PATENT SPECIFICATION

655,685

Date of Application and filing Complete Specification:
Feb. 16, 1948. No. 4538/48.

Application made in United States of America on June 18, 1947.

Complete Specification Published: Aug. 1, 1951.

3502

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

COMPLETE SPECIFICATION.

Improved Hydrocarbon Synthesis.

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 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 reduction with hydrogen of carbon monoxide, to form hydrocarbons including normally liquid hydrocarbons, and oxygenated hydrocarbons, in a catalytic process employing a fluidized mass of promoted powdered iron catalyst. In particular, it relates to operating the said process under conditions which tend to suppress the physical disintegration or fragmentation of the iron catalyst, or at least to retard such fragmentation, so as to preserve the catalyst average particle size such that it is adapted for good fluidization.

By "fluidized" catalyst, is meant a phenomenon wherein the catalyst in powder form is procured, in the presence of an upflowing gas or vapor, in a confined zone, in the form of a dense, turbulent, ebullient mass or bed.

In the accompanying drawing, an apparatus has been shown diagrammatically in which a preferred modification of this invention may be carried into effect.

It is well known in the art to conduct hydrocarbon synthesis reactions by contacting hydrogen and oxides of carbon with catalysts under various temperature and pressure conditions. The catalysts employed are usually selected from the iron group metals, namely, iron, cobalt and nickel. They are utilized either alone or on suitable carriers, such as kieselguhr, diatomaceous earth, pumice, synthetic gels, silica and alumina. Promoters such as the carbonates halides or oxides of potassium, chromium, zinc, aluminum, magnesium and the rare earth metals are used with the iron group metals.

The old art dealt with fixed or stationary bed type of operation. When it was attempted to operate the hydrocarbon synthesis process in the presence of a fluidized bed of iron catalyst, difficulties were encountered in that carbonaceous deposits on the catalyst caused the latter to undergo physical disintegration to an extent such that it would no longer be satisfactorily fluidized.

There have been a number of broad prior disclosures as to the operating conditions in a hydrocarbon synthesis process using a fluidized iron catalyst. For example, Specification No. 593,940 refers to a synthesis temperature range of 375—700° F., preferably 475—625° F., pressure conditions of up to 800 pounds per square inch, and a hydrogen to carbon monoxide ratio of between about 0.5 : 1 and about 5 : 1, preferably between about 1 : 1 and about 2.5 : 1. The range of operating conditions suggested heretofore have however been far too indefinite to yield a fully satisfactory process.

It has been recognised that synthesis reactions could be carried out without losing substantial activity of the catalyst and without securing any substantial carbon formation on the catalyst. However, when conducting operations of this character, desired product yield was low. On the other hand, if operating conditions were adjusted to secure high yields and high selectivities, undesirable carbon formation occurred followed by disintegration or fragmentation of the catalyst. Much time and effort have been spent attempting to solve this particular problem, that is, how to secure high selectivities and high yields without incurring carbon formation and physical disintegration of the catalyst and it has now been found that if the total pressure in the reaction zone, and with it the hydrogen partial pressure, is relatively high,

[*Price 2/-*]

the tendency of carbonaceous deposits to form on the catalyst is repressed.

In accordance with this invention operating conditions to secure high yields and high selectivities are maintained and concurrently physical breakdown to non-fluidizable catalyst fines by carbon formation is suppressed by maintaining in the synthesis reaction zone a hydrogen partial pressure of 150 to 275 pounds per square inch absolute, including the total hydrogen content of the fresh and recycled gases, at the point where the reactants enter the reaction zone, a total pressure of above 350 pounds per square inch but below 800 pounds per square inch, a temperature of 650° to 725° F. and a total gas feed rate of fresh and recycled gases of substantially 10 to 200 standard cu. ft. per pound of catalyst per hour. The total pressure in the synthesis zone is preferably maintained above 400—500 pounds per square inch.

Operating conditions are such as to give minimum yields of 190 cc. of butane and higher boiling constituents, or minimum yields of 250 cc. of propane and higher boiling constituents per cubic meter of carbon monoxide and hydrogen consumed. Preferred operating conditions are such as to give a minimum yield of at least 200 cc. of butane and higher boiling constituents per cubic meter of carbon monoxide and hydrogen consumed.

In employing these critical pressures in conjunction with the other operating conditions, viz. reaction temperature and total gas feed rate, designed to produce the high yields and selectivities specified, it is to be understood that these latter conditions are interrelated and that their actual value is a function of one another.

Yields and selectivities of at least 190 cc. of butane and higher boiling constituents are secured by maintaining a temperature of reaction of 650° F. to 725° F. The volumes of feed gases (measured in cu. ft. at standard conditions), per hour per pound of carbon free catalyst are consistent with catalyst activity to give high conversion of CO and H_2.

The catalyst employed may be any suitable iron base Fischer synthesis catalyst such as a synthetic ammonia catalyst, a pyrites ash catalyst, reduced red iron oxide, and the like.

The composition of the fresh feed gases to the reaction zone is preferably about 1 mol of carbon monoxide per mol of hydrogen. However, when employing an iron type of a synthetic ammonia catalyst (a high purity magnetite fused and promoted with an alkali material such as K_2CO_3 and alumina), it is preferred to use 1 mol of carbon monoxide per 2 mols of hydrogen.

EXAMPLE.

In order to demonstrate the effect of high total and in particular high hydrogen partial pressure, a number of operations were conducted using an iron type of synthetic ammonia catalyst. The composition of the fresh feed gases to the system and the Composition of the total feed gases to the reaction zone due to recycle averaged as follows:—

	Gases Vol. %	
	Fresh Feed	*To Reaction Zone*
Hydrogen	59.9	39.4
Carbon Monoxide..	29.1	14.1
Carbon Dioxide ..	7.9	26.2
Nitrogen	1.2	1.5
Unsaturates ..	—	3.0
Total Paraffins ..	1.9	15.8

The results of the various operations are summarized as follows; Runs 1 and 2 being included for comparative purposes:

Run No.		*Selectivity*		*Total Pressure Pounds Per Sq. In.*	*Hydrogen Partial Pressure lbs./sq. in. (approx.)*	*Temp.*	*V/Hr/W.*	*Carbon Increase and Catalyst Breakdown*
		C_4^+*	C_3^+**					
1	..	179	225	240	96	637	24.5	Yes
2	..	220	261	404	161	675	98.8	No
3	..	180	214	235	94	646	37.6	Yes
4	..	197	237	401	160	676	94.3	No.
5	..	220	260	400	160	673	94.7	No
6	..	214	256	400	160	676	95.9	No
7	..	226	262	404	161	664	92.9	No
8	..	219	258	399	159	670	93.7	No

*C_4^+ =butane and heavier hydrocarbons.

**C_3^+ =propane and higher hydrocarbons.

The foregoing data show the effect of high total pressure and in particular high hydrogen partial pressure in retarding "carbon" formation, and hence fragmentation of the catalyst. The term "carbon," of course, relates to the deposits, formed unavoidably in or on the catalyst during the process, and is generally a material part of which is soluble in hydrocarbon solvents and partly insoluble or "fixed". Some of the carbon may be in the form of iron carbide. The data show that a high hydrogen partial pressure, even at high temperatures and fairly severe conditions represses carbon formation so that catalyst disintegration is retarded.

Subsequent tests showed that the hydrogen partial pressure range should be from 150 to 275 pounds per square inch absolute. Even where the temperatures were high (up to 700° F.) and the molecular ratio of hydrogen to carbon monoxide in the total feed was 1.4 to 1.7 (severe conditions conducive to good yields of high quality gasoline), carbon formation was repressed but the hydrogen partial pressure had to be maintained in the upper portion of the foregoing range. Good yields of desired products were also obtained (around 200 cc. of C_4^+ hydrocarbons per standard cubic meter of hydrogen and carbon monoxide consumed).

The foregoing runs were made in a fluidized bed type of operation in an apparatus which is fairly represented in the accompanying drawing.

Referring to the drawing, 1 represents a case or reactor having a grid or screen G. It contains a bed of fluidized powder iron catalyst C. The gasiform reactants enter the reactor at the bottom, the fresh feed from line 2, the recycled material from line 3 and the total feed from line 4, as shown. The gasiform material passes upwardly through the distributing grid G into the bed of catalyst and the flow rate of the gasiform material is maintained at around say 0.5—1. feet per second "superficial" velocity (i.e. assuming no catalyst in the reactor) whereupon a dense, turbulent mass of powder in gas or vapor is formed. This fluidized bed will have an upper dense phase level at some point L depending on the gas velocity and the number of pounds of iron catalyst in the reactor. Above L, there is a dilute phase suspension and in the space between L and the top of the reactor the concentration of catalyst in gas recedes sharply upwards so that the main bulk of the catalyst is separated from the gasiform material in the reactor. If desired solids-separation devices such as "cyclone" separators, may be positioned in the upper portion of the reactor and the gasiform material forced therethrough to remove additional quantities of powdered catalyst. The product vapors are withdrawn through line 6, forced through one or more solids separating devices such as the "cyclone" separator 7, shown in the drawing, or an electrical precipitator, a filter, etc. for the purpose of removing catalyst still entrained. The thus separated catalyst may be returned to the reactor through line 8. The product substantially freed of catalyst is removed from separator 7 through line 9 and is then cooled to condense normally liquid materials in cooler 10. The cooled product passes via line 11 into a separator 12 wherein normally gaseous material is withdrawn through line 13 and recycled to line 3, a portion of this material being withdrawn from the system if desired via 14. It may be desirable to scrub out or otherwise remove the CO_2 before recycling this gaseous material through line 3. The liquid product consisting of an aqueous phase and an oil phase is removed from separator 12 through line 15 and is collected in receiver 16. These phases may be worked up to recover gasoline, gas oil, the oxygenated hydrocarbons according to conventional methods which need not be described therein.

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

1. In a process for the synthesis of hydrocarbons by reacting carbon monoxide and hydrogen in a reaction zone in contact with a fluidized bed of powdered iron catalyst, the improvement which comprises maintaining in the synthesis reaction zone a hydrogen partial pressure of 150 to 275 pounds per square inch absolute, including the total hydrogen content of the fresh and recycled gases, at the point where the reactants enter the reaction zone, a total pressure of above 350 pounds per square inch but below 800 pounds per square inch, a temperature of 650° to 725° F. and a total gas feed rate of fresh and recycled gases of substantially 10 to 200 standard cubic feet per pound of catalyst per hour, permitting the reactants to remain in contact with said catalyst for a sufficient period of time to effect the desired conversion, and recovering the desired products from said reaction zone.

2. The process of Claim 1 in which said total pressure is above 400 pounds per square inch.

3. The process of Claim 1 in which said catalyst is a high purity magnetite fused and promoted with an alkali promoter and alumina, and carbon monoxide and hydrogen are used in a fresh feed mol ratio of substantially 1 : 2.

Dated this 16th day of February, 1948.

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

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 2*s.* per copy; by post 2*s.* 1*d.* may be obtained.

This Drawing is a reproduction of the Original on a reduced scale