PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Catalytic Synthesis of Hydrocarbons

We, KOPPERS COMPANY, INC., a corporation organized under the laws of the State of Delaware, one of the United States of America, of Koppers Building, City of Pittsburgh, State of Pennsylvania, United States of America, Assignees of ALFRED RICHARD POWELL, a citizen of the United States of America, of Koppers Building, City of Pittsburgh, State of Pennsylvania, 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 the catalytic synthesis of hydrocarbons. More particularly the invention relates to a catalytic synthesis of the type carried out by the Fischer-Tropsch type of reaction wherein carbon monoxide is hydrogenated catalytically by an exothermic reaction.

The Fischer-Tropsch synthesis is now being extensively used to produce two general classes of hydrocarbons. When a cobalt catalyst is used as a synthesis catalyst the hydrocarbons formed are predominantly paraffinic while with an iron catalyst the hydrocarbons formed by the synthesis are predominantly unsaturated hydrocarbons. These unsaturated hydrocarbons produce a good motor fuel because of the high octane rating of such products.

Each of the above-mentioned catalytic reactions is highly exothermic and these facts have required the use of a very complicated reaction chamber to remove heat and to control the temperature of the catalyst bed for an efficient operation of the process.

The primary object of the present invention is to provide a process of catalytic hydrogenation of carbon monoxide by which the temperature of the catalyst bed may be easily and efficiently controlled.

Another object of the invention is to provide a process for the catalytic hydrogenation of carbon monoxide wherein the exothermic heat of reaction may be absorbed by the heat of vaporization of a liquid distributed throughout the catalyst bed.

A further object of the invention is to provide a process for the catalytic hydrogenation of carbon monoxide by which the exothermic heat of reaction may be expended by evaporating a liquid having a constant boiling point which is distributed throughout the catalytic reaction bed.

A still further object of the invention is to provide a process of catalytic hydrogenation of carbon monoxide in a catalyst bed while simultaneously controlling the catalyst bed by means of water circulated through the bed with the gases being reacted.

The various features of the invention are illustrated in the accompanying drawing which is a flow sheet of an apparatus in which a preferred form of the invention may be carried out.

It has been proposed to control the temperature in the reaction zone during the exothermic reactions in the manufacture of hydrocarbons from carbon monoxide and hydrogen by suspending the catalyst in a liquid medium which passes through the reaction zone countercurrent to the products of reaction. The catalyst and liquid suspended therein are withdrawn from the reaction zone, separated, cooled and returned to the top of the reaction zone. Alcohols, ethers, esters and heavy petroleum distillates and lubricating oils are mentioned as suitable heat controlling liquids.

In another process the carbon monoxide and hydrogen are passed through a reaction zone in concurrent flow with a fluid catalyst suspended therein and a wholly vaporizable fluid is injected into the fluid mass in the reaction chamber and passes out of the reaction zone with the reaction products. Indirect heat interchange is used to help control the temperature. Water or portions of the liquid product produced by the process are mentioned as suitable cooling liquids to be injected into the reaction zone.

The present invention consists in a process of hydrogenating carbon monoxide which comprises passing a synthesis gas as a mixture of carbon monoxide and hydrogen in the ratio as parts by volume in the range of 1:1 to 1:2 into a synthesis catalyst bed, preheating the gas mixture entering the catalyst bed to a synthesis temperature and adding sufficient water to the gases passing through the catalyst bed to absorb the exothermic heating of the synthesis reaction by evaporation of the water.

Suitable catalysts for carrying out the Fischer-Tropsch type of reaction for the hydrogenation of carbon monoxide comprise cobalt, iron or nickel, together with oxides of vanadium, uranium, magnesium or thorium which act as promoters. The oxides and metals are preferably deposited upon a carrier such as diatomaceous earth, silica gel, or alumina gases. These catalysts are usually prepared and broken into granular form for use in the present process.

It has been determined empirically by a large number of laboratory and pilot plant runs that the following equation corresponds very closely to the type products made when operating with an iron catalyst and a pressure of synthesis gas between 20 and 30 atmospheres with a synthesis gas composed of approximately equal portions of carbon monoxide and hydrogen and a temperature of approximately 240° C. in the catalyst bed:—

$$45CO + 48H_2 = 3C_8H_{16} + C_3H_6 + 3CH_4 + 15CO_2 + 15H_2O$$

When using cobalt as a catalyst and operating at a synthesis gas pressure of approximately 10 to 15 atmospheres at a temperature of approximately 200° C. with a synthesis gas composed of approximately $1\frac{3}{4}$ parts of hydrogen to one part of carbon monoxide, the following products are formed:—

$$40CO + 68H_2 = C_{20}H_{42} + C_8H_{18} + C_3H_8 + 3CH_4 + 6CO_2 + 28H_2O$$

In the synthesis reaction using an iron catalyst it is found that approximately 588 kilogram calories is evolved per cubic meter of gas. This corresponds to approximately 62 B.t.u.'s per cubic foot of gas. With the cobalt catalyst the exothermic heat of reaction is 635 kilogram calories per cubic meter or 67 B.t.u.'s per cubic foot of gas.

It is important in these reactions that the heat of reaction must be dissipated or taken care of in order to control the reaction and maintain an efficient temperature for the reaction. It has been found that water is a very excellent medium by which the exothermic heat of reaction may be dissipated because the water may be introduced into the catalytic synthesis bed and passed through the bed with the synthesis gases and as the exothermic heat of reaction is evolved this heat may be absorbed by evaporation of the water to form steam. The pressure in the synthesis bed is sufficiently high to hold the water in a liquid state until the temperature is raised above the boiling point of water at the existing pressure. It is important that approximately the right amount of water is used to absorb all of the exothermic heat of reaction and that a slight excess not over 1% leaves the reaction catalyst bed in order to insure that liquid water is present throughout the bed.

Water is an excellent temperature controlling medium because it does not react with the hydrocarbons which are formed in the reaction. It tends to wash and keep the catalyst granules clean and has a constant boiling point so that the temperature throughout the catalyst bed may be maintained at the boiling temperature of water at the pressure existing in the bed. With an iron catalyst the synthesis temperature has been found to be approximately 240° C. at synthesis-gas partial pressures of from 20 to 30 atmospheres. With a cobalt catalyst the synthesis temperature is approximately 200° C. with a synthesis-gas partial pressure of from 10 to 15 atmospheres.

The preferred method of controlling the synthesis reaction for the hydrogenation of carbon monoxide may be carried out in the apparatus illustrated in the drawing substantially as follows:

IRON CATALYST.

A mixture of carbon monoxide and hydrogen composed of 40 to 50% CO and 60 to 50% H_2 by volume is introduced through a line 10 into a compressor 12 where the pressure is increased to approximately 46.3 atmospheres or a pressure between 40 and 50 atmospheres. This compressed gas passes through a line 14 into the top of a catalytic synthesis chamber 16 having a bed of catalyst 18 therein.

As the synthesis gas passes through the line 14 it is mixed with hot synthesis reaction gases introduced through a line 19. This hot gas preheats the synthesis gas to a temperature of at least 212° C. Water is introduced into the line 14 through a line 20 and is mixed with the preheated synthesis gas entering the top of the synthesis chamber. As soon as the gases enter the catalyst bed of the chamber the temperature quickly rises from approximately 212° to 240° C. and is held at this temperature as it passes downwardly through the bed. The amount of water being introduced is sufficient to provide for all exothermic heat of reaction involved in the synthesis of the gas. At the temperature and pressure conditions outlined above approximately 75% of the synthesis gases per pass through the catalyst bed will be converted into the products shown in the formulæ above and the remaining 25% of synthesis gas passes them with the conversion products out of the bottom of the conversion chamber through a line 21. Approximately 50% of the hot gases of reaction are required for preheating the synthesis gas and this gas is taken through a line 22 and forced by means of a blower 24 back to the line 19. The recycling of the products of reaction gives an opportunity for a further hydrogenation of unconverted synthesis gas in the recycle gas, but the total conversion of synthesis gas including the recycle is preferably maintained at about 75%.

The remaining half of the products of conversion which leave the bottom of the catalyst chamber flow through the line 21 and pass in series through heat interchangers 26 and 28. These heat interchangers are preferably waste heat boilers with water being introduced at the line 30 and steam being removed through the lines 32. The waste heat boilers act to condense hydrocarbons and water which are in the products of reaction, these condensed products being removed from the bottom of the boilers through the lines 34.

The carbon dioxide in the reaction gases is not beneficial in the synthesis reaction and, since it also occupies a certain volume which tends to cut down the capacity of the apparatus, it is preferred to remove the carbon dioxide from the products of reaction. To accomplish this the cooled gases from the waste heat boiler 28 pass out through a line 36 and enter the bottom of a scrubber 38 in which the gases pass in countercurrent relation to a stream of potassium carbonate or other absorbent which is introduced into the top of the tower through a line 40. The potassium carbonate readily absorbs the carbon dioxide while allowing the hydrocarbons to pass through the scrubber 38. This potassium carbonate solution is taken from the bottom of the scrubber 38 by means of pump 42 and forced into a CO_2 removing tower 44. The potassium carbonate solution and CO_2 therein flows down across trays in the tower 44 and is heated in the bottom of the tower by means of a steam coil 46. Preferably the potassium carbonate solution entering the tower 44 has its pressure reduced through a valve 48. By the pressure reduction and the heating the carbon dioxide is driven out of the potassium carbonate solution and is exhausted through an outlet 50. The revivified potassium carbonate solution is removed from the bottom of the tower 44 by means of a pump 52 and forced through a cooler 53 into the line 40 for recirculation through the tower 38.

The reaction gases which have been freed of carbon dioxide pass out of tower 38 through a line 54 and enter the top of a second catalyst reaction chamber 56. As this gas passes through the line 54 into catalyst chamber it is preheated by means of hot gas which is introduced into the line 54 through a line 58. The hot gas flowing through the line 58 is composed of hot reaction gases that are formed in the catalyst chamber 56 and flow out of the bottom of the tower through a line 60 by which they are circulated by means of a pump 62 into the line 58. Water is introduced into the line 54 through a line 64 to supply the cooling fluid for controlling the synthesis reaction temperature. Preferably the same pressure is maintained in the tower 56 as that pressure which is maintained in the catalyst chamber 16. Approximately 50% of the products of reaction passing through the catalyst chamber 56 are recirculated by the pump 62 back through the line 58 for preheating the synthesis gases. The remaining 50% flows through the line 60 to a condenser cooler 66 where the products are condensed and may be withdrawn through a line 68. An additional 18 to 20% of the carbon monoxide is hydrogenated in the catalyst chamber 56.

COBALT CATALYST.

When a cobalt catalyst is used for the production of hydrocarbons substantially the same circulation of synthesis gas, recycle gas and water is maintained. It will be noted, however, from the formula given above that the hydrocarbons formed with the cobalt catalyst are very much heavier or higher boiling point products. Therefore periodically the catalyst chambers 16 and 56 will have to be opened to remove the waxy products. With the cobalt catalyst the synthesis gases must be heated to a minimum temperature of 176° C. and preferably the synthesis temperature to be maintained in the catalyst bed is about 200° C. The pressure in the catalyst chambers and system are lower than using a cobalt catalyst so that the heat of vaporization of water at 200° C. and about 24 atmospheres total pressure is 833 B.t.u.'s per lb. of water. Therefore, the amount of water added to the synthesis gases may be carefully regulated to put in the minimum amount of water that is necessary in order to take care of the exothermic heat of reaction and thus avoid cooling of the catalyst bed.

From the formulæ representing the synthetic reactions when using iron and cobalt catalysts it is shown that the type of hydrocarbons formed with an iron catalyst pass through the waste heat boilers and may be separated therefrom. An equal amount of water and carbon dioxide are formed in the reaction and when the CO_2 is removed the relative amount of carbon monoxide in the synthesis gas is increased. Since approximately 25% of the synthesis gas is hydrogenated in the catalyst chamber 56 this catalyst chamber may be much smaller than is the catalyst chamber 16.

The total partial pressures of the synthesis gases ($CO+H_2$) by the arrangement described above is approximately 25 atmospheres in both the catalyst chambers 16 and 56 when operating with an iron catalyst. When operating with a cobalt catalyst the partial pressures of the synthesis gases in the catalyst chambers is preferably maintained at 10 to 15 atmospheres.

When operating with either an iron or cobalt catalyst, the mixture of carbon monoxide and hydrogen may be passed through a plurality of synthesis catalyst beds in series to absorb the exothermic heat. The volume of water which is added to the reaction gas mixture entering the catalyst beds is based upon the volume of gases and the temperature of the specific catalyst bed into which the water is introduced.

Water is a very advantageous liquid for controlling the synthesis reaction because this material is formed in the synthesis reaction and has a constant boiling temperature.

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 of hydrogenating carbon monoxide to produce hydrocarbons comprising: passing a synthesis gas as a mixture of carbon monoxide and hydrogen in the ratio as parts by volume in the range of 1 : 1 to 1 : 2 into a synthesis catalyst bed, preheating the gas mixture entering the catalyst bed to a synthesis temperature and adding sufficient water to the gases passing through the catalyst bed to absorb the exothermic heat of the synthesis reaction by evaporation of the water.

2. The process according to claim 1, in which the amount of water added to the synthesis gas is such that not more than 1% of the water will leave the catalyst bed as liquid water with the products of reaction.

3. The process according to claim 1 or 2, in which the gas entering the catalyst bed is preheated to the synthesis temperature by recirculating part of the hot gases of reaction leaving the catalyst bed back for admixture with the fresh synthesis gases entering the catalyst bed.

4. The process according to any of the preceding claims, in which the synthesis temperature for the preheated gas mixture when using an iron catalyst is 212° C. with the catalyst bed maintained at approximately 240° C.

5. The process according to claim 4, in which the catalyst synthesis reaction is carried out at a total pressure of approximately 40 to 50 atmospheres pressure.

6. The process according to claim 4 or 5, in which the catalyst synthesis reaction is carried out with a partial pressure of synthesis gas of approximately 25 atmospheres.

7. The process according to any of claims 1 to 3, in which the synthesis temperature for the preheated gas mixture when using a cobalt catalyst is at least 176° C. with the catalyst bed maintained at approximately 200° C. for the reaction.

8. The process according to claim 7, in which the catalyst synthesis reaction is carried out at a total pressure of approximately 20 to 30 atmospheres.

9. The process according to claim 7 or 8, in which the catalyst synthesis reaction is carried out with a partial pressure of synthesis gas of approximately 10—15 atmospheres.

10. The process according to any of the preceding claims comprising separating water and hydrocarbons formed in the synthesis and passing the residual gas through a second synthesis bed, preheating the residual gas to a synthesis temperature and adding sufficient water to the gases passing through the second bed to absorb the exothermic heat of reaction by the evaporation of water.

11. The process as claimed in any of the preceding claims, which comprises passing the mixture of carbon monoxide and hydrogen through a plurality of synthesis catalyst beds in series in which the

gas mixture entering each bed is preheated to a synthesis temperature and adding to the gases entering each catalyst bed a sufficient amount of water to absorb the exothermic heat of synthesis reaction by evaporation of the water.

12. The process of hydrogenating carbon monoxide substantially as described with reference to the accompanying drawing.

Dated the 29th day of July, 1947.

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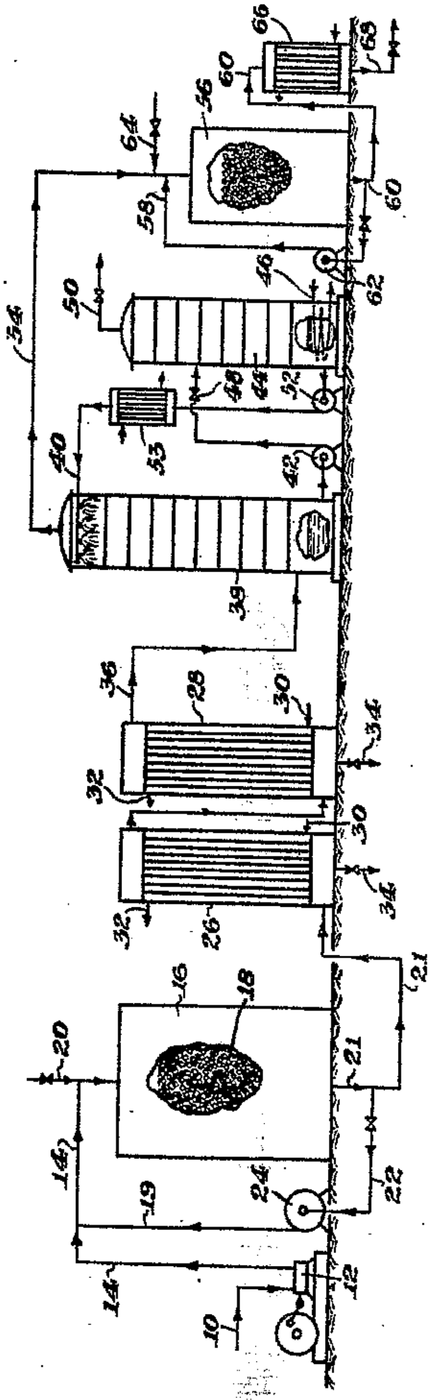
638,087 COMPLETE SPECIFICATION 1 SHEET

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



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