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PATENT SPECIFICATION



Application Date: Nov. 29, 1935. No. 33177/35.

468,434

Complete Specification Left: Nov. 19, 1936.

Complete Specification Accepted: June 29, 1937.

PROVISIONAL SPECIFICATION

Improvements in and Apparatus for the Conversion of Oxides of Carbon with 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 convert oxides of carbon, in particular carbon monoxide, with hydrogen in the presence of catalysts at elevated temperatures and at atmospheric or increased pressure into hydrocarbons or organic compounds containing oxygen.

For the purpose of carrying away the heat formed during the reaction it has already been proposed to carry out the conversion in liquid media with finely divided catalysts suspended therein. By reason of the high temperatures necessary for the conversion and the high vapour pressures of many liquids at these temperatures the said method of working has hitherto been limited to the use of organic liquids of high boiling point which are stable under the reaction conditions.

My foreign correspondents have now found that the conversion of oxides of carbon with hydrogen in the presence of catalysts and at elevated temperatures can be advantageously carried out by effecting the conversion in a liquid medium which consists of the oils which have been obtained by the conversion of an amount of the same kind of initial materials which has been perviously treated under the same or similar conditions, i.e. in the proper oil. The said liquid medium is advantageously prepared by leading the final gases and vapours formed in and leaving the reaction zone by the conversion of the initial gases through a cooling zone which is

advantageously constructed as a reflux condenser so that the vapours of the products formed which are leaving with the final gases are wholly or partly condensed and returned to the reaction zone where they form the liquid medium. The said method of working allows of a very simple and efficient leading away of the excess heat and moreover has the advantage that even very readily-boiling components of the reaction product, as for example amylene, butylene, propylene and even ethylene, or corresponding saturated hydrocarbons are returned into the reaction zone by condensation or by dissolution in the condensate flowing in the opposite direction in the cooling zone and are thus subjected to a further conversion into products of higher boiling point, whereas according to the methods hitherto used the mostly low-boiling products formed leave the reaction zone together with the final gases as the final products. Furthermore, by using suitable catalysts, it is possible according to this invention, as contrasted with the known methods, to obtain products very poor in or free from oxygen even at high pressures. The term "effecting the conversion in the proper oil" is intended to include also the manner of working in which a foreign oil is used for the commencement of the conversion but is gradually replaced by freshly formed proper oil.

According to this invention it is preferable to work at such pressures and temperatures that the liquid phase is ensured in the reaction zone, but the working in a liquid medium according to this invention also includes that state above the critical temperature of any or all of the constituents of the "liquid medium" in which the difference in density of the gaseous state shews no appreciable difference from the liquid state. The term

"conversion in a liquid medium" also includes that characteristic state in the reaction zone occurring when using reflux cooling even when the critical temperature is exceeded, which state is set up in the reaction zone by reason of the constant reflux of the cooler condensed products with gaseous components dissolved therein and which probably constitutes a mixed state of the boiling liquid phase and continuous vapour formation or disengagement of dissolved vapours.

The process may also advantageously be carried out by keeping the cooling zone wholly or partly filled with the liquid so that the gases and vapours flowing through the cooler are led through the cooled condensate which is flowing downwards in a convection current and are thereby cooled and at the same time washed.

The liquid products formed are continuously or periodically withdrawn from the reaction zone or from the cooling zone while constantly maintaining a sufficient amount of liquid medium in the reaction zone. The procedure may also be that a part of the liquid medium is led in circulation through the apparatus. The introduction and withdrawal of the circulating medium may be effected into or from the reaction zone or the cooling zone. The liquid to be introduced may be preheated or cooled depending on the special operating conditions. Thus for example the commencement of the conversion may be effected by introducing hot circulating medium.

As catalysts may be mentioned finely divided solid substances suspended in the liquid medium. When using these suspended substances, a separation of the catalysts from the products formed is necessary. It has been found, however, that catalysts in the form of pieces which remain in the reaction zone during the conversion can be used with advantage according to this invention. In order that there may be a maintaining and sufficient circulation of the liquid medium and also a sufficient reflux of the condensate, and also if desired an untroubled circulation of liquid and, with these measures, a sufficiently rapid withdrawal of heat, it has been found to be preferable to distribute the single pieces of catalyst sufficiently far apart whether it be by the formation of thin layers with intermediate empty spaces or by a bulky formation of the catalyst pieces.

The process is advantageously carried out at temperatures between 200° and 420° Centigrade and at pressures above 10 atmospheres, preferably between 50 and 250 atmospheres. Good results may,

however, also be obtained at lower pressures, as for example at atmospheric pressure.

The following Example, given with reference to the accompanying drawing which shews diagrammatically an arrangement of apparatus according to this invention, will further illustrate the nature of this invention but the invention is not restricted to this Example or to the specific arrangement shewn.

EXAMPLE.

A mixture of 1000 grams of iron powder (obtained by the decomposition of iron carbonyl), 25 grams of silicon powder, 25 grams of titanium dioxide, 50 grams of potassium permanganate and 50 grams of water is fused in a stream of oxygen, whereby the iron powder is oxidised to ferrosiferrous oxide. The resulting melt is cooled, comminuted to a grain size of from 5 to 8 millimetres and treated with hydrogen for 48 hours at 650° Centigrade.

The catalyst thus prepared is arranged in seven layers *b* each 7 centimetres in height over a length of 60 centimetres in a vertical high-pressure tube *a* having an internal diameter of 4.5 centimetres. The free space between the layers *b* of catalysts and between the single particles of catalyst and also the space up to about 30 centimetres above the uppermost layer of catalyst is filled completely with an oil boiling between 65° and 160° Centigrade. A compensating vessel *c* is provided laterally of the high-pressure tube for the reception of excess of oil formed during the conversion. Liquid final products may be withdrawn at *d*.

At the upper end of the reaction zone, which is 90 centimetres in length, there is provided a reflux condenser *e*, water being led into its cooling jacket at *f* and withdrawn at *g*.

A mixed gas containing 40 per cent. of carbon monoxide and 60 per cent. of hydrogen by volume is led in from a pipe *k* and, after distribution through a porous filter *i*, led upwards into the reaction tube *a* in which a pressure of 100 atmospheres prevails and which is heated to an internal temperature of from about 360° to 380° Centigrade by an external source of heat, as for example an electrical furnace having a temperature of 480° Centigrade. The heat set free by the conversion is absorbed by the oil which is thereby partially vaporised. The vaporised portion is condensed again in the reflux condenser and flows back into the reaction zone.

The initial gas is charged through the high-pressure tube at such a rate that 75 litres of final gas per hour are obtained; this gas is withdrawn at *l* and has the

Following composition:—

21	per cent. by volume of CO ₂
1.4	“ “ “ “ “ C _n H _{2n}
15.6	“ “ “ “ “ CO
51.8	“ “ “ “ “ H ₂
6.8	“ “ “ “ “ C _n H _{2n+2} and
3.4	“ “ “ “ “ N ₂ .

For each cubic metre of final gas 47 grams of oil are formed. The element analysis of this oil is as follows:—85.1 per cent. of C, 14.4 per cent. of H and 0.5 per cent. of O. 93 per cent. of the oil boil between 40° and 300° Centigrade.

Contrary to expectation, only a slight amount of water is formed during the conversion. The oxygen of the portion of the carbon monoxide which has reacted to form hydrocarbons is practically completely present in the form of carbon dioxide at the end of the conversion. The oil formed, in spite of the high pressure used, is, contrary to expectation, practically free from oxygen. Furthermore there is not deposition of carbon.

Dated this 29th day of November, 1935.

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

COMPLETE SPECIFICATION

Improvements in and Apparatus for the Conversion of Oxides of Carbon with 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 Frankfurt-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 convert oxides of carbon, in particular carbon monoxide, with hydrogen in the presence of catalysts at elevated temperatures and atmospheric or increased pressure into hydrocarbons, which may be gaseous, liquid or solid, or their derivatives containing oxygen.

For the purpose of carrying away the heat formed during the reaction it has been proposed to carry out the conversion in liquid media with finely divided catalysts suspended therein. By reason of

treated under the same or similar conditions, i.e. in the proper oil, and which contains substantial amounts (of at least 1 per cent. and usually between 10 and 100 per cent.) of constituents which have a boiling point within the boiling range of benzines and which therefore under the prevailing conditions of temperature and pressure are vaporised i.e., gaseous or vaporous. In other words, the boiling point of these constituents is below the reaction temperature under the pressure employed. The said constituents usually remain dissolved in the oil but they may in part also evaporate from the oil. The said liquid medium is advantageously prepared by leading the final gases and vapours formed in and leaving the reaction zone through a cooling zone which is advantageously constructed as a reflux condenser so that the vapours of the products formed which are leaving with the final gases are wholly or partly condensed and returned to the reaction zone where they form the liquid medium. The said method of working allows of a very

able catalysts, it is possible according to this invention, as contrasted with the known methods, to obtain products very poor in or free from oxygen even at high pressures. The term "effecting the conversion in the proper oil" is intended to include also the manner of working in which a foreign oil is used for the commencement of the conversion but is gradually replaced by freshly formed proper oil.

According to this invention the conversion is carried out at such pressure and temperatures that the liquid phase is ensured in the reaction zone, but the working in a liquid medium according to this invention also includes that state above the critical temperature of any or all of the constituents of the "liquid medium" in which the density of the gaseous state shews no appreciable difference from that of the liquid state. The term "conversion in a liquid medium" also includes that characteristic state in the reaction zone, occurring when using reflux cooling even when the critical temperature is exceeded, which state is set up in the reaction zone by reason of the constant reflux of the cooler condensed products with gaseous components dissolved therein and which probably constitutes a mixed state of the boiling liquid phase and continuous vapour formation or disengagement of dissolved vapours.

The process may also advantageously be carried out by keeping the cooling zone wholly or partly filled with the liquid so that the gases and vapours flowing through the cooler are led through the cooled condensate which is flowing downwards in a convection current and are thereby cooled and at the same time washed.

The liquid products formed are continuously or periodically withdrawn from the reaction zone or from the cooling zone while constantly maintaining a sufficient amount of liquid medium in the reaction zone. The procedure may also be that a part of the liquid medium is led in circulation through the apparatus. The introduction and withdrawal of the circulating medium may be effected into or from the reaction zone or the cooling zone. The liquid to be introduced may be preheated or cooled depending on the special operating conditions. Thus for example the commencement of the conversion may be effected by introducing hot circulating medium.

As catalysts may be mentioned finely divided solid substances suspended in the liquid medium. When using these suspended substances, a separation of the catalysts from the products

formed is necessary. It has been found, however, that catalysts in the form of pieces which remain in the reaction zone during the conversion can be used with advantage according to this invention. In order that there may be a maintaining and sufficient circulation of the liquid medium and also a sufficient reflux of the condensate, and also if desired an untroubled circulation of the liquid and, with these measures, a sufficiently rapid withdrawal of heat, it has been found to be preferable to distribute the catalyst so as to leave spacious interstices whether it be by the formation of thin layers with intermediate empty spaces or by a voluminous form of the catalyst pieces.

The process is advantageously carried out at temperatures between 200° and 420° Centigrade and at pressures above 10 atmospheres, preferably between 50 and 250 atmospheres. Good results may, however, also be obtained at lower pressures, as for example at atmospheric pressure.

Suitable initial gas mixtures are for example those containing from 10 to 80 per cent. of carbon monoxide and from 90 to 20 per cent., respectively, of hydrogen, preferably those containing from 30 to 70 per cent. of carbon monoxide and from 70 to 30 per cent., respectively, of hydrogen. The initial gas mixtures may also contain inert gases, such as nitrogen or they may contain carbon dioxide.

As catalysts there may be mentioned the substances usually employed for the conversion of carbon monoxide with hydrogen into hydrocarbons or their oxygen-containing derivatives. When hydrocarbons are desired it is of advantage to employ iron or its compounds, in particular oxides, preferably with activating additions, such as titanium or silicon or their compounds, in particular their oxides or heavy metals, such as uranium, manganese, tungsten, chromium, or molybdenum or their compounds or compounds of alkali metals or alkaline earth metals, such as sodium, calcium, magnesium or barium. Cobalt and nickel and their compounds or compositions containing the same may also be employed.

The following Examples are given with reference to the drawing accompanying the Provisional Specification and to the accompanying drawing which drawings show diagrammatically vertical sections of apparatus according to this invention; these Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted thereto or to the specific arrangements shown.

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EXAMPLE 1.

A mixture of 1000 grams of iron powder (obtained by the decomposition of iron carbonyl), 25 grams of silicon powder, 25 grams of titanium dioxide, 50 grams of potassium permanganate and 50 grams of water is ignited and fused in a stream of oxygen, whereby the iron powder is oxidised to ferrosiferrous oxide. The resulting melt is cooled, comminuted to a grain size of from 5 to 8 millimetres and treated with hydrogen for 48 hours at 650° Centigrade.

The catalyst thus prepared is arranged in seven layers *b* (see the drawing accompanying the Provisional Specification), each 7 centimetres in height, over a length of 60 centimetres in a vertical high-pressure tube *a* having an internal diameter of 4.5 centimetres. The free space between the layers *b* of catalysts and between the single particles of catalyst and also the space up to about 30 centimetres above the uppermost layer of catalyst is filled completely with an oil boiling between 65° and 160° Centigrade. A compensating vessel *c* is provided laterally of the high-pressure tube for the reception of excess of oil formed during the conversion. Liquid final products may be withdrawn at *d*.

At the upper end of the reaction zone, which is 90 centimetres in length, there is provided a reflux condenser *e*, water being led into its cooling jacket at *f* and withdrawn at *g*.

A mixed gas containing 40 per cent. of carbon monoxide and 60 per cent. of hydrogen by volume is led in from a pipe *k* and, after distribution through a porous filter *i*, led upwards into the reaction tube *a* in which a pressure of 100 atmospheres prevails and which is heated to an internal temperature of from about 360° to 380° Centigrade by an external source of heat, as for example an electrical furnace *h* having a temperature of 480° Centigrade. The heat set free by the conversion is absorbed by the oil which is thereby partially vaporised. The vaporised portion is condensed again in the reflux condenser and flows back into the reaction zone.

The initial gas is charged through the high-pressure tube at such a rate that 75 litres of final gas per hour are obtained; this gas is withdrawn at *l* and has the following composition:—

	21	per cent. by volume of	CO ₂
60	1.4	“ “ “ “ “	C _n H _{2n}
	15.6	“ “ “ “ “	CO
	51.8	“ “ “ “ “	H ₂
	6.8	“ “ “ “ “	C _n H _{2n+2} and
	3.4	“ “ “ “ “	N ₂ .

For each cubic metre of final gas, 47 grams of oil are formed. The element analysis of this oil is as follows:—85.1 per cent. of C, 14.4 per cent. of H and 0.5 per cent. of O. 93 per cent. of the oil boil between 40° and 300° Centigrade.

Contrary to expectation, only a slight amount of water is formed during the conversion. The oxygen of the portion of the carbon monoxide which has reacted to form hydrocarbons is practically completely present in the form of carbon dioxide at the end of the conversion. The oil formed, in spite of the high pressure used, is, contrary to expectation, practically free from oxygen. Furthermore there is no deposition of carbon.

EXAMPLE 2.

In a high pressure vessel 1 (see the accompanying drawing) which has an internal diameter of 200 millimetres and a height of 5 metres are arranged 50 kilograms of the same catalyst as described in Example 1 in layers having a distance of 7 centimetres so that the space of the reaction vessel in which the catalyst is arranged, has a height of 4 metres. The reaction vessel is filled with oil obtained in a previous operation and then brought to a temperature between 310° and 340° Centigrade by means of external heating. Preheated oil and the gas mixture to be converted consisting of 47 per cent. of carbon monoxide and 53 per cent. of hydrogen are introduced at the bottom of the reaction vessel by a pipe 8. The pressure maintained in the vessel amounts to 100 atmospheres. The reaction products including the oil present in the vessel, which latter is partly in the vaporous and partly in the liquid state, leave the reaction vessel at the top, pass through a heat exchanger 2 and are then introduced into a cooler 3 in which they are cooled to 50° Centigrade. The cooled products are led into a separator 4 from which the gaseous and vaporous constituents are withdrawn by a pipe 9, while the oil and water formed in the reaction separate in the lower part of the separator from which the water and an amount of oil corresponding to that formed in the reaction are withdrawn by a pipe 5. The remainder of the oil is conveyed from the separator 4 by a pump 6 through a heating coil 7 and then by way of the heat exchanger into the lower part of the reaction vessel 1. Since the oil maintained in the reaction vessel 1 may become gradually enriched in higher boiling constituents, part of the oil is withdrawn from time to time by the pipe 10 instead of by the pipe 5, so that an accumulation of high boiling constituents in the oil is avoided. The gas withdrawn at 9 is fur-

ther cooled and thus freed from additional light oils. Still further constituents, in particular oils of very low boiling point and normally gaseous hydrocarbons containing 3 and 4 carbon atoms, may be removed from the gas by washing with a suitable oil or by means of active carbon. The gas then remaining which still contains about one half of the carbon monoxide and hydrogen supplied into the reaction vessel 1 may be completely converted into oil in a second operation.

In the manner described 1200 cubic metres of carbon monoxide and hydrogen are introduced per day into the reaction vessel, of which about 600 cubic metres are converted while the remainder together with the carbon dioxide and methane formed in the reaction is obtained as the final gas. From each cubic metre of carbon monoxide and hydrogen having undergone the conversion there are obtained 33.9 grams of normally gaseous hydrocarbons mainly containing 3 and 4 carbon atoms, 30.7 grams of oil boiling up to 100° Centigrade, 13.1 grams of oil boiling between 100° and 150° Centigrade, 11.9 grams of oil boiling between 150° and 200° Centigrade, 11.2 grams of oil boiling between 200° and 250° Centigrade, 8.4 grams of oil boiling between 250° and 300° Centigrade, 19.1 grams of oil boiling above 300° Centigrade, 67.0 grams of water and 9.5 grams of water-soluble compounds containing oxygen. The latter compounds which are withdrawn together with the water consist of 70 per cent. of ethyl alcohol, 10 per cent. of methyl alcohol, the remainder being mainly acetaldehyde, acetone and propyl and butyl alcohols.

In the Patent Specification No. 465,668 a process for the conversion of mixtures of carbon monoxide and hydrogen into gaseous and/or liquid hydrocarbons. Contingently together with their oxygen derivatives, has been claimed which comprises contacting such a mixture at a reacting temperature with a catalyst obtained by treating previously fused ferrosiferrous oxide with a reducing gas at a temperature above 300° Centigrade, and I make no claim to this process here.

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 subject to the foregoing disclaimer what I claim is:—

1. A process for the catalytic conversion of mixtures comprising carbon monoxide and hydrogen at an elevated temperature into hydrocarbons and/or their oxygen derivatives which comprises carrying out the conversion in a liquid medium consisting of the oils obtained by a previous conversion of the same initial materials under the same or similar conditions and containing a substantial amount of constituents the boiling point of which is within the boiling range of benzines and which therefore, under the pressure employed, boil below the temperature maintained during the conversion.

2. In the process as claimed in claim 1, passing the gases and vapours issuing from the conversion space through a cooling space from which the condensed part of the said gases and vapours is returned to the conversion space.

3. In the process as claimed in claim 2, partly or wholly filling the cooling space with a liquid medium.

4. In the process as claimed in any of claims 1 to 3, arranging the catalyst so as to leave spacious interstices for circulating liquid.

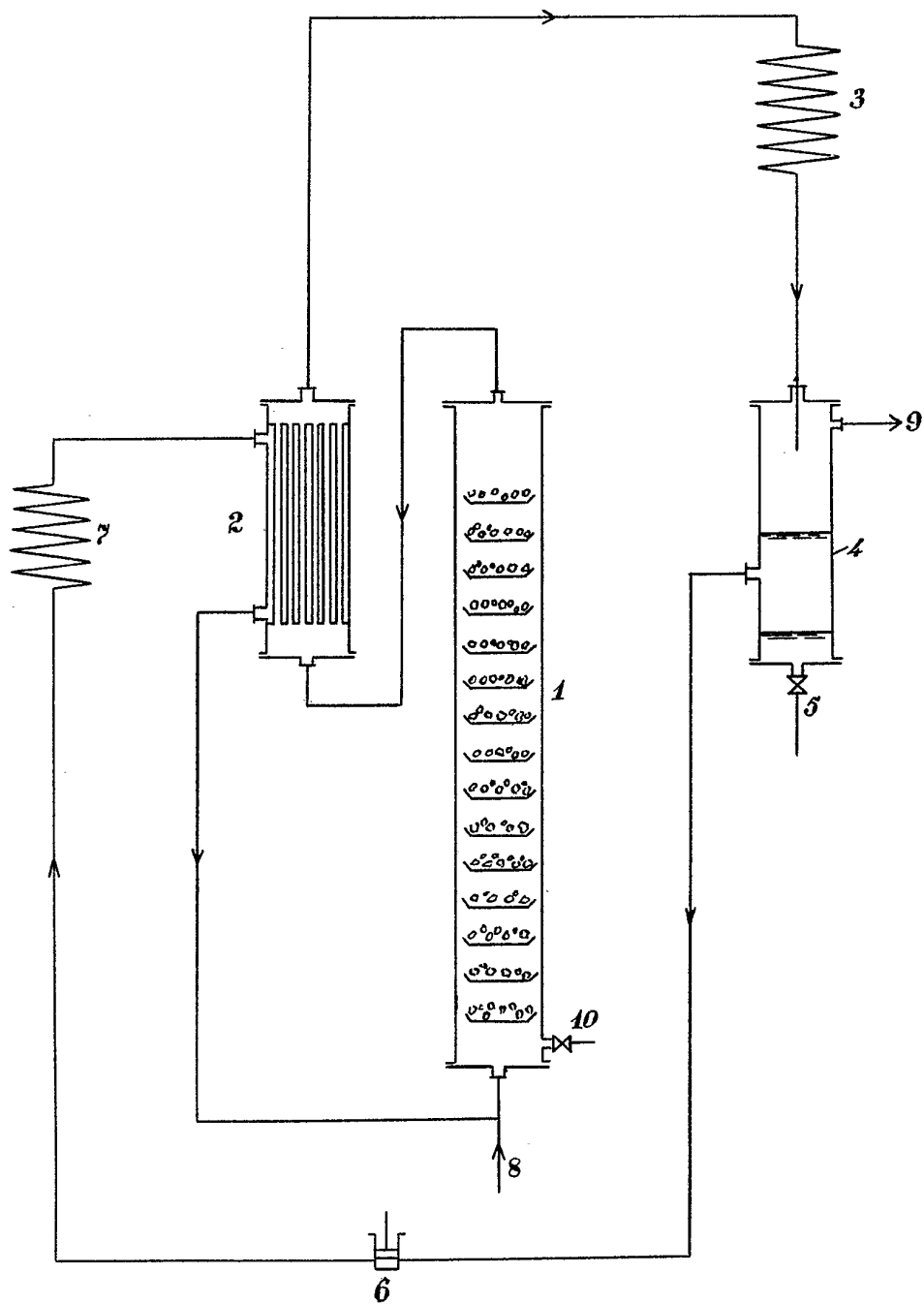
5. In the process as claimed in any of claims 1 to 4, passing part of the liquid medium in a cycle through the conversion space and/or through the cooling space.

6. Apparatus, when used for the conversion of carbon monoxide and hydrogen, comprising a reaction vessel, a reflux condenser on this vessel, a compensating vessel provided laterally of the reaction vessel for the reception of excess of oil and at the bottom of the reaction vessel an outlet for the withdrawal of final products, substantially as herein described and shewn in the drawing accompanying the provisional specification.

Dated this 19th day of November, 1936.

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

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



[This Drawing is a full-size reproduction of the Original.]

