

## PATENT SPECIFICATION.



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## PROVISIONAL SPECIFICATION

## Improvements relating to the Production of Hydrocarbons.

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 improvements in the production of hydrocarbons by reacting carbon monoxide and hydrogen.

Valuable hydrocarbons can be obtained by reacting carbon monoxide and hydrogen at relatively low temperatures and under ordinary or slightly increased pressure. Such a process can be carried out with the use of a liquid reaction medium in which the catalyst is immersed, see, for instance, my Specification No. 505,121. The use of such a liquid reaction medium facilitates the withdrawal of the considerable quantity of heat evolved in the process which causes boiling of the reaction medium, the vapour thus produced being condensed and returned to the reaction zone by means of a reflux condenser.

According to the present invention the production of hydrocarbons by reacting carbon monoxide and hydrogen is effected by introducing the reactant gases into a reaction medium prepared by dissolving in an organic liquid inert to the reactants and reaction products a salt of a metal catalytically active in the process and distilling off from the reaction medium the products as they are formed. In this way it has been found possible to effect a general improvement in the production of hydrocarbons and especially of normally liquid hydrocarbons not merely from the point of view of heat control but also with regard to the conversions obtained and with regard to the simplicity of the operating technique.

The liquid reaction medium employed may, most suitably, be of hydrocarbon nature, and may be one of relatively high boiling point for instance anthracene oil, and in this case the process may be operated so that the product distilling from the reaction zone consists substantially of the products of the reaction between carbon monoxide and hydrogen. On the other hand a lower boiling hydrocarbon may be used which will distil with

the products from the reaction zone and in this case it is necessary to return part of the condensed liquid or add fresh liquid in order to maintain the level of reaction medium within the reaction zone. It is preferred in practice to use as the liquid reaction medium a quantity of the liquid hydrocarbons which are produced by the process of the invention and there may be used in this way either a liquid of the composition produced by the reaction or a fraction thereof of any desired boiling range. When employing a reaction medium of the same composition as the condensable products of the reaction it is possible to adjust the rate of feed of carbon monoxide and hydrogen so that the products distil off at such a rate as to maintain a constant volume of liquid in the reaction zone.

Temperature control of the reaction can be effected very efficiently by circulating the reaction medium between the reaction zone and a cooler, an accurate control of temperature being possible by controlling the rate at which the reaction medium is circulated between the two vessels. On the other hand the distillation of the reaction products from the reaction medium continuously with their production itself effects a considerable removal of the heat produced in the process.

As previously indicated, a salt of the catalytically active metal used is dissolved in the reaction medium, and in this connection it is pointed out that higher fatty acid salts of the catalytic metals are generally of greatest use in view of their solubility in the reaction media used, such salts as the stearates, palmitates and laurates being very satisfactory, while other soluble salts which may be used are the salts of resin acids, and compounds of lower molecular weight such as the acetates. Nickel and cobalt are catalytic metals of great value in the process of the invention, especially when employed in conjunction with copper, and/or manganese and these metals may be used, for instance in the form of salts of the type referred to above, if desired together with activators such as thoria or other metal oxides, e.g. alumina, magnesia or zinc

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oxide, which may be suspended in the solution of catalyst salt. Iron also exerts a favourable catalytic influence on the reaction but is generally less suitable than nickel or cobalt.

The quantity of metal salt dissolved in the reaction medium can be quite small and need not exceed 1 or 2% of the weight of the action medium, while quantities much smaller than this e.g. down to 0.2 to 0.3% can be used if desired. On the other hand it is to be understood that higher proportions of the metal salts can be used if desired. As previously indicated, the reaction is one which is carried out very efficiently at relatively low temperatures, preferably not exceeding 200° C., for instance temperatures of the order of 180–200° C. Atmospheric pressure may be employed and, although somewhat higher pressure can be used, it is preferred not to exceed a pressure of

about 5 atmospheres, while if desired sub-atmospheric pressure, e.g.  $\frac{1}{2}$  to  $\frac{1}{4}$  of an atmosphere may be used.

If desired, the partial pressure of the reactants may be reduced by using a diluent gas, e.g. nitrogen, carbon dioxide, steam or methane, or other hydrocarbon gases or vapours, for instance gaseous hydrocarbons or the vapours of normal liquid hydrocarbons produced in the process itself and recycled as diluent. The quantity of diluent used may be equal to about the volume of the carbon monoxide and hydrogen mixture, or larger quantities, e.g. up to 5 or 10 parts by volume for each part of the reaction mixture may be employed.

Dated this 20th day of August, 1940.

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### COMPLETE SPECIFICATION.

#### Improvements relating to the Production of Hydrocarbons.

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 improvements in the production of hydrocarbons by reacting carbon monoxide and hydrogen.

Valuable hydrocarbons can be obtained by reacting carbon monoxide and hydrogen at relatively low temperatures and under ordinary or slightly increased pressure. Such a process can be carried out with the use of a liquid reaction medium in which the catalyst is immersed, see, for instance, my Specification No. 505,121. The use of such a liquid reaction medium facilitates the withdrawal of the considerable quantity of heat evolved in the process which causes boiling of the reaction medium, the vapour thus produced being condensed and returned to the reaction zone by means of a reflux condenser. In such processes the catalyst may also be used as a suspension in the liquid reaction medium.

According to the present invention the production of hydrocarbons by reacting carbon monoxide and hydrogen in a liquid reaction medium in the presence of a metal catalytically active in the process and distilling the products from the reaction medium as they are formed is effected by a process which is characterised in that the reaction medium is

prepared by dissolving a salt of the catalytically active metal in an organic liquid inert to the reactants and reaction products. In this way it has been found possible to effect a general improvement in the production of hydrocarbons and especially of normally liquid hydrocarbons not merely from the point of view of heat control but also with regard to the conversions obtained and with regard to the simplicity of the operating technique.

The liquid reaction medium employed may, most suitably, be of hydrocarbon nature, and may be one of high boiling point, for instance anthracene oil, and in this case the process may be operated so that the product distilling from the reaction zone consists substantially of those of the products of the reaction which boil at temperatures up to the reaction temperature together with a portion of the higher boiling products. On the other hand a lower boiling hydrocarbon may be used which will distil with the products from the reaction zone and in this case it is necessary to return part of the condensed liquid or add fresh liquid in order to maintain the level of reaction medium within the reaction zone. It is preferred in practice to use as the liquid reaction medium a quantity of the liquid hydrocarbons which are produced by the process of the invention and there may be used in this way either a liquid of the composition produced by the reaction or a fraction thereof of any

desired boiling range. When employing a reaction medium of the same composition as the condensable products of the reaction it is possible to adjust the rate of feed of carbon monoxide and hydrogen so that the products distil off at such a rate as to maintain a constant volume of liquid in the reaction zone.

Temperature control of the reaction can be effected very efficiently by circulating the reaction medium between the reaction zone and a cooler, an accurate control of temperature being possible by controlling the rate at which the reaction medium is circulated between the two vessels. On the other hand the distillation of the reaction products from the reaction medium continuously with their production itself effects a considerable removal of the heat produced in the process.

As previously indicated, a salt of the catalytically active metal used is dissolved in the reaction medium, and in this connection it is pointed out that salts of fatty acids of high molecular weight are generally of greatest use in view of their solubility in liquid hydrocarbons which, as above stated, form excellent reaction media, such salts of this kind as the stearates, palmitates and laurates being very satisfactory, while other soluble salts which may be used are the salts of resin acids, and compounds of lower molecular weight such as the acetoacetates. Nickel and cobalt are catalytic metals of great value in the process of the invention, especially when employed in conjunction with copper, and/or manganese and these metals may be used together with activators such as thorium compounds, e.g. thoria, or other metal oxides, e.g. alumina, magnesia or zinc oxide, which may be suspended in the solution of metal salt. Iron also exerts a favourable catalytic influence on the reaction but is generally less suitable than nickel or cobalt unless somewhat higher temperatures than 200° C. are used. If desired, before passage through the solution of a mixture of carbon monoxide and hydrogen for the synthesis of hydrocarbons, hydrogen alone may be passed, preferably at the temperature to be used in the synthesis. This treatment or, in its absence, the early part of the synthesis, may result in the metal salt being wholly or partly reduced to the metallic state.

The quantity of metal salt dissolved in the reaction medium can be quite small and need not exceed 1 or 2% of the weight of the reaction medium, while quantities much smaller than this e.g. down to 0.2 to 0.3% can be used if desired. On the other hand it is to be understood that higher proportions of the metal salts can

be used if desired, e.g. solutions of 10—20% concentration of even saturated solutions. As previously indicated, the reaction is one which is carried out very efficiently at relatively low temperatures, preferably not exceeding 200° C., for instance temperatures of the order of 180—200° C. Atmospheric pressure may be employed and, although somewhat higher pressure can be used, it is preferred not to exceed a pressure of about 5 atmospheres, while if desired sub-atmospheric pressure, e.g.  $\frac{1}{2}$  to  $\frac{1}{4}$  of an atmosphere may be used.

If desired the partial pressure of the reactants may be reduced by using a diluent gas, e.g. nitrogen, carbon dioxide, steam or methane, or other hydrocarbon gases or vapours for instance gaseous hydrocarbons or the vapours of normal liquid hydrocarbons produced in the process itself and recycled as diluent. The quantity of diluent used may be equal to about the volume of the carbon monoxide and hydrogen mixture, or larger quantities, e.g. up to 5 or 10 parts by volume for each part of the reaction mixture may be employed.

The following Example illustrates the invention.

#### EXAMPLE.

40 parts by weight of metallic cobalt and 3.6 parts by weight of metallic copper are dissolved in the minimum quantity of 40% nitric acid necessary. The solution is diluted to a concentration equivalent to 12.5 litres per kg. of cobalt and 10 parts by weight of thorium nitrate  $\text{Th}(\text{NO}_3)_4 \cdot 12 \text{H}_2\text{O}$  are added in the form of a 10% aqueous solution. To the mixed solution heated to its boiling point is added 150 parts by weight of sodium carbonate in the form of a 20—25% solution. The precipitated carbonates are filtered, washed free from nitrate, dried and dissolved in 400 parts by weight of lauric acid and the product is dissolved in a fraction of a hydrocarbon oil obtained by a previous synthesis and boiling above 220° C.

Hydrogen is passed through the solution at 195—200° C. for two to four hours and then a mixture of carbon monoxide with twice its volume of hydrogen is passed while maintaining the temperature of the liquid at between 195 and 200° C. The heat of reaction is partly removed by vaporisation of products obtained by the synthesis, these products being condensed and collected outside the reaction zone, and partly by circulation of the catalyst liquor through a cooler.

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 production of hydrocarbons by reacting carbon monoxide and hydrogen in a liquid reaction medium in the presence of a metal catalytically active in the process and distilling the products from the reaction medium as they are formed, characterised in that said reaction medium is prepared by dissolving a salt of the catalytically active metal in an organic liquid inert to the reactants and reaction products.

2. Process according to Claim 1 wherein the reaction medium consists of a hydrocarbon of high boiling point.

3. Process according to Claim 2 wherein a fraction of the reaction products is used as reaction medium.

4. Process according to any of the pre-

ceding claims wherein the catalyst metals are dissolved in the reaction medium in the form of salts of fatty acids of high molecular weight.

4. Process according to any of the preceding claims wherein nickel or cobalt is used in conjunction with copper and thorium.

6. Process for the production of hydrocarbons from carbon monoxide and hydrogen substantially as hereinbefore described.

7. Hydrocarbons whenever produced by any of the processes claimed in the preceding claims.

Dated this 3rd day of July, 1941.

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