PATENT SPECIFICATION

647,052

Date of Application and filing Complete Specification: Aug. 28, 1946.

No. 25868/46.

Complete Specification Published: Dec. 6, 1950.

Index at acceptance: —**Classes 1(i),** F3a1a, F3b2(a: x); **and 2(iii),** B1g.

COMPLETE SPECIFICATION

Improvements in or relating to the Catalytic Synthesis of Hydrocarbons

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 Linden, New Jersey, United States of America, and 100, West 10th Street, Wilmington, Delaware, both in the 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 relates to the manufacture of valuable products by the catalytic conversion of carbon oxides with hydrogen.

The synthetic production of liquid hydrocarbons from gas mixtures containing various proportions of carbon monoxide and hydrogen is already known and numerous catalysts, usually containing an iron group metal, have been described which are specifically active in promoting the desired reactions at certain preferred operating conditions. For example, cobalt supported on an inert carrier is used when relatively low pressures (atmospheric to 5 atmospheres) and low temperatures (375° to 425° F.) are applied in the manufacture of a substantially saturated hydrocarbon product while at the higher temperatures (450° to 750° F.) and higher pressures (5 to 25 atmospheres and higher) required for the production of unsaturated and branched-chain products of high antiknock value, iron-base catalysts are more suitable. In both cases the activity of the catalyst declines steadily during the course of the reaction chiefly due to the deposition of non-volatile conversion products, such as carbon, paraffin wax and the like, on the catalyst, as well as due to a change in the degree of oxidation of the active component.

The present invention is concerned with a continuous process for the synthesis of normally liquid hydrocarbons using a finely divided iron catalyst wherein the catalyst contaminated in the course of the synthesis operation is continuously or intermittently regenerated in a simple and economical manner.

There have been a number of prior suggestions relating to continuous processes for the contacting of a finely divided catalyst with reactant gases which broadly involve passing a suspension of the catalyst in the reactant gases upwardly through a treating zone under reaction conditions and withdrawing overhead a gaseous suspension, the catalyst in this withdrawn suspension being thereafter separated and subjected to a regeneration treatment prior to being recirculated to the treating zone. Such a process is generally applicable to a wide variety of catalytic reactions such as dehydrogenation, cracking, reforming aromatization and organic reactions in general such as the synthesis of hydrocarbons from carbon-monoxide and hydrogen. The regeneration treatment may comprise contacting the catalyst separated from the overhead products from the treating zone with a regenerating gas by forming a suspension of the catalyst in such gas and passing it through a regeneration zone under suitable conditions. After passage through the regeneration zone the catalyst is separated and returned directly to the treating zone for further use. For example in dehydrogenation or cracking operations the regenerating gas may be oxygen or air which is caused to burn off the carbonaceous deposits formed on the catalyst during the reaction treatment.

In this type of process the precise regeneration treatment will naturally vary according to the catalyst used and the nature of the catalyst contaminants. In the case of hydrocarbon synthesis catalysts, contaminants may be removed by treatment with hydrogen, solvent extraction and/or combustion with an oxygen-containing gas. Thus one prior proposal has been to superficially oxidize a fouled hydrocarbon synthesis catalyst, particularly a cobalt catalyst, and then reactive it in a prolonged batchwise treatment with hydrogen. This latter proposal involved a separate hydrogenation stage and thus added to the expense of the regeneration treatment.

The present invention is concerned with the utilization and subsequent regeneration of an iron catalyst in a conventional hydrocarbon synthesis process and involves two treating zones, viz. a synthesis zone and a regeneration zone, in each of which zones finely divided iron catalyst is maintained in the form of a dense fluidized bed having a well defined upper level and wherein withdrawal of solids is effected downwardly and that of gaseous products upwardly. Fouled catalyst is withdrawn from the synthesis zone and passed to the regeneration zone wherefrom it is recirculated to the synthesis zone. The employment of dense fluidized beds and downward draw-off of solids as opposed to the overhead withdrawal of a gaseous suspension which necessitates subsequent gas/solids separation, facilitates the controlled circulation of solids between zones. Regeneration is effected by treating the fouled catalyst in the regeneration zone with an oxygen-containing gas under conditions adapted to burn off the catalyst contaminants and oxidize the metal component thereof and it has been discovered that the reactivation of the oxidized catalyst may be effected by simply returning the oxidized catalyst to the synthesis zone wherein it undergoes the requisite hydrogenation, thus obviating the requirement for a separate hydrogenation stage.

The characteristics and conditions of many conventional methods for reactivating hydrocarbon synthesis catalyst are determined by the desire to recover substantially unchanged the highly valuable paraffin wax deposited on the deactivated catalyst. It has been found that the deposits which deactivate iron-base catalysts contain preponderating proportions of practically worthless coke-like materials and only very little, if any, valuable compounds, such as paraffin wax, whose loss or recovery does not appreciably affect the economic balance of the synthesis process. Thus the present improved regeneration treatment involves no economic loss in this respect.

In the oxidizing step, the amount of deactivating deposits which form volatile oxidation products, such as coke, tar, resins, paraffin wax, sulfur compounds, etc., is reduced to a desired extent by oxidation or combustion to form mainly carbon oxides and small amounts of water. A temperature range of from 900° to 1500° F. has been found most suitable for this step of the present process. The oxidation treatment is carried to a point at which oxidation of the metal components of the catalyst takes place. It is preferred to conduct the reconditioning process in a continuous manner in cooperation with a continuously operated synthesis process, applying the principles and conditions of the fluid solids technique, as will appear more clearly hereinafter.

The accompanying drawing which forms a part of the instant specification and which is to be read in conjunction therewith is a diagrammatic view of one form of apparatus capable of carrying out the process of this invention. More particularly referring now to the drawing, synthesis reactor 1 contains finely-divided iron-base synthesis catalyst of any suitable composition known in the art of the hydrocarbon synthesis and having a particle size of from 100 to 400 mesh, preferably about 200 mesh. The synthesis gas mixture from any source indicated generally at 2, having a molar ratio of hydrogen to carbon monoxide varying between the approximate limits of 0.5—3:1, is fed by compressor 3 through line 4 to the catalyst zone of reactor 1 and enters the latter through a distribution plate 5 at a velocity controlled within the limits of from ½ to 10 ft. per second so as to maintain the catalyst in the form of a dense, highly turbulent, fluidized mass having a well-defined upper level L_1, which is determined by the amount and specific gravity of the catalyst present in the reactor and the speed and viscosity of the synthesis gas. The pressure within reactor 1 is maintained within the approximate limits of 5 to 50 atmospheres, preferably between 10 and 20 atmospheres. Due to the phenomenon of hindered settling of catalyst particles, only a small proportion of the powdered catalyst is carried into the zone above the level L_1 which serves as a catalyst disengaging zone. For instance, the fluidized catalyst in the catalyst zone below the level L_1 may have a density of 15 to 100 lbs. per cu. ft., while the catalyst density above the level L_1 may be as low as 0.05 lbs. per cu. ft. The catalyst particles reaching the disengaging zone are separated from the reacted gas in separator 6 which may be a centrifugal or electric type separator, and the gas freed of catalyst leaves reactor 1 through line 7 and is passed through line 8 to a conventional recovery system 8^1. A portion of the gas leaving reactor 1 through line 7 may be recycled either at or about the reactor outlet temperature or at a lower temperature through line 9 to line 4 and to the reaction zone in order to assist in the fluidization of the catalyst and/or the temperature control of the reaction zone. As a result of the excellent heat-transfer characteristics of the fluidized catalyst mass contained within reactor 1, the reaction temperature may be easily kept constant within a few degrees F. at the desired temperature level which for the case of iron-base catalysts lies between the approximate limits of 450° and 800° F., preferably between 500° and 650° F. Surplus heat of the exothermic reaction may be withdrawn, and heat required for starting up the process may be supplied by any conventional means (not shown).

To maintain the activity of the catalyst at a high level, fluidized catalyst is withdrawn from reactor 1 at a point above distribution plate 5 through line 10 which may have the form of a standpipe whose contents exert a pseudo-hydrostatic pressure on the base of pipe 10 leading into line 11 wherein the catalyst is mixed with a carrier gas, preferably an oxidizing gas such as air or air enriched with oxygen supplied by pump 11^1 from line 13; steam or an inert fluidization gas may be added from line 22^1 to obtain the desired degree of fluidization. The gas in line 11 may be preheated to any desired temperature between the approximate limits of 700°—1200° F. The catalyst suspended in the carrier gas is passed from line 11 into oxidation reactor 12 which although substantially smaller is similar in construction to synthesis reactor 1, having a distribution plate 12^1 and a gas-solids separator 14. The catalyst within oxidation reactor 12 forms under the action of the gas supplied through line 11 and the combustion gases formed, a dense, highly turbulent, fluidized mass similar to that in reactor 1 forming an upper level L_{12}. The oxidizing portion of the gases supplied through line 11 is so controlled as to cause the desired combustion of the carbonaceous deposits on the catalyst at temperatures which may vary between about 1000° and 2000° F. Combustion gases leave reactor 12 through separator 14 and line 18 to be used in the system as fluidizing gas or for heat recovery or to be disposed of as desired; they may also be passed to an additional catalyst separation zone (not shown) to recover any catalyst fines carried by the combustion gases.

In most cases the amount of carbonaceous deposit on the catalyst is sufficiently large to generate more heat by combustion of the amount of carbon to be removed than is required to maintain oxidation reactor 12 at the desired temperature. In order to prevent undesired overheating in these cases, we provide for a catalyst circulation from reactor 12 downwardly through line 19 to a cooler 20 and from there through line 21 back to reactor 12. A preferably inert carrier gas such as steam, flue gas, etc., is introduced through line 22 into line 21 to carry a dilute suspension of cooled catalyst upwardly to reactor 12. It will be understood that the temperatures of cooler 20 and the amount of catalyst passed therethrough may be readily controlled so as to maintain any desired constant combustion temperature in reactor 12. If the amount of carbonaceous catalyst deposit is insufficient to separate the heat required in reactor 12, a combustible gas such as natural gas, synthesis feed or tail gas, or the like, may be supplied to reactor 12 through line 13^1 to generate additional heat of combustion.

After the desired amount of carbonaceous deposit has been removed from the catalyst in oxidation reactor 12, the fluidized catalyst is withdrawn downwardly through line 23 and passed through a stripping zone 15 wherein any oxidizing gas adhering to the catalyst may be removed by an inert stripping gas such as steam, flue gas, etc., supplied from line 22. The catalyst leaving the stripping zone 15 through line 23^1 is passed into line 4 where it is picked up by the synthesis feed gas and recycled to the reactor 1. The line 23 through the stripping zone is designed as a standpipe so that the catalyst therein is fed under its own pseudohydrostatic pressure into the gas feed line 4 and is returned to the reactor 1 as a suspension catalyst in the synthesis gas.

It should be understood that the reconditioning reactor 12 may be conveniently operated under the same pressure as synthesis reactor 1. However, if desired, either higher or lower pressures may be applied therein using such means well known in the fluid solids technique as pressurized or depressurized catalyst feed hoppers.

In order to further illustrate this invention, the following example is given which should not be construed as limiting the same in any manner whatsoever.

EXAMPLE.

Reactor 1 is operated at a dense phase capacity of about 10 cu. ft. containing about 500 lbs. of iron catalyst having an oxygen content of about 10% and a carbon content of about 20% in a fluidized catalyst phase of about 50 lbs. per cu. ft. density which is contacted by about 10,000 cu. ft. per hour of fresh synthesis gas containing 31.5% CO at a temperature of about 600° F. and a pressure of about 15 atmospheres. At these conditions, about 1.5% of the CO in the fresh gas is decomposed to form carbon deposited on the catalyst at a rate of about 1.5 lbs. per hour, while the oxygen content of the catalyst is increased by about 0.2 lbs. per hour.

In order to maintain these operating conditions, about 25 lbs. of catalyst per hour is circulated at about 600° F. from reactor 1 to reactor 12 and about 220—230 cu. ft. of air per hour is supplied to reactor 12. To maintain a combustion temperature of about 1000° F., about 400—450 lbs. of catalyst per hour is recycled through lines 19 and 21 through cooler 20 wherein the recycle catalyst stream is adjusted to a temperature of about 800° F. Catalyst containing about 15% of carbon is withdrawn through line 23 at the rate of about 23—24 lbs. per hour. The reconditioned catalyst is returned to reactor 1 at a temperature of about 400° F.

It should be understood that the rate at which the catalyst is circulated through the reconditioning reactor depends mainly on the amount of carbon to be removed per unit of catalyst and time. Thus, at the conditions outlined in the Example, if the carbon content is to be reduced from 20% to about 0.5%, about 30—40% of the catalyst charge is circulated per day through the reconditioning reactor. This figure rises to about 60—70% if the carbon content is to be reduced from 20% to about 10% and may exceed 100% at the conditions of the Example. In general, the catalyst circulation rate falls within the approximate limits of 1 and 100% per day of the catalyst charge of reactor 1.

The process of the present invention may be widely varied; for instance activators, such as alkaline earth and rare earth metal oxides may be added to the iron catalysts which may be supported on inert carrier materials, such as kieselguhr, silica gel, and the like. The reconditioning of the catalyst may also be conducted intermittently rather than continuously in full adaptation to the rate of deactivation of the catalyst. Spent catalyst may be withdrawn from the system and fresh make-up catalyst may be fed from hopper 50 through lines 52 and/or 54 to reactor 1. Pipes 10, 19, 23, 52 and 54 may be aerated in a manner known *per se* to facilitate the downward flow of solids. These and other changes may be made in the details disclosed in the foregoing specification without departure from the invention or sacrificing the advantages thereof.

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

1. In a continuous process for the synthesis of normally liquid hydrocarbons of the type in which a gas mixture containing carbon monoxide and hydrogen is contacted in a reaction zone with a finely divided iron catalyst which becomes contaminated with deposits during the course of the reaction, the improvement which comprises passing said gas mixture upwardly through said catalyst to maintain it in the form of a dense, turbulent fluidized bed having a well defined upper level, removing reaction products overhead, withdrawing a portion of contaminated catalyst downwardly from a lower portion of the reaction zone and passing it to a regeneration zone, charging an oxygen-containing gas to the regeneration zone where it contacts the contaminated catalyst maintained in the form of a dense fluidized mass having a well defined upper level, maintaining the catalyst in said regeneration zone for a time sufficient and under conditions adapted to effect regeneration by burning off the catalyst contaminants and to oxidize the iron component of the catalyst, withdrawing regenerated and oxidized catalyst downwardly from said regeneration zone and returning catalyst so withdrawn to said reaction zone.

2. The process of Claim 1 in which said regeneration zone is of substantially smaller capacity than said reaction zone.

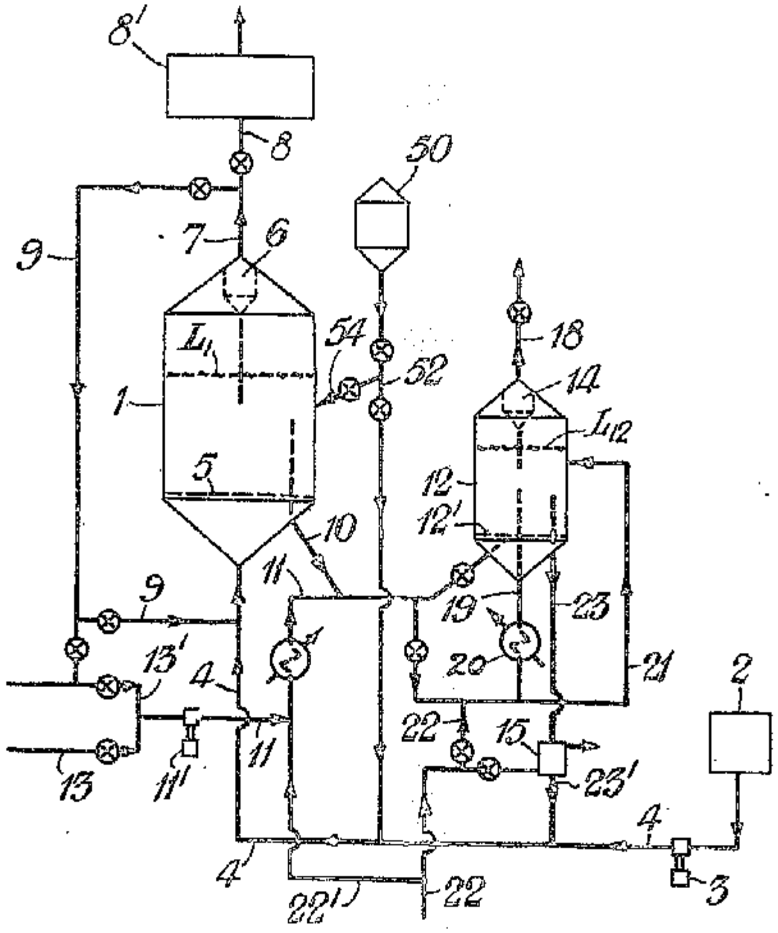
Dated this 28th day of August, 1946.
D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agents for the Applicants.

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.

647,052 COMPLETE SPECIFICATION

1 SHEET

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



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