[Second Edition.]

PATENT SPECIFICATION

Application Date: Feb. 3, 1936. *No. 3218/36.* **469,618**

Complete Specification Left: Jan. 8, 1937.

Complete Specification Accepted: July 29, 1937.

PROVISIONAL SPECIFICATION

Improvements in Carrying out Reactions 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 is already known that reactions of the oxides of carbon, and in particular of carbon monoxide, with hydrogen must proceed under very accurately maintained temperature conditions if it is desired to obtain an optimum yield of organic compounds containing more than one carbon atom, in particular of liquid hydrocarbons or their oxygen derivatives, and at the same time to obtain the best possible economy of the process.

The said reactions are exothermic; thus from a certain size of furnace upwards, at which the heat set free begins to exceed the loss by radiation, the excess of heat must be led away continuously. According to the methods of cooling hitherto known, a colder liquid or gaseous medium is brought into indirect heat exchange in the same direction or in countercurrent with the reaction material to be cooled. In the course of the path of cooling, the temperature of the cooling agent thus rises and the cooling agent loses activity by reason of the lowering of the mean temperature difference. Methods of this kind are suitable for carrying out reactions the heat requirements of which are not uniform, for example when at the commencement of the reaction a considerably greater portion of the total heat must be led away than in the middle or at the end of the reaction. If, on the other hand, the reaction proceeds with a constant evolution of heat or if the evolution of heat proceeds with but slight fluctuations, which is usually the case in reactions under low pressure, i.e. atmospheric or slightly increased pressure, then the drawback mentioned above is more evident the more uniformly the reaction proceeds.

My foreign correspondents have now found that in the said reactions of the oxides of carbon with hydrogen, in particular in the reaction of hydrogen with carbon monoxide, at atmospheric or increased pressure for the formation of liquid hydrocarbons or their derivatives, wet steam is very suitable as a cooling agent, especially wet steam the saturation of which is kept within the limits of about 60 and about 80 per cent., i.e. in which up to 40 per cent. of water is present in the liquid phase (in the form of small suspended droplets). In this way not only does the temperature of the cooling agent and consequently the temperature of the reacting substances remain constant during the absorption of heat by the cooling agent, but the heat transmission value also maintains a maximum value within the steam-concentration limits of 60 and 100 per cent. According to this invention the cooling agent is brought into indirect heat-exchange with the product undergoing reaction. Such a cooling system has the character of a cooling bath having an entirely uniform temperature such as cannot be obtained in practice by other methods. For thermal reasons a pressure range, depending on the reaction temperature to be maintained, of from 5 to 15 atmospheres is especially suitable because under the said pressures the dry steam formed by heat exchange from the wet steam is able to exert a maximum of energy. It is also advantageous to keep the cooling medium under such a pressure that the dry steam temperature is only slightly below the reaction temperature. If it is found that in the course of the cooling the steam has become dry before the end of the reaction, it is preferable to introduce water in the form of a spray or mist into the cooling chamber to such an extent that in the further course the temperature at which dry steam is formed is no longer exceeded so that no superheated steam is formed.

The wet steam to be used as the cooling agent may be prepared in various ways. For example water under the pressure used in the cooling may be heated by any

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available source of waste heat to the dry steam temperature and then allowed to evaporate whereby a wet steam having a considerable content of liquid water is formed. Alternatively, hot water under pressure, which has been heated for example by heat exchange in a reaction chamber in which a large amount of heat is evolved, may be released from pressure down to the pressure used in the cooling, the desired degree of saturation being obtained by spraying in water. The wet steam thus used for cooling can withdraw heat from the reaction vessel until the formation of dry steam. The dry steam thus obtained may be further used for heating or, while releasing to a lower pressure for the recovery of energy. A part of the condensate is preferably returned in circulation.

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

Example.

6000 cubic metres per hour of a gas mixture consisting of 2 parts of hydrogen (4000 cubic metres) to 1 part of carbon monoxide (2000 cubic metres) are led through three reaction chambers arranged one behind the other, charged with a nickel catalyst and each of 20 cubic metres content, of an apparatus for the preparation of hydrocarbons from carbon monoxide and hydrogen. The heat of reaction thus developed amounts to 600 calories per cubic metre of gas and in all 3,600,000 calories are set free per hour. Since with good insulation and by reason of the relatively low working temperature a maximum radiation loss of 100,000 calories per hour can be expected in all, 3,500,000 calories per hour must be led away. For this purpose the reaction chambers *a* are so constructed that the catalyst lies in the spaces between a bundle of tubes *b* through which is led wet steam containing 60 per cent. of steam under a pressure of 16 atmospheres which is introduced at *d*. The steam leaves the bundle of tubes at *c* in the form of dry steam. 1 kilogram of steam absorbs 200 calories; in this way there are prepared in all 17.5 metric tons of dry steam per hour which may be used for example as driving steam of a turbine plane with a good degree of efficiency. The reaction products, after leaving the last reaction chamber at *h*, are led through a heat-exchanger *e* and then through a condenser *f* in which the condensation of the products liquid at ordinary temperature takes place. The latter are separated from non-condensable constituents in a separator *g*. The initial gases are introduced at *i*, pass through the heat-exchanger *e* and the preheater *k* and then enter the first reaction chamber *a* at *l*.

Dated this 3rd day of February, 1936.

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

COMPLETE SPECIFICATION.

Improvements in Carrying out Reactions 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), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is already known that reactions of the oxides of carbon, and in particular of carbon monoxide, with hydrogen must proceed under very accurately maintained temperature conditions if it is desired to obtain an optimum yield of organic compounds containing more than one carbon atom, in particular of liquid hydrocarbons or their oxygen derivatives, and at the same time to obtain their best possible economy of the process.

The said reactions are exothermic, thus from a certain size of furnace upwards, at which the heat set free begins to exceed the loss by radiation, the excess of heat must be led away continuously. According to the methods of cooling hitherto known, a colder liquid or gaseous medium is brought into indirect heat exchange in the same direction or in countercurrent with the reaction material to be cooled. In the course of the path of cooling, the temperature of the cooling agent thus rises and the cooling agent loses activity by reason of the lowering of the mean temperature difference. Methods of this kind are suitable for carrying out reactions the heat requirements of which are not uniform, for example when at the commencement of the reaction a considerably greater portion of the total heat must be led away than in the middle or at the end of the reaction. If, on the other hand, the reaction proceeds with a constant evolution of heat or if the evolution of heat proceeds with but slight fluctuations, which is usually the case in reactions under low pressure, i.e. atmospheric or slightly increased pressure, then the drawback mentioned above is more evident the more uniformly the reaction proceeds.

My foreign correspondents have now found that in the said reactions of the oxides of carbon with hydrogen, in particular in the reaction of hydrogen with carbon monoxide, at atmospheric or increased pressure for the formation of liquid hydrocarbons or their derivatives, the excess heat may be withdrawn in a very advantageous manner by indirect heat exchange relation if wet steam is introduced into the cooling space. It is preferable to employ a wet steam the saturation of which is kept between the limits of about 60 and about 80 per cent., i.e. in which up to 40 per cent. of water is present in the liquid phase (in the form of small suspended droplets). In this way not only does the temperature of the wet steam employed as cooling agent and consequently the temperature of the reacting substances remain constant during the absorption of heat by the cooling agent, but the heat transmission value also maintains a maximum value within the steam-concentration limits of 60 and 100 per cent. Such a cooling system has the character of a cooling bath having an entirely uniform temperature such as cannot be obtained in practice by other methods. For thermal reasons a pressure range, depending on the reaction temperature to be maintained, of from 5 to 15 atmospheres is especially suitable because under the said pressure the dry steam formed by heat exchange from the wet steam is able to exert a maximum of energy. It is also advantageous to keep the cooling medium under such a pressure that the dry steam temperature is only slightly below the reaction temperature. If it is found that in the course of the cooling the steam has become dry before the end of the reaction, it is preferable to introduce water in the form of a spray or mist into the cooling chamber to such an extent that in the further course the temperature at which dry steam is formed is no longer exceeded so that no superheated steam is formed.

The wet steam to be used as the cooling agent may be prepared in various ways. For example water under the pressure used in the cooling may be heated by any available source of waste heat to the dry steam temperature and then allowed to evaporate whereby a wet steam having a considerable content of liquid water is formed. Alternatively, hot water under pressure, which has been treated for example by heat exchange in a reaction chamber in which a large amount of heat is evolved, may be released from pressure down to the pressure used in the cooling, the desired degree of saturation being obtained by spraying in water. The wet steam thus used for cooling can withdraw heat from the reaction vessel until the formation of dry steam. The dry steam thus obtained may be further used for heating or, while releasing to a lower pressure, for the recovery of energy. A part of the condensate is preferably returned in circulation.

The following Example, given with reference to the drawing accompanying the Provisional Specification in which is shewn diagrammatically an arrangement of suitable apparatus, will further illustrate how the said invention may be carried out in practice but the invention is not restricted to this Example.

EXAMPLE.

6000 cubic metres per hour of a gas mixture consisting of 2 parts of hydrogen (4000 cubic metres) to 1 part of carbon monoxide (2000 cubic metres) are led through three reaction chambers arranged one behind the other, charged with a nickel catalyst and each of 20 cubic metres content, of an apparatus for the preparation of hydrocarbons from carbon monoxide and hydrogen. The heat of reaction thus developed amounts to 600 calories per cubic metre of gas and in all 3,600,000 calories are set free per hour. Since with good insulation and by reason of the relatively low working temperature a maximum radiation loss of 100,000 calories per hour can be expected in all, 3,500,000 calories per hour must be led away. For this purpose the reaction chambers *a* are so constructed that the catalyst lies in the spaces between a bundle of tubes *b* through which is led wet steam containing 60 per cent. of steam under a pressure of 16 atmospheres which is introduced at *d*. The steam leaves the bundle of tubes at *c* in the form of dry steam. 1 kilogram of steam absorbs 200 calories; in this way there are prepared in all 17.5 metric tons of dry steam per hour which may be used for example as driving steam of a turbine plane with a good degree of efficiency. The reaction products, after leaving the last reaction chamber at *h*, are led through a heat-exchanger *e* and then through a condenser *f* in which the condensation of the products liquid at ordinary temperature takes place. The latter are separated from non-condensable constituents in a separator *g*. The initial gases are introduced at *i*, pass through the heat-exchanger *e* and the preheater *k* and then enter the first reaction chamber *a* at *l*.

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. In the conversion of oxides of carbon with hydrogen, in particular the conversion of carbon monoxide with hydrogen under atmospheric or increased pressure to form hydrocarbons or their oxygen derivatives, the step of maintaining the temperature desired for the conversion by withdrawing the excess of heat set free by indirect heat exchange relation of the reacting substances with wet steam introduced into the cooling space.

2. In the process as claimed in Claim 1, maintaining the saturation of the wet steam between the limits of about 60 and about 80 per cent.

3. In the process as claimed in Claim 1 or 2, keeping the wet steam employed as cooling agent under a pressure at which the dry steam temperature is only slightly below the reaction temperature.

4. The process for carrying out the conversion of oxides of carbon with hydrogen substantially as described in the foregoing Example.

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

Dated this 8th day of January, 1937.

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London, W.C.2,
Agents.

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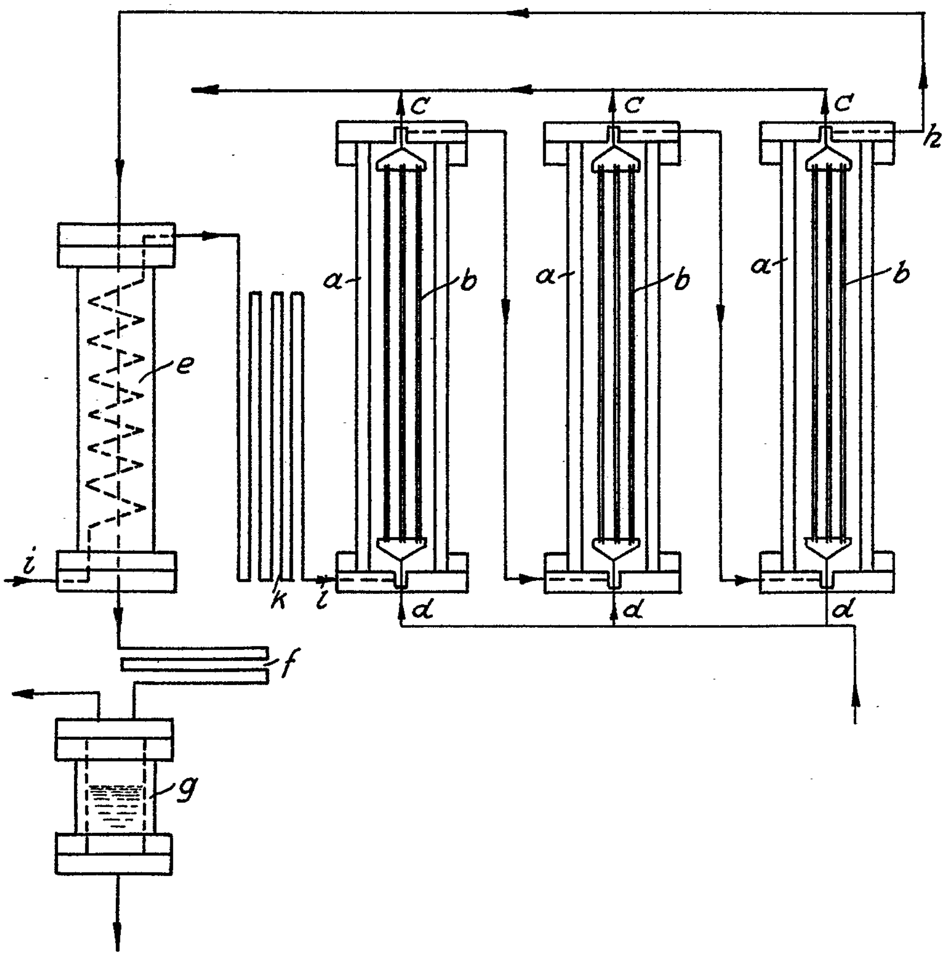
2nd Edition

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



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