PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen, and Catalyst therefor

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the catalytic reaction between carbon monoxide and hydrogen to form valuable liquid hydrocarbons. More particularly, the present invention is concerned with improvements in the reaction based on an improved composition of catalyst employed in the reaction.

The synthetic production of liquid hydrocarbons from gas mixtures containing various proportions of carbon monoxide and hydrogen is a matter of record and various operating conditions, and numerous catalysts, usually containing a metal of the iron group, have been proposed to promote the desired reactions. For example, to produce substantially saturated hydrocarbons it has been proposed to use catalysts comprising cobalt on an inert carrier at relatively low pressures of about 1 to 5 atmospheres and at temperatures from 300° to 425° F. whereas in order to produce products containing high proportions of unsaturated and/or branched chain hydrocarbons it has been found necessary to use iron catalysts at higher temperatures between 450°—750° F. at higher pressures of 15 to 40 atmospheres.

In both cases, the reaction is strongly exothermic and the utility of the catalyst declines steadily in the course of the reaction chiefly due to deposition of non-volatile conversion products such as paraffin wax, carbon, and the like on the catalyst.

The extremely exothermic character and high temperature sensitivity of the synthesis reaction and the relatively rapid catalyst deactivation have led, in recent years, to the application of the fluid solids technique wherein the synthesis gas is contacted with a turbulent bed of finely divided catalyst fluidized by the gaseous reactants and products. This technique permits continuous catalyst replacement and greatly improves heat dissipation and temperature control.

Most processes for the synthesis of hydrocarbon involve the step of producing the synthesis gas mixture of carbon monoxide and hydrogen by partial combustion of coal or natural gas with an oxidizing gas such as air or oxygen, which synthesis gas is then converted to the hydrocarbons in a second step. In the usual processes in order to produce a highly unsaturated hydrocarbon product it is generally thought desirable as mentioned above to operate this synthesis reaction at high pressure of about 400 lbs. per sq. in. using an iron catalyst. This necessitates the feeding of the synthesis gas to the reactor under high pressure and usually requires the production of the synthesis gas under high pressure, which in turn involves feeding the oxidizing gas under high pressure to the synthesis gas producer. This usually necessitates the use of expensive pure oxygen at high pressure as the oxidizing gas as it would be uneconomical to utilize air under high pressure because the recycle requirement associated with an iron catalyst would result in the undesirable recirculation of a gas containing an ever-increasing amount of nitrogen.

For the above reasons, it would be highly desirable to be able to produce valuable olefinic motor fuel products by a hydrocarbon synthesis process by the fluid solids technique wherein the synthesis gas could be prepared with air at low pressures instead of with oxygen at high pressures, and wherein the synthesis itself could be carried out at moderate instead of at high pressure.

Many attempts have already been made in this direction using fixed bed processes. Thus it has been attempted to prepare high octane motor fuel using a thoria promoted cobalt on silica gel catalyst. However, it was found that when the variables were adjusted in an effort to improve the liquid yield and quality of product, the yield of liquid products increases somewhat with pressure when the temperature is held constant, but the yield of wax increases also. This is quite undesirable because wax formation renders it extremely difficult to maintain a fluidized bed in the reactor. On the other hand, if the pressure is held constant in the relatively low pressure areas where cobalt catalyst functions well, that is, in the region of 15 to about 75 p.s.i.g., the olefin content of the product is low, and attempts to increase the olefinicity by increasing the temperature caused a decrease in liquid product yield and an increase in gas formation.

On the other hand, experience has indicated that operation with iron catalyst at the lower pressures is usually accompanied by severe carbonization of the catalyst as well as formation of wax, both making the maintenance of a fluid catalyst bed a matter of very great difficulty.

It is now found that hydrocarbon synthesis products containing high proportions of valuable unsaturated hydrocarbons can be obtained by contacting a synthesis gas mixture of carbon monoxide and hydrogen containing substantial quantities of nitrogen, for example, when prepared by oxidation of coal or natural gas with air at low pressure by contacting the said gas mixture, preferably in a once-through operation, at a temperature between 450 and 650° F. and at a pressure between 50 and 100 lbs./sq. in. gauge with a dense turbulent mass of fluidized finely divided solid catalyst comprising a silica gel support carrying a mixture of iron and cobalt and a thorium-containing promoter in which the iron and cobalt are present in a total amount of 10—85% by weight of the whole and in the proportion of from .16 to 10 parts by weight of cobalt per part of iron, and said promoter, calculated as thorium metal, is present in an amount from 1—5% by weight of the whole.

The synthesis operation is preferably carried out at a temperature between 475° and 525° F. and at a pressure between 55 and 75 lbs. per sq. in. gauge and with a gas throughout of from 2 to 30 cubic feet of synthesis gas per pound of catalyst per hour at a linear velocity of 0.1 to 3 feet per second and preferably between 0.4 and 1.5 feet per second. Furthermore, it is found that the operating range wherein these beneficial effects are realised is a relatively narrow one, and relatively small variations in reaction conditions decrease either the yield or the olefinicity, or increase wax formation.

In the synthesis of hydrocarbons from carbon monoxide and hydrogen, as described above wherein the synthesis gas contains large quantities of nitrogen, it is obvious that a once-through operation is most desirable, because otherwise large quantities of inert material would be recycled, markedly decreasing the capacity of the plant and the operation. Such nitrogen is present when the synthesis gas is prepared by partial combustion of natural gas with air at moderate pressures, which is of marked economic advantage over preparing the same by combustion with pure oxygen under pressure. Furthermore, in the synthesis of hydrocarbons from CO and H_2 employing a once-through operation, it is apparent that the optimum consumption ratio of the reactants should be the same as their ratio in the synthesis feed gas.

In the production of synthesis gas by partial oxidation with air of methane and natural gas, hydrogen and CO are produced at a 2/1 ratio. When such a gas is used as a feed to the synthesis reactor, the elimination of oxygen in the form of water rather than carbon dioxide is essential for an approximately 2/1 H_2/CO consumption ratio, in accordance with the reaction,

$$(1)\ 2nH_2 + nCO \longrightarrow (CH_2)_n + nH_2O.$$

This is essentially the course of the reaction when cobalt is employed as a synthesis catalyst, and is thus ideally suited for a once-through operation. However, as indicated above and as is well known, cobalt catalyst is not conducive to formation of olefinic hydrocarbons valuable as motor fuel. On the other hand in some cases, when an iron catalyst is employed, the over-all reaction can be more nearly represented by

$$(2)\ 3nH_2 + 3nCO \longrightarrow 2\,(CH_2)_n + nH_2O + nCO_2$$

The CO_2 that occurs along with the products of the synthesis reaction, as in (2) above, may be a result of the reversible water gas shift reaction

$$(3)\ CO + H_2O \rightleftharpoons CO_2 + H_2$$

Thus in the synthesis reaction according to (1) above, the consumption ratio of hydrogen to carbon monoxide is 2/1. However, since some of the water formed in (1) may react with some unconverted CO in accordance with (3), hydrogen is formed and CO is consumed which in effect lowers the H_2/CO consumption ratio. Carried to its limit, the ultimate effect of this reaction would be for all of the H_2O formed to react rapidly and irreversibly with CO in which the net synthesis reaction could be written as

$$(4)\ nH_2 + 2nCO \rightarrow (CH_2)_n + nCO_2$$

giving an H_2/CO consumption ratio of 0.5/1. From the above it may be seen that, starting with a 2/1 H_2/CO feed gas, the H_2/CO consumption ratio may vary from about 2/1 to almost 0.5/1 depending upon the degree to which the water gas shift reaction takes place.

During the normal synthesis with an iron catalyst, and iron is considered to be an excellent shift catalyst, the water gas constants,

$$K = \frac{(CO_2)\quad(H_2)}{(CO)\quad(H_2O)},$$

calculated from the concentrations of the water gas components in the effluent from the reactor are 60—95% of the known water-gas equilibrium constants at temperatures in the range of 550°—650° F. The known values for K at 550° F. and at 650° F. are about 50 and 23 respectively. The low calculated values indicate that the amounts of CO_2 and H_2 present are inadequate to satisfy the water gas shift equilibrium and that the reaction of CO and H_2O is slower than the synthesis reaction.

In such a once-through hydrocarbon synthesis operation at low pressures in the range of about 50 to 100 lbs. per sq. in. gauge with fluidized catalyst to prepare high yields of olefinic motor fuel it is, therefore, highly desirable that the H_2/CO consumption ratio approach as nearly as possible to the ratio in which these two constituents are present in the feed.

When employing a cobalt synthesis catalyst in the normal processes the ratio of H_2 to CO consumed is greater than the H_2 to CO ratio in the feed, up to ratios of about 2/1. On the other hand, all previously known modifications of iron synthesis catalysts give H_2 to CO consumption ratios less than the ratio of these constituents in the feed. Now, however, the surprising discovery has been made that catalysts of the compositions defined above give H_2/CO consumption ratios greater than the ratio of these constituents in the feed, thus making the process suitable for a once-through operation with synthesis gas from partial oxidation of natural gas, wherein the H_2/CO ratio is about 2/1.

The invention will best be understood by referring to the accompanying diagrammatic representation of one of the methods of carrying the invention into effect where suitable equipment and flow of material are shown.

Referring now in detail to the drawing, natural gas from any convenient source preheated in preheater 4 is passed to synthesis gas producer vessel 6, which comprises a catalytic oxidation zone. Simultaneously, air is passed through through line 18 into compressor 20, wherein it is moderately compressed to about 50—100 psig. and the compressed material is passed through line 22 and preheater 16, wherein it is preheated to about 1200° F., and introduced into synthesis generator plant 6. In generator 6 partial oxidation mainly to CO and H_2 takes place. The temperature in the oxidation zone may be of the order of 2000—2500° F. The lower portion 8 of generator 6 may comprise a catalytic reformer bed, containing a reforming catalyst such as nickel or copper on magnesia, and any CO_2 and H_2O formed as a result of combustion in the upper part of the generator will reform unreacted methane to produce further quantities of H_2 and CO.

The hot synthesis gases leaving generator 6, which are at a temperature of about 1600°—1800° F. are passed through line 10 and are preferably employed to preheat the incoming natural gas and air in preheaters 4 and 16, respectively, the synthesis gas stream being divided for this purpose to pass through lines 12 and 14, and through lines 25 and 26. The reunited synthesis gas stream in line 27, which has been cooled as indicated to about 450°—600° F., and may be further cooled if desired, is passed to the bottom of hydrocarbon synthesis reactor 28. The latter is preferably in the form of a vertical cylinder with a conical base and an upper expanded section, and has a grid (or screen) 30 located in the lower section to effect good gas distribution.

Within reactor 28, a mass of catalyst

is maintained in the form of a finely divided powder having a particle size distribution from about 100—400 mesh, preferably about 150 to 200 mesh supplied to the reactor 28 from hopper 34 via line 36.

The synthesis gas mixture, having a molar ratio of H_2CO of about 2 to 1, flows upwardly through grid 30. The superficial linear velocity of the gas within the reactor is kept within the approximate range of 0.1—3 feet per second, preferably about 0.4—1.5 feet per second so as to maintain the catalyst in the form of a dense, highly turbulent fluidized mass having a well defined upper level 38 and an apparent density of from about 30 to 125 lbs. per cubic foot, depending upon the fluidization conditions.

The pressure within reactor 28 is kept within the limits of 50 to 100 psig., preferably about 55—75 psig. and the temperature is maintained constant within the limits of 450° to 650° F., preferably 475° to 525° F. Surplus heat from the exothermic reaction may be withdrawn by any conventional means, such as external cooling coil 32.

Only a small portion of the powdered catalyst is carried into the disengaging section of the reactor above level 38, and these catalyst particles are separated from the reaction products in a conventional gas-solids separator, such as cyclone 40 and returned to the dense bed via dip pipe 42. The rate of gas throughput in terms of cubic feet of gas (H_2+CO) per pound of catalyst per hour, or V/Hr./W, is in the range of 2 to 20, and is so adjusted as to give the desired conversion without need for any recycle of tail gas.

Product vapor and gases are withdrawn overhead from reactor 28 and are passed through line 44 and condenser 46 to liquid products separator 48, wherein liquid products are separated from gases. The liquid products, containing high yields of olefins with little or no oxygenated hydrocarbons may be withdrawn through line 52 for further processing, such as fractionation, cracking of the gas oil fraction, isomerization, polymerization, hydroforming, etc., all in a manner known *per se*.

The uncondensed gases, comprising lower molecular weight hydrocarbons as well as unreacted synthesis gas and nitrogen are preferably passed through line 50 to a fluidized solids, active carbon adsorbtion plant, wherein light hydrocarbons may be removed, and recovered by desorption, at the lower pressures of the present operation. This represents a considerably more economical process than the conventional oil absorption of tail gas.

Instead of producing synthesis gas from partial combustion of natural gas or methane by air at low pressures, synthesis gas may also be prepared by the water gas reaction from coal. In such case, depending on how heat is furnished to the process, either by direct combustion of coke or coal within the water gas generator with air or by recycling of hot combustion solids from a burner vessel, the synthesis gas may or may not contain appreciable quantities of nitrogen. However, the ratio of H_2/CO in synthesis gas prepared from coal is about 1/1, and such a synthesis gas may be passed through a shift converter to increase the feed gas ratio from about 1/1 to about 2/1. In such a system, also, a desulfurizing step would be introduced, such as the passing of the synthesis gases through spent synthesis catalyst to remove sulfur.

The cobalt-iron catalyst which is used according to the invention preferably contains from 3 to 25% by weight of iron and from 5 to 30% by weight of cobalt and from 1 to 5% by weight of thoria, calculated as thorium metal, and from 60—89% by weight of silica gel calculated as silica.

One prefered cobalt-iron catalyst may be prepared in the following manner: Fourteen wt. per cent. cobalt, 14 wt. % iron and 4.4 wt. % thorium (all provided in the form of the corresponding hydrated nitrate salts) were milled in a Simpson mixer with 67.6% silica (provided as silica hydrogel containing about 18% solids) and the wet mixture was then passed through a colloid mill. The above composite was dried at about 250° F. and then further heated for 48 hours at 420° F. and for an additional 5 to 6 hours at 550° F. to complete the decomposition of the nitrates. The resulting dried material was then ground to a suitable size and reduced with hydrogen at 700° F. and atmospheric pressure.

EXAMPLE.

The following example shows the effect of temperature on the activity, selectivity, and unsaturation of the product using a mixed cobalt/iron catalyst in accordance with the invention. For a comparative basis, data obtained under similar reaction conditions for a cobalt catalyst promoted with an alkali promoter but containing no iron are included. In all cases the pressure was 75 p.s.i.g., the H_2/CO ratio 1/1, and the feed rate 200—400 volumes of synthesis gas per volume of catalyst per hour, this feed rate converted to volume of gas per weight of catalyst per hour being within the range previously quoted.

Temperature °F.	430	450	500	525	550
Catalyst A					
25.2% Co					
2.8% Fe					
4.4% Th					
67.6% SiO_2					
CO conversion, % output	41	44	60	—	81
H_2 conversion, % output	82	82	93	—	93
C_4+yield, cc/m^3 H_2+CO cons.	228	221	180	—	128
Bromide No. of collected oil	45	48	85	—	97
Product appearance	clear	clear	clear	—	clear
Catalyst B					
30% Co					
1% ThO_2					
3% MgO					
66% SiO_2					
2% Na*					
(* As Na_2CO_3 based on Co)					
CO conversion, % output	18	30	54	57	74
H_2 conversion, % output	39	53	85	87	89
C_4+, cc/m^3 H_2+CO cons.	216	226	187	148	113
Bromine No. of collected oil	34	33	56	54	62
Product appearance	waxy	waxy	slightly waxy	clear	clear

The above data show for the iron-cobalt catalyst a steady increase in H_2 and in CO conversion with temperature. Selectivity to valuable C_4+ liquid products was found to decrease with increasing reaction temperature at about the same rate with each of the catalysts. However, the unsaturation of the oil product, as indicated by the bromine number, was appreciably higher in all cases for the iron-cobalt catalyst than for the cobalt catalyst promoted with alkali. The unsaturation was found to improve far more rapidly as the temperature was increased with the former than with the latter catalyst. Thus at about 500° F. operating temperature, when the yields of liquid product were about equivalent in both cases, 180—187 cc C_4+/m^3 of H_2+CO converted, the cobalt-iron catalyst of the invention produced a total oil product having a bromide number of 85, corresponding to a liquid product unsaturation of 59, the gasoline fraction (Initial to 430° F.) of which had an estimated unsaturation of about 66%. Under the same conditions the alkali promoted cobalt catalyst without iron produced a total oil product which had a bromine number of only 56, corresponding to an unsaturation value of 42%. Increasing the operating temperature up to 550° F. with each of these catalysts increased the product bromide number in each case, though to a far higher value for the iron-cobalt (97) than for the alkali promoted cobalt (62). Furthermore, the oil product from the iron-cobalt product was clear and much less waxy than that produced at the same temperature with the alkali promoted cobalt catalyst.

Experiments have also been carried out to determine the effect of variation in the proportion of iron and cobalt in the catalyst employed in this invention and these experiments have pointed to the following:

1. The use according to the invention of the cobalt-iron catalyst gives a uniformly high H_2/CO consumption ratio despite variation in iron content and despite use of a low H_2/CO ratio gas.

2. The per cent. unsaturation of the synthesis product is high and is relatively independent of the cobalt-iron ratio when this ratio is 1/1 or higher.

3. Cobalt-iron ratios of 1/1 or less appear to favor higher C_4+ selectivities.

4. The butene-2/butene-1 ratio in the synthesis product is high, which is in marked contrast to the low ratios obtained with iron catalysts. This means that since

alpha olefins are low, further treating of the product for octane improvement, such as by isomerization, is simplified. This is also true in respect to treatment to convert oxygenated hydrocarbons to olefins; such compounds are found only in negligible quantities in the product from the iron-cobalt catalyst as against an iron catalyst, in the product from which they may be present in amounts equivalent to 2—4% oxygen.

Thus in accordance with the invention hydrocarbon synthesis operations may be carried out at low pressures to give high yields of unsaturated compounds and minimum quantities of wax. By dispensing with the oxygen unit and operating the synthesis gas generator with air investment costs are substantially decreased from the level where a high pressure type of operation requiring an oxygen unit is employed.

What we claim is:—

1. A process for producing relatively high yields of olefinic hydrocarbons from a synthesis gas containing carbon monoxide and hydrogen together with substantial quantities of nitrogen which comprises contacting said gas mixture, preferably in a once-through operation, at a temperature between 450 and 650° F. and at a pressure between 50 and 100 lbs./sq. in. gauge with a dense turbulent mass of fluidized finely divided catalyst comprising a silica gel support carrying a mixture of cobalt and iron and a thorium-containing promoter, said catalyst containing, based on the total weight of the catalyst, from 10—35% by weight of the mixture of cobalt and iron in the proportions of from 0.16 to 10 parts of cobalt per part of iron, and from 1—5% by weight of said promoter calculated as thorium metal.

2. A process as claimed in Claim 1 wherein the synthesis operation is carried out at pressure between 55 and 57 lbs. per sq. in. gauge.

3. A process as claimed in Claim 1 or 2 wherein the synthesis operation is carried out at a temperature between 475 and 525° F.

4. A process as claimed in any one of claims 1—3, wherein the catalyst contains from 3 to 25% by weight of iron, from 5 to 30% by weight of cobalt, from 1—5% by weight of thoria calculated as the metal, and from 60 to 89% by weight of silica gel calculated as silica.

5. A process as claimed in Claim 4, wherein the catalyst comprises 14% by weight of iron, 14% by weight of cobalt, 4.4% by weight of thoria calculated as the metal, and 67.6% by weight of silica gel calculated as silica.

6. A process as claimed in any of claims 1—5 wherein the synthesis gas is obtained from the partial combustion of natural gas with air in the presence of an oxidation catalyst preferably in the form of a dense turbulent bed of fluidized finely divided solid particles, at a low pressure between 50 and 100 lbs. per sq. in. gauge.

7. A process as claimed in Claim 6 wherein the synthesis gas contains carbon monoxide and hydrogen in the proportion of 2 molecules of hydrogen per molecule of carbon monoxide.

8. A process as claimed in claim 6 or 7 wherein the synthesis gas is cooled to the temperature in the reaction zone before being introduced therein.

9. A process as claimed in any one of claims 1—8 wherein the synthesis gas is passed through said mass of catalyst at the rate of 2 to 20 cubic feet of gas per pound of catalyst per hour and at a linear velocity of 0.1 to 3 feet per second and preferably between 0.4 and 1.5 feet per second.

10. A catalyst for the production of olefins from a synthesis gas mixture containing carbon monoxide and hydrogen together with a substantial quantity of nitrogen at relatively low pressure, comprising a silica gel support carrying a mixture of cobalt and iron and a thorium-containing promoter, the cobalt and iron together constituting 10—35% by weight of the total catalyst and being present in the proportion of from 0.16 to 10 parts by weight of cobalt per part of iron, and the promoter being present in an amount from 1—5% by weight, calculated as thorium metal, based on the total weight of the catalyst.

11. A catalyst as claimed in Claim 10 comprising from 3 to 25% by weight of iron, from 5 to 30% by weight of cobalt and from 60 to 89% by weight of silica gel calculated as silica.

12. A catalyst as claimed in Claim 11 comprising 14% by weight of cobalt, 14% by weight of iron, 4.4% by weight of thoria calculated as the metal, and 67.7% by weight of silica gel calculated as silica.

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1 SHEET

This drawing is a reproduction of the Original on a reduced scale.