[Second Edition]

PATENT SPECIFICATION

598,380

Convention Date (United States of America): Dec. 14, 1944.
Application Date (in United Kingdom): June 18, 1945. No. 15489/45.
Complete Specification Accepted: Feb. 17, 1948.

3484

COMPLETE SPECIFICATION

Improvements in or relating to the Synthesis of Liquid 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, 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 Fischer-Tropsch synthesis of normally liquid hydrocarbons from carbon monoxide and hydrogen.

Heretofore and prior to the present invention others have effected the synthesis of hydrocarbon oils by reacting CO and hydrogen properly proportioned stoichiometrically in the presence of a suitable catalyst under known conditions of temperature, pressure and feed rates. The present invention has to do with improvements in this type of synthesis where it is carried out employing the so-called fluid catalyst technique or, in other words, where the catalyst in the form of a powder is suspended in the reaction gases during the reaction.

In a fluid hydrocarbon synthesis reactor operating in a commercial plant where the production rate should be maintained at a maximum consistent with the overall equipment design, it is desirable to have some means of compensating for fluctuation in the rate of reaction.

It can be assumed that the total feed rate of synthesis gas will be maintained approximately constant and that the level of catalyst in the fluid reactor will also be maintained approximately constant in order to take advantage of optimum use of cooling surface in the reactor and in order to avoid cases where high catalyst levels might cause undue entrainment of catalyst in hydrocarbon vapors issuing from the reactor. On the other hand, the natural aging of catalyst with time would tend to give less conversion for a fixed catalyst level and fixed feed rate. Likewise, fluctuations in the composition of the synthesis gas may cause the reaction rate either to increase or to decrease. A decrease in catalyst activity can be compensated for to some extent by increasing the temperature level of operation, but this is in general unsatisfactory from a standpoint of product distribution. The present method renders the reaction rate constant without having recourse to increases or decreases in the temperature level. This method is to control the reaction rate by controlling the activity of the catalyst, which is accomplished either by fortifying the catalyst with more active material (which may be the active component without a carrier, or may be a carrier more highly impregnated with the active component) or by weakening the catalyst by adding a solid diluent (which may be the material that is used as a catalyst base).

In order to provide a better understanding of the invention, the accompanying drawing shows diagrammatically a suitable apparatus which may be used in carrying these improvements into effect.

Referring to the drawing, a mixture of hydrogen and carbon monoxide in the approximate molar ratio of 2 to 1 and preferably containing less than 10% inert materials such as N_2 or CH_4 or CO_2 is introduced into the system through line (10) to a synthesis reactor (12). This reactor contains a body of fluidized catalyst which is in the form of a powder having a particle size of from 30 to 400 mesh. The catalyst may be Co promoted with MgO or ThO_2 supported on kieselguhr, clays, or synthetic gel bases, such as silica gel. Other catalysts, such as those containing iron, may also be used. The reactor is provided with a foraminous member G through which the incoming gases pass, the foraminous member aiding in the uniform distribution of the gas throughout the catalyst. The reactor is also provided with cooling tubes immersed in the fluidized catalyst mass, whereby heat of reaction is removed and the temperature of the catalyst bed is controlled and maintained at the desired level. This removal of heat is accomplished by boiling some liquid, such as water, within the

[*Price 2/-*]

cooling tubes. By controlling the linear velocity of the gas within the limits of, say, 0.2 to 5 ft./second, preferably 1/2 to 1-1/2 ft./second, a dense suspension of catalyst in gas is formed. By controlling the amount of catalyst which is present in the reactor and the upward velocity of the gas, the dense phase will have an upper level at L, say 10 feet above the grid G. As previously indicated, in a commercial plant it is desirable to maintain the upper level L more or less constant. But, as previously indicated, as the reaction period progresses, the rate of reaction and therefore the formation of the desired product tends to decrease due to a falling off in the activity of the catalyst. Consequently, means are provided for increasing the activity of the catalyst by continuously feeding thereto from a supply hopper (13) through pipe (14) a quantity of the active component of the catalyst. Thus, suppose that the catalyst is cobalt activated with thoria and carried on a base. There may then be added cobalt in powder form, or cobalt and thoria, or cobalt and magnesia, or other active metal suitable for catalyzing the synthesis reaction from storage hopper (13) by line (14). The powdered catalyst added may be either in the form of pure metal and metal oxide or in the conventional form of a supported catalyst wherein the metal and metal oxide are supported in a relatively higher concentration on such materials as kieselguhr, clays, or synthetic gel bases. The rate of addition of the fresh catalytic material through line (14) will depend upon many factors, such as the percentage or concentration of active metal and metal oxide promoter in the added catalyst, and also upon the conditions maintained in reactor (12). Thus, in general, where higher rates of production and higher temperatures are maintained, increased catalyst replacement rates will be required to maintain uniform activity. The average range of the rate of addition of fresh catalyst will be from about 0.05 to 1.0% of the catalyst inventory per day. In order to maintain a fixed level of fluidized catalyst in the reactor, it will be necessary as hereinafter described to remove an amount of used catalyst equivalent to that introduced through line (14).

Now, referring again to the general conditions in the reactor, the preferred reaction conditions are the following:

	Broad Range	Preferred Range
Temperature - - - - - - -	370—650° F.	360—450° F.
Pressure - - - - - - -	atmos.—750 psig.	atmos.—125 psig.
Residence Time in Reactor - - -	5—60 sec.	10—30 sec.
Catalyst - - - - - - -	32% Co: 5% Th: kieselguhr etc. balance	
Molar Ratio H_2 to Co - - - - - -	1—3	1.90—2.10

Under the conditions stated, the reaction products issue through a line (20) and are delivered to a purification, condensation and recovery system indicated at (22). The method of recovering hydrocarbon oil boiling within the naphtha and gas oil range does not go to the heart of the invention, and the expert in this art will understand that the oil in line (20) will require after-treatment, such as aromatization, reforming, catalytic cracking, and the like, to provide a finished gasoline of good quality. It is also pointed out that good practice requires the use of solid separating devices either in the top of the reactor (12) or disposed in the line (20) to recover catalyst, and also scrubbing of the vapors with heavy liquid oil to free the oil vapors of entrained catalyst. These methods of recovering the last traces of catalyst from the crude product vapors are conventional and need not be described at length herein because they do not go to the heart of the invention.

It should be pointed out, however, in this connection, that the vapors in the space S above level L in reactor (12) carry only minor amounts of catalyst. That is to say, where the density of the suspension between grid G and level L in the reactor may be from 15 to 30 lbs./cu. ft., the density of the vapors issuing from the top of the reaction zone may be of the order of 0.0025 to 0.0030 lbs./cu. ft.

It is also pointed out that during the synthesis reaction heavy oils and/or wax materials are formed on the catalyst and therefore it is desirable to withdraw this catalyst continuously through a standpipe (15) and subject it to washing with, say, a hydrocarbon oil in a zone which is indicated at (16) for the purpose of reactivating and purifying the catalyst, after which washing treatment the catalyst may be returned to the reaction zone. An amount of catalyst, withdrawn through standpipe (15), may be permanently removed from the system to compensate for the amount of fresh catalyst added through line (14). Alternatively or simultaneously, a portion of catalyst recovered from the overhead system (22) may be permanently rejected.

The flexibility of the invention also provides against the contingency of maintaining a constant catalyst activity where operating conditions favor an increase in catalyst activity. Such is the case in transition periods of operation, wherein, for example, the temperature of reaction is being increased. In this case, an inert powder, such as unimpregnated kieselguhr or clay or a synthetic gel, may be added through line (14).

To summarize briefly, the invention comprises maintenance of uniform activity of the catalyst employed in the synthesis of hydrocarbons from a gaseous mixture of hydrogen and carbon monoxide. Catalysts for this reaction consist of an active metal, a metallic oxide promoter, and a suitable support. Fluctuations in the rate of reaction are compensated in the proposed procedure by addition of fresh components of the catalyst mixture. Catalyst in the reaction zone may be fortified by adding catalytically active metal and/or the oxide promoter continuously or at pre-defined intervals. If, at any time, abnormally high conversions should be obtained, another modification of the invention comprises addition of a solid diluent, such as the catalyst support.

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. A process for the preparation of liquid hydrocarbons from carbon monoxide and hydrogen, wherein a mixture of carbon monoxide and hydrogen is passed through a reaction zone containing a fluidised catalyst comprising a Fischer Tropsch hydrogenation catalyst on an inert support, the reaction zone being maintained under reaction conditions of temperature and pressure, and the catalytic activity being maintained substantially constant by adding fresh hydrogenation catalyst and/or catalyst promoter or a solid inert diluent to the reaction zone, to increase or decrease the catalyst activity as required.

2. A process according to Claim 1, wherein the fresh catalyst added to the reaction zone is substantially pure hydrogenation catalyst, or is hydrogenation catalyst on a carrier in a higher concentration than that of the catalyst already present in the reaction zone.

3. A process according to Claim 1, wherein the inert diluent is the same as the said inert support.

4. A process according to any of the preceding claims, wherein the hydrogenation catalyst is cobalt promoted with magnesia or thoria and the support is Kieselguhr, clay or a synthetic gel such as silica gel.

5. A process according to any of the preceding claims, wherein contaminated catalyst is continuously withdrawn from the reaction zone, washed with a hydrocarbon oil and recycled to the reaction zone.

6. A process according to any of the preceding claims, wherein an amount of catalyst is withdrawn from the reaction zone, corresponding to the amount of fresh catalyst or inert diluent added, the total quantity of catalyst in the reaction zone being maintained substantially constant.

7. A process according to any of the preceding claims, wherein the reaction conditions and catalyst compositions are those hereinbefore specified.

Dated this 18th day of June, 1945.

D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agents for the Applicants.

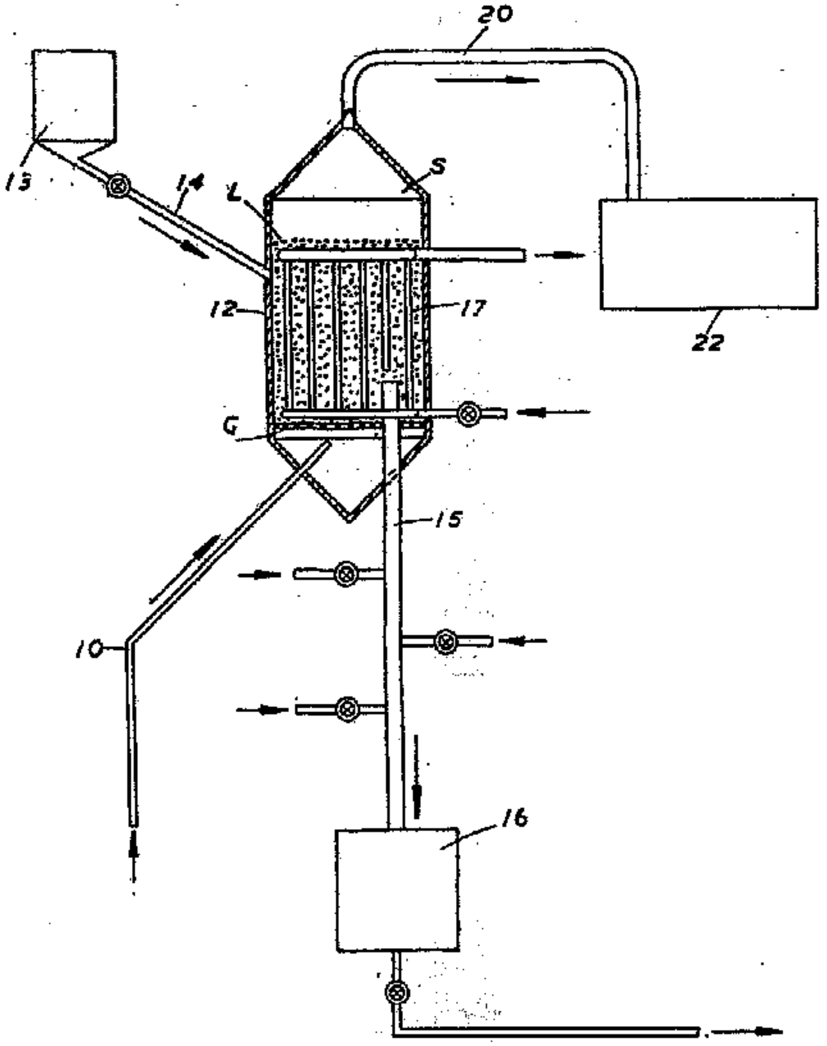
London: Printed for His Majesty's Stationery Office, by Charles & Read Ltd. – 1950. Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.

598,380 COMPLETE SPECIFICATION

1 SHEET

[Second Edition]

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



Charles & Read Ltd.