oil and solid hydrocarbons and
6.0 per cent. by volume of alcohols.

Dated this 20th day of June, 1938.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

## COMPLETE SPECIFICATION

# Improvements in the Preparation of Hydrocarbons 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,) 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 carry out the catalytic conversion of carbon monoxide with hydrogen into hydrocarbons having more than one carbon atom in the molecule in contact with stationary catalysts and in the presence of a liquid medium, in particular an oil obtained by the conversion of an amount of the same initial materials previously treated under the same or similar conditions, a so-called "proper oil", containing a considerable amount of constituents which are gaseous or vaporous under the temperature and pressure conditions employed.

The said liquid medium may be passed in the same direction as or in counter-current to the synthesis gases. However, when carrying out the conversion on an industrial scale and employing as the liquid medium in a counter-current cycle an oil, for example a "proper oil", containing constituents of low boiling point, the difficulty is encountered that the large amount of hot gases flowing through the reaction vessel readily entrains the said constituents so that they are not present during the conversion in the desired amounts and as the conversion proceeds much more slowly if only the higher boiling fractions which remain liquid are present, the yields per unit of space and time of the desired conversion products are considerably reduced.

If the liquid is passed in the same direction as the gases to be reacted, the said entraining of the low boiling constituents of the liquid by the gases takes place to a considerably smaller extent. The maintenance of a uniform temperature throughout the whole reaction vessel is, however, rendered difficult because by reason of the exothermic nature of the reaction the products become increasingly hotter during their passage through the catalytic space and thus towards the end of the reaction vessel the lower boiling constituents are vaporised to an undesirably great extent without it being possible to return them to the reaction vessel, for example, by reflux cooling, against the strong gas current.

My foreign correspondents have now found that the said reaction in contact with stationary catalysts and in the presence of a liquid medium, in particular a "proper oil", containing a considerable amount of constituents which are gaseous or vaporous under the reaction conditions, can be carried out in a very advantageous manner by introducing the liquid medium into different zones of the reaction space through separate points of introduction in or adjacent to the said zones.

The liquid medium is introduced into the various zones in regulated amounts and at temperatures suitable for proper temperature regulation.

The liquid medium is preferably passed through the reaction space in a cycle. The supply of the same to the different zones may be effected in various ways. For example, the circulating medium may all be passed through the reaction space and fresh medium supplied at one or more other places, the circulating medium may, however, also be divided into a number of parts and then passed into the reaction space at different places, fresh liquid medium then being added at one or more of these places or also at one or more other places.

When working in this way, the synthesis gases may be passed either in the same direction as or in counter-current to the liquid medium. It is advantageous to work with co-current flow.

The process of the present invention renders it possible, in spite of the great evolution of heat, to maintain a practically uniform temperature throughout the whole reaction space. A very high yield per unit of time and space may therefore be obtained, especially when working at high pressures, without by-reactions, such as formation of methane and deposition of carbon, occasioned by increase in temperature taking place.

The conversion may be carried out under the usual conditions of temperature and pressure, preferably at temperatures between about 200° and 420° Centigrade and under ordinary pressure or thereabout or elevated pressure, for example, above 10 atmospheres, such as 20, 50, 100, 200, 500 or 700 atmospheres or more. The relative proportions of the initial gases may be varied within wide limits; the ratio of the amounts of carbon monoxide to hydrogen generally speaking lies between about 4:1 and 1:4 (measured volumetrically) preferably between about 2:1 to 1:3, for example, about 1:1 to 1:2. It is often advantageous to work with an excess of carbon monoxide. Diluent gases, such as carbon dioxide, nitrogen and/or methane may also be present. The liquid medium is usually added in an amount of from about 0.2 to 5 parts by volume to 100 parts by volume of initial gas (measured at atmospheric pressure and room temperature).

As the final products of the reaction there are obtained by interaction of carbon monoxide and hydrogen in addition to gaseous and solid hydrocarbons, mainly liquid hydrocarbons, and this is the only or main reaction taking place in the process in accordance with the present invention. The proportions of the individual products (benzine, middle oil, lubricating oil, paraffin wax) in the total product vary according to the reaction conditions used.

The invention will be further described with reference to the drawing accompanying the Provisional Specification. In Figure 1 is illustrated diagrammatically a plant suitable for carrying out the process according to this invention in practice, but the invention is not restricted to the use of the particular plant shown.

Referring to Figure 1, the circulating liquid medium is passed by the circulating pump *f* through the heat-exchanger *b* and the preheater *i* into the reaction vessel *a*. The synthesis gas is introduced at *g*. The liquid leaves the vessel *a* together with the residual gas at *k* and is passed through the heat-exchanger *b*, into the cooler *c* and then into the separator *d* in which is effected the separation of the liquid constituents (including the water formed which separates at the bottom) from the gas. Fresh liquid medium is introduced through the pipes *h* into various zones of the reaction vessel. The part of the liquid medium which is not returned from the separator *d* through *f* is withdrawn together with the water at *l*.

The following Example, given with reference to Figure 2, of the drawing accompanying the Provisional Specification, will further illustrate how the invention may be carried out in practice, but it should be understood that the invention is not restricted to this Example.

EXAMPLE.

The reaction vessel K is a high pressure tube of 150 millimetres internal diameter and 5.8 metres height which is filled with a catalyst in the form of pieces of from 8 to 12 millimetres in grain size. The catalyst is prepared by fusing or sintering iron with small additions of titanium oxide, manganous oxide and potassium hydroxide in a current of oxygen and is treated at 650° Centigrade with hydrogen before being charged into the tube. Into the reaction vessel K there are introduced per hour at G 87 cubic metres of a gas of the following composition:

| | | |
|---|---|---|
| 6.0 | per cent. of | $CO_2$ |
| 0.4 | ,, | $C_nH_{2n}$ |
| 44.8 | ,, | CO |
| 40.0 | ,, | $H_2$ |
| 4.4 | ,, | $C_nH_{2n-2}$ |
| 4.4 | ,, | $N_2$. |

At the same time as the gas, there are introduced per hour at H about 0.6 cubic metre of oil which has been preheated to about 290° Centigrade in the preheater W. The oil and gas flow through the vessel K in the same direction, leave the same together at E, flow in counter-current to colder circulating oil through the heat-exchanger A and the cooler D in which they are cooled to about 70° to 80° Centigrade. In the separator S, the condensed oil together with the greater part of the water containing alcohol formed during the reaction is separated from the gas. The excess of oil and the water are withdrawn at B, while the remaining oil is returned as circulating medium to the vessel K through the circulatory pump P through the heat exchanger A and the oil preheater W.

The circulating medium consists of the following fractions:

18 per cent. by volume boiling up to 150° Centigrade,
21 per cent. by volume boiling from 150° to 200° Centigrade,
33 per cent. by volume boiling from 200° to 300° Centigrade,
28 per cent. by volume boil above 300° Centigrade.

When, after starting the conversion, the temperature in the upper part of the vessel K rises to more than 295° to 300° Centigrade, a part of the circulating oil is branched off at V and passed without preheating through a tube R which is insulated up to its outlet end and which projects 1.5 metres into the reaction vessel K. By the additional supply of oil, a uniform temperature of from 280° to 300° Centigrade can be maintained in the reaction vessel.

The mixture of final gas and benzine vapour leaving the separator S is further cooled, whereby a large part of the benzine hydrocarbons is separated in the liquid state. The residual final gas obtained in an amount of 50 cubic metres per hour has the following composition:

| | | |
|---|---|---|
| 33.4 | per cent. of | $CO_2$ |
| 3.0 | ,, | $C_nH_{2n}$ |
| 21.0 | ,, | CO |
| 21.8 | ,, | $H_2$ |
| 13.0 | ,, | $C_nH_{2n+2}$ |
| 7.8 | ,, | $N_2$. |

By passing it over active carbon, further amounts of "gasol" (a product substantially consisting of hydrocarbons having 3 and 4 carbon atoms and contingently small amounts of those having 5 carbon atoms in the molecule) and light benzine are recovered; the remaining gas may, after removal of carbon dioxide and if desired replenishment with fresh gas, be brought into further reaction in a second stage or returned to the same reaction space.

The products formed with a yield of 8.2 kilograms per hour consist of
25.0 per cent. by weight of "gasol",
69.0 per cent. by weight of benzine, oil and solid hydrocarbons
6.0 per cent. by weight of alcohols.

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 catalytic conversion of carbon monoxide with hydrogen into hydrocarbons with more than one carbon atom in the molecule, in contact with stationary catalysts and in the presence of a liquid medium containing a considerable amount of constituents which are gaseous or vaporous under the reaction conditions, which comprises introducing the liquid medium into different zones of the reaction space through separate points of introduction in or adjacent to the said zones.

2. A process as claimed in claim 1, which comprises introducing the liquid medium into the various zones in regulated amounts and at temperatures suitable for proper temperature regulation.

3. A process as claimed in claim 1 or 2, which comprises employing as the liquid medium a "proper oil".

4. A process as claimed in any of claims 1 to 3, which comprises passing the liquid medium through the reaction space in a cycle.

5. A process as claimed in claim 4, which comprises passing the liquid medium through the reaction space in the same direction as or in counter-current to the gas to be converted.

6. A process as claimed in any of claims 1 to 5, which comprises converting synthesis gases in which the proportion by volume of carbon monoxide to hydrogen is between about 4:1 and 1:4, preferably between about 2:1 and 1:3.

7. A process as claimed in any of claims 1 to 6, which comprises converting synthesis gases in which the proportion by volume of carbon monoxide to hydrogen is between about 1:1 and 1:2.

8. A process as claimed in any of claims 1 to 7, which comprises carrying out the conversion at temperatures between about 200° and 420° Centigrade.

9. A process as claimed in any of claims 1 to 8, which comprises carrying out the conversion at pressures of from about 10 to 700 atmospheres or more.

10. A process as claimed in any of claims 1 to 8, which comprises carrying out the conversion at ordinary pressure or thereabout.

11. A process for the conversion of carbon monoxide with hydrogen, substantially as described in the foregoing Example.

12. A process for the conversion of carbon monoxide with hydrogen substantially as hereinbefore described with reference to the drawing accompanying the Provisional Specification.

13. Hydrocarbons with more than one carbon atom in the molecule, whenever obtained in the process of any of the preceding claiming clauses.

Dated the 9th day of May, 1939.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 1

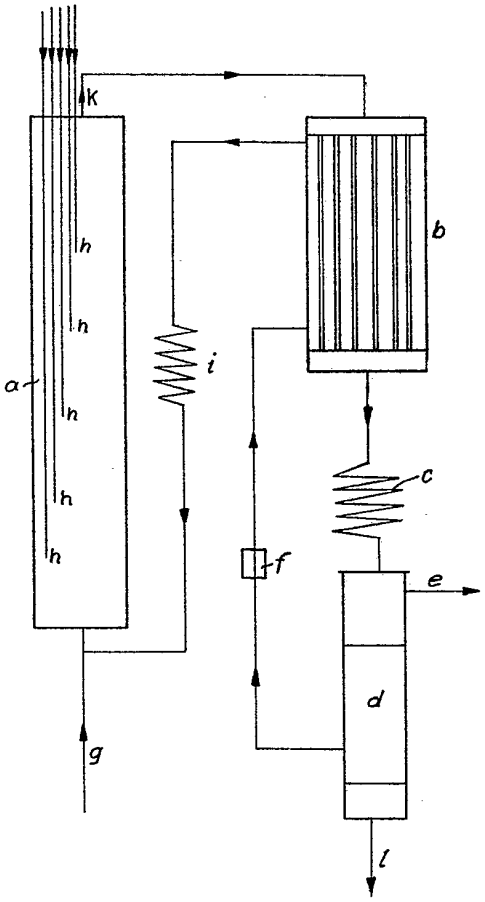
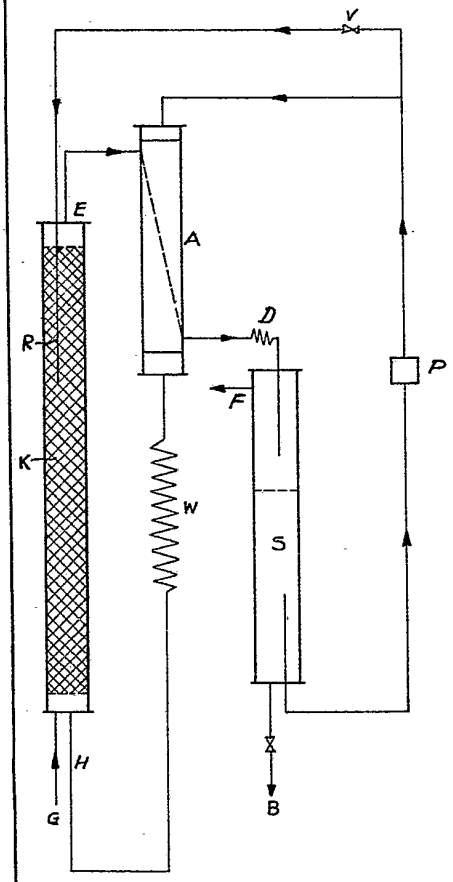



Fig. 2

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