

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

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:—

The present invention relates to improvements in the art of synthesizing hydrocarbons and oxygenated hydrocarbons from a gaseous mixture containing carbon monoxide and hydrogen. In particular, the present improvements relate to improved cooling means for controlling temperatures in the highly exothermic reaction wherein carbon monoxide is reduced by a hydrogen-containing gas.

The synthesis of hydrocarbons, including normally liquid hydrocarbons such as gasoline, has recently acquired a new and important status in the petroleum industry for the reason that the provable crude oil reserves in the United States of America have reached a foreseeable exhaustion in the not too distant future. In that situation, therefore, the industry has turned to other possible sources for maintaining the required supply of commercial gasolines. Many petroleum technologists are of the opinion that the natural gas resources of the United States are of such an extent that it is possible that, if a commercially feasible process can be found for converting this natural gas into gasoline and other normally liquid hydrocarbons, then the concern regarding the exhaustion of the crude oil resources would be very greatly alleviated. At the present time, therefore, the industry is conducting research directed toward producing gasoline from natural gas as a starting material, with the fervent hope that the gasoline may be so produced at a price comparable to gaso-

line produced from crude petroleum oil. Of course starting materials other than natural gas are being investigated. For example, the possibility of gasifying some of the bituminous and low grade coals to form mixtures containing carbon monoxide and hydrogen as feed gases to a hydrocarbon synthesis operation is being simultaneously investigated and studied. In general, therefore, the problem of maintaining the tremendous quantity of gasoline required through the future years is a real problem and one to which the petroleum industry is certainly giving a great deal of attention at the present time.

The present invention has to do with improvements in the synthesis process itself, and does not particularly have regard to the manner in which the synthesis gas, so-called, is produced—that is, the gaseous mixture containing carbon monoxide and hydrogen which is charged to the hydrocarbon synthesis reaction zone; and therefore, the present specification and claims are restricted to that particular phase of the overall problem.

Prior to this invention, others had synthesized hydrocarbons, including normally liquid hydrocarbons. It is understood that the first work in this field was done abroad. Perhaps the first commercial operation in which hydrocarbons, including gasoline, were synthesized by the reduction of carbon monoxide with hydrogen was the so-called Fischer-Tropsch process. This process, according to the literature, was conducted in the presence of a catalyst in which the active component was cobalt and was carried out in a case or reactor containing one or more stationary beds of catalyst. After that, it was found by others that iron, preferably activated with a relatively small amount of a substance such as sodium fluoride or carbonate, also was an active catalyst in the hydrocarbon synthesis reaction. Still later, the so-called

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"fluid catalyst technique," employing iron as the catalyst, was used in synthesizing hydrocarbons by the reduction of carbon monoxide, the catalyst being promoted iron. At the present time, it is believed that iron is a more satisfactory catalyst than cobalt, principally because the gasoline fraction obtained from the iron-using process is very definitely superior in anti-detonation quality to that formed in the older cobalt-catalyst-using process.

In the catalytic cracking of hydrocarbon oils, the fluid catalyst technique has proved highly successful. This is due to many desirable attributes, including the fact that the fluid bed of catalyst can be maintained in a substantially homogeneous thermal condition due to the thorough mixing which the agitated particles in the fluidized bed afford, to the economies involved in continuity of operation, to the possibility of maintaining catalyst activity at a high level by withdrawing catalyst as desired and regenerating the catalyst and returning it to the reaction zone, and numerous other advantages.

In spite of the experience which the industry gained as a result of the development of fluid catalyst cracking, the application of this principle to hydrocarbon synthesis reactions was not accomplished without difficulties. This, of course, is readily explained because, since cracking oil is one thing and synthesizing a hydrocarbon from the intermediates, carbon monoxide and hydrogen, is quite another chemical process, it is not surprising that each would have its own peculiar problems. While the cracking of gas oil to form a cracked gasoline is an endothermic reaction, the reduction of carbon monoxide with hydrogen is highly exothermic. The adaptation therefore of the fluid catalyst technique for hydrocarbon synthesis was confronted at the outset with a new heat control problem.

The answer to the problem is not merely the disposition of cooling coils within the reactor, or surrounding the reactor in heat exchange relationship therewith. In such an arrangement, the heat transferred from the fluidized bed per unit area of cooling surface is directly proportional to the temperature difference between the bed of catalyst and the cooling medium and to the overall heat transfer coefficient between the catalyst bed and the cooling medium. In order to conserve heat transfer surface, it is desirable to operate at the highest rate of heat transfer from the bed to the cooling coils per unit area and a maximum temperature difference should exist between the bed of catalyst and the cooling medium. But it has been found, for example, that when the temperature of the cooling medium is maintained within the range of from about 525° F. to 550° F. or below that, the heat transfer coefficient is markedly reduced, which in turn of course reduces the heat transfer rate per unit area of cooling surface. This is true when using a powdered iron catalyst and operating at pressures within the range of from 200 to 500 pounds per square inch and particularly for pressures between 300 and 400 pounds per square inch (optimum pressure conditions in most instances) and where the catalyst bed is at a temperature of from 625° F. to 775° F. As will hereinafter more fully appear, experiments demonstrate that there is a critical temperature range of the circulating cooling medium for most efficient heat transfer, and that is the essence of the present improvements in the hydrocarbon synthesis process.

The object of the present invention, therefore, is to control the temperature of a fluidized bed of catalyst during the hydrocarbon synthesis process in a manner which is more efficient than those previously used.

Another object of the invention is to keep the temperature of a fluid bed of iron catalyst constant throughout during the hydrocarbon synthesis process by regulating the rate of heat flow, per unit area, from the bed of catalyst to a cooling surface in heat exchange relationship therewith.

Another object of the invention is to maintain a fluidized bed of iron catalyst employed in the hydrocarbon synthesis reaction at a substantially uniform temperature throughout with a reduced amount of cooling surface in heat exchange relationship with the fluidized bed of catalyst.

The accompanying drawing shows a flow plan representing a fluid catalyst hydrocarbon synthesis plant, the drawing depicting the system partially diagrammatically and partially in sectional view.

Referring in detail to the drawing, (1) represents a case or reactor having a cylindrical main portion and a conical base. Disposed within the reactor in the lower portion of the cylindrical section is a foraminous member (2). Disposed within the reactor is a bank of cooling tubes (3) terminating in headers or boiler plates (4) and (5) and through which is caused to circulate a fluid cooling medium. In addition, however, the reactor (1) is provided with a jacket (6) which surrounds the major portion of the main

section of the reactor, as shown, and through which jacket a cooling fluid is caused to circulate.

In operating the process, fresh feed enters the system through line (7). This feed contains hydrogen and carbon monoxide but may also contain some carbon dioxide and some water and also other inert gases normally present in synthesis gas. The feed is compressed in a pump (8) and thence forced through a valved line (9) into a heater (10). If the gas pressure in line (7) is sufficiently high, of course, the fresh gas may bypass the compressor as indicated in the drawing. The fresh gas feed is withdrawn from the heater (10) through line (11) and discharged into the conical section of reactor (1) where it passes up through the grid or screen (2) into contact with the catalyst (C). The catalyst in the preferred modification of the invention is powdered iron having a particle size within the approximate limits of from 20 to 200 microns, with over 50% having a particle size of from 40 to 100 microns. The gasiform material is caused to flow upwardly in the reaction zone at a controlled rate, say a superficial velocity of from $\frac{1}{2}$ to 3 feet per second. The result of the slow gas flow rate in conjunction with the particle size is to form a dense, turbulent, ebullient mass which has come to be known as the fluidized bed. Depending on the amount of catalyst present in the bed, the same will have an upper dense phase level at (L). Above the dense phase level is a dilute phase in which the concentration of catalyst decreases upwardly.

The process so operated affects a separation of the main bulk of the catalyst within the reactor and only entrained fines pass overhead with the exiting product stream. Usually, there are disposed in the upper portion of the reactor a plurality of solids separating devices such as centrifugal separators (S) through which the issuing gasiform material is forced for the purpose of separating substantially the last traces of entrained catalyst and returning the same to the dense phase through a plurality of dip pipes (d). The product stream is withdrawn from the reactor through line (12), cooled in (13) and delivered to a purification and recovery system. It will not be necessary to describe in detail the method of cooling and collecting the gasoline and other desired products, since this may be

accomplished by conventional methods. It should be pointed out, however, that unreacted carbon monoxide and hydrogen, with perhaps some of the carbon dioxide and water, may be returned to the reaction zone through a recycle line (14), a pump (15) and a heater (16).

As stated, the improvements relate to improved means for controlling temperature within the reaction zone, and to this end, therefore, a cooling medium such as water, diphenyl, mixtures of diphenyl and diphenyl oxide, suitable hydrocarbon fractions or other material having a satisfactory boiling temperature range, enters the system through line (17), then is pumped by pump (18) into a boiler drum (20) via line (19), where heat is extracted from the circulating cooling fluid by evaporation of a portion thereof, followed by utilization of the vapors to generate power (in means not shown). A portion of the vapors in line (21) may be condensed in cooler (22) and returned to drum (20). Pressure on the cooling system is controlled by any conventional pressure control instrument. The cooled fluid is withdrawn from the boiler drum (20) by line (23) and discharged into header (5), and thereafter forced through the bank of tubes (3) through which it passes in heat exchange relationship with the fluidized bed of catalyst, extracting heat from the latter and being withdrawn through a valved line (24) and returned to the boiler drum (20) for the removal of heat. Another portion of the circulating cooling medium in line (23) is passed via line (25) into jacket (6) at a bottom portion thereof, forced upwardly there- through in heat exchange relationship with the fluidized bed of catalyst, withdrawn at an upper portion of said jacket through line (26), and returned via line (24) to the boiler drum (20).

Referring again to the boiler drum (20), the liquid level is controlled by any known instrument (27) adapted to control the rate of addition of fresh or recycled cooling medium.

Thus, the operation of an improved hydrocarbon synthesis plant embodying the improvements has been described as to the flow of reactants therethrough, and in particular as to the flow of the temperature-controlling fluids.

As to operating conditions in reactor (1), good results are obtained employing the following:

	Temperature	- - - - -	550—750° F.
	Pressure	- - - - -	150—800 lbs./sq. in.
	Fresh Feed to the Reactor	- -	5—250 standard cu. ft. per pound of catalyst in reactor
5	Total Feed Including Recycle	-	5—300 standard cu. ft. per pound of catalyst in reactor.

As previously stated, the invention has to do with efficient temperature control. It will be appreciated that the disposition of cooling coils reduces the capacity of a given reactor in amount related to the space occupied by the said cooling coils, and consequently a definite advantage accrues to a cooling system which operates satisfactorily employing the minimum amount of cooling tube surface. It has been found that a high heat transfer rate can be maintained and that the amount of cooling surface required

can be very substantially reduced. 20

It has been found, for example, that during a certain run in the fluid hydrocarbon synthesis plant operating during the course of some 13 days, in which operation the catalyst was powdered iron and the cooling medium was a liquefied mixture of diphenyl and diphenyl oxide (a well-known temperature control fluid), under the conditions further stated below, the following conditions of temperature and heat transfer prevailed: 25 30

	Run No.	12A	12B	12B	12B	12C	12D
	Day	1st	10th	10th	10th	12th	13th
	Reactor Pressure, psig.	394	400	396	396	400	399
35	Avg. Cat. Bed Temp., °F.	636	667	705	769	663	645
	Temp. °F. of Cooling Medium	579	542	483	520	410	595
	Heat Trans. Coef. Btu/Hr./Sq. Ft./°F.	71	42	14	12	18	55

The foregoing data show that, as the cooling medium temperature was reduced to below the 525° F. to 550° F. range, the heat transfer coefficient decreased markedly. However, when the temperature was again raised above 550° F., the coefficient was increased. Consequently, these data show that cooling medium temperatures below 525—550° F. are not advisable and that better results are obtained employing a lesser temperature differential between the cooling medium and the bed. Attention is directed to the fact that the foregoing operation was conducted under a reactor pressure of about 400 pounds per square inch. 40 45 50

Any cooling medium may be used in which temperature can be controlled. At pressures in the range of from 500 to 800 pounds per square inch, and operating in the same temperature range given in the foregoing table, namely, from about 625° F. to about 775° F., the cooling medium should not be maintained below the approximate range of from 600° F. to 650° F. 55 60

On the other hand, for pressures below 200 pounds per square inch, say from 100 to 200 pounds per square inch, and operating so that the bed has a temperature generally within the range set forth above, the cooling medium should be at a temperature within the range of about 400—450° F. 65 70

Thus, where the synthesis proceeds under a pressure in the general range of 100 to 800 lbs. per square inch, the temperature of the cooling medium should be in the range from 400—650° F. For pressures of 200 to 500 pounds per square inch, the temperature difference between the bed and the cooling medium should preferably be not more than about 150° F. 75 80

To recapitulate briefly, therefore, it has been found that when maintaining the most efficient heat transfer between the cooling system and the hot fluidized bed of powdered iron catalyst in a hydrocarbon synthesis operation, there is a critical temperature differential between the temperature of the cooling system and the bed which provides a maximum rate of heat transfer and thus has the desirable effect of reducing the amount of equipment and utilities necessary to effect good temperature control. 85 90 95

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:— 100

1. An improved hydrocarbon synthesis process for the formation of hydrocarbons and oxygenated hydrocarbons by the reduction of carbon monoxide with hydrogen in a reaction zone in the presence of a fluidized bed of iron 105

catalyst, wherein excess heat is removed by a cooling medium maintained at such a temperature that the coefficient of heat transfer and the temperature differential between the bed and the cooling medium are correlated to give a rate of heat transfer in the region of its maximum.

2. A hydrocarbon synthesis according to Claim 1 for the formation of hydrocarbons and oxygenated hydrocarbons by the reduction of carbon monoxide with hydrogen under superatmospheric pressure and in the presence of a fluidized bed of powdered iron catalyst at temperatures within the range 625° F. to 775° F., wherein heat is abstracted from said synthesis reaction by causing a temperature control fluid to circulate in heat exchange relationship with said bed of catalyst, a high heat transfer coefficient being maintained between the bed of catalyst and the cooling medium by maintaining the temperature of the cooling medium within the range of from about 400° F. to 650° F., where the synthesis proceeds under a pressure within the range of from about 100 to 800 pounds per square inch, the higher cooling medium temperatures being employed in conjunction with the higher pressure.

3. The process according to Claim 2,

in which the synthesis is carried out under a pressure of from about 100 to 200 pounds per square inch and in which the cooling medium is maintained at a temperature within the range of from about 400° F. to 450° F.

4. The process according to Claim 2, in which the synthesis is carried out under a pressure of from about 500 to 800 pounds per square inch and in which the cooling medium is maintained at a temperature within the range of from about 600° F. to 650° F.

5. The process according to Claim 2, in which the synthesis is carried out under a pressure of from about 200 to 500 pounds per square inch and in which the cooling medium is maintained at a lower temperature than the bed of catalyst but at a temperature not more than about 150° F. below the temperature of the bed of catalyst.

6. The improved hydrocarbon synthesis process substantially as hereinbefore described.

Dated this 1st day of April, 1948.

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