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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

An Improved Hydrocarbon Synthesis Process

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 nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention is concerned with an improved hydrocarbon synthesis process. The invention is more particularly directed to an improved hydrocarbon synthesis process in which the composition of the synthesis gas is controlled within critical limits to secure a minimum deposition of carbon and a maximum production of desired hydrocarbon and oxygenated hydrocarbon constituents. The invention is more particularly directed to a process wherein gases containing methane are converted to produce a synthesis feed gas of a critical composition. This conversion can be effected by oxidation of methane with water and carbon dioxide over an oxidation catalyst or by direct oxidation of methane with air or oxygen with or without an oxidation catalyst. In accordance with our invention, the composition of the synthesis feed gas is controlled so that the mol. ratio of hydrogen to carbon monoxide is not less than 3 to 1 and is preferably in the range from 4 to 6, to 1. Simultaneously the concentration of the carbon dioxide is maintained at a relatively high level so that the mol. ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide is equal to or less than 2 and is preferably not over 1.5.

It is well known in the art to conduct hydrocarbon synthesis reactions by contacting hydrogen and oxides of carbon with catalysts under various temperature and pressure conditions. The catalyst employed is usually selected from the iron group metals, as for example, iron,

cobalt, and nickel. The catalysts are utilized either alone or on suitable carriers, such as kieselguhr, diatomaceous earth, synthetic gels, silica and alumina. Promoters such as oxides of chromium, zinc, aluminum, magnesium, alkali metals and the rare earth metals are used with the iron group metals. These catalysts are employed either in fixed-bed or in fluid catalyst operations. In fluid operations the catalyst generally comprises particles having particle sizes in the range from 0 to 200 microns and higher. These particles are maintained in a fluid ebullient bed by means of up-flowing gases the velocity of which is in the range from 0.1 to 5.0 ft. per second.

The temperature employed in the synthesis reaction vary widely as for example, in the range from about 300° F. to about 800° F. and are generally in the range from about 350° F. to about 750° F. The pressures likewise vary considerably and are a function of other operating conditions, such as catalyst employed, activity of the catalyst, character of the feed gases, and the temperatures utilized. Pressures in the range from about 1 to 100 and higher atmospheres have been suggested. The character of the feed gases introduced into the synthesis reaction zone depends somewhat on the particular temperatures and pressures and upon the catalyst employed.

Our invention is particularly concerned with the production of a mixture of hydrogen and carbon monoxide from hydrocarbons, particularly methane or from natural gas which is particularly adapted for use in a hydrocarbon synthesis reaction. One method for the production of such mixtures consists of oxidizing the methane with a suitable oxidation catalyst. A typical catalyst for such a conversion comprises 27% nickel oxide and 3% magnesium oxide on kaolin. Nickel on other supports has also been found to be satisfactory. This reaction is generally conducted by pass-

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ing the hydrocarbon gas mixed with steam and carbon dioxide in suitable proportions over the catalyst at temperatures from about 1300° F. to about 1800° F.

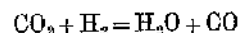
5 The ratios of carbon dioxide to methane and steam to methane in the feed are adjusted to produce the desired composition of gaseous product. For example, to produce a gas containing hydrogen and carbon monoxide in the ratio of 2/1 at 10 1500° F. a suitable ratio of steam to methane is 1.3 when the carbon dioxide to methane ratio is 0.68. With a feed mixture of this composition there is sufficient excess oxygen to prevent deposition 15 of carbon on the catalyst. In another process for producing mixtures of hydrogen and carbon monoxide, methane is oxidized directly with pure oxygen using 20 mol. ratios of oxygen to methane between 0.7:1 and 1.1:1 at temperatures of about 2000° F. to 2400° F. with or without the addition of water and carbon dioxide. 25 Either of the above methods of producing hydrogen and carbon monoxide or any other suitable method may be used in conjunction with our invention.

We have now discovered that providing the character of the feed 30 synthesis gases is controlled in accordance with our invention, unexpected desirable results are secured in that carbon deposition is minimized and that conversion and selectivities are 35 increased. Selectivity is here defined as the fraction of the synthesis gas consumed which produces desirable products such as hydrocarbons having three and four carbon atoms in the molecule and heavier hydrocarbons and 40 oxygenated hydrocarbons such as alcohols, ketones, and acids.

In accordance with our invention, we control the ratio of hydrogen to carbon 45 monoxide in the synthesis gas at not less than 3 to 1 on a molecular ratio and preferably 4 to 6 mols. of hydrogen per mol. of carbon monoxide. Simultaneously, in accordance with our process, we maintain a relatively high concentration of 50 carbon dioxide. The concentration of CO₂ is adjusted so that the mol. ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide is at or below 2 and preferably not in excess 55 of 1.5.

The process of our invention may be readily understood by reference to Figures 1 and 2 of the accompanying drawing. 60 Referring specifically to Figure 1, in the synthesis of hydrocarbons it is sometimes advantageous to recirculate some of the unconverted gases to the synthesis reactor. The composition of the feed to 65 the reactor is therefore in this case

dependent upon the composition of the exit gas and the composition of the fresh synthesis gas. Furthermore, it is desirable to consider the composition of this feed mixture after it has come to equilibrium with respect to the water-gas shift reaction as follows:



On the abscissa of Figure 1 is shown the ratio of H₂/CO in various feed mixtures. 75 As the above equilibration has taken place the ordinate shows the rate of carbon deposition which took place when synthesis was effected with these various feed mixtures. It is evident from Figure 1 80 that the rate of carbon deposition increases critically below hydrogen to carbon dioxide ratios of 3 and particularly at ratios of 2.5 and lower. High carbon deposition is of course extremely deleterious to the process. The points designated by solid circles in Figure 1 show 85 operations in which the H₂/CO ratio in the total feed was maintained high through the addition of water directly to the synthesis reactor. This process has the effect of decreasing the carbon formation but had the disadvantage of decreasing the activity of the synthesis catalysts so that conversions of H₂ + CO on the 95 order of 60 to 89% were obtained. The points designated as open squares show operations in which the H₂/CO ratio was maintained high by the process described in this invention wherein the ratio 100

$$\frac{\text{H}_2 - \text{CO}_2}{\text{CO} + \text{CO}_2}$$

was maintained from 1.5 to 2.0. In these operations the H₂ + CO conversion was from 97 to 98%.

In order to further illustrate our invention, an embodiment of the same is shown 105 in Figure 2. Feed gases comprising hydrocarbons, water gas and carbon dioxide are introduced into conversion zone (10) by means of lines (1), (2) and (3) respectively. These feed gases may contain 110 from about 30 to 50% methane, from about 20 to 60% carbon dioxide, and from about 20 to 60% steam. A typical composition of a suitable feed for producing 115 desirable synthesis gas comprises about 40% methane, 40% steam and 20% carbon dioxide. Conversion zone (10) contains an oxidizing catalyst, as for example, nickel. The operation is conducted at a temperature in the range from 120 about 1300° F. to 1800° F. with feed rates from 50 to 500 volumes methane or equivalent per volume of catalyst per hour.

After a sufficient time of contact to secure the desired reaction, reaction gases are withdrawn from conversion zone (10) by means of line (4) and introduced into converter zone (20). The gases withdrawn from conversion zone (10) comprise gases having a hydrogen concentration in the range from about 40% to 66%, a carbon monoxide concentration in the range from about 45 to 30%, a carbon dioxide concentration in the range from about 0.1 to 10%, and a nitrogen concentration in the range from about 0 to 5%.

Steam or water is introduced into converting zone (20) by means of line (5). The temperature is maintained in the range from 800° to 1000° F., the pressures in the range from 1 to 100 atmospheres and 2 to 10 times the theoretical amount of water employed. The catalyst used may be red iron oxide in any suitable form. After a sufficient time of contact, the gases are withdrawn from converting zone (20) by means of line (6) and introduced into synthesis zone (30) wherein the gases are contacted with a suitable synthesis catalyst, as for example, a metal selected from the iron group. The preferred catalyst comprises iron. Temperature and pressure conditions in synthesis zone (30) are maintained at a level to secure the desired reaction. In general, with iron catalysts

the temperatures are in the range from 500° to 750° F. and the pressures from 10 to 50 atmospheres. Synthesis products are withdrawn from zone (30) by means of line (9) and handled in any manner desirable. It is sometimes advantageous to recirculate unreacted synthesis gas in which case part of the gas stream leaving synthesis zone (30) through line (9) will be separated from water and liquid hydrocarbons and returned to the inlet of synthesis zone (30). In some operations it may be desirable to recirculate exit gases from line (9) to the conversion zone (10). Line (7) and valve (8) are provided to by-pass converter zone (20) which by-pass line may be utilized to secure the desired analysis in the feed gases to zone (30).

In order to further illustrate our invention the following example is given:

EXAMPLE 1.

Two operations were made employing varying types of synthesis feed gas. In Operation A synthesis gas comprising hydrogen to carbon monoxide in the mol. ratio of 2 to 1 was employed. In Operation B a feed comprising hydrogen to carbon monoxide in a mol. ratio of 4 to 1 was employed. Furthermore, the feed gas contained 10% carbon dioxide. The results of the respective operations are as follows:—

	Fresh Feed to Synthesis Reactor										Operation	
											A	B
70	H ₂ %	-	-	-	-	-	-	-	-	-	58	64
	CO, %	-	-	-	-	-	-	-	-	-	29	16
	CO ₂ %	-	-	-	-	-	-	-	-	-	9	16
	CH ₄ , N ₂ , % etc.	-	-	-	-	-	-	-	-	-	4	4
75	H ₂ - CO ₂	-	-	-	-	-	-	-	-	-	1.3	1.5
	CO + CO ₂	-	-	-	-	-	-	-	-	-	2.0	4.0
	H ₂ /CO	-	-	-	-	-	-	-	-	-	2.0	4.0
	Synthesis Temperature, °F.	-	-	-	-	-	-	-	-	-	650	650
80	Synthesis Press., Atms.	-	-	-	-	-	-	-	-	-	28	28
	H ₂ + CO Conversion	-	-	-	-	-	-	-	-	-	95.0	97.5
	Ultimate yields per cubic meter of hydrogen and carbon monoxide consumed	-	-	-	-	-	-	-	-	-		
	cc. C ₁ + HC's + WS Oxy Cpds.*	-	-	-	-	-	-	-	-	-	263	281
85	cc. C ₁ + HC's + WS Oxy Cpds.*	-	-	-	-	-	-	-	-	-	219	229
	cc. C ₂ + HC's	-	-	-	-	-	-	-	-	-	183	184
	Water soluble oxygenated compounds by difference	-	-	-	-	-	-	-	-	-	26	45

*C₂ and heavier hydrocarbons plus water soluble oxygenated compounds

From the above data it is evident that a synthesis gas of the ordinary composition in which the ratio of hydrogen to carbon dioxide is 2 to 1 such as would be made by oxidizing methane over nickel catalyst or by burning methane with oxygen gives yields, particularly of C_2 and heavier plus "alcohols and acids" which are inferior to those obtained in Operation B. In Operation B the feed gas was of a composition which is obtained by our invention as shown in Figure 2.

EXAMPLE 2.

Our invention is further illustrated by the following typical gas compositions and a method of preparing the same. The particular gas composition described is the one employed in Operation B of Example 1. The following gas composition was introduced into a conversion furnace containing nickel catalyst. The temperature of the furnace was 1530° F. and the pressure was about 2 atmospheres.

25	CH_4	36.8
	CO_2	19.0
	H_2O	36.2
	N_2	8.0

The gas leaving the conversion furnace, after condensation of the water had the following composition.

30	CO_2	5%
	H_2	60%
	CO	30%
35	N_2	5%

A portion of this gas, amounting to 42%, was passed through a converter-furnace together with excess steam to produce a gas which, when dried, consists of 27% CO_2 ; 69% H_2 and 4% N_2 . This was mixed with the remainder of the gas from the reformer to produce the desired mixture of the following composition:

40	CO_2	16%
	H_2	64%
45	CO	16%
	N_2	4%

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. An improved process for the synthesis of hydrocarbons containing three and more carbon atoms in the molecule which comprises introducing into a synthesis reaction zone a feed mixture comprising carbon monoxide and hydrogen, said feed mixture being characterized in

that the ratio of hydrogen to carbon monoxide is not less than 3 mols of hydrogen per mol. of carbon monoxide, said feed mixture also being characterized in that the concentration of the carbon dioxide is maintained at a relatively high level so that the mol. ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide is not in excess of 2, and maintaining said reaction zone at a temperature and pressure adapted to produce the desired synthesis reaction.

2. A process according to Claim 1 wherein the mol. ratio of hydrogen to carbon monoxide is in the range from 4 mols of hydrogen to 6 mols of hydrogen per mol. of carbon monoxide.

3. A process according to Claim 1 wherein the mol ratio of hydrogen to carbon monoxide is in the range from 4 mols of hydrogen to 6 mols of hydrogen per mol. of carbon monoxide, and wherein the concentration of carbon dioxide is maintained at a relatively high level so that the ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide, is not in excess of 1.5.

4. An improved process for the synthesis of hydrocarbons which comprises oxidizing hydrocarbon mixture containing methane under conditions to produce gases comprising carbon monoxide and hydrogen, segregating a portion of said product gases and passing the same with steam to a converter furnace, removing the reaction gases from the converter furnace and recombining the same with said product gases, adjusting operating conditions so that the mol. ratio of hydrogen to carbon monoxide in the mixed stream is in the range from 4 mols. of hydrogen to 6 mols. of hydrogen per mol. of carbon monoxide and that the concentration of the carbon dioxide is at a relatively high level so that the ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide is not greater than 1.5, introducing said mixed gas stream into a hydrocarbon synthesis reaction zone containing an iron type catalyst, maintaining said hydrocarbon synthesis reaction zone at temperatures and pressures adapted to secure synthesis and removing synthesis products therefrom.

5. A process according to Claim 4 wherein said catalyst in said hydrocarbon synthesis reaction zone comprises a fluidized iron catalyst.

6. A process according to Claim 4 wherein said converter furnace is maintained at a temperature in the range from about 800° F. to 1000° F. and wherein 2 to 10 times the theoretical amount of steam is employed.

7. In a hydrocarbon synthesis reaction

wherein feed gases comprising hydrogen and carbon monoxide are contacted with an iron type catalyst the improvement for increasing the yield of oxygenated products which comprises maintaining the mol. ratio of hydrogen to carbon monoxide not less than 3 mols. of hydrogen per mol. of carbon monoxide and simultaneously maintaining the concentration of the carbon dioxide at a relatively high level so that the mol. ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide is not more than 2.

15 8. A process according to Claim 7 wherein the mol. ratio of hydrogen to carbon monoxide is in the range from 4

mols. of hydrogen to 6 mols. of hydrogen per mol. of carbon monoxide.

9. A process according to Claim 7 20 wherein the mol. ratio of hydrogen to carbon monoxide is in the range from 4 mols. of hydrogen to 6 mols. of hydrogen per mol. of carbon monoxide, and wherein the concentration of carbon dioxide is 25 maintained at a relatively high level so that the ratio of hydrogen minus carbon dioxide over carbon monoxide plus carbon dioxide, is not in excess of 1.5.

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Fig. 1.

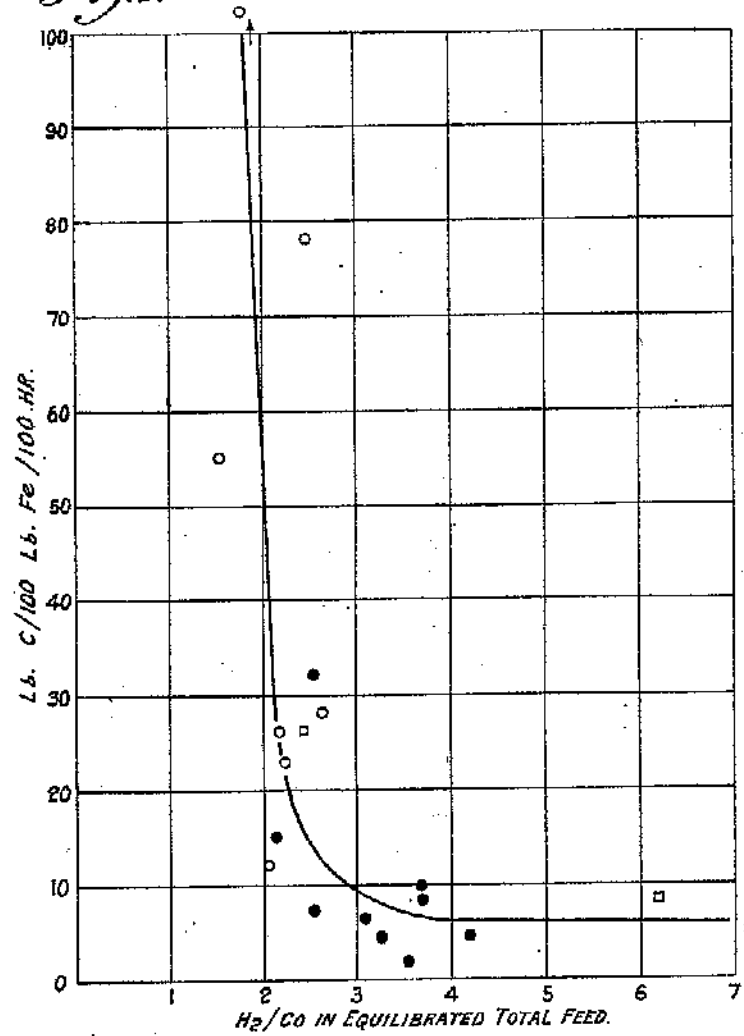


Fig. 2.

