# PATENT SPECIFICATION

Application Date: June 13, 1941. No. 7485/41.

551,312

Complete Specification Left: May 20, 1942.

Complete Specification Accepted: Feb. 17, 1943.

## PROVISIONAL SPECIFICATION

## Exothermic Chemical Processes

We, WALTER HENRY GROOMBRIDGE and RONALD PAGE, both British subjects, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention relates to exothermic chemical processes and more particularly such processes carried out between gaseous reagents such as carbon monoxide and hydrogen.

In many chemical reactions of an exothermic nature carried out on a commercial scale, the heat evolved is removed from the reaction zone by the boiling of a liquid in thermal contact therewith. Since the heat of vaporisation of most liquids is so much greater than the heat which can be conducted away merely by a current of liquid below its boiling point, this method offers many advantages in practice. There is, however, considerable difficulty in designing plant which is easily capable of assembly and re-assembly after it has been taken down, for example for the replacement of reactivation of catlyst contained in the reaction zone. This difficulty becomes more important when the reaction is carried out under pressure so that a difference of pressure exists between the contents of the reaction vessel and the container for the cooling liquid, since it becomes necessary for the joints between the two vessels to be pressure-tight. Water is the liquid most commonly employed owing to the fact that it is available in large quantities and is of constant boiling point so that there is no chance of a variation in the reaction temperature resulting from variation in the quality of the cooling liquid employed. In many reactions, however, and in fact in all reactions carried out at temperatures above 100° C., the use of water makes it necessary to use the cooling liquid under super atmospheric pressure and accordingly there may exist a difference in pressure between the reaction vessel and the container for the cooling liquid as well as between each and the atmosphere. The present invention is concerned with a method of and apparatus for obviating this difficulty and the invention is of greatest importance in connection with the production of hydrocarbons by subjecting carbon monoxide and hydrogen to reaction at pressures above atmospheric. The invention will be described more particularly in connection with this particular application.

According to the invention, hydrocarbons are produced by subjecting carbon monoxide and hydrogen to reaction in a reaction vessel in thermal contact with a boiling liquid and the outlet from the reaction vessel is in communication with the surface of the cooling liquid, the reaction products and vapour from the cooling liquid being withdrawn together.

The synthesis of hydrocarbons from carbon monoxide and hydrogen can be carried out very effectively at ordinary atmospheric pressure but, by increasing the pressure to 5—7 atmospheres or somewhat more, the apparatus used can be correspondingly reduced in size without reducing the quantity of hydrocarbons produced and without any considerable change in their nature. It is even possible to produce at such pressures a quantity of hydrocarbons per unit quantity of reaction gases equal to that obtainable with the same quantity of reaction gases at atmospheric pressure while using the substantially smaller quantity of catalyst which is needed in the smaller apparatus. Increasing the pressure much above 10 atmospheres does not however produce corresponding advantages in view of the increased proportion of methane then found in the product. If, therefore, it is not desired to form substantial quantities of methane by the process pressures of above 20 atmospheres are usually best avoided. On the other hand if steps are taken to utilize the methane, e.g. by conversion with steam into oxides of carbon and hydrogen or by cracking or partial combustion into acetylene, the process can be conducted economically at such higher pressures. At even higher pressures useful oxygen-containing products may also be obtained.

With active catalysts, e.g. those of the cobalt-thoria type, the process is usually carried out at temperatures of 190—210° C. and water boiling at this temperature develops a pressure of some 16—18 or 20 atmospheres. Nevertheless water can be used as the cooling fluid in the process even when it is desired to use a synthesis presure of no more than, say, 5—7 atmospheres by dissolving therein a salt in sufficient quantity to reduce its vapour tension so that the resulting solution boils at the desired reaction temperature under the pressure at which it is desired to carry out the reaction. For example, if it is desired to carry out the reaction. For example, if it is desired to carry out the synthesis of hydrocarbons from carbon monoxide and hydrogen at 6 or 7 atmospheres sufficient of the salt is dissolved in the cooling water to produce a solution boiling under this pressure at 190—210° C. Calcium chloride is a salt of most general application in this connection, although other salts may be used including calcium bromide, magnesium chloride or bromide, sodium chloride or bromide, potassium carbonate, or zinc chloride. Caustic soda and caustic potash may also be used to raise the boiling point of the water used.

As an alternative to altering the boiling point of the cooling water in the manner described, there may be used as cooling liquid a suitable liquid boiling at the temperature and pressure obtained in the reaction zone. Thus, ethylene glycol may be used for temperatures somewhat above those normally employed in the synthesis of hydrocarbons when using a cobalt-thoria catalyst, for example, at the temperatures which are most suitable for a catalyst having a basis of iron.

It is preferred to use a cooling liquid which is immiscible with the hydrocarbons produced in the synthesis owing to the simplicity of the subsequent separation of the condensate coming from the reaction zone and cooling bath. When using an aqueous salt solution, only water distils with the hydrocarbons with which it is immiscible and from which it is therefore readily separated while the composition of the cooling liquid may be maintained constant by supplying fresh water in a measure as it is evaporated from the salt solution.

As previously indicated a valuable feature of the present invention is the simplicity of the apparatus needed for adopting the novel procedure. In its simplest form, the apparatus may comprise an outer container for the cooling liquid, this container being provided with an outlet for reaction gases and vapour from the cooling liquid and also with an inlet for fresh cooling liquid to replace that evaporated. Secured to the head of such a container there may be provided a tube plate and above it an inlet header provided with an inlet for reaction gases. The tube plate may be provided with tubes expanded into openings in the plate and depending into reaction vessels within the cooling liquid. The reaction vessels may, very conveniently, be of cylindrical form, closed at their lower ends and hung from the tubes referred to, for example by means of pins passing through the tubes and engaging with slots in the reaction vessels in the manner of bayonet joints. By arranging that the tubes extend to the base of the reaction vessels and providing catalyst in the annular space thus formed, the reaction gases will be preheated during their passage to the bottom of the reaction vessels and will then pass upwardly through the catalyst and be withdrawn from the open top, where they mix with the vapours from the cooling liquid and are withdrawn from the vessel.

It will be appreciated that an important advantage of apparatus constructed in the manner described above is that reaction vessels of an insubstantial nature may be used as, whatever the pressure at which the synthesis is carried out, this pressure exists both inside and outside the reaction vessels.

While the invention has been described more particularly in connection with the production of hydrocarbons from carbon monoxide and hydrogen, it will be appreciated that the method and apparatus described are applicable to other exothermic processes, especially those carried out in the vapour phase.

Dated this 12th day of June, 1941.

STEPHENS & ALLEN,
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York House, Gordon Avenue, Stanmore,
Middlesex.

## COMPLETE SPECIFICATION

## Exothermic Chemical Processes

We, WALTER HENRY GROOMBRIDGE and RONALD PAGE, both British subjects, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to exothermic chemical processes and more particularly, such processes carried out between gaseous reagents such as carbon monoxide and hydrogen.

In many chemical reactions of an exothermic nature carried out on a commercial scale, the heat evolved is removed from the reaction zone by the boiling of a liquid in thermal contact therewith. Since the heat of vaporisation of most liquids is so much greater than the heat which can be conducted away merely by a current of liquid below its boiling point, this method offers many advantages in practice. There is, however, considerable difficulty in designing plant which is easily capable of assembly and re-assembly after it has been taken down, for example for the replacement or reactivation of catalyst contained in the reaction zone. This difficulty becomes more important when the reaction is carried out under pressure so that a difference of pressure exists between the contents of the reaction vessel and the container for the cooling liquid, since it becomes necessary for the joints between the two vessels to be pressure-tight. Water is the liquid most commonly employed owing to the fact that it is available in large quantities and is of constant boiling point so that there is no chance of a variation in the reaction temperature resulting from variation in the quality of the cooling liquid employed. In many reactions, however, and in fact in all reactions carried out at temperatures above 100° C., the use of water makes it necessary to use the cooling liquid under super atmospheric pressure and accordingly there may exist a difference in pressure between the reaction vessel and the container for the cooling liquid as well as between each and the atmosphere. The present invention is concerned with a method of and apparatus for obviating this difficulty and the invention is of greatest importance in connection with the production of hydrocarbons by subjecting carbon monoxide and hydrogen to reaction at pressures above atmospheric. The invention will be described more particularly in connection with this particular application.

According to the invention, hydrocarbons are produced by subjecting carbon monoxide and hydrogen to reaction in a reaction zone in thermal contact with a liquid which is boiled by the heat liberated in the reaction zone and the outlet from the reaction vessel is in communication with the surface of the boiling liquid being withdrawn together.

The synthesis of hydrocarbons from carbon monoxide and hydrogen can be carried out very effectively at ordinary atmospheric pressure but, by increasing the pressure to 5—7 atmospheres or somewhat more, the apparatus used can be correspondingly reduced in size without reducing the quantity of hydrocarbons produced and without any considerable change in their nature. It is even possible to produce at such pressures a quantity of hydrocarbons per unit quantity of reaction gases equal to that obtainable with the same quantity of reaction gases at atmospheric pressure while using the substantially smaller quantity of catalyst which is needed in the smaller apparatus. Increasing the pressure much above 10 atmospheres does not however produce corresponding advantages in view of the increased proportion of methane then found in the product. If, therefore, it is not desired to form substantial quantities of methane by the process pressures of above 20 atmospheres are usually best avoided. On the other hand is steps are taken to utilize the methane, e.g. by conversion with steam into oxides of carbon and hydrogen or by cracking or partial combustion into acetylene, the process can be conducted economically at such higher pressures. At even higher pressures useful oxygen-containing products may also be obtained.

With active catalysts, e.g. those of the cobalt-thoria type, the process is usually carried out at temperatures of 190—210° C. and water boiling at this temperature develops a pressure of some 16—18 or 20 atmospheres. Nevertheless water can be used as the cooling fluid in the process even when it is desired to use a synthesis pressure of no more than, say, 5—7 atmospheres by dissolving therein a salt in sufficient quantity to reduce its vapour tension so that the resulting solution boils at the desired reaction temperature under the pressure at which it is desired to carry out the reaction. For example, if it is desired to carry out the synthesis of hydrocarbon from carbon monoxide and hydrogen at 6 or 7 atmospheres sufficient of the salt is dissolved in the cooling water to produce a solution boiling under this pressure at 190—210° C. Calcium chloride is a salt of most general application in this connection, although other salts may be used including calcium bromide, magnesium chloride or bromide, sodium chloride or bromide, potassium carbonate, or zinc chloride. Caustic soda and caustic potash may also be used to raise the boiling point of the water used.

As an alternative to altering the boiling point of the cooling water in the manner described, there may be used as cooling liquid a suitable liquid boiling at the temperature and pressure obtained in the reaction zone. Thus, ethylene glycol may be used for temperatures somewhat above those normally employed in the synthesis of hydrocarbons when using a cobalt-thoria catalyst, for example, at the temperatures which are most suitable for a catalyst having a basis of iron.

It is preferred to use a cooling liquid which is immiscible with the hydrocarbons produced in the synthesis owing to the simplicity of the subsequent separation of the condensate coming from the reaction zone and cooling bath. When using an aqueous salt solution, only water distils with the hydrocarbons with which it is immiscible and from which it is therefore readily separated while the composition of the cooling liquid may be maintained constant by supplying fresh water in a measure as it is evaporated from the salt solution.

As previously indicated a valuable feature of the present invention is the simplicity of the apparatus needed for adopting the novel procedure. In its simplest form, the apparatus may comprise an outer container for the cooling liquid, this container being provided with an outlet for reaction gases and vapour from the cooling liquid and also with an inlet for fresh cooling liquid to replace that evaporated. Secured to the head of such a container there may be provided a tube plate and above it an inlet header provided with an inlet for reaction gases. The tube plate may be provided with tubes expanded into openings in the plate and depending into reaction vessels within the cooling liquid. The reaction vessels may, very conveniently, be of cylindrical form, closed at their lower ends and hung from the tubes referred to, for example by means of pins passing through the tubes and engaging with slots in the reaction vessels in the manner of bayonet joints. By arranging that the tubes extend to near the base of the reaction vessels and providing catalyst in the annular space thus formed, the reaction gases will be preheated during their passage to the bottom of the reaction vessels and will then pass upwardly through the catalyst and be withdrawn from the open top, where they mix with the vapours from the cooling liquid and are withdrawn from the vessel.

It will be appreciated that an important advantage of apparatus constructed in the manner described above is that reaction vessels of an insubstantial nature may be used as whatever the pressure at which the synthesis is carried out, this pressure exists both inside and outside the reaction vessels.

While the invention has been described more particularly in connection with the production of hydrocarbons from carbon monoxide and hydrogen, it will be appreciated that the method and apparatus described are applicable to other exothermic processes, especially those carried out in the vapour phase.

The accompanying drawings illustrate a form of apparatus which is suitable for use in carrying out the synthesis of hydrocarbons from carbon monoxide and hydrogen with the aid of the invention.

In the drawings, Fig. 1 shows diagrammatically in section the apparatus comprising reaction vessels and container for cooling liquid, Fig. 2 shows a suitable form of reaction vessel and Fig. 3 an inlet tube for introducing the reactant gases into the reaction vessel.

Referring to the drawings, the container 1 for cooling liquid, flanged as at 2, carries on the flange a tube-plate 3 and the flange 4 of a header 5 provided with inlet 6, flange 2, tube-plate 3 and flange 4 being secured together by bolts 7. The tube-plate 3 carries inlet tubes 8 expanded into openings therein, these inlet tubes carrying pins 9, fitting into slots 10 in reaction vessels 11 and thereby supporting the reaction vessels. The container 1 is provided with an inlet 12 for cooling liquid and an outlet 13 for reaction products and vapour from the cooling liquid.

In operation, catalyst 14 is charged into the annular space between inlet tubes 8 and the inner walls of the reaction vessels 11 and cooling liquid 15 is fed into the container 1 through inlet 12 until it rises somewhat above the surface of the catalyst 14. The reaction is started usually by supplying hot liquid 15 to raise the temperature of the catalyst to the reaction temperature, whereupon the mixture of carbon monoxide and hydrogen is passed in through inlet 6, header 5, inlet tubes 8 to the catalyst 14, the products being withdrawn by the outlet 13. Once the reaction starts heat is liberated and boils the cooling liquid 15, the vapour thus produced being removed with the reaction products through outlet 13, cooling liquid being supplied to maintain the level in the container 1 by inlet 12. This level can be seen by means of suitable sight glass (not shown).

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

1. Method of carrying out an exothermic chemical reaction in a reaction zone in thermal contact with a liquid boiled by the heat liberated in the reaction zone, wherein the outlet from the reaction zone is in communication with the surface of the boiling liquid and the reaction products and vapour from the boiling liquid are withdrawn together.

2. Process for the production of hydrocarbons from carbon monoxide and hydrogen in a reaction zone in thermal contact with a liquid boiled by the heat liberated in the reaction zone, wherein the outlet from the reaction zone is in communication with the surface of the boiling liquid and the reaction products and vapour from the boiling liquid are withdrawn together.

3. Process according to Claim 1 or 2, wherein the reaction is conducted at superatmospheric pressure.

4. Process according to Claim 3, wherein the liquid in thermal contact with the reaction zone is an aqueous solution containing a quantity of solute chosen so that the solution boils at the desired reaction temperature.

5. Process according to Claim 4, wherein the liquid in thermal contact with the reaction zone is an aqueous solution of calcium chloride.

6. Process according to Claim 3, wherein an organic liquid of suitable boiling point is employed as cooling liquid.

7. Method of carrying out the production of hydrocarbons from carbon monoxide and hydrogen and other exothermic chemical reactions substantially as hereinbefore described.

8. Apparatus for use in carrying out exothermic chemical reactions at a temperature controlled by a boiling liquid, which comprises a reaction vessel situated within a container for cooling liquid, said reaction vessel being provided with an inlet for reactants and an outlet for reaction products, said outlet being in communication with the interior of said container and an outlet provided on said container.

9. Apparatus according to Claim 8, wherein a plurality of reaction vessels are provided within a common container for cooling liquid, said reaction vessels being of tubular form and mounted vertically with closed lower ends and an inlet tube for reactants is situated within each reaction vessel and passes down to near the bottom thereof.

10. Apparatus according to Claim 9, wherein said inlet tubes are suspended from a tube-plate closing the container for cooling liquid and each inlet tube supports the reaction vessel it serves.

Dated this 18th day of May, 1942.
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FIG 1

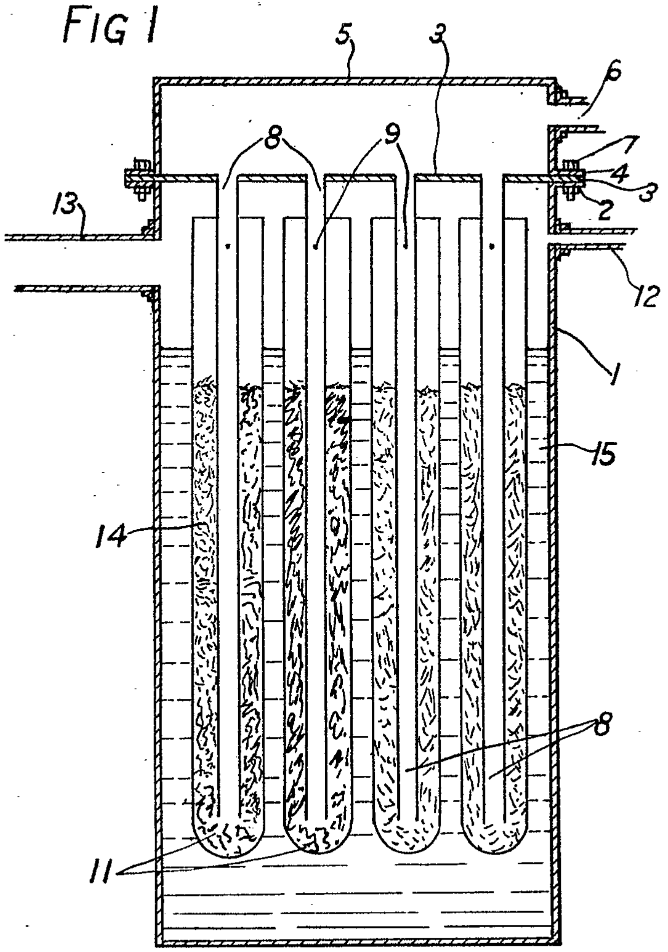


FIG 3

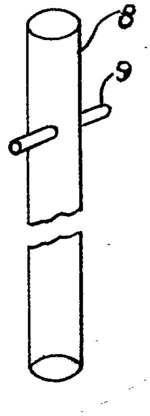
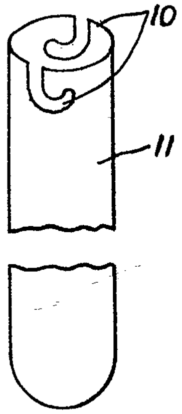


FIG 2



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

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