PATENT SPECIFICATION

625,841

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COMPLETE SPECIFICATION

An improved process for the Catalytic manufacture of Hydrocarbons and Oxygenated Hydrocarbons

I, CONRAD ARNOLD, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention (a communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America), 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 relates to improvements in the art of synthesizing hydrocarbons and oxygenated hydrocarbons by a catalytic reaction involving carbon monoxide and hydrogen as reactants. More particularly, the present improvements relate to methods of cleansing the catalyst which, in the course of the foregoing reaction, acquires deposits of oily and waxy material and also deposits which contain oxygen, all of which will appear more fully in the following description, the drawing forming a part of the present specification, and the claims.

Methods have previously been described for cleansing or regenerating a catalyst of the type here in question by hydrogenating in situ the deposits formed on the catalyst during the process of reacting carbon monoxide and hydrogen, by reacting added hydrogen over and above that required to react with the carbon monoxide and, by that means, hydrogenating the heavy oily and waxy material on the catalyst to volatile compounds, thereby rendering the deposits adaptable for removal.

Further in Specification No. 587,456 which although not published at the date of the present application, yet bears an earlier date, there is claimed a process for the preparation of valuable organic products by the reduction of carbon oxides with hydrogen comprising supplying a finely divided solid catalyst to a column of substantial height, maintaining the catalyst in a mobile state in said column, passing a stream of catalyst from the bottom of said column into a gas stream to form a suspension therein of said catalyst, passing said suspension of catalyst in a mixture with the gaseous reagents through a reaction zone, separating the catalyst from the gasiform stream leaving the reaction zone and supplying at least a portion of said separated catalyst directly to said column of substantial height. In this process it is further claimed to regenerate with hydrogen at a temperature of from 500-700°F. or higher, a portion of the contaminated catalyst separated from the gasiform stream leaving the reaction zone and then to return the regenerated catalyst thereto.

According to the present invention, the fouled catalyst is removed from the synthesis reactor and hydrogenated in a separate vessel at a temperature of at least 900°F. and for a sufficient time to effect removal of at least 80% of the contaminants on the catalyst. The hydrogenation of the catalyst in the second vessel has the advantage that the hydrogenation may be carried out at the optimum temperature and pressure for the hydrogenation, the additional hydrogen and products of hydrogenation are not mixed with the hydrocarbon synthesis product, and the carbon to hydrogen ratio in the reaction zone will not be affected by the hydrogenation of the deposits on the catalyst.

The improvements are carried out in a so-called "fluid catalyst" type of operation, that is to say, an operation in which the catalyst in the form of a powder is suspended in the reactants in the reaction zone. This suspension is formed by causing the reactants to flow upwardly in the reaction zone at a velocity which is sufficient to maintain the catalyst in a turbulent, dense suspension above which the catalyst is maintained in dilute suspension, the dense phase being characterized by the fact that due to its turbulence, the catalyst is maintained at a substantially uniform temperature throughout its mass. In the hydrogenator the catalyst may also be in the form of a dense, turbulent ebullient mass suspended in the hydrogen-containing gas, although under certain conditions it may be preferred to maintain it in the form of an "aerated," freely flowing mass through which the hydrogen gas passes quickly and without inducing violent turbulence within the bed.

In the course of the synthesis within the dense suspension of catalyst in the reactor, hydrocarbons of a wide range of molecular weight may be formed. At the same time oxygenated compounds may also be formed. In either case, the molecular weight varies from that of methane and other normally gaseous material to high boiling materials, the latter of which at room temperature may be solid. The operating conditions of temperature and pressure in the reaction zone determine the amount of the heavier hydrocarbons and oxygenated hydrocarbons which may be removed as a gas with the other gasiform materials leaving the reactor. Under certain conditions of operation the rate of production of the heavier hydrocarbons and oxygenated hydrocarbons exceeds the rate of removal of the said heavier hydrocarbons and oxygenated compounds leaving the reactor. Consequently, condensation occurs and these heavier materials are deposited on the catalyst in the form of liquids or solid materials. If the quantity of this deposit retained by the catalyst is allowed to build up, a condition may be reached wherein the catalyst particles begin to stick together, thereby losing their adaptability to be fluidized or formed into the suspensions previously mentioned. Even before this occurs the oxygenated hydrocarbon compounds deposited on the catalyst tend to cause physical disintegration thereof, with the production of unwarranted quantities of catalyst fines. While it is true that some catalyst will pass from the reactor with the crude gasiform material, the actual amount of this catalyst so withdrawn from the reactor, although it may contain a heavy deposit thereon, will normally be insufficient to prevent accumulation of the deposit on the catalyst within the vessel to the extent that its adaptability to be fluidized is inhibited and that extensive disintegration of the catalyst begins. Hence, it is conventional to remove catalyst from the reactor and to treat it with a solvent to remove the materials contained thereon. Not only is this an expensive operation but it is impossible to remove completely the deposit from the catalyst by solvent extraction. It is also possible to burn the deposit from the catalyst, but in this case the catalyst must be reduced before re-employment and it frequently suffers deterioration during the cycle.

From the standpoint of long maintenance of catalyst activity and of suitable quality for good catalyst fluidization, it would be preferable to operate with no deposition of heavy hydrocarbons or heavy oxygenated hydrocarbons on the catalyst since the deposits will eventually decrease the activity of the catalyst in promoting synthesis and also result in a non-fluid bed. To prevent the deposition of contaminants on the catalyst, it would require a modification of the process wherein the production of heavy oil is eliminated either by the use of very selective catalysts or by adjusting the conversion temperature and pressure conditions so that all of the heavy oils are vaporized and carried out of the reactor along with the reactants. But the conditions thus required are not compatible with the most economical utilization of the reactor and, hence, preferred operation would be one wherein a certain amount of heavy oil, wax, and oxygenated hydrocarbons are formed but in which the accumulation of such material on the catalyst is controlled in order not to lose its fluidity or activity.

It is, therefore, the main object of this invention to provide a process for the removal of high boiling materials from an operating hydrocarbon synthesis catalyst in a manner which is efficient, economical, and in nowise interferes with the operation of the hydrocarbon synthesis process itself under optimum conditions.

In the accompanying drawing, an apparatus has been shown diagrammatically in Fig. 1 in which a preferred modification of this invention may be carried into effect; and in Fig. 2, the effect of temperature in carbon removal from the catalyst upon hydrogenation of the latter has been shown by means of a graph.

Referring in detail to Fig. 1, 1 represents a reactor of the so-called hindered settling type, that is to say, a reactor in which there is maintained in the reactor a dense, fluidized mass of iron catalyst in reactants. A mixture of carbon monoxide and hydrogen suitably proportioned enters the system through line 10, passes through a compressor 12, and is then discharged into the bottom of reactor 1, wherein it passes upwardly through a foraminous member 13 into a body of catalyst C, which is in the form of a dense suspension. This catalyst may be, for example, an iron catalyst deposited on kieselguhr. The gases flow upwardly through the catalyst at a velocity of from 1/2 to 10 feet per second but, generally, proper bed density or suspension density is effected by causing the gas to flow at a rate of about 1-1/2 feet per second where the catalyst has a particle size of 5 to 200 microns. As stated, this velocity causes the formation of a dense suspension of catalyst in gasiform material and by controlling the actual amount of catalyst in the reactor, the dense suspension will have an upper level at L, above which the concentration of catalyst in gasiform material decreases so that in the space from L to the top of the reactor, disengaging of catalyst from gasiform material takes place to a considerable degree so that the gases issuing from the reactor contain a relatively small amount of catalyst. Stated otherwise, the dense suspension between 13 and L may have a density of 10 to 70 pounds per cubic foot, whereas the gases exiting from the reactor through line 17 may have a density of 0.001 to 0.1 pounds per cubic foot. As indicated, the crude product issues through line 17 and then may be forced through one or more dust separators, such as electrical precipitators or "cyclones" 19, for the purpose of removing a further portion of catalyst and then the vapors are withdrawn through a line 21 and discharged into a fractionating tower 23 where they are subjected to fractional distillation. In the fractional distillation column or tower 23, the normally gaseous material containing hydrocarbons, hydrogen, carbon monoxide, carbon dioxide and water is withdrawn overhead through line 30 and discharged into a water condenser 32 where it is cooled to a temperature below the condensation point of the water vapor, whereupon the cooled material is withdrawn through line 35 and discharged into a separator 37 from which water and light hydrocarbons are withdrawn from the bottom while the uncondensed material is recirculated via line 40 to line 10. A gasoline fraction is recovered from the fractionating tower 23 through line 42 and subjected to purification and further refining in conventional equipment (not shown). A heavy fraction may be recovered from the bottom of fractionating tower or column 23 through line 45 and utilized in a manner which does not go to the heart of the present invention. The description of the process for synthesizing hydrocarbons from carbon monoxide and hydrogen given hereinbefore represents a conventional method of operating a system employing the so-called fluid catalyst technique and does not include the improvements embodying the present invention, which latter, as stated, refer to improved methods for removing oily, waxy deposits from the catalyst.

Referring again to the reactor 1, as previously indicated waxy deposits accumulate on the catalyst and are removed as follows. Catalyst is withdrawn from the reactor 1 through a drawoff standpipe 50 controlled by a valve 52. As usual, the standpipe is provided with gas taps 55 into which a slow current of gas may be injected for the purpose of "fluidizing" the catalyst or, in other words, increasing its fluidity. This fouled catalyst is then discharged into a stream of hydrogen-containing gas introduced into the system through line 60. This hydrogen-containing gas may be heated in a furnace or other suitable means (not shown) before mixing with the catalyst. The suspension of catalyst in the hydrogen-containing gas thus formed is discharged into the bottom of hydrogenator 65, passing upwardly through a foraminous plate or grid 67 into the main body of the reactor where it is maintained in dense phase suspension, above which is a dilute phase suspension, by controlling the superficial velocity of the gas in the same manner as employed in forming the suspensions in reactor 1. The fouled catalyst may also be discharged directly from standpipe 50 through valve 52, into the hydrogenation vessel 65, into which catalyst-free hydrogen gas may be introduced through grid 67. Hereinafter operating data and results obtained will be set forth but for the present it is merely stated that conditions of temperature are maintained within the hydrogenation zone so as to cause hydrogenation of the deposits on the catalyst to convert the said deposits into volatile decomposition products. The volatile products resulting from the hydrogenation reaction are withdrawn from the system through line 70 and delivered to equipment (not shown) for the purpose of recovering therefrom valuable products such as normally liquid hydrocarbons. The thus purified catalyst is withdrawn through a drawoff pipe 72, preferably through an "aerated" standpipe of the type 50, previously described, and discharged into, say, a stream of hydrogen or CO in the line 73 to form a suspension therein, which suspension is then returned to the reaction zone.

In the foregoing description, which is diagrammatic, a full showing of numerous mechanical aids and accessory apparatus, such as flow meters, valves, pumps, and the like, have been omitted, in the interest of simplicity, but the engineer will understand that in a commercial unit this accessory apparatus would be included to enable the unit to be operated smoothly and efficiently.

As has been previously stated the temperature at which the hydrogenation is carried out in hydrogenator 65 is at least 900°F. in atmospheric pressure operations. Attention is directed to Figure 2 wherein a fouled catalyst was treated at various temperatures, the graph showing that with operation above the indicated temperature level, the removal of carbon may be as great as about 93.1 per cent of that originally on the said catalyst while below this level it is of the order of 20 per cent or less. The chart was drawn from hydrogenation experiments on a deposit-contaminated powdered iron catalyst in a hydrogenation zone maintained under 1 atmosphere of hydrogen pressure at temperatures ranging from 650°F. to 1100°F. and amply demonstrates the efficiency of carbon removal above 900°F. Before the hydrogenation runs were made the "wax" content and also the total carbon content in weight per cent was determined on each of the four samples of contaminated iron catalysts hydrogenated. By the term "wax" in the present application is meant only those deposits on the catalyst which are soluble in benzene and which are substantially composed of hydrogen and carbon only while the total carbon, as determined by combustion, may contain oxygenated compounds and is in large part insoluble in benzene. In this connection carbon and hydrogen analyses indicated that the "wax" contained 86.5 weight per cent carbon and 13.5 per cent hydrogen. It is also clear from the appended table that the wax represented only 1/10 to 1/3 of the total carbon deposit. The samples hydrogenated were obtained from a fluid hydrocarbon synthesis pilot plant operating on the same general principle as that illustrated in Figure 1. The operating conditions for the hydrogenation and the results thereof are set forth in the below Table I:—

TABLE I

				Wt. % Carbon		
Catalyst Sample	Wt. % Wax*	Hydrogen Hrs.	Treatment Temp., °F.	Before H_2 Treatment	After H_2 Treatment	% C. Removal
A	12.7	4	650	33.2	29.4	11.5
		16	650	33.2	28.4	14.5
B	9.2	4	650	35.2	33.1	6.0
		16	700	35.2	29.0	17.5
C	5.1	4	650	38.6	35.2	9.0
		16	800	38.6	31.2	19.1
D	5.6	16	900	40.6	7.9	81.5
		16	1000	40.6	4.2	89.7
		2	1100	40.6	2.8	93.1

*Contains approximately 86.5% carbon and 13.5% hydrogen.

The foregoing table as well as the chart in Figure 2 clearly shows that there is a break in the temperature-carbon removal curve during the hydrogenation process at a temperature of from 800 to 900°F. and that at least a temperature of 900°F. must be maintained to effect satisfactory removal of the carbonaceous deposit from the catalyst.

In commercial operation the operating pressure in the hydrogenator 65 will most economically approximate the pressure in the reaction vessel 1 in order to facilitate the circulation of catalyst. The operating temperature and the holding time of the solid and the hydrogen gas flow rate are established by the degree of cleanup desired, suitable conditions being, for example, 400 pounds per square inch pressure, 900°F. temperature, 15 minutes catalyst holding time, and a hydrogen flow rate of 500 cubic ft. of hydrogen at standard conditions per pound of catalyst treated.

To recapitulate briefly, it has been found that the contaminants formed on a catalyst during its use in the synthesis of hydrocarbons and oxygenated hydrocarbons may be effectively removed in the hydrogenation zone by treatment of the catalyst with a hydrogen-containing gas at a temperature of at least 900°F., higher temperatures being also permissible. This hydrogenation operation will remove deposits on the catalyst not removable by the conventional washing with solvents as well as those removable thereby and with better results than removal by oxidation. It has the further advantage that the hydrogenation in conjunction with the main synthesis reaction is adapted to be operated continuously and cheaply.

Having now particularly described and ascertained the nature of the said invention, and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A method of forming hydrocarbons and oxygenated hydrocarbons which comprises reacting the carbon monoxide and hydrogen in the presence of a powdered iron catalyst which is maintained in the reaction zone in the form of a dense fluid mass in the reactant gases, maintaining the reaction zone at an elevated temperature under superatmospheric pressure, withdrawing the catalyst contaminated by carbon-containing deposits during the said reaction, conveying the said contaminated catalyst into a separate hydrogenation zone, forming a dense fluidized suspension of said contaminated catalyst in said hydrogenation zone, maintaining a temperature of at least 900°F. in said hydrogenation zone, permitting the contaminated catalyst to remain resident in the said hydrogenation zone for a sufficient time to effect removal of at least 80% of the said contaminants, withdrawing the cleansed catalyst from the said hydrogenation zone, and returning the cleansed catalyst to the reaction zone.

2. A method as claimed in Claim 1 in which the hydrogenation is carried out under superatmospheric pressure.

3. A method as claimed in Claim 2 in which the hydrogenation is carried out under a pressure of the same order as that prevailing in the reaction zone.

4. A method as claimed in any of Claims 1—3 wherein the catalyst is metallic iron.

Dated this 2nd day of October, 1946.

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Agents for the Applicant.

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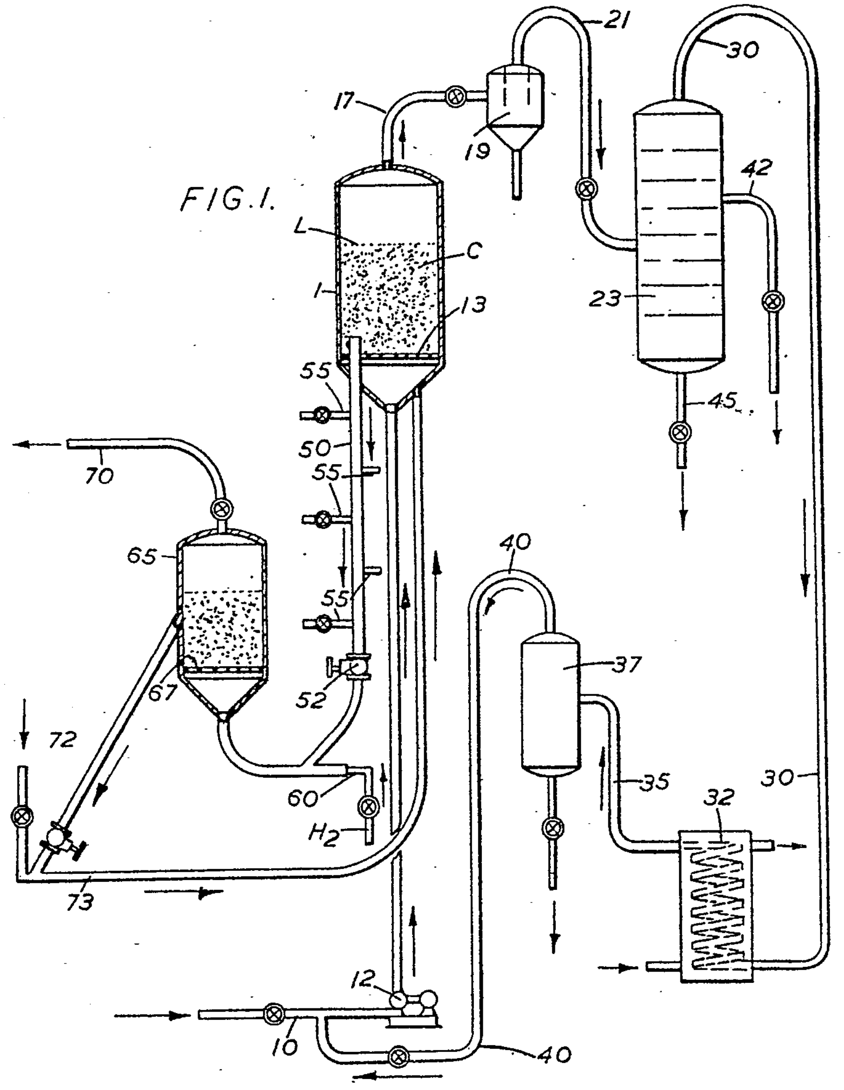
[This Drawing is a reproduction of the Original on a reduced scale.]

FIG. 1.



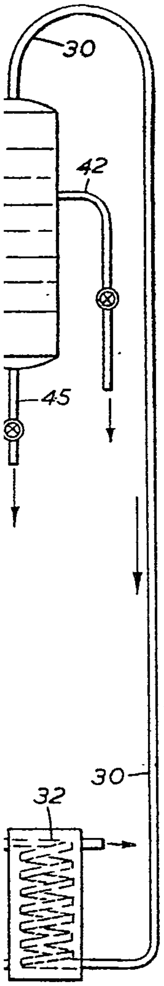
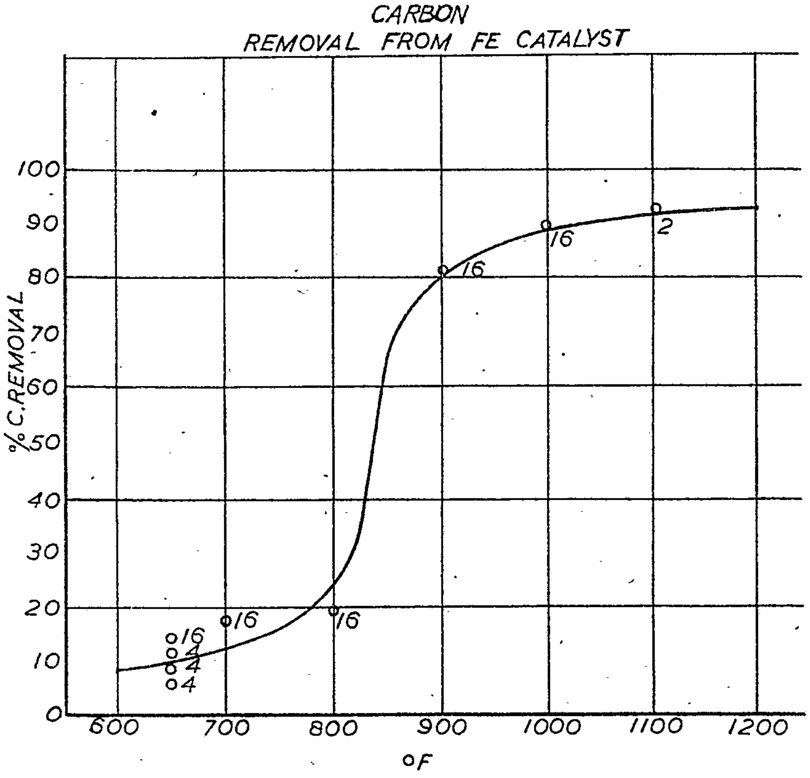


FIG. 2.



H. M. S. O. (Ty. P.)

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

FIG. 1.

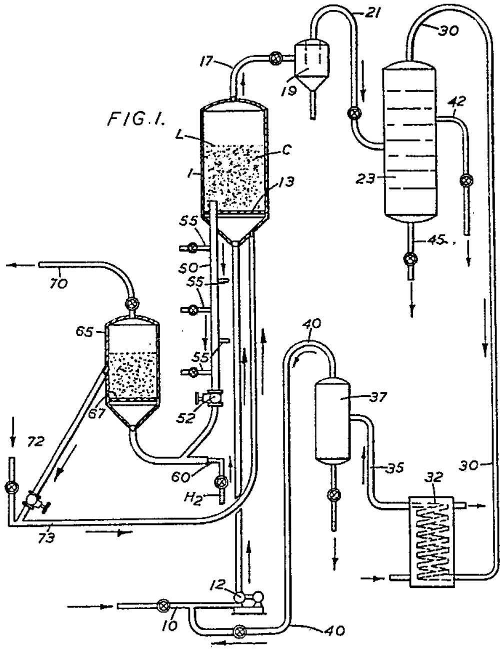
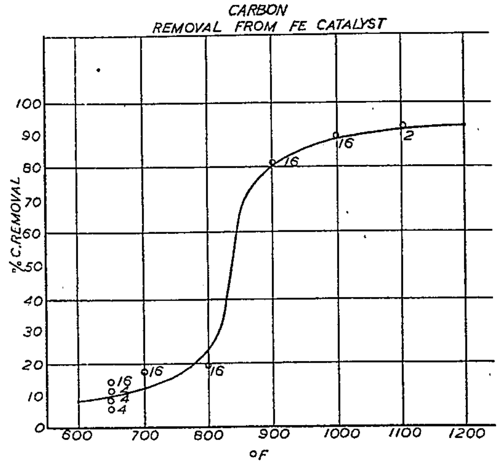


FIG. 2.



H.M.S.O. (Ty. P.)