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COMPLETE SPECIFICATION

An Improved Process for the Synthesis of Hydrocarbons

(A communication from 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).

I, CONRAD ARNOLD, a British subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, 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 an improver Fischer synthesis of hydrocarbons.

It is a main object of the present invention to effect the synthesis of normally liquid hydrocarbons from carbon monoxide and hydrogen in the presence of a fluidized catalyst under operating conditions and employed means directed toward effecting increased efficiency.

It is a specific object of this invention to maintain a fluidized mass of catalyst in a high state of activity and as an aid thereto continuously or intermittently removing waxy and oily material therefrom.

In the accompanying drawing, there is shown diagrammatically an apparatus layout in which a preferred modification of the invention may be carried into effect.

In the synthesis of hydrocarbons from carbon monoxide and hydrogen performed in the presence of a fluidized mass of catalyst, it is necessary to limit the amount of wax or liquid oil carried on the catalyst to a value below that at which the fluidizing characteristics of the catalyst become adversely affected. To accomplish this result according to the present invention, a portion of the catalyst is withdrawn continuously or intermittently from the reaction zone, and subjected to a de-waxing or de-oiling cleansing treatment and then returned to the reactor, the cleansing of the catalyst being accomplished by heating to volatilize and remove oily and/or waxy material therefrom.

The removal of oil or wax from the catalyst can be accomplished by means of solvents as disclosed in co-pending Application No. 15746/45 (Serial No. 600,580). As previously indicated, the present invention relates to the removal of oily and waxy material from the catalyst by means of volatilization.

In carrying the invention into practical effect the synthesis reaction and the oil or wax removal step are each preferably conducted in two or more stages. For purposes of illustrating the invention, a two-stage operation will be described, with reference to the apparatus illustrated in the accompanying drawing.

Referring to the drawing (1) and (1A) represent a pair of vertical cylindrical reactors of the type commonly used in fluid catalyst systems. In general these reactors are cylindrical in their main portion but have conical bases and crown pieces and also carry a screen or grid located in the bottom thereof, through which the gasiform material passes as it enters the mass of fluidized catalyst. In the drawing the synthesis gas comprising a mixture of CO to H_2 in which the ratio of H_2 to CO is about two to one by volume, enters the system via line (2), passes through a heater (5) (if a heater is necessary) and then enters at the bottom of reactor (1) as shown in the drawing. These reactors have been described in prior disclosures and since the form and structure of the said reactors do not go to the heart of the present invention, it will not be necessary to describe them herein. The reactors (1) and (1A) are operated so that the main bulk of catalyst is withdrawn from the bottom through lines (3) and (3A) from reactors (1) and (1A) respectively, and the hot catalyst is passed through coolers (4) and (4A) respectively to remove a portion of the exothermic heat which is released in the said reactors. It is within the purview of the invention to dispose the cooling means within the reactor and in this case there would be no outside circulation as shown through coolers (4) and (4A). The fluidized state of the catalyst in the reactors (1) and (1A) is maintained, as is known, by controlling the net upward velocity of the gases or vapors in the range of from ½ to 5 ft. per second, preferably from 1½ to 3 ft. per second where the catalyst has a particle size of from 100 to 400 mesh. This flow rate results in the formation of a dense phase suspension having an upper level which level depends on the amount of catalyst left in the reactor. Above this dense phase upper level, the concentration of catalyst in the gases drops sharply so that the reaction gases withdrawn from the reactors through lines (6) and (6A) contain only a relatively small quantity of catalyst. It is preferable to pass the gases in (6) and (6A) through dust collectors such as centrifugal separators or electrical precipitators to remove the last traces of catalyst. The reaction products are condensed in coolers (7) and (7A) and collected in receiving drums (10) and (10A).

It will be noted that the catalyst withdrawn from reactor (1) after passing through a cooler (4) is in part passed through a line (12), carrying a flow-control valve (13), into line (2) where it is mixed with the incoming gas formed into a suspension in line (2) and then carried back to the reactor. However, another portion of the catalyst passes via line (14) after it is admixed with gaseous material from line (15) and formed into a suspension, through a heater (20) and thence via line (21) into reactor (1A). It should be pointed out that the uncondensed vapors in line (15) may contain quantities of carbon dioxide, and since this is a diluent it may be advisable to pass the cooled vapors through a scrubber (S) containing an aqueous solution of, say, sodium hydroxide or some other known material in which carbon dioxide is soluble for the purpose of removing the said carbon dioxide.

It is also pointed out that in a large installation, heater (20) may not be required and therefore its use is optional depending upon conditions. Reactor (1A) operates as both a synthesis reactor on the unconverted CO and H_2 coming from reactor (1) and as a stripper for the wax and oil deposited on the catalyst. The gas leaving (1) is cooled to condense out the heavy constituents so that it can re-vaporize heavy components from the catalyst removed from reactor (1) and is aided in effecting this vaporization by operating reactor (1A) at a lower pressure and a higher temperature than used in (1). The stripping of oily and waxy material from the catalyst in reactor (1A) is further aided by withdrawing a portion of the gaseous material from (10A) through line (22), pumping it by pump (23) through a heater (24) and thence discharging it by line (25) to reactor (1A). The material in line (25) carries in suspension catalyst recovered from cooler (4A) via line (26) carrying a flow-control valve (27) which permits the withdrawal of catalyst from the cooler (4A) and is discharged into the gasiform material in line (22) where it is formed into a suspension. Another portion of the catalyst cooled in (4A) is withdrawn through a pipe (30) carrying flow-control valve (31) and delivered into said gas line (2) where it is formed into a suspension and carried into reactor (1) in the manner indicated in the drawing.

Referring again to receiving drum (10A) into which the product from reactor (1A) is first delivered, it will be noted from the drawing that a pipe (40) projects from the top of the receiving drum (10A), passes through a cooler (41) and by this conduit means gasiform material in (10A) may be withdrawn from the latter through (40), cooled and condensed in (41) and collected in a second receiving drum (10B) which is maintained at a temperature of about 100° F. The water and product formed in the process is withdrawn from (10), (10A) and (10B). Water is withdrawn through lines (49), (49A) and (49B) and the crude product from lines (50), (50A) and (50B).

As to operating conditions, the following are preferred. The catalysts mentioned in the tubular view below contain the following ingredients. The Co-MgO catalyst contains cobalt, the active component, magnesia as a promoter and kieselguhr as the carrier. For example, the catalyst may contain 32% cobalt, 63% kieselguhr and 5% magnesia by weight. The iron catalyst is over 45% iron with possibly 5% of oxides of alkali metals, copper or aluminum.

REACTOR I

	Broad Range		Preferred Range	
Catalyst	Co—MgO	Fe	Co—MgO	Fe
1. Temperature °F.	375—450	450—700	390—435	550—650
2. Pressure p.s.i.g.	10—150	50—500	15—105	100—300
3. Fresh Feed Rate Vol. $CO + H_2$/Vol. Cat./hr.	50—500	50—1000	100—300	200—700
4. Conversion of CO %	50—90	50—90	60—75	60—75
5. Ratio H_2/CO	$\frac{2}{1}$	$\frac{1 \text{ to } 1.5}{1}$	$\frac{2}{1}$	$\frac{1.1 \text{ to } 1.25}{1}$

REACTOR 1A.

	Broad Range		Preferred Range	
Catalyst	Co—MgO	Fe	Co—MgO	Fe
1. Temperature °F. Higher than Reactor I	5—100	5—250	10—50	10—100
2. Pressure p.s.i.g. lower than Reactor I	10—150	50—500	15—105	100—300
3. Feed Rate	Gas from Reactor I Within space velocity limits indicated for Reactor I			
4. Total Conversion CO %	65—100	65—100	79—95	75—95
5. Recycle Gas Vol/Vol. Feed Gas	0.5—10	0.5—10	1—5	1—5

Another important aspect of the invention is that the reactor (1A) is of smaller volume than (1) and preferably has a size of about one-third that of the larger reactor. While a two-stage operation has been described for synthesizing hydrocarbons from CO and H_2, it is to be distinctly understood that three or more stages may be used to accomplish this result.

To recapitulate briefly, the present invention is based on the proposition that hydrocarbons may be synthesized from CO and H_2 continuously using the so-called fluid catalyst type of operation, hereinbefore described. In this type of operation materials which are liquid under operating conditions interfere with and impede good operation of the system because they interfere with the fluidization of the catalyst. Therefore, in order to correct this insufficiency the catalyst is continuously or intermittently withdrawn from the reaction zone and stripped of liquid or waxy material by volatilizing off the said oily or waxy material and returned in substantially dry condition to the reaction zone where it is better adapted to be fluidized.

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 process for the synthesis of normally liquid hydrocarbons by the reaction of carbon monoxide and hydrogen in the presence of a Fischer synthesis catalyst, wherein the catalyst is maintained as a fluidised mass in a reaction zone maintained at Fischer synthesis conditions of temperature and pressure, catalyst contaminated with wax and oil being continuously or intermittently withdrawn from the reaction zone and passed to a

stripping zone in which it is heated to volatilise the wax and oil, the dewaxed catalyst being recycled to the reaction zone.

2. A process according to Claim 1, wherein a stripping gas or vapour is passed through the stripping zone to aid the volatilisation of the wax and oil.

3. A process according to Claim 1 or Claim 2, wherein the stripping zone is a second reaction zone, a gaseous fraction of the reacted products from the first reaction together with a part of the contaminated catalyst withdrawn from the first reaction zone being charged into the second reaction zone, and dewaxed catalyst being continuously withdrawn from the second reaction zone and recycled to the first reaction zone.

4. A process according to Claim 3, wherein a gaseous fraction of the reacted products from the second reaction zone is admixed with a part of the dewaxed catalyst withdrawn from the second reaction zone, and the admixture recycled to the second reaction zone.

5. A process according to any of the preceding claims, wherein the catalyst recycled to the reaction zone or zones is first cooled.

6. A process according to any of the preceding claims, wherein the temperature and presure in the stripping zone are higher and lower respectively than those in the reaction zone.

7. A process according to Claim 6, wherein a cobalt-magnesia catalyst is employed and the temperature is from 5—100° F. higher and the pressure from 10—600 lb./sq. in. lower in the stripping zone than in the reaction zone.

8. A process according to any of Claims 3 to 7, wherein the second reaction zone is substantially smaller than the first reaction zone, preferably about one third as big.

9. A process according to any of Claims 3 to 8, wherein the reaction conditions, catalysts, and ratios of carbon monoxide to hydrogen are those hereinbefore set forth.

10. A process according to any of Claims 3 to 9, wherein the gaseous fraction withdrawn from the first reaction zone and passed to the second reaction zone, is first passed through an absorption chamber for the removal of carbon dioxide.

Dated this 21st day of January, 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]