PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of Controlling Exothermic Catalytic Gas Reactions

We, UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organised under the Laws of the State of Delaware, United States of America, of 310, South Michigan Avenue, Chicago 4, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides a method of controlling exothermic catalytic gas reactions by maintaining the temperatures of such reactions substantially constant throughout the reaction zone. It is more particularly concerned with a method of controlling, within desired narrow limits, the reaction temperature in the catalytic conversion of carbon monoxide and hydrogen to hydrocarbons.

In many catalytic processes involving the reaction of gases, the temperature maintained determines the nature of the reaction products and, in order to produce the desired products, the temperature must be maintained within close limits. In many such reactions the liberation of heat by the reaction itself makes it difficult to maintain the required temperature. Accordingly, many successful laboratory reactions are not commercially feasible because of design problems in furnishing the large amount of heat transfer surface necessary to remove the exothermic heat of reaction. Furthermore, in many commercial processes involving the reaction of gases the rate of reaction is limited by the amount of heat that can be removed from the reaction zone.

For example, liquid hydrocarbons boiling within the motor fuel range can be produced by passing carbon monoxide and hydrogen in the ratio of about one part of carbon monoxide to about two parts of hydrogen by volume over a suitable hydrogenating and polymerizing catalyst provided the temperature is maintained between about 190° and 210° C. However, if the temperature is maintained substantially above this range, carbon is deposited on the catalyst and excessive quantities of gaseous hydrocarbons such as methane are produced. At temperatures below this range very little if any reaction is brought about. London catalyst life and more uniform product quality are obtained if the temperature is maintained within ± 3° C. of the optimum temperature. This reaction liberates about 4050 kilogram-calories for each kilogram of hydrocarbon produced. It will be readily apparent therefore that an exceedingly difficult heat dissipation problem is involved to remove such a large amount of heat from the reaction zone and at the same time maintain the reaction temperature within such close limits.

Examples of other gaseous reactions conducted in the presence of solid catalysts to which this invention is applicable are the hydrogenation of iso-octene to iso-octane, the oxidation of carbon monoxide to carbon dioxide, the conversion of hydrogen and nitrogen to ammonia, and the oxidation of naphthalene to phthalic anhydride. In all of these processes there is a net decrease in the volume of the gases as the reaction proceeds. While this invention is applicable to reactions of this type, it has particular advantage in the synthesis of hydrocarbons from a mixture of carbon monoxide and hydrogen.

Accordingly, the present invention provides a method for maintaining a substantially constant temperature throughout a reaction zone during the exothermic catalytic reaction therein of gaseous reactants and in which reaction there is a net decrease in the volume of gases as the reaction proceeds, which method comprises heating to approximately reaction temperature and then passing through the reaction zone countercurrently to the flow of reactants and in direct contact therewith, a liquid mixture inert under the reaction conditions existing in the reaction zone and consisting essentially of a volatile component and a relatively non-volatile component, the volatile component being vaporisable at the aforesaid reaction conditions and the non-volatile component having a negligible vapour pressure at the reaction temperature, absorbing exothermic heat of said reaction by vaporization of said volatile component and regulating the amounts of said components charged to the reaction zone in said mixture so that said volatile component is substantially completely vaporized during its passage through the reaction zone and so that a substantially constant ratio is maintained throughout the reaction zone between the molal concentrations of said volatile component in the vapor and in the liquid thereby preventing any appreciable temperature gradient in the reaction zone.

In a more specific embodiment the invention consists in conducting highly exothermic gas reactions within closely controlled temperature limits by a method which comprises heating to approximately reaction temperature and then passing into the reaction zone countercurrently to the flow of gaseous reactants and in direct contact therewith, a liquid mixture inert under the reaction conditions and consisting essentially of about $R(N_i-N_f)$ mols per hour of a volatile component having a vapor pressure at the reaction temperature and when pure of $\frac{RP}{R-1}$, and about $\frac{RN_i}{R-1}$ mols per hour of the relatively non-volatile liquid component having a negligible vapor pressure at reaction temperature, where R is equal to the number of mols of liquid vaporized per mol of decrease in gas volume, N_i is the mols per hour of gaseous reactants charged to the reactor, N_f is the mols per hour of product and unconverted reactant gases leaving the reactor, and P is the absolute pressure within the reactor.

A major problem in Fischer-Tropsch synthesis reactions, which are typical of the reactions to which this invention is directed, is to remove the large heat of reaction while maintaining a very precise temperature control. A method of control has been proposed which comprises passing a stream of vaporizable oil down through the catalyst bed countercurrent to the process gas stream. If the oil is at or near its boiling point at the plant pressure when it is admitted to the catalyst bed, it will be able to absorb heat through vaporization during its passage through the bed and therefore will absorb the heat liberated by the reaction. The temperature, however, will not be uniform at all points within the catalyst bed. For example, when the gas stream is negligible in comparison with the oil stream and heat is supplied extraneously to the reactor, fractional distillation will occur and the temperature of the oil will increase toward the bottom of the bed. The magnitude of this effect, of course, will depend upon the boiling range of the oil charged. On the other hand, if a pure compound or very narrow boiling range fraction were charged in an actual operation, the temperature of the oil would decrease toward the bottom of the bed because of the decreasing partial pressure of the oil vapors, said decrease being caused by the relative increase in the number of mols of the reactants. While these effects tend to compensate one another, it is not sufficient to have an approximate compensation. The reaction temperature must be kept within a narrow range of not more than 6° C. throughout the bed. Furthermore, although it is possible to maintain the temperature at the bottom and at the top of the catalyst bed at the same value in exothermic gas reactions when using a single vaporizable liquid as the heat absorption medium, experience has indicated that the temperature at any point within the bed will be higher than the end temperatures.

However, the method of the present invention, utilizing a mixture of a volatile and a relatively non-volatile liquid, avoids the former difficulties by having the non-volatile liquid act as a regulator of the molal concentration of the volatile component in the liquid phase. In such a system, for the temperature to be the same at all points, the mol fraction of the light component in the liquid phase must bear a constant relationship to the mol fraction of the light component in the vapor phase, that is, at all points in the reaction zone the ratio of the mol fraction of the light component in the liquid phase to the mol fraction of the light component in the vapor phase must be substantially the same. Owing to the continuous vaporization of the lighter component, as required to absorb the heat evolved by the reaction, the mol fraction of the light component in the vapor phase increases from the reactant gas inlet to the product gas outlet. Accordingly an appropriate quantity of heavier component must be employed to assure a corresponding increase, from reactant inlet to product outlet, in the mol fraction of the light component in the liquid phase. The aforesaid expression $\frac{RN_i}{R-1}$ defines the quantity of non-volatile component that will accomplish this result.

Briefly stated, the invention as applied to the conversion of carbon monoxide and hydrogen to hydrocarbons comprises passing a gaseous mixture of carbon monoxide and hydrogen upwardly through a bed of suitable solid catalyst, for example cobalt on kieselguhr under conditions of time, temperature, and pressure to convert at least a portion of the carbon monoxide and hydrogen to hydrocarbons. To absorb the heat liberated during the reaction, a mixture of liquids is charged to the top of the catalyst bed. The light component of this mixture is a pure liquid compound or a relatively narrow boiling range liquid which has a vapor pressure at the reaction temperature of $\frac{RP}{R-1}$ where R is the number of mols of liquid vaporized per mol of shrinkage in total synthesis vapor and P is the absolute pressure within the reactor. The term total synthesis vapor is meant to include hydrogen, carbon monoxide, carbon dioxide, water, inerts, and all of the hydrocarbon and oxygenated products of the reaction and to exclude the vaporized heat absorption medium. The heavy component of the mixture is a liquid with a substantially negligible vapor pressure relative to that of the light component. The mixture is charged to the reactor at the rate of approximately

$$R[(N_i - N_f) + \frac{N_i}{R-1}]$$

mols per hour of which $R(N_i - N_f)$ mols per hour is the light component and the remainder that is: $\frac{RN_i}{R-1}$ mols per hour, is the heavy component. N_i is the inlet gas rate to the reactor expressed as mols per hour. N_f is the mols per hour of outlet gas including water and hydrocarbon reaction products but not vaporized heat absorption medium. As this mixture of the light and heavy components flows down through the catalyst bed, the light component is vaporized at a rate such that the heat of reaction is absorbed as it is liberated. The liquid mixture should be preheated to approximately the reaction temperature before being charged to the catalyst bed. The vaporized light component leaves the reactor with the reaction products and the unconverted carbon monoxide and hydrogen and is separated therefrom and may be returned for further use. The heavy component flows down through the bed and is withdrawn from the bottom of the reactor; it too may be recovered for further use. An additional advantage derived from this method of controlling the reaction temperature is that the heavy component tends to dissolve and remove from the catalyst any waxlike reaction products that tend to form thereon.

The light and heavy components may be substantially pure compounds which substantially remain chemically inert during the reaction of the gaseous reactants and preferably boil at temperatures at least 55° C. apart. The light and heavy components, however, do not have to exactly meet the specifications set forth above in order to obtain a satisfactory uniformity of temperature throughout the reaction zone. Instead of using a pure compound as the light component, a narrow boiling liquid fraction may be used. The heavy component should have an initial boiling point of at least 55° C. and preferably about 85° C. above the end boiling point of the light fraction. Thus if it is desired to carry out a Fischer-Tropsch synthesis reaction at a temperature of 204° C. and a superatmospheric pressure of 6.8 atmospheres with a value of $R=5$, the light component should have a vapor pressure of approximately 9.7 atmospheres at 204° C. or a normal boiling point of about 99° C. A saturated hydrocarbon fraction boiling from 93° to 105° C. would be suitable. The heavy component could then be the gas oil fraction of the reaction product.

Although the vapor pressures and rates of the components are most conveniently and accurately determined from the formulas given above, they can also be determined in another manner. To illustrate, based upon a consideration of the reactor temperature and pressure, the reactant charge rate, and the degree of conversion, a vaporizable component of appropriate volatility may be selected. The rate at which the light component is charged to the reactor will then be such that the amount of this light component is just sufficient to absorb the heat of reaction through vaporization. The volatility will be such that the actual temperature in the catalyst bed will be approximately equal to the previously selected or predetermined reaction temperature. The actual temperature however will not be uniform throughout the bed, but can be made uniform by charging along with the light component, the correct amount of a non-volatile component. The latter rate can be found by charging increasing amounts of the non-volatile component to the top of the bed and noting the temperature difference between two different points in the bed. When this difference equals zero, the correct rate has been reached.

The liquids preferred as temperature control means are hydrocarbons of suitable boiling range. However, other organic materials such as oxygenated compounds and the like may also be used. The liquids employed should be substantially inert under the conditions prevailing in the conversion zone; they should substantially remain chemically unchanged during the conversion of the gaseous reactants. It has frequently been found that appropriate fractions of the reaction products meet the necessary requirements.

The invention is applicable not only to processes involving exothermic gas reactions in the presence of a stationary bed of solid catalyst, but it is also applicable to processes of this nature employing moving beds of solid catalyst. In moving bed processes the catalyst is transported by physical or mechanical means through a reaction zone as a single continuous bed or as a series of smaller beds. For the processes of this invention the direction of travel of the catalyst within the reactor may be either upward or downward.

What we claim is:—

1. A method for maintaining a substantially constant temperature throughout a reaction zone during the exothermic catalytic reaction therein of gaseous reactants and in which reaction there is a net decrease in the volume of gases as the reaction proceeds, which method comprises heating to approximately reaction temperature and then passing through the reaction zone countercurrently to the flow of reactants and in direct contact therewith, a liquid mixture inert under the conditions existing in the reaction zone and consisting essentially of a volatile component and a relatively non-volatile component said volatile component being vaporisable at said reaction conditions and said non-volatile component having a negligible vapour pressure at the reaction temperature, absorbing exothermic heat of said reaction by vaporization of said volatile component and regulating the amounts of said components charged to the reaction zone in said mixture so that said volatile component is substantially completely vaporized during its passage through the reaction zone and so that a substantially constant ratio is maintained throughout the reaction zone between the molal concentrations of said volatile component in the vapor and in the liquid thereby preventing any appreciable temperature gradient in the reaction zone.

2. A method for maintaining a substantially constant temperature throughout a reaction zone during the catalytic conversion therein of carbon monoxide and hydrogen into hydrocarbons, which method comprises heating to approximately reaction temperature and then passing through said reaction zone countercurrently to and in direct contact with said reactants flowing upwardly in gaseous state a liquid mixture inert under the conditions existing in the reaction zone and consisting essentially of a volatile component and a relatively non-volatile component said volatile component being vaporisable at said reaction conditions and said non-volatile component having a negligible vapour pressure at the reaction temperature, absorbing exothermic heat of said reaction by vaporization of said volatile component and regulating the amounts of said components charged to the reaction zone in said mixture so that said volatile component is substantially completely vaporized during its passage through the reaction zone and so that a substantially constant ratio is maintained throughout the reaction zone between the molal concentrations of said volatile component in the vapor and in the liquid thereby preventing any appreciable temperature gradient in the reaction zone.

3. Method as claimed in claim 1 or 2, further characterized in that there is charged to the reaction zone about $R(N_1 - N_2)$ mols per hour of a volatile liquid component having a vapor pressure at the reaction temperature and when pure of $\frac{RP}{R-1}$, and about $\frac{RN_1}{R-1}$ where R equals the mols of liquid vaporized per mol of decrease in gas volume, N_1 equals the mols per hour of gaseous reactants charged to the reaction zone, N_2 equals the mols per hour of product and unconverted reactant gases leaving the reaction zone and P equals the absolute pressure within the reaction zone.

4. Method as claimed in any of the claims 1 to 3, wherein gaseous reaction products containing the vaporized volatile component of the liquid mixture are withdrawn from the reaction zone and the said volatile component is separated from the reaction products, the relatively non-volatile component of the liquid mixture is withdrawn from the reaction zone, and the recovered components are returned to the process for further use.

5. Method as claimed in any of the claims 1 to 4, wherein the volatile component of the liquid mixture is a substantially pure compound boiling at least 55° C. lower than the temperature at which the relatively non-volatile component of the liquid mixture begins to boil.

6. Method as claimed in any of the claims 1 to 4, wherein the volatile component of the liquid mixture is a narrow-boiling liquid fraction which has an end boiling point at least 55° C. lower than the temperature at which the relatively non-volatile heavy component of the liquid mixture begins to boil.

7. Method as claimed in claim 2, wherein the volatile component of the liquid mixture consists essentially of a narrow-boiling range paraffin hydro-carbon fraction and the relatively non-volatile component of the liquid mixture consists essentially of a hydrocarbon fraction remaining substantially liquid at the reaction conditions.

8. The method of controlling exothermic catalytic gas reactions substantially as herein described.

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