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PATENT SPECIFICATION



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PROVISIONAL SPECIFICATION

Improvements in the Manufacture of Hydrocarbons from Carbon Monoxide and Hydrogen

I, HENRY DREYFUS, a British subject, of Celandese 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 by reaction between carbon monoxide and hydrogen.

When mixtures of carbon monoxide and hydrogen are heated at a suitable temperature in the presence of strongly hydrogenating catalysts different products are formed according to the conditions employed. For example at relatively high temperatures and under atmospheric pressure, methane is produced in large quantities, while at lower temperatures normally liquid hydrocarbons are the main products. For example, using a nickel catalyst, at temperatures of 230°–250° C. methane is produced, while at temperatures of 160°–180° C. normally liquid hydrocarbons are the main products.

There is, however, one difficulty which arises in carrying out the synthesis of normally liquid hydrocarbons from carbon monoxide and hydrogen. It is found that the catalyst used gradually loses its initial activity and after a more or less short period becomes commercially useless and must be regenerated. It is believed that this gradual poisoning of the catalyst is due, at least in large part, to the deposition or formation thereon of wax-like materials which reduce the active surface available for catalysing the reaction.

According to the present invention the synthesis of hydrocarbons from carbon monoxide and hydrogen is carried out under pressures substantially lower than atmospheric pressure. It is found that by operating at such pressures, the life of the catalyst can be very considerably extended. It is thus possible to work continuously for longer periods without having to stop the reaction and regenerate the catalyst.

Advantageously the reaction is carried out under a pressure of at most half an

atmosphere; preferably the pressure is less than 0.25, e.g. 0.1 atmosphere.

It is of further advantage to operate not only under reduced absolute pressure, but also in the presence of a diluent whereby also the partial pressure of the reactants and products is reduced. For example the carbon monoxide and hydrogen may be diluted with nitrogen or better still with a gas or vapour which is chemically related to the carbon monoxide or the hydrogen such as carbon dioxide or hydrocarbon gases or vapours. The diluent may, if desired, comprise hydrocarbons produced from carbon monoxide and hydrogen in an earlier stage or operation. The amount of diluent may, for example, be 1½, 3, 5 or 10 or more parts by volume for each part of carbon monoxide.

The conditions employed in the synthesis depend on the products which are desired. As catalysts there may be employed metals of Group 8. For example cobalt and iron are particularly useful when it is desired to produce normally liquid hydrocarbons, while nickel is most valuable when methane is to be produced. The catalysts may, for example, be activated with alumina, magnesia, zinc oxide or other activating agents. The catalysts, whether alone or mixed with other catalysts or with activating agents, may be employed in association with a carrier; for example they may be deposited on charcoal, silica gel, pumice, asbestos or the like. On the other hand self-supporting catalyst masses may be used with advantage, and in particular a special nickel-alumina or similar catalyst prepared in the cold as described in Specification No. 465,157 of British Celandese Limited and others is 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 temperature employed may, for example, be between 150° and 300° C. and like the catalyst the exact tempera-

ture depends on the products required. For example when employing an activated cobalt catalyst to produce normally liquid hydrocarbons a temperature of the order of 180° to 200° C. may be employed, while similar products are produced using an activated iron catalyst at temperatures in the neighbourhood of 250° C. On the other hand, when it is desired to produce methane a nickel-alumina catalyst may be employed at a temperature of, for example, about 350° C.

The hydrogen and carbon monoxide in the initial gas mixture may be present in approximately equal amounts, 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 three or four 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. A decrease in the proportion of hydrogen increases the proportion of unsaturated hydrocarbons produced.

The reaction may, for example, be carried out by passing the gas mixtures through heated tubes containing the catalyst. Preferably the dimensions and structure of the tubes are such that a high degree of turbulence is imparted to the gas so as to ensure good contact between the gas and the catalyst and to secure

efficient heating throughout the gas mixture. For example relatively narrow tubes may be used with a high rate of gas flow, or masses of catalyst may be so disposed as to break up the gas stream. A similar effect may be attained by inserting baffles at suitable intervals along the length of the reaction tube. If desired the interior of the reaction tube and/or any baffles contained therein may be made of or lined with a catalytic metal. Instead of tubes there may be used reaction zones of annular cross-section or any suitable type of apparatus.

The gas may be subjected to a single passage through the reaction zone, 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 reaction zones or by recycling it through a single reaction zone. Between the successive passages through the reaction zones or between successive cycles 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 29th day of May, 1937.
STEPHENS & ALLEN.
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22 & 23, Hanover Square,
London, W.1.

COMPLETE SPECIFICATION

Improvements in the Manufacture of Hydrocarbons 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 by reaction between carbon monoxide and hydrogen.

When mixtures of carbon monoxide and hydrogen are heated at a suitable temperature in the presence of strongly hydrogenating catalysts different products are formed according to the conditions employed. For example at rela-

tively high temperatures and under atmospheric pressure, methane is produced in large quantities, while at lower temperatures normally liquid hydrocarbons are the main products. Thus using a nickel catalyst, at temperatures of 230°—250° C. methane is produced, while at temperatures of 160°—180° C. normally liquid hydrocarbons are the main products.

There is, however, one difficulty which arises in carrying out the synthesis of normally liquid hydrocarbons from carbon monoxide and hydrogen. It is found that the catalyst used gradually loses its initial activity and after a more

or less short period becomes commercially useless and must be regenerated. It is believed that this gradual poisoning of the catalyst is due, at least in large part, to the deposition or formation thereon of wax-like materials which reduce the active surface available for catalysing the reaction.

Although a few proposals have been set forth for the synthesis of hydrocarbons from carbon monoxide and hydrogen, in which it is stated that pressures above atmospheric, or atmospheric or diminished pressures may be used, neither definite values for such diminished pressures, nor any reason for or advantage arising out of their use has been given.

I have now found that by carrying out the synthesis of hydrocarbons from carbon monoxide and hydrogen under an absolute pressure of at most half an atmosphere, the life of the catalyst can be very considerably extended. It is thus possible to work continuously for longer periods without having to stop the reaction and regenerate the catalyst. Preferably the pressure is between about 0.25 and 0.1 atmosphere, though still lower pressures can be used.

It is of further advantage to operate not only under reduced absolute pressure, but also in the presence of a diluent whereby the partial pressure of the reactants and products is further reduced. For example the carbon monoxide and hydrogen may be diluted with nitrogen or better with steam, carbon dioxide or hydrocarbon gases or vapours. The diluent may if desired comprise hydrocarbons produced from carbon monoxide and hydrogen in an earlier stage of operation. The amount of diluent may, for example, be 1, 3, 5 or 10 or more parts by volume for each part of carbon monoxide.

The conditions employed in the synthesis depend on the products which are desired. As catalysts there may be employed metals of Group 8. For example cobalt and iron are particularly useful when it is desired to produce normally liquid hydrocarbons, while nickel is most valuable when methane is to be produced. The catalysts may be activated, for example with alumina, thoria, magnesia, zinc oxide or other activating agents. The catalysts, whether alone or mixed with other catalysts or with activating agents, may be employed in association with a carrier; for example they may be deposited on charcoal, silica gel, pumice, asbestos or the like. On the other hand self-supporting catalyst masses may be used with advantage, and in particular a special nickel-alumina or

similar catalyst prepared in the cold as described in Specification No. 465,157 of British Celanese Limited and others, is 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 temperature employed may, for example, be between 150° and 300° C. and like the catalyst the exact temperature depends on the products required. For example when employing an activated cobalt catalyst to produce normally liquid hydrocarbons a temperature of the order of 180° to 200° C. may be employed, while similar products are produced using an activated iron catalyst at temperatures in the neighbourhood of 250° C. On the other hand, when it is desired to produce methane a nickel-alumina catalyst may be employed at a temperature of, for example, about 350° C.

The hydrogen and carbon monoxide in the initial gas mixture may be present in approximately equal amounts, 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 three or four 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. A decrease in the proportion of hydrogen increases the proportion of unsaturated hydrocarbons produced. If desired the carbon monoxide may even be in excess, thus increasing the tendency to produce unsaturates.

The reaction may be carried out by passing the gas mixtures through heated tubes containing the catalyst. Preferably the dimensions and structure of the tubes are such that a high degree of turbulence is imparted to the gas so as to ensure good contact between the gas and the catalyst and to secure efficient heating throughout the gas mixture. For example relatively narrow tubes may be used with a high rate of gas flow, or masses of catalyst may be so disposed as to break up the gas stream. A similar effect may be attained by inserting baffles at suitable intervals along the length of the reaction tube. If desired the interior of the reaction tube and/or

any baffles contained therein may be made of or lined with a catalytic metal. Instead of tubes there may be used reaction zones of annular cross-section or any other suitable type of apparatus.

The gas may be subjected to a single passage through the reaction zone, 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 reaction zones or by recycling it through a single reaction zone. Between the successive passages through the reaction zones or between successive cycles 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.

The following Example illustrates the invention, but does not in any way limit it:—

EXAMPLE.

Carbon monoxide mixed with twice its volume of hydrogen is passed under a pressure of 0.2 atmosphere through a tube containing a cobalt catalyst, activated with thoria, at a temperature of 180° C. The gases and vapours leaving the reaction zone are cooled, and the greater part of the hydrocarbons formed condensed. The vapours remaining, consisting for the most part of unchanged reactants with some light hydrocarbons and usually a little carbon dioxide, are mixed with fresh carbon monoxide and hydrogen, and again passed over the catalyst.

This example may be modified by employing in admixture with the carbon monoxide and hydrogen 3 to 6 volumes of steam or carbon dioxide for each volume of carbon monoxide present. Steam condensing with the hydrocarbons formed may be separated therefrom by decanta-

tion.

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 manufacture of hydrocarbons by reaction between carbon monoxide and hydrogen in the presence of a hydrogenating catalyst, in which the reactant gases, while in contact with the catalyst, are under an absolute pressure of at most half an atmosphere.

2. Process according to Claim 1, wherein the gases are under a pressure between 0.1 and 0.25 atmosphere.

3. Process according to Claim 1 or 2, wherein also the partial pressure of the gases is reduced by a diluent gas or vapour.

4. Process according to Claim 3, wherein there is employed as diluent steam, carbon dioxide or hydrocarbon gases or vapours.

5. Process according to any of the preceding claims, wherein the catalyst comprises a metal of Group 8 of the Periodic Table promoted with a metal oxide.

6. Process according to any of the preceding claims, wherein the reaction is effected at a temperature between 150° and 350° C.

7. Process according to any of the preceding claims, wherein the reactant gases contain more hydrogen than carbon monoxide.

8. A manufacture of hydrocarbons by reaction between carbon monoxide and hydrogen in the presence of a hydrogenating catalyst substantially as hereinbefore described.

9. Hydrocarbons whenever made by the process of any of the preceding claims.

Dated this 24th day of March, 1938.

STEPHENS & ALLEN,
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