

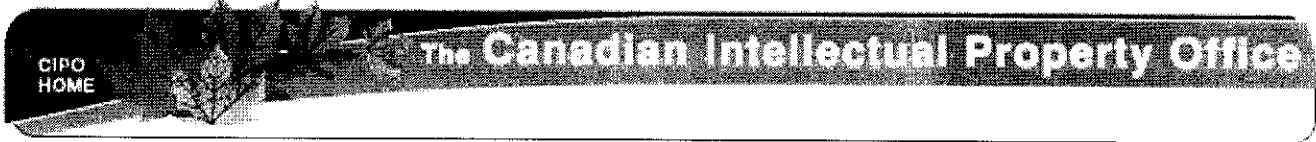


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12/20/2001 - 16:04:56

(11) CA 526366

(12) Patent:

(54) PRODUCTION OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN IN THE PRESENCE OF RECYCLED GAS PHASE

(54) PRODUCTION D'HYDROCARBURES D'OXYDE DE CARBONE ET D'HYDROGENE EN PRESENCE DE PHASE DE GAZ RECYCLE

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(74)		
(45)		June 12, 1956
(22)		
(43)		
(52)		260/753.5
(51)		N/A
		No
(30)		None
		N/A
		Unknown

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

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The present invention relates to the catalytic reduction of carbon monoxide with hydrogen in the production of hydrocarbon and/or oxygenated hydrocarbon compounds having two or more carbon atoms and particularly those of normally liquid character.

The usual process for synthesizing liquid hydrocarbons involving passage of a mixture of hydrogen and carbon monoxide in contact with a catalyst of the iron group at elevated temperatures, and generally elevated pressure, is normally characterized by the production of excessive quantities of undesired methane. That is to say, product distribution when operating to produce normally liquid products is usually such as to involve an objectionable loss of yield in the formation of substantial proportions of methane.

In accordance with the present invention, it has been discovered that the production of normally liquid hydrocarbons may be caused to proceed without substantial or material methane formation; that is, with approximately no net methane formation and in no case more than 3 to 5 per cent net methane formation based upon the carbon monoxide converted, provided that the normally gaseous products of reaction are recycled to the reactor in combination with the fresh feed synthesis gas at a critical rate bearing a predetermined relationship to the molar ratio of hydrogen to carbon monoxide in the fresh feed gases.

More specifically, it has been determined that, with typical synthesis feed gas, the net methane formation is quite high in the case of once through catalytic operations of the present character without recycle of the tail gases and that the net methane formation sharply

decreases with increase in the recycle ratio of the aforesaid gaseous reaction products, reaching a minimum value of zero or thereabouts at a critical value for each inlet fresh feed composition, thereafter increasing sharply with further increase in recycle ratio. In short, the curve of net methane production reverses sharply, reaching a minimum within a relatively narrow range of recycle ratio critical for each specific hydrogen to carbon monoxide ratio of the fresh feed.

The relationship between the hydrogen - carbon monoxide ratio, aforesaid, and the required recycle ratio for the optimum condition of minimum methane formation is determined by the following relationship:

$$Y = \frac{4.46}{X} - 0.64 \pm 0.3$$

where

X is the molar ratio of hydrogen to carbon monoxide in the fresh feed synthesis gas supplied to the reactor containing the synthesis catalyst; and

Y is the recycle ratio which the normally gaseous reaction products from the reactor bears to the fresh feed reactant gases; expressed as the ratio between the number of standard cubic feet normally gaseous products of reaction recycled, and the number of standard cubic feet of fresh feed synthesis gas being supplied to the system per unit time of operation.

The foregoing relationship expressed a range within which the curve of net methane formation reaches a minimum of close to zero, and not more than a 5 per cent net formation of methane, outside of which range of operation this products tends to be formed in excessive quantities.

Under such conditions the suppression of methane formation results in correspondingly increased yield of higher hydrocarbons containing more than three carbon atoms, and particularly normally liquid products when reaction conditions are appropriately selected for the predominant production of such fractions.

In carrying out the present invention a fresh feed synthesis gas is passed in contact with a typical hydrocarbon synthesis catalyst at a conventional elevated temperature and under conventional pressure at which the product is predominantly, essentially, or to the greatest extent practicable, in the liquid boiling range. Contact time is that suitable to result in a good conversion of reactants, advantageously the typical degree of conversion met with in practice with due regard to such things as reactor design, catalyst deterioration, and other factors involved in overall economical operation. The gasiform reaction products are withdrawn from contact with catalyst, cooled to a convenient temperature to condense the normally liquid constituents, which are separated, and the residual, normally gaseous reaction products are recycled, in the appropriate ratio to the incoming stream of synthesis gas, repeatedly passing in contact with the catalyst in this manner.

The fresh feed synthesis gas employed comprises essentially hydrogen and carbon monoxide in varying molar ratios depending upon its origin. The typical synthesis gas contains approximately 2 mols of hydrogen to 1 mol of carbon monoxide, but in practice the molar ratio may vary between extremes of about 1.0 to about 4.0. As indicated above, the present invention is operative throughout this range

and preferably within the narrow range of $H_2:CO$ ratio extending from about 1.5 to about 2.5.

While the typical synthesis gas may contain small amounts of additional modifying gases such as carbon dioxide, methane and water vapor as well as inerts such as nitrogen, the present invention, in accordance with its preferred embodiment, is limited to use of a synthesis gas in which the methane, carbon dioxide and water vapor, are not present or are maintained at a negligible value below 5 per cent and preferably below 3 per cent respectively on a molar basis. In general, substantially greater quantities of these undesired diluents tend to alter the optimum recycle ratio, the carbon dioxide, in greater quantities than 5 per cent, calling for a somewhat greater recycle ratio than that indicated above, and the other two components of this group requiring a somewhat lower recycle ratio. Accordingly, it is apparent that with this offsetting effect, the invention in its broadest aspect may tolerate somewhat higher proportions of these undesired diluents, particularly in the case where methane or water vapor or combinations thereof are present, together with somewhat comparable proportions of carbon dioxide.

The present invention, while concerned broadly with the usual catalysts for the present hydrocarbon synthesis process, is particularly advantageous in connection with catalysts of the iron type, that is to say, the usual so-called catalyst of metallic iron, iron carbide, iron oxide or other iron compound preferably reduced, conditioned and properly prepared. The catalyst may include any usual activator or promoter such as an oxide of an alkali metal, or alkaline earth metal, titania, alundum, and many others.

The synthesis gas is passed in contact with the catalyst in any suitable type of reactor, as, for example, a typical fluidized reactor system, wherein the catalyst in finely divided form is maintained in a dense phase condition by the upflowing gases, the appropriate reaction temperature being maintained by suitable cooling surfaces in contact with the fluidized mass. Alternatively, heat exchange may be effected in any convenient manner practiced in the art, as by introduction of vaporizable liquids, by recycling cool catalyst or thermophore through the reaction zone, or the like.

The gases are passed in contact with the catalyst at the usual predetermined reaction temperature characteristic of the particular catalyst in question. The temperature accordingly, per se, forms no part of the present invention, provided typical conventional temperatures are selected with due regard for the catalyst in question. Broadly, the range of operating temperatures extends from about 350°F. to about 700°F., in the case of iron catalysts, from 550°F. to 700°F. with a typical range of from about 600°F. to 650°F. where liquid hydrocarbon products are desired.

Operating pressures, in the case of the iron catalysts, are, most advantageously, in an elevated range, as for example, from about 150 - 250 pounds per square inch gauge. It is significant to note that within reasonable normal limits the character of the synthesis gas, catalyst, temperature, pressure and contact time do not materially effect the critical aspects of the present invention. That is to say, in a normal operating range predetermined for the production of any desired product containing more than one carbon atom, the critical relationship between recycle rate

and fresh feed composition is not materially altered.

In particular, contact time and space velocity may be varied within wide limits, indicating that the synthesis reaction involved is quite rapid and goes forward to a comparable degree of completion in any practical type of reactor wherein good contact is effected between the catalyst and reactants for more than an inappreciable period of time.

The effluent products of reaction are withdrawn from the reactor, cooled and condensed to a convenient temperature, as for example, 70°F. to 200°F., or below, and preferably not over about 100°F., and the normally liquid products separated. Separation may be carried out in a conventional manner so that the condensed water layer is removed from the condensed oily layer comprising liquid hydrocarbon, or oxygenated hydrocarbon products.

The resulting normally gaseous constituents remaining are recycled in the appropriate ratio as above in admixture with the fresh feed gas passing to the reactor. With a fresh feed synthesis gas produced by the partial oxidation of methane, for example, and containing about 2 mol parts of hydrogen to one of carbon monoxide, the factor X in the formula is equal to 2.0. Accordingly, the value of Y determined by the foregoing relationship falls in the range of from about 1.3 to about 1.9, preferably intermediate between these two limits where a minimum net methane formation is desired.

In the case of a fresh feed synthesis gas having a hydrogen - carbon monoxide mol ratio of about 1.0, the value of Y as determined by substituting X in the foregoing

formula has a range of from about 3.52 to 4.12. On the other hand, with a value of X equal to 2.5, the range of Y becomes about 0.84 to about 1.44.

In accordance with one specific example, a synthesis gas consisting of about 64 per cent hydrogen, and 32 per cent carbon monoxide by volume, about 1-1/2 per cent of methane, about 1 per cent of carbon dioxide and about less than 1 per cent of water vapor, is passed upwardly, at a space velocity of about 1000 v/v/hr. in contact with a fluidized mass of catalyst comprising an iron powder of finer than 200 mesh, about 20 per cent passing a 325 mesh sieve, and containing about 1 per cent of alumina (Al_2O_3), and about 0.5 per cent of sodium oxide (Na_2O).

The temperature of the mass of catalyst is maintained more or less uniformly at about 625°F. by appropriate cooling surfaces immersed in the contact mass. The reaction pressure is about 200 pounds per square inch gauge. The effluent gasiform reaction products are withdrawn from the upper surfaces of the catalyst, condensed and separated at about 100°F. and the residual normally gaseous products are recycled to the incoming fresh feed at a recycle ratio of about 1.5.

In other words, the stream of recycle gas is adjusted to a rate which equals about 1.5 standard cubic feet of the normally gaseous products of reaction per standard cubic feet of fresh feed synthesis gas introduced to the reactor. The combined feed passes upwardly through the lower portion of the contact mass at an estimated rate of about 1.5 linear feet per second, and sufficient to maintain the catalyst particles in a uniform state of dense phase fluidization.

Over a period of 48 hours operation, the total products withdrawn show a 94.4 per cent conversion of carbon monoxide introduced to the system, of which about 78 per cent are normally liquid hydrocarbons predominantly within the motor gasoline boiling range, and about 8 per cent are oxygenated hydrocarbons in the nature of alcohols. The net formation of methane during this period is about 1 per cent based on the carbon monoxide converted, and there is a net formation of carbon dioxide, on the same basis, equal to about 9 per cent. The production of normally gaseous hydrocarbons other than methane amounts to about 3 per cent, on a like basis.

In accordance with another example, the fresh feed synthesis gas comprises essentially hydrogen and carbon monoxide in the approximate ratio of 1.0, and the process conditions are otherwise the same as above, except that the recycle ratio is equal to 3.8. While the deficiency of hydrogen in the feed inherently results in conversion of some carbon monoxide to carbon dioxide at the expense of hydrocarbon yield, the hydrocarbon quality and product distribution is essentially the same as in the foregoing example with a net methane formation of 1 to 2 per cent.

It is to be noted that the present invention, in its broadest aspect, is not limited to the production of liquid hydrocarbons in the motor gasoline boiling range, but may be varied in accordance with any predetermined requirement to produce predominantly lower or higher hydrocarbons by varying the temperatures and pressures in accordance with conventional practice. Thus, in an extreme case, lighter fractions, such as ethylene, propane, or butane, may be controlledly produced at typical higher operating temperatures, and somewhat lower pressures, than above, still with minimum formation of undesired methane, provided the foregoing critical relationship of the recycle ratio and fresh

feed composition is observed.

Conversely, higher boiling products up to waxes may be prepared usually at relatively lower temperatures. In general, as is known, higher pressures and somewhat higher temperatures favor the production of oxygenated hydrocarbons. These known details, however, do not, per se, form any part of the present invention, nor alter the principles herein enunciated, and may be selected from conventional practice.

The present invention accordingly provides a convenient means for substantially completely eliminating the undesired formation of by-product methane and directing the product distribution toward the predominant production of predetermined hydrocarbon fractions containing more than one carbon atom. The invention accordingly is not materially affected by relatively wide variations in operating conditions provided that they are selected within the usual range for the production of the desired product and that the fresh feed gas and recycle ratio bear the foregoing relationship. In other words, minimum methane formation occurs within the critical limits defined specifically above, and advantageously intermediate between the range of the limits in the central portion of the said range. In other words, the preferred results occur where the value of the recycle ratio occurs about or approximately the more limited value of Y determined by the following relationship:

$$Y = \frac{4.46}{X} - 0.64$$

Obviously, many modifications and variations of the invention as set forth above 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 of privilege is claimed are defined as follows:

1. In the process for the synthesis of normally liquid hydrocarbons and oxygenated hydrocarbons, by the catalytic reduction of carbon monoxide with hydrogen, wherein a synthesis gas comprising hydrogen and carbon monoxide in a relative molar ratio in the range from about 1:1 to about 4:1 is passed in contact with a dense fluid phase mass of solid particle, iron, hydrocarbon synthesis catalyst in a reaction zone at an elevated temperature in the range of about 550-700°F. and normally liquid products are recovered from the effluent reaction stream, the improvement which comprises restricting the net formation of methane to a minimum by withdrawing the entire reaction product effluent from contact with the catalyst, separating the normally liquid products of reaction therefrom and exclusively recycling to the inlet of the reaction zone the residual mixture of normally gaseous products of reaction, at a predetermined recycle rate within the range expressed by the value of Y in the relationship:

$$Y = \frac{4.46}{X} - 0.64 \pm 0.3$$

where X is the molar ratio of hydrogen to carbon monoxide in the fresh feed reactant synthesis gas; and Y is the recycle ratio expressed as the ratio which the standard volume rate of recycle of the normally gaseous reaction products bears to the standard volume rate of feed of fresh feed reactant gases supplied to contact with the catalyst, and recovering desired products of reaction from the separated liquid.

2. In the process for the synthesis of normally liquid hydrocarbons and oxygenated hydrocarbons by the catalytic

reduction of carbon monoxide with hydrogen, wherein a synthesis gas comprising hydrogen and carbon monoxide in a relative molar ratio in the range from about 1:1 to about 4:1 is passed in contact with a dense fluid phase mass of solid particle, iron, hydrocarbon synthesis catalyst in a reaction zone at an elevated temperature in the range of about 550-700°F. and normally liquid products are recovered from the effluent reaction stream, the improvement which comprises restricting the net formation of methane to a minimum by withdrawing the entire reaction product effluent from contact with the catalyst, separating the normally liquid products of reaction therefrom and exclusively recycling to the inlet of the reaction zone the residual mixture of normally gaseous products of reaction after separation of said normally liquid products of reaction at a predetermined recycle rate approximating the value of Y in the relationship:

$$Y = \frac{4.46}{X} - 0.64$$

where X is the molar ratio of hydrogen to carbon monoxide in the fresh feed reactant synthesis gas; and Y is the recycle ratio expressed as the ratio which the standard volume rate of recycle of the normally gaseous reaction products bears to the standard volume rate of feed of fresh feed reactant gases supplied to contact with the catalyst, and recovering desired products of reaction from the separated liquid.

3. The method according to Claim 1 wherein the molar ratio of hydrogen to carbon monoxide in said synthesis gas is in the range of about 1.5:1 to about 2.5:1.

4. The method according to Claim 1 wherein said synthesis gas contains less than about five percent by volume, respectively, of carbon dioxide, methane and water vapor.

5. The method according to Claim 1 wherein said synthesis gas contains less than about three percent by volume, respectively, of carbon dioxide, methane and water vapor.