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(12) **Patent:**

(54) SYNTHESIS OF HYDROCARBONS

(54) SYNTHESE D'HYDROCARBURES

[illegible]

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ABSTRACT:

CLAIMS: Show all claims

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The present invention relates to catalytic vapor phase reactions and more particularly to the synthesis of hydrocarbons and/or oxygenated hydrocarbons by the catalytic reduction of a carbon oxide with hydrogen.

In the process whereby hydrogen and carbon monoxide are reacted catalytically in the presence of a catalyst of the iron group to form hydrocarbons and oxygenated hydrocarbons, it appears that the reactants interact at the catalytic surfaces by a process akin to adsorption, the hydrocarbon reaction products being desorbed thereafter. However, in the normal course of the reaction complete desorption of the products, particularly the higher molecular weight compounds, does not fully occur and thus, at least over a period of operation, the catalytic process becomes impaired by an accumulation of heavy molecular weight products. With early types of processes, frequent stripping, regeneration or revivification of the catalyst was resorted to, and in more recent processes it has been the practice to continuously circulate or submit the catalyst to the stripping action of a suitable stripping gas in a zone separate from the reaction zone. Such processes, with which we are familiar, circulate the catalyst at or about reaction temperature between the reaction zone and the stripping zone.

In accordance with the present invention, it has been found advantageous to carry the synthesis reaction to completion in the reaction zone and to carry out stripping of adsorbed products in a separate zone operating at a lower temperature than the reaction temperature. More specifically, it has been discovered that at lower temperatures the stripping action is fully as efficient and effective and, in many cases more so, than where the usual reaction temperatures are employed.

More specifically, the stripping temperature is at least about 50°F. below the reaction temperature prevailing in the associated synthesis of hydrocarbons by the catalytic reduction of carbon oxide with hydrogen. That is to say, the upper temperature limit of the stripping range is about 50°F. below the reaction temperature and preferably below this limit as will hereinafter be more fully disclosed.

It is, of course, disadvantageous to carry out the stripping step at excessively low temperatures below which the products adsorbed on the catalytic surface are capable of removal. This, however, as will be apparent from the foregoing, depends in some measure upon the character of the adsorbed products which in turn is dependent upon the specific conditions prevailing in the reactor and the type of product for which the reaction is being operated. In short, the character of the deposits to be removed in the stripping step may vary to some extent with the boiling range of the product for which the synthesis reaction is operated, and may range from relatively heavy compounds down to relatively lighter boiling fractions.

When operating conventional synthesis processes for the production of motor gasoline with an iron type catalyst in the temperature range of about 550-700°F. and preferably between about 600 and 650°F., it has been found that generally the stripping process is particularly effective down to temperatures of about 500°F.

To take a particular example, in the conventional operation of the process with an iron catalyst for the purpose of producing hydrocarbons predominantly in the motor gasoline boiling range, temperatures of around 625°F. and pressures of around 200 pounds per square inch gauge will usually prevail. The stripping of the adsorbed materials can be effectively carried out at temperatures advantageously, for example, within the range of 50°F. to about 100°F. below the reaction temperature.

From the foregoing it will be apparent that the invention is, in its braod aspect, applicable to all hydrocarbon synthesis processes involving other catalysts, such as cobalt, nickel or ruthenium, for the reduction of carbon oxide with hydrogen. Each of these processes, functions within a characteristic range of operating temperature and pressure to produce hydrocarbons or oxygenated hydrocarbons or mixtures thereof of any desired molecular weight. In any event, it has been found that the top limit of stripping temperatures indicated above, namely, at least about 50°F. below the reaction temperature, results in the advantages of this invention. It is frequently desirable to strip the spent or partially spent catalyst at even a lower temperature, generally about 100°F. below the reaction temperature.

It is apparent that this principle affords an effective standard by which the optimum upper limit of the stripping temperature can be conveniently correlated to any specific catalytic reaction of the present type. In short, irrespective of the catalyst employed, the desorption process will progress effectively within the range determined by the temperature differentials indicated above.

The present invention is advantageous in that the character of the desorbed products and the catalyst itself is not altered disadvantageously by excessive thermal conditions in the stripping zone. In other words, the amount of thermal cracking and corresponding free carbon formation are materially reduced. As a result, less catalyst fouling occurs and the catalyst life is appreciably longer. The lower stripping temperature also avoids or materially minimizes chemical or physical changes in the catalyst.

Another related advantage of the present invention follows from the fact that the catalyst, where it is circulated between the reaction zone and the substantially cooler stripping zone, is returned to the exothermic reaction zone at a lower temperature and thus is subjected to less severe average temperature conditions in the presence of reactants.

A yet further advantage resides in the fact that the stripping gases have a less detrimental effect upon the catalyst in the stripping zone, and permit its return to the reaction zone in a condition most favorable for promoting the catalytic reaction. More specifically, a properly prepared and run-in catalyst assumes a condition of carbide and metal content ideal for the synthesis reaction, which can be severely altered by conventional stripping media which generally are considered inert. Water vapor and carbon dioxide, which are widely suggested as stripping media, we have found to be capable of oxidizing an iron catalyst when stripping is carried out at synthesis reaction temperatures or higher. Hydrogen, another conventional stripping agent, similarly is capable of decarbiding the catalyst beyond a point optimum for the reaction in question. In accordance with the present invention, however, these undesirable effects are restricted or prevented by the selection of an appropriate lower temperature without impairment of the prime object of liberating and recovering the adsorbed products.

Similarly, when hydrogen is employed as a stripping agent, the extent of the reaction which usually occurs between the hydrogen and adsorbed hydrocarbons may be appreciably limited, with recovery of more desirable products and with a substantially decreased hydrogen consumption.

While the present invention is applicable to any of the conventional contact methods, it is particularly adaptable to systems operating under the so-called fluidization technique in accordance with which, the catalyst is in the form of a fluent powder suspended in the flow of reactant gases, so that each particle is in effect surrounded by gases or vapors in which it exhibits more or less random motion. The catalyst particles undergo "hindered settling" or slippage in the gaseous stream and assume a condition similar to a boiling liquid with an upper boundary or surface in the nature of a pseudo-liquid level. Alternatively, by increase in the linear flow velocity of the reactants, the catalyst can be largely or substantially entrained in the gaseous flow emerging from the reaction zone. As is known, the fluidized mass of powder possesses heat transfer properties comparable to those of a boiling liquid and, accordingly, permits maintenance of a uniform temperature throughout the reaction zone which may be accurately predetermined and controlled by provision of suitable cooling surfaces.

Moreover, the fluid-like character of the contact mass enables it to be readily caused to flow in cyclic relation through successive reaction and stripping zones.

In order to more clearly illustrate the invention, reference is made to the figure of the attached drawing which exemplifies one preferred embodiment suitable for carrying out the process. Therein, the apparatus, illustrated more or less diagrammatically, includes a reactor 1 to which the fresh feed reactant gases are introduced from a source, not shown, through a conduit 2. These gases, comprising a mixture of hydrogen and carbon monoxide, for example, pass upwardly in the reactor through a mass of powdered fluidized catalyst contained therein, and are withdrawn through an upper outlet conduit 3 after their emergence from the upper surface of the catalyst bed. A suitable filter 4, preferably formed of a porous refractory material such as alundum, embraces the inlet extremity of the conduit 3 and serves to separate gasiform reaction products from any entrained solid particles. Obviously, any other suitable form of separating device may be employed such as conventional magnetic or cyclone separators, whereby the gases may continue through any suitable means for use or recovery, free from catalyst contamination.

The reaction zone, namely the internal portion of the reactor occupied by the mass of fluidized catalyst, is surrounded by a cooling jacket 5 maintained at a predetermined cooling temperature by any suitable coolant supplied through inlet 6 and removed from outlet 7.

The upper or expanded portion of the reaction vessel 1 includes, at one side, a receiving hopper 8 open at its top and disposed in the approximate plane of the normally operating pseudo-liquid level of the catalyst. Catalyst accumulating in the hopper 8 passes downwardly through standpipe 9 at a rate controlled by mechanical star feeder 10, into stripping chamber 11. The stripping chamber is jacketed as at 12 in a suitable manner for promptly cooling the contents to any suitable temperature below the temperature of the reaction zone. Coolant is circulated through jacket 12 by way of inlet 13 and outlet 14. Catalyst is continuously withdrawn from stripping chamber 11 through standpipe 15 at a rate controlled by star feeder 16 or any other suitable or equivalent form of valve or flow-controlling device. Stripping gas is passed into the lower portion of the chamber 11 from a source, not shown, through an inlet pipe 17 and an injection nozzle 18, so that the cooled catalyst is subjected to a stripping action.

It will be understood that the stripping gas flow is such as to maintain a good state of fluidization favorable to the attainment of the desired temperatures within stripping chamber 11.

The catalyst passing the star feeder 16 drops into an inlet conduit 19, where it is picked up in a stream of incoming gases and returned directly into the bottom of the reactor 1. The incoming gases in conduit 19 may consist of the fresh feed synthesis gas to the reactor, in which case, inlet pipe 2 may be omitted. On the other hand, conduit 19 may advantageously supply any desired portion of the noncondensibles in the effluent from pipe 3 continuously recycled for maximum utilization of reactants.

As indicated above, the linear velocity of gas flow in the reactor is advantageously adjusted to fluidize the catalyst powder and provide a turbulent but dense mass of catalyst. With an iron-type catalyst, 85% by weight of the particles of which pass through a 325-mesh screen, a velocity of about 1 to 2 feet per second is recommended.

It is to be particularly noted that by the means disclosed in the above embodiment, it is possible to maintain a specific predetermined differential between the catalyst in the stripping chamber 11 and that in the reactor. That is to say, the fluidized catalyst in the stripper, as is well known in connection with the technique of fluidization, uniformly holds a predetermined temperature determined by the coolant in the external jacket 12. Accordingly, a relatively small stream of catalyst from the standpipe 9, striking the fluidized mass in the stripper, is immediately cooled, instantaneously reaching the lower temperature of the catalyst in the stripping zone. Whereas in many arrangements an intermediate cooling zone or chamber might be necessary and desirable, such is made unnecessary by the present embodiment.

The effluent stripping gases are conducted away from the stripping chamber through the pipe 20 after passing a suitable filter or separating element 21 which removes any entrained solid particles. The effluent gases may be passed directly by way of pipe 22 having valve 23 to the aforementioned pipe 3 for recovery of the contained hydrocarbons concurrently with those in the effluent from the reactor, or alternatively may be conveyed by pipe 24, provided with valve 25, to separate means for treatment or recovery.

The synthesis reaction progresses in the reaction zone with the formation of finished hydrocarbons and/or oxygenated hydrocarbons which pass outwardly with any byproducts through the outlet pipe 3. Used catalyst with adsorbed products is continuously withdrawn to stripping chamber 11 where it is rapidly cooled and subjected to the action of the stripping gas. The stripped vapors, together with the stripping gas, are passed to conventional means for the recovery of hydrocarbons and the stripped catalyst is continuously returned to the reaction zone.

It is important to point out that in the foregoing embodiment the cooling jackets disclosed may be and preferably are substituted by more efficient heat exchange means, for example, a multiplicity of cooling tubes supplied internally with a suitable coolant and immersed directly in the fluidized powder to be cooled. As is well known, such cooling devices are normally so streamlined as not to impair fluidization or flow of solids and to prevent the occurrence of dead spots in the catalyst mass. They, moreover, may be supplied with a suitable coolant such as water, mercury or Dowtherm, and may be maintained, by pressure control or otherwise, at any desired specific temperature corresponding to that required in the respective zones.

In accordance with one specific illustrative procedure exemplifying the present invention a synthesis gas together with recycle gas is passed through a mass of powdered iron catalyst at a linear velocity of about 1.2 feet per second. The depth of the catalyst mass is approximately 18 feet. The synthesis gas contains about 89% hydrogen and carbon monoxide in the molar ratio of substantially 2:1 and also includes about 7% carbon dioxide, 2% methane and 2% inert gases like nitrogen. The fresh feed gas is admixed with about an equal volume of recycle gas obtained by condensing and separating from the reactor effluent all compounds condensable at a temperature of 100°F. and a pressure of 250 pounds per square inch gauge.

The mass of catalyst in the reactor consists of powdered iron catalyst of less than 200 mesh size, 85% of which passes a 325-mesh screen, and containing about 1.7% potassium oxide (K_2O). The linear gas velocity of about 1.2 feet per second is calculated as the velocity of the gas passing through the reactor at reaction temperature, neglecting the actual presence of catalyst powder. The reaction zone is maintained at a temperature of 650°F. and a pressure of 250 pounds per square inch gauge. Catalyst continuously migrates upwardly to the pseudo-liquid level at which the reaction gases separate themselves from the bulk of the powdered catalyst and passes directly into a laterally spaced, cooling zone wherein it flows downwardly at a temperature of 550°F. Stripping is carried out by stripping gases introduced into the lower portion of the cooling and stripping zone. The stripping gas consists of flue gas containing about 5% hydrogen and remainder essentially carbon dioxide and nitrogen, and is passed up through the stripping zone at a linear velocity of about 1/10 foot per second. The cooled, stripped catalyst is introduced into the recycle gas stream flowing to the reactor and thus is reinjected into the reaction zone at a temperature of about 550°F. and at a catalyst circulation rate such that the entire volume of catalyst in the reaction zone is replaced about five times every hour.

The effluent gases from the reaction and stripping zones are collected and subjected to condensation and separation to obtain a hydrocarbon fraction essentially in the gasoline boiling range. The total hydrocarbon yield, based on carbon monoxide in the fresh feed, is equal to about 95% of the theoretical conversion.

The catalyst returned to the reaction zone appears to have high catalytic activity judged in terms of hydrocarbon production. Furthermore, the catalyst has a substantially longer life than when operating at stripping temperatures equal to or greater than the reaction temperature. Moreover, when the process is operated identically as in the foregoing example, but without cooling the catalyst in the stripping zone, the yield of liquid hydrocarbons is decreased by 3 to 5%.

While the foregoing example concerns the use of a flue gas as a stripping agent, it will be apparent that any conventional stripping agent may be employed, such, for example, as water vapor, hydrogen, carbon dioxide or nitrogen. Also, methane, or other normally gaseous hydrocarbons such as ethane, ethylene, propane and the like are sometimes useful as stripping agents. While each of the numerous stripping agents may be characterized by respective advantages and disadvantages, these are inherent in the conventional use of the particular gas selected and do not affect the broad objectives of the present invention, namely, to promote stripping under thermal conditions which minimize the disadvantageous effects and which result in an overall improvement in yield with minimum catalyst deterioration.

Moreover, while reference has been made in the foregoing example to iron catalyst, any equivalent catalyst comprising, e.g., a metal of the iron group or ruthenium may be substituted with the appropriate adjustment of the reactor temperatures and pressures, those characteristic of optimum operation for the desired product, and a corresponding adjustment of the stripping temperatures in accordance with the foregoing principles.

So, also, while the use of the fluidization technique involves many advantages, the invention may be readily carried out by those skilled in the art in connection with various methods of catalyst use. Thus, for example, where a non-fluidized but loose particle catalyst is employed, any suitable mechanical means may be employed for its transfer from the reaction to the stripping zone with appropriate reduction in temperature. In addition, the temperature reduction, in lieu of methods heretofore exemplified, may be achieved by using a relatively cool stream of stripping gas and, in place of continuous operation, it is possible to conduct the process with a fixed catalyst bed by periodically terminating the reaction, cooling the catalyst mass and stripping the cooled mass with a suitable gas in such a manner that the same vessel successively incorporates the reaction and stripping functions.

The catalysts employed may embody, or be treated with, any promoters or activators known in the art, such, for example, as the alkali metal and alkaline earth metal compounds, alumina, titania, thoria, and others. So, also, the catalysts may be prepared in unsupported condition or supported upon a carrier such as diatomaceous earth, magnesia or any of the numerous clays and carbons used for this purpose.

Many other specific modifications and adaptations of the present invention will be obvious to those skilled in the art from a consideration of the foregoing more or less exemplary disclosure and it is therefore understood that the invention is not limited to any such details except as defined by the following claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the synthesis of hydrocarbons, oxygenated hydrocarbons and the like, by the reduction of carbon oxide with hydrogen in the presence of a fluidized catalyst therefor, the steps which comprise passing a synthesis gas containing essentially hydrogen and a carbon oxide in contact with a mass of said catalyst under reaction conditions including an elevated temperature above about 550°F. and accumulating some adsorbed reaction products upon the catalyst surfaces, recovering reaction products from contact with the catalyst, discontinuing contact of said synthesis gas with at least a portion of said catalyst having an accumulation of reaction products adsorbed thereon, effecting the stripping of substantially all of said accumulation of adsorbed reaction products from said portion of catalyst by cooling said portion of catalyst to a temperature in the range of at least about 50°F. below said elevated temperature but not substantially less than 500°F. and subjecting said cooled catalyst to passage of a stream of stripping gas in contact therewith, while within said temperature range until said adsorbed reaction products are stripped from the catalyst, and thereafter subjecting the stripped catalyst to contact with synthesis gas at said elevated reaction temperature.

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2. The method as defined in Claim 1 wherein the said elevated temperature is in the range of from about 550°F. to about 700°F.

3. The method as defined in Claim 1 wherein the said elevated temperature is in the range of from about 600°F. to about 650°F.

4. The method as defined in Claim 1 wherein the said elevated temperature is in the range of from about 600°F. to about 650°F., and wherein the catalyst is cooled to and stripped at a temperature of about 100°F. below said elevated reaction temperature.

5. The method as defined in Claim 1 wherein the catalyst comprises iron.

6. In the synthesis of hydrocarbons, oxygenated hydrocarbons and the like by the reduction of carbon oxide with hydrogen in the presence of a fluidized synthesis catalyst, the steps which comprise passing a synthesis gas containing essentially hydrogen and carbon oxide in contact with a mass of said catalyst in a reaction zone under reaction conditions including an elevated reaction temperature and accumulating some adsorbed reaction products upon the catalyst surfaces, recovering reaction products from contact with said catalyst, discontinuing contact of said synthesis gas with at least a portion of said catalyst having an accumulation of reaction products adsorbed thereon, effecting the stripping of substantially all of said accumulation of adsorbed reaction products from said portion of catalyst by cooling said portion of catalyst to a temperature in the range of at least about 50° to 100°F. below said elevated reaction temperature and

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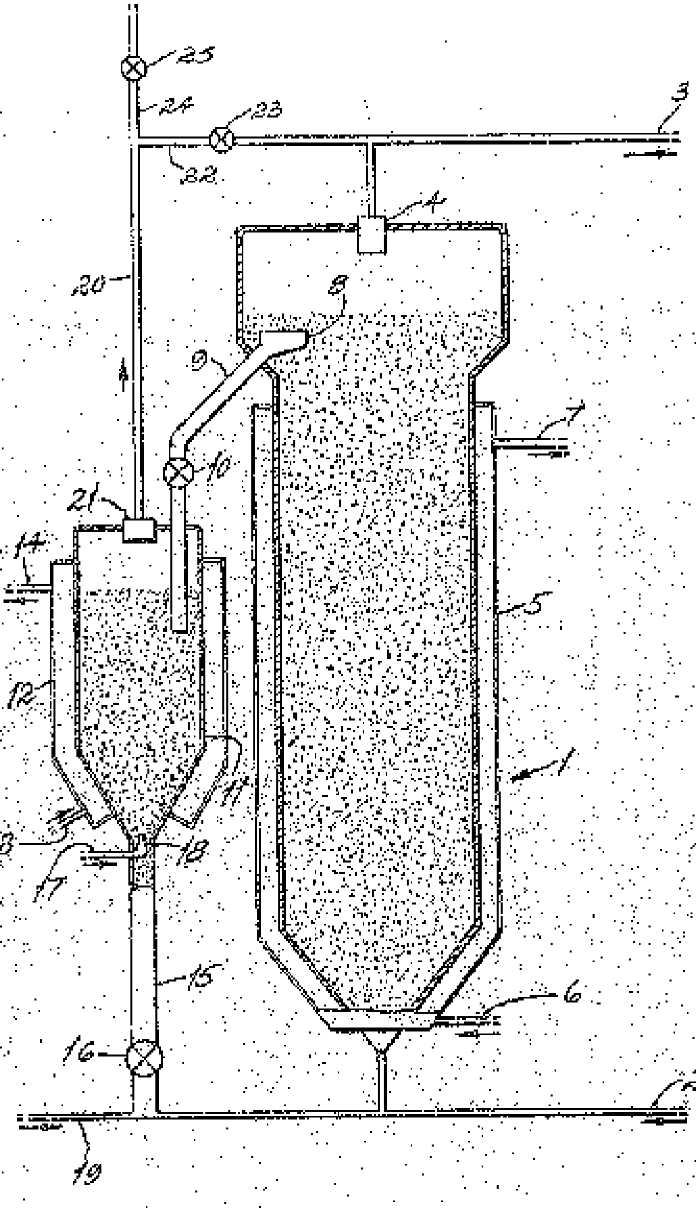
subjecting said cooled catalyst to passage of a stream of stripping gas in contact therewith while within said temperature range until said adsorbed reaction products are stripped from said catalyst, and thereafter subjecting the stripped catalyst to contact with synthesis gas at said elevated reaction temperature.

7. The method according to Claim 6 wherein the said synthesis catalyst comprises iron.

8. The method according to Claim 6, wherein the said passage of stripping gas in contact with the catalyst is effected in a stripping zone separate from the reaction zone and wherein catalyst is withdrawn from the reaction zone to the stripping zone and thereafter returned to the reaction zone after removal of accumulated adsorbed reaction products.

9. The method according to Claim 6, wherein said synthesis catalyst comprises a fluid phase of solid catalyst particles and wherein a portion at least of the fluid phase is circulated out of the reaction zone into a stripping zone, subjected to stripping by passage of said stream of stripping gas in contact therewith, and returned to the reaction zone after said removal of accumulated adsorbed reaction products.

10. The method according to Claim 6, wherein the stripping temperature of from about 50° to 100°F. below said elevated reaction temperature is not less than about 500°F.



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Certified to be the drawings referred to in the specification hereunto annexed.

Ottawa, Ontario, Canada, February 12th, 1946.