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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION.

## Improvements in or relating to the Synthesis of Hydrocarbons and Oxygenated Derivatives.

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 the hydrogenation of the oxides of carbon and in particular, to two-stage processing involving first, the formation of oxygenated hydrocarbons and secondly, the formation of hydrocarbons suitable for use as motor fuels.

The contacting under various temperatures and pressures of the oxides of carbon, particularly carbon monoxide, with hydrogen in the presence of catalyst is the means by which a variety of hydrocarbon and oxygenated hydrocarbon compounds may be prepared. The temperatures and pressures employed in the processing vary widely and depend upon factors such as the type of catalyst the nature of the feed, and final products desired. The catalyst employed usually consists of a large percentage of either iron, cobalt, or nickel with minor amounts of activating substances such as alumina and potassium. In order to obtain high efficiencies, particular reaction conditions, limited stage operations and recycling features are commonly employed.

The present invention is an improvement over prior art processing in that it effects a better utilization of catalyst masses and prevents their deterioration by controlling the character and volume of the feed stock. Within the aims of the invention is the prevention of the formation of carbon deposits on the catalyst by using a relatively high percentage of water in synthesis operations for the preparation of oxygenated organic compounds.

Broadly the invention provides a two stage process employing in the first stage a feed gas mixture containing carbon monoxide and hydrogen together with 2—8% by volume of water based on the combined volume of carbon monoxide and hydrogen. This feed gas mixture is contacted with an iron group catalyst under synthesis conditions conducive to the formation of oxygenated hydrocarbons, which are thereafter separated in a conventional manner. The unconverted gases from the first stage are then contacted in a second stage with previously used catalyst from the first stage under conditions conducive to the formation of normally liquid hydrocarbons particularly for use as motor fuel.

The preferred catalyst comprises a major proportion of iron promoted with a minor proportion, preferably from 1—8% of an alkali compound. As promoters, potassium compounds are preferred, particularly potassium carbonate or fluoride. The preferred water vapour content of the feed gases to the first stage is from 3—5%. The catalyst is preferably sintered or pretreated with carbon monoxide or a mixture thereof with hydrogen so as to contain from 1 to 3% carbon as carbide. The procedures which may be used for this pretreatment are not part of the present invention.

When operating in the above manner reduction of carbon deposition on the catalyst and the selectivity of the processing for the formation of oxygenated organic compounds in the first reactor is improved by the presence of the water. The used catalyst from this first reactor is thus suitable for further use in the second stage of hydrocarbon synthesis.

Processing according to the invention usually involves 60 to 80% conversion of the hydrogen-carbon monoxide mixture in the first stage. High yields of light oxygenated organic compounds are obtained from the water layer of the reaction product from the first stage of the processing. Thus, when processing with an iron catalyst and a synthesis gas containing hydrogen and carbon monoxide in a molecular

proportion from about 1 to 2 to 1, preferably a mol ratio of 1.8, at a temperature from about 350°F. to about 600°F. preferably from about 450°F. to about 550°F., a pressure from about 200 to about 700 pounds per sq. inch preferably from about 450 to about 550 pounds per sq. inch, a feed rate of between about 2 and about 30, and preferably between about 5 and about 20 cu. ft./lb. catalyst/hr., and a recycle of 1 to 2 relative to the initial feed gas, yields of the order of 40 to 75 cc. of light oxygenated organic compounds in the aqueous layer of the reaction product per cubic meter of mixture of hydrogen and carbon monoxide consumption are obtained, while in the corresponding oil layer, from 25% to 50% yield of alcohols of the $C_3$ to $C_{18}$ range are obtained.

The desired ratio of oxygenated products in the water and oil layers controls the operating conditions. In the oxygenated products about 70% of the combined oxygen is found in the oil layer when the temperature is about 450°F., to about 40% when the temperature is about 550°F. Thus, the temperature may be varied to give the optimum type of product.

The unreacted hydrogen and carbon monoxide from the oxygenated hydrocarbon synthesis unit is then passed to a hydrocarbon synthesis zone wherein the hydrogen and carbon monoxide are reacted to form hydrocarbons, predominantly above the $C_3$ range. In this second reaction zone, due to the high hydrogen content of the gas from the first reactor and the catalyst characteristics, the carbon deposition on the catalyst is low.

In the second reaction stage the processing conditions may be about the same as those given above for the first reaction stage. The temperature, however, commonly employed is between about 550°F. and about 750°F., and the pressure from 200 to 500 lbs. per square inch and the space velocity from 10 to 75 cubic feet of feed gases per lb. of catalyst per hour. Within these ranges of operating conditions, it is preferable to operate between about 625°F. and about 675°F., a pressure from about 350 to about 450 lbs. per square inch and at a space velocity of between about 15 and about 40 cubic feet of synthesis gas per lb. of catalyst per hour. These preferable temperature and pressure conditions are advantageous with the recycle ratio from about 2 to 5.

In the first stage of the process the use of temperatures in the lower portion of the operating range is advantageous for the production of the higher molecular weight oxygenated hydrocarbons. In the second stage of the process the higher the temperature, the lower the molecular weight and the more unsaturated are the reaction products. In general, the lower reaction temperatures in the first stage of the process are coupled with the higher temperatures in the second stage of the process. Similarly, a high reaction temperature in the first stage of the process is usually coupled with a temperature in the lower portion of the operating range in the second stage of the process. In both reaction stages a low temperature of operation is usually coupled with a low pressure operation and a high temperature of operation is coupled with a high pressure operation. By these interrelationships of the temperatures of the reactions in the two stages, high overall conversion of the feed stock occurs while the nature of the reaction products can thus be varied as desired.

In order that the invention may be more fully understood, the following description of a particular embodiment is presented. In the accompanying drawing, a flow diagram is presented of processing according to a particular embodiment.

Hydrogen and carbon monoxide in volume ratio of 1.8 are passed through line 9 into reaction unit 10. Water vapour in the amount of 4% by volume of the hydrogen and carbon monoxide mixture is passed from line 8 into line 9. The catalyst is passed into the reaction unit from storage vessel 5 through line 6. In general, the gravity of the fluidized mass admitted through line 6 is about 100-130 lbs. per cubic ft. The reaction unit 10 consists, in this particular embodiment, of a cylindrical portion 11 capped by a dome portion 12 and a conical base 13. Within the reaction vessel near the junction of the cylindrical portion 11 and the conical base 13 is a porous plate or grid 14. The unit 10 has a catalyst withdrawal line 15 and an overhead line 16 at the uppermost portion of the dome section 12. In the dome portion 12, one or more cyclone separating units as indicated by the reference numeral 17 are located. From the cyclone separator 17 is the dip pipe 18 for the returning of catalyst material from the cyclone.

In the reaction unit 10, the catalyst material is maintained in a highly fluidized condition as a result of the finely divided material of the catalyst and the upward passage of the gaseous materials from the base of the tower through the distributing grid 14. Within the unit 10, the fluidized mass presents a general appearance of a boiling liquid with a general level L at some point in the vessel some distance below the dome portion of the vessel. In this particular embodiment, the catalyst has a composition of 77% iron, 5% $K_2O$, less than 10% oxygen, the remainder

being silica, alumina and other minor constituents. The reaction conditions within the unit include a temperature of between about 350-600°F., preferably between 450-550°F., a pressure of 450 psig. and a recycle ratio of 1 to 2 of recycle to fresh feed gas. The recycle gas is passed into unit 10 through line 19. The particle size of the catalyst is in the range from 10 to 80 microns of which about 65% is between about 20 to 40 micron size, the remaining portion distributed in the range between 10 to 20 microns and to 80 microns. The superficial velocity of the gases passed upwards through the reaction unit 10 is usually 1.5 ft. per second and in this embodiment is maintained about 1 ft. per second. The space velocity is maintained between about 2 to about 30 and preferably about 10 cubic ft. of $H_2$ and CO fresh feed at standard conditions per lb. of catalyst per hour. Under these conditions, the catalyst height is about 5 to 20 feet.

Under the conditions of processing as specifically stated, a predominantly gaseous phase separation in the dome portion of the reaction unit passes through the cyclone separator 17 and thence through line 16 into treating equipment 20. Under the processing conditions in the unit 10 about 75-80% of the hydrogen-carbon monoxide mixture is converted to oxygenated hydrocarbons.

In the recovery unit 20, cooling of the products occurs. Also in the recovery unit 20, separation is effected between the gaseous and liquid phase products and also phase separation between the water-soluble and the oil soluble products. The gaseous products are removed through line 21, the aqueous products through line 22 and the oil products through line 23. A portion of the gaseous product is recycled through line 19 to the reaction unit 10. The aqueous products removed through line 22 are removed from the system by further processing and separation of the desired constituents. Similarly, the oil soluble products removed through line 23 are removed from the system for the desired products. The remainder of the gaseous products are passed through line 24 into the reaction unit 30. Also additional supply of the feed $H_2$ and CO mixture may be added to this feed to the unit 30 through line 25. The catalyst removed from the unit 10 through line 15 also passes into the unit 30. Fluidizing gas may be injected into the line 15 as desired.

The unit 30 is similar in design to unit 10. It consists of a cylindrical section 31, a dome section 32 and a conical base section 33. Similarly near the junction of the cylindrical section 31 and conical base section 33 is the grid or vapour distributing plate 34. The unit is similarly equipped with a catalyst withdrawal line 35, an overhead line 36, a cyclone separating equipment 37 and a catalyst fines return line 38. Similarly, in the unit 30 a level P at a point some distance, usually about 2/3 of the height of the cylindrical portion is maintained.

In the unit 30, a temperature of 675°F., a pressure of 400 psig., a superficial velocity of gases passed upwards of about 1 ft. per second, a space velocity between 10 and 30 and preferably 25 cubic ft. of gas per hour per lb. of catalyst are maintained. Under such conditions of processing, a substantially gaseous phase separation occurs in the top of the unit 30. This gas containing minor amounts of entrained catalyst particles passes through the cyclone separator and thence through line 36 to treating equipment 40. In equipment 40, separation and purification of the desired products is effected and passed from the system through line 41. The gaseous products are removed from equipment 40 through line 42 and passed into line 24. The catalyst withdrawn through line 35 is passed to reactivating equipment as desired.

As an example of such processing from the reaction unit 10, 150-160 cc. of hydrocarbons heavier than propane and propylene and the low molecular weight alcohols were obtained in an amount of 40-50 cc. per cubic meter of hydrogen and carbon monoxide consumption. In the oil layer of the reaction product from vessel 10, 35% of product mainly alcohols in the $C_8$ to $C_{15}$ range were obtained. From the reaction unit 30, the following yield products are obtained per cubic meter of $H_2$ and CO consumed, 180 cc. of hydrocarbons heavier than propane and propylene and only 20 cc. of water soluble oxygenated compounds. The oxygenated hydrocarbon in the oil layer was 20% of these hydrocarbons. The composition of the water soluble oxygenated compounds were about 60% ethanol and normal propanol with traces of methanol, butanol and higher alcohols. Of the remaining 40%, about 20% was acetic and higher acids, 10% aldehydes and 10% ketones.

The overall conversion of $H_2$ and CO in the two reactors was above 93%. The selectivity of the reacted CO to carbon in reactor 10 was less than 0.2% while that in the second reactor 30 was less than 0.5%. Should this degree of $H_2$ and CO conversion be attempted in a single reactor with sufficiently severe operating conditions the yield of water soluble oxygenated compounds would be from 25 to 30 $CC/M^3$ of $H_2$ and CO consumed and the selectivity of CO to carbon would be above 0.5% which would have required a large replace-

ment of catalyst to maintain the necessary catalyst size to give satisfactory fluidization in the reactor.

As will be appreciated from the foregoing description the preferred catalyst is iron, but other hydrocarbon synthesis catalysts of the iron group may also be used in the process of the invention and when this is so, the optimum synthesis operating conditions may be determined empirically.

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 two stage process for the synthesis of hydrocarbons and oxygenated hydrocarbons which comprises contacting in a first stage a gas mixture containing carbon monoxide and hydrogen together with 2-8% by volume of water vapour based on the combined volume of carbon monoxide and hydrogen with an iron group catalyst under synthesis conditions conducive to the formation of oxygenated hydrocarbons, separating the oxygenated products thus formed, contacting the unconverted gases in a second stage with previously used catalyst from the first stage under synthesis conditions conducive to the formation of normally liquid hydrocarbons and separating said normally liquid hydrocarbons.

2. A process according to Claim 1, wherein the catalyst comprises a major proportion of iron and a minor proportion, preferably from 1—8%, of an alkali compound as promoter.

3. A process for preparing hydrocarbons and oxygenated hydrocarbons by the hydrogenation of carbon monoxide which comprises contacting in a first stage a gaseous mixture containing hydrogen and carbon monoxide in molecular proportion from about 1 to 2 to 1 and water vapour in the amount of 2 to 8% by volume of the combined volume of hydrogen and carbon monoxide with a catalyst containing a major amount of iron at a temperature from 350°F. to 600°F., a pressure from 200 to 700 pounds per square inch, a space velocity from 2 to 30 cubic ft. of gaseous mixture per hour per lb. of catalyst, removing the reaction products, treating the reaction products to separate gaseous and liquid oxygenated hydrocarbons, contacting the unconverted gases in a second stage with a portion of previously used catalyst at a temperature from 550°F. to 750°F., a pressure from 200 to 500 pounds per square inch and space velocity of 10 to 75 cubic ft. of gas per hour per lb. of catalyst and recovering the hydrocarbons thus formed.

4. A process according to Claim 3, wherein the synthesis conditions in the first stage comprise a temperature from 450 to 550°F., a pressure from 450 to 550 lbs. per square inch and a space velocity from 5-20 cubic ft. of gaseous mixture per hour per lb. of catalyst.

5. A process according to Claim 3 or 4, wherein the synthesis conditions in the second stage comprise a temperature from 625 to 675°F., a pressure from 350 to 450 lbs. per square inch and a space velocity from 15 to 40 cubic ft. of gas per hour per lb. of catalyst.

6. A process according to any one of Claims 3—5, wherein the catalyst is promoted with a minor amount, preferably from 1—8%, of an alkali compound.

7. A process according to Claim 6, wherein the catalyst is promoted with a potassium compound, preferably potassium carbonate or floride.

8. A process according to any one of the preceding claims, wherein the gaseous mixture in said first stage contains from 3 to 5% by volume of water vapour based on the combined volume of carbon monoxide and hydrogen in said gas mixture.

9. A process for preparing hydrocarbons and oxygenated hydrocarbons by the hydrogenation of carbon monoxide which comprises contacting a gaseous mixture containing hydrogen and carbon monoxide in the molecular ratio of 1.8 and water vapour in the amount of 4% by volume of said combined mixture of hydrogen and carbon monoxide with a finely divided catalyst containing 77% iron and 5% $K_2O$ at a temperature of about 450° to 550°F. and a pressure of 450 pounds per square inch and a space velocity of 10 cubic ft. of gaseous mixture per lb. of catalyst per hour, removing a portion of the used catalyst, treating the reaction products to separate gaseous and liquid oxygenated hydrocarbons, contacting the unconverted gases with a portion of said used catalyst at a temperature of 675°F., a pressure of 400 pounds per square inch and a space velocity of 25 cubic ft. of gas per hour per lb. of catalyst and recovering the hydrocarbons thus formed.

10. A process according to any one of the preceding claims, wherein the catalyst is in finely divided form and is maintained in a fluidized condition by the passage therethrough of the gaseous reactants.

Dated this 19th day of May, 1948.

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