PATENT SPECIFICATION

647,079

Date of Application and filing Complete Specification: Feb. 20, 1948.
No. 5071/48.
Application made in United States of America on May 24, 1947.
Complete Specification Published: Dec. 6, 1950.

3483

Index at acceptance:—**Class 2(iii), B1g.**

COMPLETE SPECIFICATION

Control of Carbon in Hydrocarbon Synthesis

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized 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:—

This invention relates to improvements in the art of synthesizing hydrocarbons from carbon monoxide and hydrogen. Prior to this invention others have synthesized hydrocarbons boiling in the gasoline and higher ranges by reacting together carbon monoxide and hydrogen in the presence of a suitable catalyst at reaction temperatures and pressures. Prior to this invention cobalt promoted with thoria has been used as a catalyst for promoting the synthesis wherein carbon monoxide and hydrogen react to form hydrocarbons.

More recently, iron has been employed as a catalyst in the hydrocarbon synthesis, employing carbon oxide and hydrogen as reactants. In the synthesis of hydrocarbons from carbon monoxide and hydrogen, a ratio of about one mol of carbon monoxide to one mol of hydrogen has been employed when the catalyst was iron. It has also been found that this ratio of hydrogen to carbon monoxide using an iron catalyst may be varied somewhat with improved results, i.e., it is found that best results are obtained when the ratio of hydrogen to carbon monoxide is at least 1.5 mol of hydrogen per mol of carbon monoxide in the fresh feed because this higher ratio gives a higher conversion of the feed gas to desirable products and reduces carbon deposition on the catalyst and physical disintegration of the catalyst.

The present invention however comprises a process for the synthesis of hydrocarbons and oxygenated hydrocarbons comprising contacting a gaseous mixture containing carbon monoxide, carbondioxide and hydrogen with a fluidised bed of powdered iron catalyst in a reaction zone at synthesis temperatures and under superatmospheric pressure, the hydrogen partial pressure in the reaction zone amounting to at least 100 pounds per square inch and the carbon dioxide partial pressure in the zone amounting to at least 125 pounds per square inch and preferably over 150 pounds per square inch.

Preferably the total pressure in the reaction zone should be over 400 pounds per square inch.

This process results in higher yields of normally liquid hydrocarbons and oxygenated compounds, and tends to repress the formation of large quantities of carbonaceous material on the catalyst. A great aid to the success of this process is the use of an iron catalyst sintered in hydrogen for such a catalyst is resistant to fragmentation. It is highly important that the average particle size of the powdered iron catalyst be maintained within certain limits hereinafter set forth. But carbonaceous deposits on the catalyst tend to cause fragmentation or physical disintegration thereof with the result that the powdered iron catalyst is reduced to a state of fineness that it cannot be procured in a fluidized state. A catalyst "sintered" (i.e. heated to a temperature of incipient fusion) in hydrogen exhibits a superior strength to one sintered in air or oxygen.

In the accompanying drawing, a suitable apparatus in which a preferred modification of this invention may be carried into effect is shown.

Numeral 1 represents a hindered settling reactor containing a body of iron catalyst in the form of a powder having a particle size of from about 40 to 80 microns but with appreciable quantities, say 25 per cent, of sizes less than 40 microns. A mixture of carbon monoxide, carbon dioxide, and hydrogen is introduced into the present system through line 10, the ratio of hydrogen to carbon monoxide on a mol

[Price

to mol basis being approximately 1.7 to 2 mols of hydrogen per mol of carbon monoxide, the ratio of carbon dioxide to carbon monoxide in the feed being 0.2 to 0.3 mols of carbon dioxide per mol of carbon monoxide. The mixture of hydrogen and the oxides of carbon preheated, say, to about 200° to 300° F. or thereabouts, in line 10 is discharged via line 11 into the bottom of reactor 1, passes up through a foraminous member G and then contacts the fluidized catalyst C. The catalyst is formed into a fluidized mass in the reaction zone by regulating the superficial velocity of the gasiform material in the reaction zone within the limits of from about ½ to 1½ feet per second so as to form a dense, turbulent, ebullient suspension now referred to in the art as a "fluidized" catalyst. The dense phase of the fluidized catalyst has an upper level at L, above which a dilute suspension exists. The dense phase suspension may weigh from 30 to 80 pounds per cubic foot while the upper portion of the dilute phase contains mostly catalyst fines. The dense suspension from the foraminous member G to the level L extends a distance of from 15 to 40 feet and above that, in a disengaging space from L to the top of the reactor, the height may be from 10 to 20 feet, in which latter space the bulk of the catalyst separates from the gasiform material and descends by gravity toward the dense phase suspension. Ordinarily, gas-solids contacting devices 3 are disposed in the upper part of reactor 1. These gas-solids contacting devices may be, for example, centrifugal separators and are disposed therein for the purpose of separating entrained catalyst from the gases. The crude products issue from the reactor 1 through line 4 and, if desired, may be passed through one or more gas-liquid contacting devices, such as an oil scrubber 5, for the purpose of removing substantially the last traces of catalyst fines. The use of an oil scrubber to remove catalyst fines is, *per se*, not novel. It has been previously used, for example in catalytic cracking operations, and operates to cause the gases containing fines to contact a high boiling oil which may be one of the products of the reaction. For instance, the scrubbing oil may be a cold gas oil. The amount of scrubbing oil and the rate of its circulation to the scrubber are such that the products boiling above, say, 450° F., at atmospheric pressure are condensed while the products boiling up to 450° F. remain vaporized. The final effect of the scrubbing treatment is to remove substantially the last traces of catalyst from the gasiform material, as previously stated. The reaction products issue from the oil scrubber 5 through line 6, are further cooled in a condenser 7 below the boiling point of water, and discharged into a separator 8 from which normally liquid hydrocarbons and water are removed from the bottom through line 9. The gasiform fraction is led by line 13 into a second cold oil scrubber 14 from which light hydrocarbons are removed, leaving undissolved residual gases, including carbon monoxide, carbon dioxide, hydrogen, and normally gaseous hydrocarbons, such as methane, which undissolved constituents are recycled via line 20 to the reactor. The oil scrubber 14 may be omitted and the gasiform material withdrawn from separation drum 8 recycled to the reactor via lines 13 and 11. This latter type of oil scrubbing is well known to petroleum refinery engineers, and need not be described in detail. The main purposes, of course, of the oil scrubber, when used, is to remove hydrocarbons from vapors containing them.

As required, tail gas may be withdrawn and rejected from the system through valved line 21. The valve in line 21 may also be operated to control the gas pressure in the system. As will more fully appear hereinafter, the operation of the valve in line 21 is highly instrumental in maintaining the process in operation according to the present invention, for, as previously indicated, the desired partial pressure of hydrogen and carbon dioxide in the system has been attained by means of the composition of the reactants and/or by imposing suitable total pressure on the system.

As stated, the object of the invention is to operate the hydrocarbon synthesis process in the presence of a fluidized iron catalyst so as to obtain high yields of hydrocarbons, including normally liquid hydrocarbons, and also high yields of oxygenated hydrocarbons, as well as to suppress carbonaceous deposition of the catalyst. This is accomplished by maintaining a high partial pressure of carbon dioxide in the reaction zone, and also a high hydrogen partial pressure in the reaction zone.

There are at least two ways of attaining the desired hydrogen and carbon dioxide partial pressure as follows:—

1. By increasing the total pressure in the system.

2. By adding carbon dioxide from an extraneous source and controlling the ratio of recycled gas with respect to fresh feed, both in conjunction with a hydrogen to carbon monoxide ratio in the fresh feed of at least 1.5:1.

To explain (1) above, it is believed to be clear that, by simply imposing a greater pressure on the system in accordance with Dalton's Law, the partial pressure of hydrogen and the partial pressure of carbon dioxide will both be increased. For example, if the total pressure on the system is 200 pounds per square inch absolute and the partial pressure of carbon dioxide is 75 pounds per square inch, the partial pressure of carbon dioxide becomes 150 pounds per square inch when the total pressure on the system is increased to 400 pounds per square inch absolute. In like manner, the partial pressure of hydrogen will be increased.

With respect to item (2) immediately above, since, as the process is ordinarily operated with carbon monoxide conversion such that at least 90% of the carbon monoxide feed is reacted, and since the process is ordinarily operated so that at least a portion of the tail gas is recycled to the reaction zone, and further, since the fresh feed contains at least 5 volumes of hydrogen per volume of carbon dioxide, but the recycled tail gas contains about 3 volumes of carbon dioxide per volume of hydrogen, the volumes of fresh feed gas per volume of recycled gas can be proportioned to give the desired partial pressures of carbon dioxide and hydrogen in the reaction zone, it being understood that the total pressure on the system must be sufficient to maintain both the carbon dioxide and the hydrogen at the proper pressure levels.

It is pertinent at this point to emphasize that the gas exiting from the reaction zone approximates closely the composition of the main portion of the gasiform material in the reaction zone, for due to the intimate mixing afforded by the fluidized bed of catalyst, experience has shown that the fresh reactants entering the reaction zone are mainly converted in the lowermost portion of the said zone.

By resorting to any of the foregoing expedients, the carbon dioxide partial pressure in the reaction zone may be maintained at the desired level, namely, at a minimum value of 125 pounds per square inch partial pressure.

When the CO_2 partial pressure in the reactor is maintained above 125 pounds per square inch up to about 250 pounds per square inch absolute, better yields of hydrocarbons and "alcohols" or oxygenated products are formed per volume of CO and H_2 consumed. Also, it is necessary to maintain the hydrogen partial pressure in the inlet gases at at least 100 pounds per square inch up to 750 pounds per square inch absolute, to avoid carbon formation and catalyst disintegration. This is demonstrated in the following data, the first set showing the benefits from increasing partial pressure of the H_2 and CO_2 by increasing the total pressure and the second set showing the improved yields and maintenance of catalyst size by changing the CO_2 in the fresh feed and altering the CO_2 in the total feed by altering the recycle to fresh feed volumetric ratio.

Case	A	B
Catalyst Iron (pyrites Ash + 2% K_2CO_3 oxidized at 1000° F., reduced at 700° F.)		
Temperature °F.	644	630
Total pressure per square inch, absolute	442	229
Fresh Feed, H_2/CO	1.92	1.93
CO_2/CO	.26	.28
Recycle ratio	2.0	1.2
Total feed analysis, %—CO_2	34.8	28.6
CO	12.8	16.1
H_2	31.2	41.0
Other*	21.2	14.3
Exit gas analysis, %—CO_2	50.7	45.6
CO	2.7	2.6
H_2	16.5	27.4
Other*	30.1	24.9
Partial pressure, per square inch, absolute —CO_2 (ave)	176	83
H_2 (inlet)	129	94
Conversion—% $CO + H_2$ fresh feed	96.7	91

Case	A	B
Yields – cc/M3CO + H_2 Cons. ** C_4+ Hydrocarbons	192	163
Oxygenated products in water layer	34	31
Carbon formation—Lbs. C/100 Lb. Fe in reactor/100 hours	44	89
Catalyst disintegration	Satisfactory	Very severe

* Nitrogen, methane, ethane, etc.

**Cubic centimeters of C_4 + hydrocarbons per cubic meter of ($CO + H_2$) consumed.

The data clearly show that when the partial pressure of CO_2 is reduced from 176 to 83 pounds in the reactor, average of the inlet and outlet partial pressures, the yield of C_4+ hydrocarbons on $CO+H_2$ consumed decreased from 192 to 163 cc/M³ of product. At the same time there was a decrease in water soluble compounds, expressed as ethyl alcohol equivalent of carbon in the water layer, from 34 to 31 cc/M³H_2+CO consumed. The decrease in inlet hydrogen partial pressure from 129 to 94 pounds per square inch absolute increased the carbon deposition rate from 44 to 89 pounds carbon per 100 pounds Fe in reactor per 100 hours of operation, causing very severe catalyst disintegration and requiring withdrawal of half of the catalyst in the reactor and replacement with new catalyst each day to maintain operations.

The following experiments show the effect of changing the CO_2 and H_2 partial pressures by altering the feed composition and recycle ratios at the same total pressure, viz., 415 pounds per square inch absolute.

	C	D	E
Catalyst—Red iron oxide promoted with 0.5—1.0% K_2CO_3			
Temperature °F.	650	650	650
Fresh Feed, H_2/CO	1.9	1.7	1.9
CO_2/CO	.27	.33	0
Recycle Ratio	0	2.5	2.8
Total feed analysis—%—CO_2	8.5	42	16
CO	31.0	13	12
H_2	60.0	24	27
Other*	0.5	21	45
Exit gas analysis—%—CO_2	38.0	56	22
CO	6.3	5	4
H_2	43.0	11	13
Other*	12.7	28	61
Partial pressure, pounds per square inch absolute			
CO_2 (Ave)	96	205	72
H_2 (Inlet)	250	100	112
Conversion, % $CO+H_2$, fresh feed	70	96	98
Yields—cc/M³ $CO+H_2$*** Cons. C_4+Hydrocarbons	109	168	149
Oxygenated products in water layer****	34	43	39
Carbon formation	about 10 lbs. carbon/100 lb. Fe in reactor/100 hours		
Catalyst disintegration	low		

* Nitrogen, methane, ethane, etc.

*** cc/M³ $CO+H_2$ = cubic centimeters of C_4+hydrocarbons per cubic meter of CO and H_2 consumed.

**** Cubic centimeters of oxygenated hydrocarbons on same basis as C_4+hydrocarbons.

Since the hydrogen partial pressure in reaction zone was 100 pounds per square inch or over and further since this catalyst was sintered in hydrogen at 1600° F., making it more resistant to disintegration by carbon, the carbon formation rate was low and the catalyst resisted disintegration, an 800 hour run was made with no severe catalyst disintegration.

The effect of the CO_2 on the yields of C_4+ hydrocarbons and oxygenated products, (again ethyl alcohol equivalent of carbon in water layer), is clearly shown in the two sets of data. When the CO_2 partial pressure was increased from 96 to 205 pounds per square inch, absolute, by using 2.5 recycle gas gas ratio rather than one pass operations, (columns C and D), the yields of C_4+ hydrocarbons increased from 109 to 168 cc/M^3% H_2 + CO consumed and the yield of oxygenated products increased from 34 to 43 cc/M^3 H_2 + CO consumed.

A CO_2 partial pressure increase by increasing the CO_2 content of the fresh feed gas with the same recycle, cases E and D, where the CO_2/CO ratio of the fresh feed was increased from 0 to 0.33 raising the CO_2 partial pressure in the reactor from 72 to 205 pounds per square inch, absolute, gave an increase in C_4+ yields from 149 to 168 cc/M^3 CO + H_2 consumed and the oxygenated products from 39 to 43 cc/M^3 CO + H_2 consumed.

Various processes have been proposed for the production of hydrocarbons and oxygenated hydrocarbons from gases containing carbon monoxide and hydrogen, for example, Specifications Nos. 478,318 and 510,514 both disclose the presence of substantial amounts of carbon dioxide in the reaction zone. However, neither of them suggest the use of fluidised catalysts where the deposition of carbon on the catalyst is more severe.

In the Specification of our Patent No. 627,905, which was not published at the date of application of the present case, is claimed 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 which may contain a fluidised iron catalyst 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 characterised 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.

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. The method of synthesizing hydrocarbons and oxygenated hydrocarbons which comprises contacting a gaseous mixture containing carbon monoxide, carbon dioxide and hydrogen with a fluidized bed of powdered iron catalyst in a reaction zone at synthesis temperatures and under super-atmospheric pressure, the hydrogen partial pressure in the reaction zone amounting to at least one hundred pounds per square inch and that of the carbon dioxide amounting to at least 125 pounds per square inch, and recovering from said reaction zone a hydrocarbon product and oxygenated hydrocarbons.

2. The method according to claim 1 in which a total pressure of over 400 pounds per square inch absolute is imposed on the reactants in the reaction zone.

3. The method according to claims 1 and 2 in which the ratio of CO_2 to CO in the total feed to the reaction zone is increased by recycling to the reaction zone normally gaseous portions of the withdrawn product.

4. The method according to claims 1 to 3 in which the catalyst is sintered in hydrogen prior to use in the process.

5. The method of claim 4 in which the catalyst is red iron oxide sintered in hydrogen at 160° F.

6. The method as claimed in any of the preceding claims including the step of maintaining a carbon dioxide partial pressure in excess of about 150 pounds per square inch absolute whereby increased yields of oxygenated compounds are obtained.

Dated this 20th day of February, 1948.
DAVID T. CROSS,
16, Charles II Street, Haymarket,
London, S.W.1.
Agent for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1950.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.

[This Drawing is a reproduction of the Original on a reduced scale.]