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(12) Patent:

(54) HYDROCARBON MANUFACTURE

(54) FABRICATION D'HYDROCARBURES

Availability of images:(72) Inventors (Country): HENRY DREYFUS (Not Available)(73) Owners (Country): HENRY DREYFUS(71) Applicants (Country):(74) Agents:(45) Issued on: Mar. 9, 1943(22) Filed on:(43) Entered on:(52) Canadian Class (CPC): 260/678.7(51) International Class (IPC): N/AParent Cooperation Treaty (PCT): No(30) Application priority data: NoneAvailability of images: N/ALanguage of filing: UnknownABSTRACT:CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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

According to the invention hydrocarbons are manufactured by subjecting a mixture comprising carbon monoxide, hydrogen and a diluent gas or vapour to elevated temperatures in the presence of a catalyst.

As the diluent gas or vapour there may be employed for example a relatively inert gas or vapour, e.g. nitrogen. Particularly good results are obtained when the diluent comprises a gas or vapour which is chemically related to one or other of the reagents or to the products, as, for example, steam and especially carbon dioxide and hydrocarbon gases and vapours. If desired any two or more diluents may be employed; for example, carbon dioxide may be used together with one or more hydrocarbons, or two or more hydrocarbons may be employed, or nitrogen with carbon dioxide and/or one or more hydrocarbons.

A number of methods may be adapted for producing mixtures of carbon monoxide and hydrogen with various diluents. For example, carbon monoxide, hydrogen and the diluent or diluents may all be obtained from separate sources and mixed together in the desired proportions. For example hydrocarbons for use as diluents may be obtained from oil-cracking or coal-hydrogenation operations, or from other industrial processes, or part of the hydrocarbons produced by the process of the invention may be recycled and employed to dilute a further batch or quantity of reagent gases.

In another method, a mixture of carbon monoxide and hydrogen may be produced in a single operation, and a

1
diluent gas or vapour, for example from one of the
sources enumerated above, added to this mixture. For
example, a mixture of carbon monoxide and hydrogen
may be made by the partial combustion of less valuable
5 hydrocarbons, especially methane and its lower homologues.
In such a treatment it is preferable to use the heat
liberated in the partial combustion to help to bring the
reagent gases and diluents to the temperature required
for the process of the invention; for instance the gases
10 obtained by the partial combustion may be mixed with
diluent and led to the reaction zone under conditions
such that their sensible heat is substantially retained.
This method of operating provides a new process whereby
methane or its lower homologues may be readily transformed
15 into higher hydrocarbons and especially into liquid hydro-
carbons suitable for use as motor fuel.

In a modification of this method the partial combustion
of the methane or other hydrocarbon may be so regulated
that carbon dioxide or unoxidised hydrocarbon remains after
20 the combustion, and part or all of the diluent required may
be obtained in this way.

Other methods of producing the required gas or vapour
mixture consist in making the diluent and one or both
reagent gases in a single reaction. For example, if
25 carbon monoxide is caused to react with a limited amount
of steam in the presence of a catalyst, e.g. iron or nickel,
there is produced a gas mixture containing carbon monoxide,
hydrogen and carbon dioxide in proportions depending on the
original proportions of carbon monoxide and steam and the
30 other reaction conditions. Moreover the mixture may be

enriched with further quantities of either or both reactants, or further carbon dioxide or other diluent, e.g. steam or preferably hydrocarbons, may be added.

In another method carbon monoxide may be allowed to react with a limited amount of oxygen or air to give a mixture of carbon monoxide and carbon dioxide; the use of air has the advantage that a further dilution of the gas mixture, with nitrogen, is attained without extra trouble or expense. The mixture of oxides of carbon, with or without nitrogen, so produced may be mixed with the desired amount of hydrogen.

Mixtures of hydrogen and hydrocarbon gases or vapours are formed in various industrial processes, for example in the cracking and refining of hydrocarbon oils, and such mixtures, after the addition of the required amount of carbon monoxide, may be employed, other diluents being added if desired.

In a further method the diluent may be actually formed in the reaction zone. For example a mixture of carbon monoxide, any desired proportion of hydrogen, and steam may be introduced into the reaction zone, and the steam, besides acting itself as a diluent, may react with part of the carbon monoxide to produce hydrogen and carbon dioxide. When hydrogen and carbon dioxide are to be made in the reaction zone by this method, it is preferable to have in the reaction zone a catalyst for the reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ as well as a catalyst for the reduction of carbon monoxide with hydrogen to give hydrocarbons. These two catalysts may be in admixture with each other or may be arranged so that the gas flows

first over the catalyst for the reaction $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$
and then over the catalyst for the hydrocarbon synthesis.

It may sometimes be most advantageous to employ as catalyst
a single substance which catalyses both reactions, e.g.

5 nickel. In any case it will usually be preferable to arrange
that successive parts of the reaction zone are heated to
different degrees; thus the temperature in the first part
of the zone may be about $400^\circ - 500^\circ \text{C}$. so as to promote
the reaction between carbon monoxide and steam, and the
10 second part of the zone may be maintained at a temperature
suited to the reaction between carbon monoxide and hydrogen,
as is more fully described below. If desired instead of
or as well as having some hydrogen in the mixture before
the reduction of the steam, sufficient may be added afterwards
15 to bring the carbon monoxide and hydrogen ratio to the
desired figure.

The proportion of diluent present in the reaction
mixture may vary over a wide range; preferably at least
as much diluent as carbon monoxide is present, and advan-
20 tageously for each part of carbon monoxide there may be
present 1 $\frac{1}{2}$, 2, 3, 5, 10 or more parts by volume of diluent.

While the volume of hydrogen present in the reaction
mixture may be less than or equal to that of the carbon
monoxide, it is preferable to employ an excess of hydrogen.
25 For example, the mixture may contain 1 $\frac{1}{2}$, 2, 3, 4, or even
more volumes of hydrogen for each volume of carbon monoxide.

The temperature to be employed will vary according to
the products desired. For example, for the production of
normally liquid hydrocarbons, the gases may be subjected to
30 a temperature between 150° and 250°C ., and especially

between 180° and 200° C. When hydrocarbons of lower molecular weight are required, the temperature employed may exceed 250° C., and may, for instance, be about 300°, 400°, 500° C., or higher. For example, temperatures of the order of 330° to 380° or 400° C. are particularly useful when methane is the desired product. If desired, the gases may be preheated before entering the reaction zone. Preferably the pressure is atmospheric or does not greatly exceed atmospheric.

The method of operating the process may also vary with the nature of the principal products which are desired. Thus when permanent gases, e.g. methane and ethane, are the main products of the reaction, good results may be obtained by a straight run method, the reaction mixture being fed into the reaction zone or zones at one end and products being withdrawn at the other. If substantial quantities of condensable hydrocarbons are formed, these may be separated from the gaseous products and employed as diluent in the treatment of further quantities of hydrogen and carbon monoxide. If desired a cyclic method may be adopted wherein the gases and vapours leaving the reaction zone or zones are fed back to some earlier point in the system for further reaction. In this case the hydrocarbons formed in an earlier passage through the zone act as diluent in a later one. When the hydrocarbon content has built up to a sufficient extent the cycle may be broken and the products withdrawn.

When liquefiable hydrocarbons are the main products of the reaction, a straight-run process may again be used; cyclic processes are however of value; for example after

each passage of the reagents through the reaction zone liquefiable hydrocarbons may be removed therefrom by condensation either wholly or, if part of the hydrocarbons is to be recycled as diluent, to any desired degree.

5 Further reagent gases, with or without further quantities of diluent, may be introduced into the cycle to replace those which have already reacted.

While the reaction, especially in a straight-run process, may be carried out as a single stage operation, 10 particularly when methane is the principal product desired, it is frequently advantageous to employ a plurality of stages. The reaction proceeds more slowly at the relatively low temperatures employed to produce liquefiable hydro- 15 carbons, and therefore a multi-stage process is particularly valuable when liquid hydrocarbons are required. Preferably liquid hydrocarbons formed in any one stage are wholly or largely removed, e.g. by condensation, immediately after that stage.

Among the catalysts which may be employed are suitable 20 metallic and other hydrogenating catalysts, for example metals of the eighth group of the Periodic Table, especially nickel and cobalt. These hydrogenating catalysts may be employed in admixture with other catalysts or activating agents, preferably dehydrating catalysts, e.g. alumina, 25 magnesia, thorina and the like. The catalysts, whether simple or mixed, 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 shaped nickel-alumina or similar catalyst prepared as described in Canadian Application S. No. 435,197 filed 21st October, 1935.

The catalyst may, for example, be contained in heated tubes through which the gas mixtures are passed. Preferably the dimensions and structure of the tubes are such that a high degree of turbulence is imparted to the gases so as to ensure good contact between the gases and the catalyst and to secure efficient heating throughout the gas mixture. For example, relatively narrow tubes may be used with a correspondingly high rate of gas flow, or the 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. The tubes and/or the baffles contained therein may be made of, or lined or covered with, a catalytic metal.

Instead of tubes, there may be employed reaction zones of annular cross-section, or any other suitable type of apparatus may be used. For example, the reagents and diluent may be passed through a heated inert liquid containing a catalyst in solution or suspension.

The following Examples illustrate the invention but are not to be regarded as limiting it in any way:-

EXAMPLE 1.

A mixture of 4 volumes of methane and 1 volume of oxygen is passed at atmospheric pressure through a narrow tube packed with a thorium-promoted nickel catalyst maintained at 900° C. to produce a mixture of carbon monoxide, hydrogen

and methane; the resulting mixture is cooled rapidly to 200° C. and passed, with a contact time of about $\frac{1}{4}$ minute, through a thorium-promoted nickel catalyst in a similar tube maintained at 200° C. The outflowing mixture is cooled to separate benzene, and the residual gas, consisting largely of methane, may be admixed with further methane and oxygen to supply fresh mixture for use in the process.

EXAMPLE 2.

Oil gas, substantially freed from unsaturated hydrocarbons by acid absorption and containing 60 - 75% of methane and other gaseous paraffins, is mixed with carbon monoxide in amount equal to about half that of the free hydrogen present and is passed at atmospheric pressure over a thorium-activated cobalt catalyst at 180° C. with a contact time of $\frac{5}{4}$ minute. The product is cooled to condense benzene.

EXAMPLE 3.

A mixture of 2 volumes of water gas and 1 volume of steam is passed at atmospheric pressure through a tube packed with iron oxide at 450° C. and then through a tube packed with a thorium-activated nickel catalyst heated to 400° C. The product contains a high proportion of methane.

EXAMPLE 4.

A mixture of 2 volumes of water gas and 1 volume of steam is passed at atmospheric pressure through a tube packed with iron oxide at 450° C. The resulting gaseous mixture is cooled rapidly to 180° C., cooling being assisted by the addition of 1 volume of carbon dioxide, and the whole

is passed through a tube packed with a thorium-
activated cobalt catalyst and maintained at 180 C.
The benzene produced is separated by cooling.

5 In any of the examples the hydrocarbon synthesis
step may be conducted in two or more stages, and in
such case it is preferable to condense part or all
of the higher boiling materials, such as benzene, out
of the gases before subjecting them to the second or
any subsequent stage.

10 Having described my invention what I desire to
secure by Letters Patent is:-

1. Process for the production of hydrocarbons, which comprises passing a mixture of carbon monoxide and steam over a mixture of a catalyst adapted to produce carbon dioxide and hydrogen therefrom and a catalyst for the reduction of carbon monoxide with hydrogen, the gas mixture first coming into contact with the catalyst mixture at a temperature of 400° to 500°C . and then at a temperature of 150° to 250°C .

2. Process for the production of hydrocarbons, which comprises passing a mixture of carbon monoxide and steam over a nickel catalyst, the gases first coming into contact with the catalyst at a temperature of 400° to 500°C . and then at a temperature of 150° to 250°C .

C 3. Process for the production of hydrocarbons which comprises passing a mixture of carbon monoxide and steam over a catalytic mass adapted to produce carbon dioxide and hydrogen from the said mixture, and to catalyze the reduction of carbon monoxide with hydrogen, the gas mixture first coming into contact with the catalytic mass at a temperature of 400° to 500°C . to convert part of the carbon monoxide to carbon dioxide, and then while the steam content of the gas mixture formed at said temperature is maintained, into contact with the catalytic mass at a temperature of 150° to 250°C .