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3489

COMPLETE SPECIFICATION

Improved Fischer 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 Linden, 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 the manufacture of products by the Fischer Synthesis involving the interreaction of oxides of carbon and hydrogen resulting in the production of substances such as methanol and other alcohols, liquid hydrocarbons and oxygenated organic compounds. The invention is more particularly concerned with the manufacture of valuable hydrocarbon products containing more than one carbon atom in the molecule by the hydrogenation of carbon monoxide. The invention is especially concerned with an improved method for controlling the amount of high molecular weight products which are adsorbed by the catalyst and is to be used in connection with the so-called fluid-solids technique wherein during the synthesis of the hydrocarbons, the catalyst is in the form of powder and is maintained in a dense suspension in the reaction zone intermixed with the reactants. This is accomplished by causing the reactants to flow upwardly in the reaction zone at a velocity which is sufficient to maintain the catalyst in a turbulent condition within the dense suspension previously referred to. In this type of operation the products obtained in the synthesis together with any unreacted materials and a small amount of entrained catalyst issue from a point at the top of the reactor after having passed through several cyclone separators which serve to remove most of the catalyst from the gasiform material by centrifugal action. The catalyst separated by the cyclones is returned to the reaction zone.

In the course of the synthesis within the dense suspension, hydrocarbons of a wide range of molecular weight may be formed. The molecular weight varies from that of methane to high boiling materials some of which at room temperature exist in the solid form and hence are commonly known as waxes. The operating conditions of temperature and pressure in the reaction zone determine the amount of the heavier hydrocarbons which may be removed as gas with the other gasiform materials leaving the reactor. Under certain conditions of operation the rate of production of the heavier hydrocarbons exceeds the rate of removal with the materials leaving the reactor. Consequently condensation occurs and these heavier hydrocarbons are then contained on the catalyst in the form of liquids. If the quantity of liquid contained on the catalyst is allowed to build up, a condition is reached at which the catalyst particles begin to stick together, thereby losing true fluid characteristics. The small amount of catalyst which is not removed from the gases leaving the top of the reactor will also contain liquid materials, if such have been deposited thereon in the reactor. The amount of catalyst plus contained liquid removed in this fashion may still be insufficient to prevent further accumulations of liquid on the catalyst within the reactor without reaching the "sticking" non fluid conditions, referred to above. Hence, it is necessary to provide for direct removal of catalyst from the reactor with subsequent removal of the heavy liquids or waxes contained thereon. From the standpoint of catalyst activity, it would be most advantageous to operate with substantially no deposit of oil or wax on the catalyst since excessive deposit decreases the catalyst activity in promoting synthesis. However, to prevent the deposit requires a modification of the process wherein the production of a

[*Price 1/-*]

heavy oil is eliminated either by the use of very selective catalysts or by adjusting the conversion temperature and pressure conditions so that all of the heavy oils are vaporized and carried out of the reactor along with the reactants. The conditions thus required are not compatible with the most economical utilization of the reactor and hence a preferred operation would be one wherein a certain amount of heavy oil or wax would be allowed to accumulate on the catalyst, without losing fluidity.

It is therefore the main object of this invention to provide a process for the synthesis of hydrocarbons from carbon oxides and hydrogen in which a certain amount of the wax is maintained upon the catalyst without the catalyst losing its fluid properties.

It has been proposed in the past to perform a Fischer synthesis using a moving bed of catalyst, i.e. a body of catalyst which moves steadily through a reaction zone on a moving band or by means of scrapers or some similar means, and in such a process it has been proposed to withdraw spent catalyst from the reaction zone, wash it free from wax with a suitable solvent and return the washed catalyst to the reaction zone.

The present invention is concerned with a Fischer synthesis process in which the catalyst is maintained in a fluidised condition in the reaction zone. In these circumstances, the problem of catalyst contamination takes on a significance not present in the older moving bed process, since, as already stated, waxy contamination on the catalyst when present in an amount over a certain limit, causes the catalyst to lose its fluidisable characteristics.

When using the fluidised catalyst technique for a Fischer synthesis, it has been proposed to pass contaminated catalyst withdrawn from the reaction zone through a stripping zone in which it is stripped with steam or inert gas, for the purpose of removing volatile constituents from the catalyst. Such a procedure is not generally satisfactory for the removal of waxes or the heavier contamination with which the present process is concerned.

The present invention comprises a process for the synthesis of liquid hydrocarbons and oxygenated organic compounds 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 heavy oil being continuously withdrawn from the reaction zone and passed to an extraction zone in which at least the greater part of the wax and oil is removed by solvent extraction, the dewaxed catalyst being recycled to the reaction zone, and the amount of wax and oil removed in the extraction zone being such that the recycled catalyst and the catalyst mass in the reaction zone are fluidisable.

The amount so removed, together with the rate at which catalyst is removed from the reactor for washing will preferably be so adjusted that the catalyst in the reactor will, on the average, contain no more than 90% of the amount of oil or wax which it can carry and still maintain true fluid characteristics. Generally this amount is not more than 25% by weight of the catalyst and for some catalysts is as low as 15%.

Other objects of this invention, not at this time more particularly enumerated, will be understood from the following detailed description and accompanying drawing. For purposes of illustration it is assumed that the feed gases comprise hydrogen and carbon monoxide and that the reaction is conducted under conditions to produce hydrocarbon constituents containing more than one carbon atom in the molecule. Referring therefore to the drawing the synthesis gases are introduced into the system by means of line 1, compressed in compressor 2, and mixed with recycle gases from line 3 and catalyst from reactor standpipe 4. The mixture is conducted through cooler 5 and introduced into reactor 6 through line 7. Fresh make-up catalyst may be introduced into the catalyst-synthesis gas mixture from catalyst hopper 8 through line 9.

The catalyst suspension is introduced into the lower portion of the reaction vessel and is passed upwardly therethrough. Thus the more dense catalyst particles will lag behind the less dense suspending gases or vapours and the catalyst concentration in the reaction zone will therefore be substantially greater than in the suspension of catalyst supplied thereto. The gases and/or vapours pass upwardly through the reaction zone at such a rate that the solid catalyst particles and gases and/or vapours form a dense phase mass which acts as if it had a level similar to a boiling liquid. The catalyst within this mass has a concentration much more dense than the catalyst in the gas and/or vapours above the level. In practice there is a clear line of demarcation between these two phases which produces the level. However, the level is not quiescent but is under agitation similar to the surface of a boiling liquid. The formation of such a dense phase mass with its pseudo level occurs whenever the gas velocity is between 0.5 and 5 feet per second, preferably when the inlet velocity of the gases does not exceed 1.5 feet per second and the outlet velocity is not less than 0.3 feet per second. Although the level furnishes a point of sudden decrease in catalyst density, it is understood that the density of the catalyst within this dense phase mass increases towards the bottom. With the velocities mentioned there is uniform size distribution of the catalyst entrained in the exit gases.

The temperature of the reaction zone 6 may be controlled by the amount and temperature of the materials supplied thereto, and/or by heat exchange through the walls. Since in the processes of this invention, the reactions are generally exothermic, and great increases in temperature in the reaction zone should be avoided, it is one feature of this invention to continuously remove a portion of the dense phase mass of catalyst from the bottom of the reaction zone through standpipe 4 where it is mixed with incoming feed vapours, cooled in exchanger 5 and returned to the reaction zone. Standpipe 4 is a long vertical column which is of sufficient height to provide the desired pressure for circulating the catalyst. This pressure is similar to the hydraulic or hydrostatic pressure head of a fluid column, the pressure being a direct function of the density of the catalyst powder and of the column's height. This device is particularly effective as a means for circulating the catalyst and removing excess heat by heat exchange thus avoiding any apparatus having moving parts coming in contact with the catalyst. The lower end of column 4 is provided with a suitable valve 10 for regulating the amount of catalyst discharging therefrom. A conventional slide valve having an adjusted slide which can be adjusted to regulate the size of the orifice through which the powder passes is suitable for this purpose, although other types of valves may be used. This valve may be operated normally or automatically. A drop in pressure across the valve 10 of about 2 to about 5 lbs. per sq. in. is generally desired in order to provide adequate control of the flow of catalyst powder.

The reaction products and catalyst suspended therein are withdrawn from reaction zone 6 by line 11 and pass into catalyst separating zones 12 and 13. The gaseous products are withdrawn through line 14 while catalyst separated from the gases and/or vapours in separators 12 and 13 is returned to the dense phase in reaction zone 6 through lines 15 and 16 respectively. Under the usual conditions of temperature and pressure obtained in the reaction zone the catalyst in the dense phase mass in the reactor 6 adsorbs some of the heavier hydrocarbon products of the reaction which eventually cause it to lose true fluid characteristics. In order to prevent this, a portion of the catalyst is continuously removed from standpipe 4 by line 23 and subjected to a treatment whereby these heavier products are removed.

It has been determined that an upper limit exists in the ability of a finely divided synthesis catalyst to carry adsorbed oils or wax and still maintain fluid characteristics. This depends upon the physical and chemical characteristics of the catalyst, but in general the amount of adsorbed oils or wax may vary up to 25% based on the weight of the catalyst without the catalyst losing its fluid characteristics. In order to provide a safe limit for operating without losing fluidity it is preferred that the oil content of the catalyst in the reactor be maintained between 1 and 90% of the oil-carrying capacity of the catalyst from a fluidity standpoint. According to the preferred method of operation for this invention the catalyst should not contain more than 15% by weight of oil or wax.

Accordingly the catalyst removed from standpipe 4 through line 23 is introduced into a wax removal zone 24 where it is subjected to the action of a solvent introduced through line 25. This solvent may be an oil such as naphtha or a hydrocarbon such as benzene or a liquefied hydrocarbon such as pentane or butane. It may also be a suitable fraction of the synthetic product.

The amount of catalyst washed in zone 24 is inversely proportional to the efficiency of the washing procedure. For economical reasons in order to reduce the amount of catalyst to be circulated, the efficiency of the washing procedure should be such that at least 50% and preferably 100% of the wax and/or oil is removed. In order to maintain the desired wax/catalyst ratio in the reactor it is necessary to withdraw, wash and recycle (assuming 100% wax and oil removal) one lb. of catalyst per hour for each unit weight of wax or oil to be retained on each lb. of catalyst in the reactor.

For example if it be assumed that the

process according to the present invention will produce 4,750 barrels per day of 55° A.P.I. synthetic oil with a heavy oil or wax production of 5% based on the synthetic oil produced then the amount of heavy oil or wax remaining in the reactor per hour is:

$$\frac{4{,}750 \times 265^{*} \times .05}{24} = 2{,}620 \text{ lbs./hr.}$$

(*265 is the weight in lbs. of each brl. of synthetic oil).

If it is desired to maintain the average concentration of heavy oil or wax on the catalyst in the reactor at 0.15 lbs. per lb. of catalyst, then the amount of catalyst to be washed (assuming 100% wax and oil removal in the washing zone) will be:

$$\frac{2{,}620}{0.15} = 17{,}500 \text{ lbs./hr.}$$

If on the other hand the efficiency of the washing procedure is only 50% then 0.075 lb. of oil or wax will be retained on the catalyst being recycled to the reactor and the amount of catalyst washed must be doubled, or,

$$\frac{2{,}620}{0.075} = 35{,}000 \text{ lbs./hr.}$$

The solvent containing the dissolved wax or oil is withdrawn through line 26 and treated to separate it from the dissolved material. Solvent-treated catalyst is removed from the wax removal zone through line 27 and introduced into line 3 carrying synthesis gases and recycled to reactor 6 through cooler 5 and line 7. As stated above it is preferable to carry out this extraction so that preferably no more than 15% of oil or wax by weight will be contained on the catalyst within the reactor.

The reagents, catalysts and operating conditions used in the above described process will naturally be varied according to the nature of the products desired, these conditions being already known. For example in the synthesis of hydrocarbons from carbon monoxide and hydrogen, the reaction is preferably conducted at substantially atmospheric or moderately elevated pressures with catalyst, containing metallic cobalt, iron, nickel or copper which may be in admixture with promoters such as oxides of chromium, zinc, aluminum, magnesium and the rare earth metals and which may be deposited on carriers such as kieselguhr and pumice and clay and synthetic gels such as the hydrates of silica and/or alumina. The gases are preferably substantially free from sulphur and oxygen and for cobalt catalysts are supplied in a ratio of about one mol of carbon monoxide to two mols of hydrogen, the total gaseous feed containing, for example, about 25-30% of carbon monoxide and 50-60% hydrogen, the remainder being nitrogen or other substantially inert gases. For iron catalysts a 1:1 ratio of H_2/CO is preferred. The temperature of reaction may be maintained between 350° and 450° F. with catalysts containing compoumds of cobalt and magnesia; with catalysts containing iron, temperatures of between 550° and 650° F. are used. In general the operating temperatures will be between 350° and 700° F. depending on the catalyst and conditions used. Furthermore, while the description has been limited to a fluid catalyst process in which the catalyst is circulated through a cooling zone to control the temperature in the reactor, it is to be understood that any other type of fluid process may be used, for example, the temperature control may be obtained by cooling surfaces within the reactor or in any other desired manner.

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 for the synthesis of liquid hydrocarbons and oxygenated organic compounds 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 heavy oil being continuously withdrawn from the reaction zone and passed to an extraction zone in which at least the greater portion of the wax and oil is removed by solvent extraction, the dewaxed catalyst being recycled to the reaction zone, and the amount of wax and oil removed in the extraction zone being such that the recycled catalyst and the catalyst mass in the reaction zone are fluidisable.

2. A process according to Claim 1, where at least 50% of the wax and oil present on the catalyst passing through the extraction zone is removed, and the amount of catalyst passed through the extraction zone is such that the catalyst in the reaction zone contains no more than 90% of the amount of wax and oil which it can carry without loss of its fluidisable characteristics.

3. A process according to Claim 1 or Claim 2, wherein the degree of extraction in the extraction zone, and amount of catalyst passing through the extraction zone are so controlled that the catalyst

in the reaction zone contains from 15-25% by weight of adsorbed wax and oil.

4. A process according to Claim 1 or Claim 2, wherein the degree of extraction in the extraction zone and the amount of catalyst passing through the extraction zone are so controlled that the catalyst in the reaction zone contains not more than 15% by weight of adsorbed wax and oil.

5. A process according to any of the preceding claims, wherein the percentage of wax and oil present in the reaction zone is kept constant, the efficiency of the solvent extraction is from 50% to 100%, and the catalyst throughput through the extraction zone is inversely proportional to the extraction efficiency.

6. A process according to any of the preceding claims, wherein the solvent is a naphtha, benzene or liquid pentane or butane.

7. A process according to any of the preceding claims, wherein the proportions of carbon monoxide to hydrogen, catalysts and operating conditions in the reaction zone are those hereinbefore set forth.

Dated this 20th day of June, 1945.

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