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(54) PROCESS FOR CATALYTIC CONVERSION OF CARBON OXIDES IN HYDROCARBONS

(54) PROCEDE POUR CONVERSION CATALYTIQUE D'OXYDES DE CARBONE DANS HYDROCARBURES

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This invention relates to the catalytic conversion of carbon oxides and hydrogen into hydrocarbons and particularly into hydrocarbons rich in olefins.

Broadly, the invention contemplates carrying out the synthesis reaction under conditions adapted to effect substantially complete conversion of available carbon in the synthesis feed gas into hydrocarbons and particularly into hydrocarbons containing a large proportion of olefins while suppressing the formation of methane and at least substantially reducing the net production of carbon dioxide.

The effluent stream of reaction products from the reaction zone containing hydrocarbons, steam, carbon dioxide and relatively small amounts of hydrogen and carbon monoxide is advantageously cooled to condense steam and normally liquid hydrocarbons. The gaseous fraction thereof is subjected to contact with a chemical agent such as sulphuric acid, cuprous chloride, etc. under conditions such that olefinic constituents of the gas are converted into normally liquid products which are readily separated from the residual gas. A portion of the resulting residual gas is recycled to the synthesis reaction. Carbon dioxide is removed from the non recycled portion of the residual gas, as for example by absorption in ethanolamine solution, and the recovered carbon dioxide recycled to the synthesis reaction. The gas from which carbon dioxide has been removed, having a relatively low content of carbon monoxide and hydrogen, can be discharged as fuel gas.

The invention contemplates carrying out the synthesis operation so as to produce a highly olefinic product low in methane and also so that the amount of unconverted

carbon monoxide and hydrogen in the effluent stream of reaction products is small, so much so that the residual gases after removal of carbon dioxide may be discharged from the system without the necessity for recovering carbon monoxide and hydrogen therefrom.

The aforesaid gaseous fraction of the effluent from the synthesis reaction contains a large amount of olefins, i.e., 70 to 90% by volume. The invention contemplates removal of these olefins from the recycle gas because these olefins undergo objectionable degradation reactions when recycled to the synthesis reaction, producing methane and paraffin hydrocarbons as well as heavier and less valuable olefins. The so-removed olefins are thus available for conversion into desirable products.

In addition, only the net product of the olefin free gas needs to be scrubbed to recover carbon dioxide for recycling to the synthesis reaction.

In accordance with the invention, the gaseous fraction of the effluent from the reaction zone containing gaseous olefins and paraffins as well as a substantial amount of carbon dioxide may be subjected to contact with sulphuric acid so as to convert olefinic constituents thereof into their corresponding sulphates, in which form they can be readily separated from carbon dioxide and gaseous paraffins.

The treatment with sulphuric acid or other reagent may be carried out in stages, as will be described later, employing in each stage conditions of temperatures, pressure and reagent concentration, etc., adapted to selectively

remove a particular olefin. The resulting olefin compounds may be separately disposed of as desired. Olefin sulfates, for example, may be passed to an alkylation reaction wherein the olefins are reacted with an isoparaffin such as isobutane to form alkylated hydrocarbons.

Specifically the invention contemplates carrying out the synthesis reaction for the production of olefins in the presence of added carbon dioxide maintaining the ratio of mols of hydrogen to mols of both carbon monoxide and carbon dioxide passing to the reaction zone not in excess of 1 and preferably not less than about 0.6.

In addition, the invention contemplates maintaining the molar ratio  $\frac{\text{CO}_2 (\text{H}_2 - 2 \text{COA})}{\text{CO} \times \text{H}_2\text{O}}$  of reactants passing to the reaction zone substantially greater than  $0.0202e^{\left(\frac{7350}{T+400}\right)}$  where "A" is the fraction of the carbon monoxide converted in the reaction zone and which will usually range from about 0.95 to 0.995, "e" is the base of Napierian logarithms, e.g., 2.7183, and "T" is the reaction temperature in degrees Fahrenheit.

The numerical value of this latter molar ratio is substantially greater than the value of the equilibrium constant for the water gas shift reaction which is about 70 for a reaction temperature of 500°F., about 31 for a reaction temperature of 600°F., and about 16 for a reaction temperature of 700°F. Thus, when effecting the synthesis with a fluidized iron powder catalyst at a temperature of about 600°F., this second molar ratio should be maintained at least in the range of 60 and above, and advantageously in the range of about 100 to 160.

It is advantageous to effect initial contact between the synthesis feed gas and the catalyst at a substantially lower temperature than that prevailing during subsequent contact between the reactants and the catalyst within the reaction zone or zones. The catalyst particle temperature at the point of initial contact with synthesis gas is advantageously about 50°F. lower and may range from at least 10 to 100°F. lower than the catalyst temperature at the point of final contact. Under these conditions, the predominating initial reaction in the region of initial contact is  $2\text{Fe} + \text{CO} + \text{H}_2 = \text{Fe}_2\text{C} + \text{H}_2\text{O}$ . Subsequently and above the region on initial contact the predominating reaction is  $\text{Fe}_2\text{C} + \text{H}_2 = \text{CH}_2 + 2\text{Fe}$ . At the higher temperature prevailing in the upper portion of the reaction zone or in a succeeding reactor for that matter the reaction  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$  is favored.

For example with a reaction zone containing the previously mentioned iron catalyst, the catalyst temperature in the gas inlet region of the zone is advantageously 550°F., or lower, or while in the product outlet region it is about 600°F.

Under ordinary circumstances the synthesis of hydrocarbons from carbon monoxide and hydrogen is accompanied by the formation of large amounts of carbon dioxide. Carbon dioxide so produced results in some measure from the carbiding reaction between the catalyst metal and carbon monoxide, which reaction is advantageous from the standpoint of maintaining an excess of the carbide in the reaction.

A feature of the present invention involves effecting consumption of carbon dioxide so produced in this carbiding reaction by reacting it with available hydrogen to form additional carbon monoxide for use in the synthesis and

thus maintain a high concentration of carbon monoxide in the synthesis reaction zone. Hydrogen may be added so as to assure the presence of the desired quantity of hydrogen in the reaction zone.

Water or steam is also a product of the reaction between carbon dioxide and hydrogen and is also formed to a large extent by other reactions taking place during the course of the synthesis. It is contemplated maintaining the concentration of water in the reaction system as low as possible in order to favor the reaction between carbon dioxide and hydrogen with consequent increase in the formation of carbon monoxide. Accordingly, it is contemplated removing water from the synthesis gas feed or reducing the water content at least to approximately the amount with which the gas is saturated under the conditions of temperature and pressure prevailing in the reaction zone. Also where the reaction is carried out in a plurality of stages, to each of which fresh synthesis gas flows in parallel, provision may be made for removing water from the reactant streams flowing between stages in series flow.

By operating under the aforesaid conditions, a much greater conversion of the available carbon in the synthesis feed gas into desirable compounds is realized, for example into  $C_2$  and higher molecular weight hydrocarbons. It is contemplated effecting substantially complete conversion in each stage of the carbon monoxide passing thereto, for example about 99% conversion, although operating conditions may be regulated so that from 95 to 99.5% conversion is effected in each stage or in the reaction zone.

The net production of carbon dioxide from the

conversion process is substantially entirely avoided when charging a synthesis gas containing at least 2 mols of hydrogen per mol of carbon monoxide, and carbon dioxide may be actually consumed in the reaction.

The amount of carbon dioxide added to a reaction stage or to the reaction zone depends upon the composition of the synthesis feed gas passing thereto. The synthesis gas may contain a small amount of carbon dioxide. If the hydrogen present is less than that theoretically required to react with the carbon monoxide present to produce olefins and water, then the amount of carbon dioxide added is less since carbon dioxide is produced in the reaction under such conditions.

By way of example, when charging synthesis gas containing carbon monoxide, carbon dioxide and hydrogen to a reaction zone wherein it is subjected to contact with a fluidized iron catalyst at a temperature of approximately 600°F. and under a pressure of approximately 200 pounds per square inch gauge, the ratio of mols of hydrogen to mols of carbon monoxide plus carbon dioxide passing to the reaction zone is maintained at about 0.6. The molar ratio  $\frac{CO_2 (H_2 - 2 COA)}{CO \times H_2O}$  is maintained at about 160. Under these conditions, the following yields are obtained as mol per cent of carbon monoxide converted:

C <sub>1</sub> + C <sub>2</sub> hydrocarbons	3.6
C <sub>3</sub> and heavier hydrocarbons	91
Water soluble oxygenated compounds	<u>5.4</u>
	100.0

The C<sub>2</sub> fraction of the hydrocarbon products will contain about 50 to 60% unsaturated hydrocarbons while the C<sub>3</sub> and heavier fraction will comprise about 70 to 85% unsaturated hydrocarbons.

In order to illustrate the mode of operating the overall process, reference will now be made to the accompanying drawing. A hydrocarbon gas such as methane is drawn from a source not shown through a pipe 1 and conducted to a generator 2. Oxygen or air or other suitable oxygen rich gas is conducted from a source not shown through a pipe 3 to the generator 2. The generator is operated under conditions of temperature and pressure so as to produce a synthesis gas of predetermined composition, for example containing carbon monoxide and hydrogen in the proportion of about 1 mol of carbon monoxide to 2 mols of hydrogen.

The resulting gas is passed through a heat exchanger 4 wherein it is cooled to a temperature suitable for introduction to the synthesis reaction which in the case of an iron catalyst is in the range about 550 to 600°F. Moisture condensed from the gas can be removed in the separator 4a.

The synthesis gas flows through a pipe 5 into the lower portion of a reactor 6 wherein the gas is brought into contact with a fluidized catalyst comprising iron powder containing about 1 to 2% potassium oxide and about 2 to 3% alumina.

An effluent stream of reaction products is continuously removed from the reactor 6 through a pipe 7 to a heat exchanger 8 wherein it is reduced to a temperature in the range about 60 to 150°F. The cooled stream flows through pipe 9 to a separator 10 wherein condensed hydrocarbons and steam collect. The water and hydrocarbons separate into layers and the water is drawn off through a pipe 11 while the liquid hydrocarbons are drawn through a pipe 12.

The residual gas comprising gaseous hydrocarbons



having from 1 to 5 carbon atoms per molecule and containing a substantial amount of carbon dioxide and small amounts of hydrogen, carbon monoxide and some nitrogen is drawn off through a pipe 13. Nitrogen will be present in this residual gas in the event that air or other nitrogen containing gas is used in the generation of the synthesis gas.

The liquid hydrocarbons removed through the pipe 12 will comprise mainly hydrocarbons having more than 5 carbon atoms per molecule and may contain small amounts of oxygenated compounds as well as small amounts of normally gaseous hydrocarbons such as butane.

This liquid stream is passed to a fractionator or stabilizer 15 wherein normally gaseous constituents are removed therefrom through a pipe 16. The stabilized hydrocarbons are drawn off through a pipe 17 and may be passed all or in part to a reforming unit 18.

The reforming step may comprise treatment of the hydrocarbons with bauxite or other clay-type material at a temperature in the range about 700 to 900°F. so as to remove oxygenated compounds and increase the octane rating of the hydrocarbons.

The gas discharged through the pipe 16 may be passed all or in part to the pipe 13. The resulting gas mixture is conducted from the pipe 13 to a chemical treatment unit 20 wherein the gaseous stream passing therethrough is subjected to contact with sulphuric acid or other suitable chemical agent under conditions such that the olefins are converted to compounds which are readily separated from the gaseous paraffin hydrocarbons.

The unit 20 may comprise a plural stage absorption

system wherein the individual olefins are reacted with sulphuric acid of requisite concentration to form the corresponding olefin sulfates. The resulting sulfate mixtures or solutions can be passed through a pipe 21 to an alkylation unit 22 wherein the sulphates are treated with an isoparaffin such as isobutane drawn from a source not shown through a pipe 23. The alkylation operation is of conventional type using concentrated sulphuric acid as the catalyst and is carried out so as to produce alkylated hydrocarbons suitable as high anti-knock motor fuel which may be blended all or in part with the reformed hydrocarbons.

The absorption tower treatment can be carried out in a plurality of stages. Thus in one stage the gaseous feed may be treated with sulphuric acid of about 65% concentration so as to remove isobutylene. In another stage the gas may be treated with acid of about 85 to 90% concentration so as to remove propylene and the normal butylenes, while in a separate stage the gas may be treated with acid of about 95% concentration so as to remove ethylene. The resulting olefin sulphate mixtures may be disposed of other than as olefin feed to alkylation reactions.

Instead of using sulphuric acid it is contemplated that other chemical reagents may be employed, for example cuprous chloride may be used so as to form addition compounds with the olefins, from which compounds the olefins may subsequently be liberated.

It is contemplated that the olefins may be selectively removed from the reactor effluent gas. Thus  $C_3$  and higher olefins may be removed while ethylene remains in the gas flowing through pipes 25 and 32. In this latter case

ethylene can be recycled to the reactor instead of being disposed of as fuel gas. If desired, ethylene can be selectively removed from the reactor effluent gas and recycled to the reactor, thus providing hydrocarbon recycle substantially free from methane and other hydrocarbons.

The residual gas from the unit 20 comprising paraffin hydrocarbons such as ethane, propane, etc. and carbon dioxide, etc. is removed through a pipe 25, the major portion thereof being passed to a scrubbing tower 26 wherein it is subjected to contact with ethanolamine or other chemical reagents adapted to remove carbon dioxide from the gas.

The enriched solution is drawn off through a pipe 27 to a stripper 28 wherein the carbon dioxide is removed from the scrubbing agent and discharged through a pipe 29, the lean solution being drawn off through pipe 30 for return to the tower 26.

The residual gas from the tower 26 comprising saturated gaseous hydrocarbons, nitrogen and small amounts of hydrogen and carbon monoxide is discharged through a pipe 31.

The carbon dioxide discharged through pipe 29 is recycled through pipe 33 to the reactor 6 in an amount sufficient to maintain the aforesaid ratios of reactants passing to the reactor 6.

The portion of the gas flowing through pipe 25 which is not scrubbed is passed directly through pipe 32 to the pipe 33 for recycling to the reactor. In this way some of the residual unreacted carbon monoxide and hydrogen is recycled to the reactor. Recycling of this stream is advantageous from the standpoint of maintaining fluidization of the catalyst not only when starting up but also during onstream operation.

In the event that additional hydrogen is required it may be supplied through pipe 34.

An advantage of the process of this invention resides in the relatively low content of unreacted carbon monoxide and hydrogen in the gas being discharged through the pipe 13, which in turn is due to the high conversion of carbon monoxide into  $C_2$  and higher molecular weight hydrocarbons. This in turn permits utilizing air in place of oxygen in the generator 2. Nitrogen can be eliminated from the system in the fuel gas without the necessity of employing complicated absorption towers and auxiliary apparatus because the residual gas is so lean in carbon monoxide and hydrogen that recovery of these particular constituents is unnecessary. Use of ethylene only as the hydrocarbon component of the recycle gas as previously suggested is advantageous when air rather than oxygen is used in the synthesis gas generation.

While mention has been made of using an iron catalyst, it is contemplated that catalysts containing other metals of the iron group, such as cobalt, nickel, ruthenium, etc., may be used. The catalysts may contain other promoters, for example the oxides of uranium, vanadium and magnesium. In addition, the catalyst may be of the supported type using as supporting materials diatomaceous earth, silica gel, Filtrols, etc.

The reaction temperature in the reactor 6 will depend upon the type of catalyst used and may range from 200 to 700°F. Likewise, the pressure may range from atmospheric to several hundred atmospheres.

It is also contemplated that other than fluidized catalyst systems may be used. Thus, the catalyst may be

employed in stationary or moving bed form.

Obviously many modifications and variations of the invention as above set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

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

1. In the catalytic hydrogenation of carbon monoxide for the production of hydrocarbons, oxygenated hydrocarbons and mixtures thereof, wherein synthesis gas containing hydrogen and carbon monoxide in the molar ratio of at least 2:1 is passed in contact with a fluidized solid particle iron hydrocarbon synthesis catalyst in a reaction zone at an operating temperature in the range of about 550-700°F. to effect substantial conversion of the reactants into desired products of reaction, the improvement which comprises continuously supplying to the reaction zone a gaseous feed mixture comprising said hydrogen and carbon monoxide together with carbon dioxide and not more than a small concentration of water vapor, maintaining the reaction zone substantially uniformly at said reaction temperature, regulating the relative proportions of the constituents of said gaseous feed mixture such that the ratio of mols of hydrogen to mols of carbon monoxide plus carbon dioxide is in the range of about 0.6 to 1.0, and such that the molar ratio

$$\frac{(\text{CO}_2) \times (\text{H}_2 - 2\text{COA})}{\text{CO} \times \text{H}_2\text{O}}$$

is at least twice as great as the numerical value of the equilibrium constant for the water-gas shift reaction at the temperature prevailing in said reaction zone, where A is the fraction of carbon monoxide converted in said reaction zone, thereby substantially completely suppressing carbon dioxide formation within said reaction zone, effecting substantially complete conversion of carbon monoxide into said desired products and withdrawing effluent products of reaction from the reaction zone.

2. The method according to claim 1, wherein the catalyst in the reaction zone is maintained in a substantially uniform state of dense phase fluidization.

3. The method according to claim 1, wherein about 0.95 to 0.995 of the feed carbon monoxide is converted into desired products of reaction in the reaction zone.

4. The process for the production of desired hydrocarbons, oxygenated hydrocarbons and mixtures thereof by the catalytic hydrogenation of carbon monoxide with the conversion of substantially all of the feed carbon monoxide into said desired products and with repressed formation of carbon dioxide, which comprises feeding a gaseous mixture of carbon monoxide, hydrogen, water vapor and carbon dioxide into a reaction zone containing a fluidized solid particle iron hydrocarbon synthesis catalyst, contacting said gaseous mixture with said fluidized catalyst at a reaction temperature in the range of about 550-700°F. until about 0.95 to about 0.995 of said feed carbon monoxide has been converted into desired products of reaction, maintaining the composition of said gaseous feed mixture such that the molar ratio of hydrogen to carbon monoxide is at least 2:1, and the proportion of carbon dioxide is such that the molar ratio

$$\frac{(\text{CO}_2) \times (\text{H}_2 - 2\text{COA})}{\text{CO} \times \text{H}_2\text{O}}$$

is at least twice as great as the numerical value of the equilibrium constant for the water-gas shift reaction at the temperature prevailing in the reaction zone, where A is the constant between about 0.95 and 0.995, representing the fraction of the feed carbon monoxide which is to be converted into said desired products, withdrawing effluent products of reaction from the reaction zone and recovering the desired products of reaction therefrom.

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5. The method according to claim 4, wherein the composition of said gaseous feed mixture is such that the ratio of the mols of hydrogen to the sum of the mols of carbon monoxide and carbon dioxide is in the range from 0.6 to 1.0.

6. The process for the production of desired hydrocarbons, oxygenated hydrocarbons and mixtures thereof by the catalytic hydrogenation of carbon monoxide with the conversion of substantially all of the feed carbon monoxide into said desired products and with repressed formation of carbon dioxide, which comprises feeding a gaseous mixture of carbon monoxide, hydrogen, water vapor and carbon dioxide through a reaction zone containing a fluidized solid particle iron hydrocarbon synthesis catalyst, contacting said gaseous mixture with said fluidized catalyst at a reaction temperature in the range about 550-700°F., until about 0.95 to about 0.995 of said feed carbon monoxide has been converted into desired products of reaction, maintaining the composition of said gaseous feed mixture such that the molar ratio of hydrogen to carbon monoxide is at least 2:1, and the proportion of carbon dioxide is sufficient to repress action of the water gas shift reaction in that direction which consumes carbon monoxide and water vapor with the formation of carbon dioxide such that the conversion of the feed carbon monoxide into undesired carbon dioxide by the water-gas shift reaction is substantially inhibited, withdrawing effluent products of reaction from the reaction zone and recovering the desired products of reaction therefrom.

A