[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Hydrocarbons and other Products from Carbon Monoxide and Hydrogen.

I, HENRY DREYFUS, a British subject, of Celanese House, 22 & 23, Hanover Square, London, W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of hydrocarbons and other products by reaction between carbon monoxide and hydrogen.

When carbon monoxide and hydrogen are brought into contact with suitable catalysts at elevated temperatures they can be made to unite with the formation of various types of product. For example at high temperatures and under very high pressures certain catalysts, e.g. zinc chromate, promote the synthesis of lower fatty alcohols and other oxygenated organic compounds. Under lower pressures, for example atmospheric pressure, these oxygenated compounds are usually not obtained. On the other hand, especially when metals of Group 8 of the Periodic Table are used as catalysts, it is possible to obtain, according to the temperature and other conditions, large yields either of methane or of higher hydrocarbons including normally liquid hydrocarbons. There are, however, two difficulties which arise particularly in the hydrocarbon synthesis. The first of these is that small quantities of wax-like bodies are often formed; these may be deposited on the catalyst, thereby greatly decreasing its efficiency. The second is that owing to the exothermic nature of the reaction over-heating of the catalyst and consequent undesired reactions are liable to occur.

I have found that these difficulties can both be to a large extent overcome if the synthesis is carried out under certain special conditions. According to the invention the catalyst is immersed in a liquid medium which boils or which contains a constituent or constituents which boil, at or about the temperature and pressure which it is desired to employ for the synthesis. The carbon monoxide and hydrogen are bubbled through the liquid medium in contact with the catalyst. Preferably the catalyst chamber is provided with a reflux condenser by means of which the vaporised medium may be condensed and returned to the synthesis zone.

As the liquid medium it is preferable to employ a hydrocarbon or a mixture of hydrocarbons. Such a mixture may have a narrow boiling point range or it may merely contain substantial quantities of components boiling at the desired temperature. Preferably the liquid medium is substantially free from sulphur or sulphur compounds or other substances which might tend to poison the catalyst. Thus, for example, a purified petroleum fraction may be employed as the liquid medium, but it is preferred to use an oil which itself has been prepared by the reduction of carbon monoxide.

The temperature, pressure and catalyst employed vary with the product desired. As already mentioned, if it is desired to produce oxygenated organic compounds a zinc chromate or other catalyst should be employed and the gases caused to react under high pressure. However, the invention is of greatest value when applied to the synthesis of hydrocarbons under atmospheric or similar pressures. If it is desired to produce mainly methane there may be used a nickel catalyst at temperatures of about 230—250° C. If it is desired to produce normally liquid hydrocarbons as the main products an activated cobalt catalyst may be used at a temperature of about 180—200° C., or an activated iron catalyst at a temperature in the neighbourhood of 250° C. The catalyst may be activated by means of substances having a promoting action, for example alumina, magnesia or zinc oxide. A method of making a special nickel catalyst promoted with alumina is described in Specification No. 465,157 of British Celanese Limited and others, and this is found to be particularly useful for making methane. Analogous methods of making iron and especially cobalt catalysts may be adopted when normally liquid hydrocarbons are to be the main products.

The initial gas mixture may contain hydrogen and carbon monoxide in

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approximately equal volumes, but preferably an excess of hydrogen is used. For example good results are obtained by using twice as much hydrogen as carbon monoxide by volume, but mixtures containing still higher proportions of hydrogen, for example 3 or 4 times as much hydrogen as carbon monoxide, may be used if desired. Generally speaking, the higher the proportion of hydrogen the greater the tendency to produce methane. Thus an increase in the proportion of hydrogen may with advantage be accompanied by a decrease in the temperature employed if it is desired to produce normally liquid hydrocarbons. Decrease in the proportion of hydrogen tends to increase the proportion of unsaturated hydrocarbons produced.

If desired the carbon monoxide and hydrogen may be diluted with nitrogen or with a gas or vapour which is chemically related to carbon monoxide or to hydrogen, for example carbon dioxide or hydrocarbon gases or vapours. The diluent may, if desired, comprise light hydrocarbons produced from carbon monoxide and hydrogen. The amount of diluent may, for example, be $1\frac{1}{2}$, 3, 5 or 10 or more parts by volume for each part of carbon monoxide.

The gas may be subjected to a single passage in contact with the catalyst, especially when it is desired to produce methane. However, when normally liquid hydrocarbons are to be produced, and therefore lower temperatures are employed, the reaction tends to proceed somewhat more slowly and it may, therefore, be advisable to subject the gas mixture repeatedly to the reaction conditions either by passing it through a number of catalyst zones or by recycling it through a single catalyst zone. Between successive passages through the catalyst zones or between successive stages in a recycling process normally liquid hydrocarbons may be condensed out of the gas mixture and so removed. If desired a certain proportion of such normally liquid hydrocarbons may be allowed to remain in the gas mixture or may be returned thereto to act as diluent.

Dated this 5th day of November, 1937.

STEPHENS & ALLEN,
Chartered Patent Agents,
Celanese House,
22 & 23 Hanover Square, London, W.1.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Hydrocarbons and other Products from Carbon Monoxide and Hydrogen.

I, HENRY DREYFUS, a British subject, of Celanese House, 22 & 23, Hanover Square, London, W.1, 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 the manufacture of hydrocarbons and other products form carbon monoxide and hydrogen.

When carbon monoxide and hydrogen are brought into contact with suitable catalysts at elevated temperatures they can be made to unite with the formation of various types of product. For example at high temperatures and under very high pressures certain catalysts, e.g. zinc chromate, promote the synthesis of lower fatty alcohols and other oxygenated organic compounds. Under lower pressures, for example atmospheric pressure, these oxygenated compounds are usually not obtained. On the other hand, especially when metals of Group 8 of the Periodic Table are used as catalysts, it is possible to obtain, according to the temperature and other conditions, large yields either of methane or of higher hydrocarbons including normally liquid hydrocarbons. There are, however, two difficulties which are, particularly in the hydrocarbon synthesis. The first of these is that small quantities of wax-like bodies are often formed; these may be deposited on the catalyst, thereby greatly decreasing its efficiency. The second is that owing to the exothermic nature of the reaction, overheating of the catalyst and consequent undesired reactions are liable to occur. To overcome or reduce the importance of these difficulties is an object of the present invention.

It has been suggested in Specification No. 468,434 that the catalyst should be immersed in a liquid medium which has itself been produced by the hydrocarbon synthesis and which contains a substantial amount of constituents which, under the pressure prevailing in the reaction zone, boil below the temperature at which the reaction is to be carried out. During the reaction part or all of these low boiling constituents of the liquid medium is of course vaporised, and these vapours are cendensed in a reflux condenser and returned to the reaction zone.

According to the present invention the catalyst is submerged in a body of a liquid medium which either boils completely within the permissible range of temperatures for the reaction under the pressure employed, or boils partly within this range, and for the rest above it. As the synthesis proceeds, the heat evolved vaporises part of the liquid medium boiling within the desired temperature range and the vapours are condensed and returned to the catalyst zone. The amount of the liquid medium boiling within the said temperature range is such that a substantial part of it is always in the liquid phase. By this means a very close control of the reaction temperature is achieved.

In carrying out the invention the catalyst is immersed in the liquid medium and the reaction gases are passed through the liquid medium and in contact with the catalyst. Preferably the catalyst chamber is provided with a reflux condenser by means of which the vaporised medium may be condensed and returned to the synthesis zone.

As the liquid medium it is preferable to employ a hydrocarbon or a mixture of hydrocarbons. Such a mixture may have a very narrow boiling point range or it may contain substantial quantities of components boiling at the desired temperature together with components boiling at higher temperatures. Preferably the liquid medium is substantially free from sulphur or sulphur compounds or other substances which might tend to poison the catalyst. Thus, for example, a purified petroleum fraction may be employed as the liquid medium, but it is preferred to use an oil which itself has been prepared by the reduction of carbon monoxide.

The temperature, pressure and catalyst employed vary with the product desired. As already mentioned, if it is desired to produce oxygenated organic compounds a zinc chromate or other catalyst should be employed and the gases caused to react under high pressure. However, the invention is of greatest value when applied to the synthesis of hydrocarbons under atmospheric or similar pressures. If it is desired to produce mainly methone there may be used a nickel catalyst at temperatures of about 230°—250° C. If it is desired to produce normally liquid hydrocarbons as the main products an activated cobalt catalyst may be used at a temperature of about 180°—200° C., or an activated iron catalyst at a temperature in the neighbourhood of 250° C. The catalyst may be activated by means of substances having a promoting action, for example alumina, thoria, magnesia or zinc oxide. A method of making a special nickel catalyst promoted with alumina is described in Specification No. 465,157 of British Celanese Limited and others, and this is found to be particularly useful for making methane. Analogous methods of making promoted iron and especially promoted cobalt catalysts may be adopted when normally liquid hydrocarbons are to be the main products.

The new process affords a ready means whereby the temperature of the catalyst and of the gases in contact therewith can be regulated very accurately, by careful adjustment of the pressure in the reaction zone and, with the pressure, of the boiling point of the liquid medium. When making hydrocarbons or other products, using a substantially atmospheric pressure, it is preferable to use a liquid medium which under atmospheric pressure boils, at least in part, exactly at or only slightly lower than the lowest temperature to be used in the reaction, as by so doing it is possible to make any desired temperature adjustments by the application of the minimum of excess pressure. Since the reaction will in general give any particular desired products only over a temperature range of at most a few degrees, the increase or decrease of pressure required is but small.

The initial gas mixture may contain hydrogen and carbon monoxide in approximately equal volumes or carbon monoxide in excess, but preferably an excess of hydrogen is used. For example good results are obtained by using twice as much hydrogen as carbon monoxide by volume, but mixtures containing still higher proportions of hydrogen, for example 3 or 4 times as much hydrogen as carbon monoxide, may be used if desired. Generally speaking, the higher the proportion of hydrogen the greater the tendency to produce methane. Thus an increase in the proportion of hydrogen may with advantage be accompanied by a decrease in the temperature employed if it is desired to produce normally liquid hydrocarbons. Decrease in the proportion of hydrogen tends to increase the proportion of unsaturated hydrocarbons produced.

If desired the carbon monoxide and hydrogen may be diluted with nitrogen, carbon dioxide or hydrocarbon gases or vapours. The diluent may, if desired, comprise light hydrocarbons (i.e. hydrocarbons which under the pressure in the reaction zone have a boiling point lower than the reaction temperature) produced from carbon monoxide and hydrogen. The amount of doluent may, for example, be 1½, 3, 5 or 10 or more parts by volume for each part of carbon monoxide.

The gas may be subjected to a single passage in contact with the catalyst, especially when it is desired to produce methane. However, when normally liquid hydrocarbons are to be produced, and therefore lower temperatures are employed, the reaction tends to proceed somewhat more slowly and it may, therefore, be advisable to subject the gas mixture repeatedly to the reaction conditions either by passing it through a number of catalyst zones or by recycling it through a single catalyst zone. Between successive passages through the catalyst zones or between successive stages in a recycling process normally liquid hydrocarbons may be condensed out of the gas mixture and so removed. If desired a suitable proportion of light normally liquid hydrocarbons may be allowed to remain in the gas mixture or may be returned thereto to act as diluent. When high pressures are used and oxygenated derivatives made, the process may likewise be carried out in a single stage or in a number of stages, for example by recycling the synthesis gases.

Although by the new process an efficient temperature control is possible without further cooling means, for example pipes or the like through which a cooling medium circulates, such means, internal and/or external, may be used if desired to supplement the cooling effect of the vaporisation of the liquid medium. Such means may also be used to heat up the liquid medium and the catalyst before the reaction begins.

The following Example illustrates without in any way limiting the invention:—

EXAMPLE.

A cobalt catalyst, promoted with thoria, is immersed in a hydrocarbon fraction, produced by reaction between carbon monoxide and hydrogen, and boiling for the most part between 180° and 185° C., and for the rest at higher temperatures up to about 250° C., under a pressure in the neighbourhood of atmospheric. A mixture of hydrogen and carbon monoxide, containing twice as much hydrogen as carbon monoxide by volume, is preheated to about 180° C. and passed in the form of fine bubbles through the hydrocarbon fraction and in contact with the catalyst. Initially heat is supplied to the hydrocarbon fraction to raise its temperature to about 180° C., but after the reaction has begun the exothermic nature of the reaction supplies more than enough heat to compensate for losses. Part of the excess heat is removed with the products of the reaction, and part causes the hydrocarbon fraction to boil. The vapours of the hydrocarbon fraction so produced, together with the products of the reaction, are passed into a reflux condenser maintained at a temperature just below that of the reaction, whereby all the vapours of boiling point about or above this temperature, whether formed by vaporisation of the hydrocarbon fraction or in the reaction, are condensed and returned to the catalyst zone. As the volume of hydrocarbon liquid in the catalyst zone increases owing to the formation of high boiling hydrocarbons, the excess is drawn off by an overflow at the desired level, fitted with a liquid seal. The gases and vapours which have passed through the reflux condenser are then further cooled, to separate condensible products of the reaction, and after being mixed with further carbon monoxide and hydrogen, are again heated and returned to the reaction zone.

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. Process for the manufacture of hydrocarbons and oxygen-containing derivatives of hydrocarbons by reaction between carbon monoxide and hydrogen at elevated temperatures in the presence of a catalyst, wherein the catalyst is submerged in a body of liquid medium which either boils completely within the permissible range of temperatures for the reaction under the pressure employed, or boils partly within this range, and for the rest above it, the reaction gases being passed through the liquid medium and in contact with the catalyst, so that the heat evolved in the reaction vaporises a part only of the liquid medium boiling within the said range of temperatures.

2. Process according to Claim 1, wherein the liquid medium comprises a mixture of hydrocarbons.

3. Process according to Claim 1 or 2, wherein the boiling point of the liquid medium during the reaction is controlled by adjusting the pressure on the liquid medium.

4. Process according to any of Claims 1—3, wherein the liquid medium which is vaporised during the reaction and any vaporised reaction products of similar boiling point in admixture therewith, are condensed in a reflux condenser and returned to the reaction zone.

5. Process according to any of the preceding claims, wherein the liquid medium comprises a mixture of hydrocarbons themselves produced by reaction between carbon monoxide and hydrogen.

6. Process according to any of the pre-

ceding claims, wherein oxygen-containing derivatives of hydrocarbons are obtained by the reaction between carbon monoxide and hydrogen under pressures considerably higher than atmospheric in the presence of an appropriate catalyst.

7. Process according to any of Claims 1—5, wherein hydrocarbons are obtained by the reaction between carbon monoxide and hydrogen under pressures in the neighbourhood of or equal to atmospheric in the presence of an appropriate catalyst.

8. Process for the manufacture of hydrocarbons and oxygen-containing derivatives of hydrocarbons, substantially as hereinbefore described.

9. Hydrocarbons and oxygen-containing derivatives of hydrocarbons, whenever made by the process of any of the preceding claims.

Dated this 21st day of September, 1938.
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