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COMPLETE SPECIFICATION

Improved Process for the Synthesis of Hydrocarbons

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:—

The present invention is concerned with an improved hydrocarbon synthesis process. It more particularly relates to an improved hydrocarbon synthesis operation wherein the respective streams are handled in a manner to segregate and recover oxygenated compounds produced in the reaction. By operating in accordance with the present process higher yields of improved products are secured.

It is well known in the art to conduct hydrocarbon synthesis reactions by contacting hydrogen and oxides of carbon with catalysts under various temperature and pressure conditions. The catalysts employed are usually selected from the iron group metals, as, for example, iron, cobalt and nickel. They are utilized either alone or on suitable carriers such as kieselguhr, diatomaceous earth, pumice, synthetic gels, silica and alumina. Promoters such as the carbonates or halides of the alkali metals, particularly potassium, are used with the iron group metals. These catalysts are employed either in fixed bed or in fluid catalyst operations.

The temperatures employed vary widely, as, for example, in the range from about 400° F. to about 800° F. and are generally in the range from about 500° F. to about 700° F. The particular temperature employed will depend upon, among other factors, the type of non-gaseous hydrocarbon product desired, the character and the activity of the particular catalyst utilized, the throughput and composition of the synthesis gases and upon the reaction pressure. For instance, when utilizing a mixture of feed gases comprising carbon monoxide and hydrogen in the ratio of one mol of carbon monoxide per two mols of hydrogen at pressures in the range atmospheric to 100 lbs. per square inch, and in the presence of a cobalt catalyst, the reaction temperature is generally in the range from about 340° F. to about 500° F. On the other hand, if similar feed gases are utilized employing 300 lb. per square inch pressure and an iron catalyst, the temperature is generally in the range from about 500° to about 700° F.

The pressures likewise vary considerably and are a function of other operative conditions such as catalyst employed, activity of the catalyst, character of the feed gases and the temperatures utilized. Pressures in the range from 1 to 100 atmospheres have been suggested. When utilizing an iron type catalyst, it has been proposed to use pressures in the range from about 25 to 750 lbs. gauge although preferred pressures have been in the range below about 300 lbs. gauge. When employing cobalt catalysts, the pressures generally employed have been somewhat lower, generally around atmospheric pressure, and seldom in excess of 100 lbs. per square inch gauge. The character of the feed gases depends somewhat upon the temperatures and pressures and upon the catalysts employed. For example, when employing a cobalt type catalyst, it is preferred to use one mol of carbon monoxide to two mols of hydrogen, while, when an iron catalyst is utilized, equal mols of hydrogen and carbon monoxide in the feed synthesis gases are desirable. The volumes of feed gases utilized per volume of catalysts likewise vary considerably. In general, it is preferred to use from about 500 to 2000 volumes of feed gases per volume of catalyst per

[*Price* 2/-]

hour. Also, it is frequently desirable to recycle the synthesis tail gas to the reactor. The recycle gas to fresh feed ratio may be from 0.5 to 7.5 of recycle gas to one of fresh feed.

Operations such as described are generally conducted under conditions to secure the maximum yield of hydrocarbon constituents containing four or more carbon atoms in the molecule. However, under the conditions of the operation, various side reactions occur which result in the production of valuable oxygenated compounds. In accordance with the invention, we propose to recover and segregate these valuable oxygenated compounds from the hydrocarbon constituents in a manner to secure improved yields of the various reaction products.

The recovery and utilization of oxygenated products from a hydrocarbon synthesis have heretofore been suggested. For example in a process for the production of a high octane fuel, the recovery of selected oxygenated compounds for addition to the product fuel has been proposed. In this latter process the product from the synthesis operation is condensed under pressure to yield an oil and an aqueous layer which may be separated by decantation. Thereafter from the aqueous layer acetone and methanol are separated by appropriate distillation from the other alcohols present and are mixed with the final fuel.

The present process is directed primarily to the recovery of C_2—C_5 alcohols and it has been found that by keeping within the limits prescribed that in addition to those compounds such as acetone and methanol which do not form azeotropes with water, that higher boiling neutral ogygenated compounds, particularly ethyl, propyl, butyl and amyl alcohols, can be separated by azeotropic distillation.

In accordance with the present invention, the reactant gases removed overhead from the synthesis reaction zone are cooled to condense the same at a temperature in the approximate range of from 40° to 100° F. The condensate is passed to a separation zone wherein an oil phase and an aqueous phase segregate. The aqueous phase is distilled in a distillation zone to remove overhead an alcohol rich stream boiling below approximately 212° F. and to recover as bottoms a fraction containing acids and residual undistilled water. A portion of the aqueous bottoms fraction is then preferably contacted with the oil phase condensate to extract neutral oxygenated hydrocarbons therefrom although it will be understood that water from other sources could also be used. The product containing the neutral oxygenated hydrocarbons extracted from the oil phase condensate is then desirably separated from the oil phase and admixed with the aqueous phase undergoing distillation.

In a preferred embodiment the bottoms from the initial distillation zone are passed to a secondary distillation zone and distilled under conditions to remove overhead an aqueous stream containing some oxygenated organic compounds and to remove as bottoms, a stream containing less volatile oxygenated compounds. This aqueous overhead stream from the secondary distillation zone is used to countercurrently treat the oil stream segregated in the separation zone. By operating in accordance with the present process, unexpectedly desirable results are secured and improved yields of high quality products are secured.

The process of the invention may be readily understood by reference to the accompanying drawing illustrating one modification of the same. Feed gases comprising oxides of carbon and hydrogen are introduced into reaction zone (1) by means of feed line (2). Temperature and pressure conditions are maintained in reaction zone (1) to secure the desired reaction products. For the purpose of illustration it is assumed that the catalyst comprises an iron type catalyst and that the temperature in the reaction zone is maintained in the range from about 550° F. to about 650° F. and that the pressure is maintained in the range from about 200 to about 300 pounds per square inch. After a sufficient time of contact, the reaction gases are removed overhead from reaction zone (1) by means of line (3), passed through condensing zone (4) at approximately 40 to 100° F. and introduced into gas separation zone (5). Uncondensed gases may be withdrawn from the system by means of line (6). However, at least a portion of the uncondensed gases are preferably recycled to reaction zone (1) by means of recycle line (7) and controlled by means of control valve (8).

The condensate is withdrawn from gas separation zone (5) through valve (9) and passed into a liquid separation zone (10) by means of line (11). Segregation between the oil phase and the aqueous phase occurs in liquid separation zone (10). The aqueous phase is withdrawn from the bottom of liquid separation zone (10) by means of line (12) and passed into initial distillation zone (13). Temperature and pressure conditions in initial distillation zone (13) are controlled so as to remove overhead, by means of line (14), an alcohol rich phase boiling below approximately 212° F. This alcohol rich overhead stream is cooled and condensed in condensing zone (15) and passed into separation zone (16). Uncondensed constituents are removed from separation zone (16) by means of line (17) while the condensed stream comprising essentially alcohols is removed from the bottom of separation zone (16) by means of line (18). These streams removed by means of line (17) and (18) may be further treated or handled in any manner desirable in order to segregate fractions of the desired specification.

The bottom stream from initial distillation zone (13) is removed by means of line (19) and introduced into secondary distillation zone (20). Temperature and pressure conditions are maintained in secondary distillation zone (20) so as to remove overhead, by means of line (21), a phase rich in water although containing some oxygenated compounds. The aqueous phase may be withdrawn from the system by means of line (22), but is preferably recycled by means of line (23) and handled in a manner as hereafter described. A stream containing the higher boiling oxygenated compounds is removed as a bottoms from secondary distillation zone (20) by means of line (24) and handled in any manner desirable. This stream may be further treated or distilled in a manner to segregate various fractions having the desired specifications.

In accordance with the preferred modification of the invention, the oil phase segregated in liquid separation zone (10) is removed by means of line (27) and introduced into the bottom of initial countercurrent treating zone (28). The oil phase flows upwardly through zone (28) and is withdrawn by means of line (29) and introduced into the bottom of secondary countercurrent treating zone (30). The oil phase flows upwardly through countercurrent treating zone (30) and countercurrently contacts the downflowing aqueous phase which is secured by condensing at least a portion of the overhead from zone (20) in condensing zone (25). This aqueous condensed phase is introduced into the top of countercurrent treating zone (30) by means of line (26). The treated oil phase is withdrawn by means of line (31) and is substantially completely free of oxygenated compounds. The aqueous phase is withdrawn from the bottom of secondary countercurrent treating zone (30) by means of line (32) and introduced into the top of initial countercurrent treating zone (28). This aqueous phase is withdrawn from the bottom of initial countercurrent treating zone (28) by means of line (33) and recycled to initial distillation zone (13), by combining this stream with the liquid stream passing from liquid separation zone (10) to initial distillation zone (13) by means of line (12).

To recapitulate the invention essentially comprises condensing at approximately 40 to 100° F. the reactant gases removed overhead from the reaction zone and segregating an oil phase and an aqueous phase. The aqueous phase is distilled in a distillation zone to remove overhead a phase comprising essentially alcohols and distilling over at a temperature below approximately 210° F. The bottom stream from the initial distillation zone is then preferably distiled in a manner to remove overhead a stream comprising essentially water, and to segregate a bottom stream comprising essentially higher boiling oxygenated compounds. The overhead stream from the secondary distillation zone is preferably used to countercurrently treat the oil phase and is recycled to the initial distillation zone.

By operating in the described manner, unexpected desirable results are secured. The oxygenated compounds produced during hydrocarbon synthesis are distributed between the oil and water phases in an amount which is a function of the relative volume of product oil and water and the molecular weight and type of the oxygenated compounds produced. The latter factor determines the relative solubility of the oxygenated compounds in the two phases. In normal operations the ratio of water produced to oil produced may vary over the range from about 0.8 to 3.0 volumes of water per volume of oil, depending upon the operating conditions and catalyst employed during the synthesis operation. Accordingly, there is a wide variation in the proportion of the total oxygenated compounds existing in the water phase and this extends over the range from about 35 to 80%. It is obvious, therefore, that under certain conditions treatment of only the water phase for recovery of oxygenated products may result in large losses of these valuable products. Accordingly, it is highly desirable to contact the oil with the water phase after substantially reducing its content of oxygenated product. In order to most effectively transfer the oxygenated products from the oil to the water phase, the operation is carried out countercurrently. As previously pointed out however, water other than that obtained from the bottoms fraction of the distilled aqueous phase can also be used.

Another advantage in removing the oxygenated compounds from the oil phase lies in the subsequent disposition of the oil. Since the oxygenated products in the oil phase are generally of higher molecular weight than those normally present in the water phase, it is obvious that these will be present through the entire boiling range of the gasoline and therefore could not be removed by fractionation. By removing these oxygenated compounds by the technique herein described, subsequent treating by a method such as bauxite treating, in order to make a suitable gasoline, may be eliminated or its severity reduced so that treating losses will be smaller.

Temperatures and pressure conditions of the process are as follows. The temperature in condensing zone (4) is maintained, as previously indicated, in the approximate range of 40 to 100° F., preferably in the range from 50 to 60° F. The preferred pressure in zone (4) will be equal to the operating pressure in the synthesis reactor zone (1). In general, it is preferred that a pressure of about 1 atmosphere be employed in the initial and secondary distillation zones although in certain cases it may be desirable to operate these zones at super-atmospheric pressure, in an amount up to the pressure existing in the synthesis zone (1). The temperature at the top of the initial distillation zone (13) should be below approximately 212° F., temperatures in the range of 208° or 210° F. to 212° F. being preferred. The temperatures at the top of the secondary distillation zone (20) are preferably in the range from 212° F. to 220° F. and desirably in the range from 213° F. to 216° F.

It is preferred that the overhead stream removed from the secondary distillation zone be condensed and cooled to a temperature of approximately 100° F. The amount of aqueous phase used to countercurrently treat the oil streams in the countercurrent treating zones is preferably in the range of 3 volumes to 50 volumes of water per volume of oil being treated. In general, it is desired that these units be run at a temperature in the range from 50° F. to 150° F. and at substantially atmospheric pressure. In order to illustrate the invention the following examples are given:—

EXAMPLE 1.

A sample of oil product was extracted in 10 successive treatments, each treatment consisting of 2 vols. of distilled water per volume of oil. The following data illustrate the extent to which the oxygenated compounds were removed by the batch treatment with water.

EXTRACTION OF OXYGENATED COMPOUNDS FROM OIL PHASE BY MEANS OF H_2O.

Dump #	Total Wash Water Vol./Vol. of Original Oil	Oxygenated Compounds Content of Oil-Wt. %	% Total Oxygenated Compounds Removed	Oxygenated Compounds Removed—cc/m³ of Converted Feed
0	0	3.8%	0	0
1	2.0	2.0	47	5.1
2	3.9	1.5	61	6.8
5	9.6	0.6	84	9.6
10	18.9	0.4	90	11.5

The data show that after 5 dumps 84% of the oxygenated materials originally present in the oil phase had been removed.

The production of oxygenated compounds during the hydrocarbon synthesis operation is affected greatly by both operating conditions and the type of catalyst employed. For example, the hydrogen content of the total feed gas influences the type of oxygenated compounds produced. When using high concentrations of hydrogen the yields of alcohols are increased while at the same time lower yields of aldehydes and ketones are obtained. Likewise, increased operating pressure promotes the formation of oxygenated compounds. Temperature, recycle ratio, conversion and hydrogen to carbon monoxide fresh feed ratio are also factors in determining the yield of oxygenated compounds. As mentioned, these variables affect not only the total yield and type of oxygenated compounds, but also the molecular weight of the oxygenated product and, therefore, the distribution of these compounds between the oil and water phases. In view of the above, it will be appreciated that the following example illustrating the invention merely indicates one possible set of results.

EXAMPLE II.

A hydrocarbon synthesis reaction was conducted at a temperature of 625° F. and at a pressure of 300 pounds per square inch. About 750 volumes of synthesis gas per volume of catalyst per hour was used. The recycle ratio was approximately 2 volumes of recycle gas per volume of fresh feed. The catalyst employed was an iron catalyst promoted with 1½% of potassium carbonate. The overhead reacting gas stream was cooled to a temperature of about 60° F. The yield of hydrocarbons comprising 4 carbon atoms in the molecule and higher boiling constituents, including the oxygenated compounds therein, was 175 cc.'s per cubic meter of hydrogen and carbon monoxide converted. The yield of the aqueous phase was about 235 cc.'s per cubic meter of hydrogen and carbon monoxide converted. The temperature in the initial distillation zone was maintained to remove overhead constituents whose aqueous azeotropes boiled below about 212° F. The overhead stream from the initial distillation zone comprised about 16½ volume per cent. of the aqueous phase and contained oxygenated compounds in about 90% concentration. The oxygenated compounds comprised mainly alcohols having 2, 3, 4 and 5 carbon atoms in the molecule, together with some low boiling aldehydes and ketones. Specific alcohols are, for example, ethyl alcohol, propyl alcohol, butyl alcohol and amyl alcohol. The acids were in the bottoms fraction together with esters and other higher boiling alcohols, aldehydes and ketones. These higher boiling oxygenated compounds in aqueous solution pass to the secondary distillation zone which was maintained at a temperature just sufficient to remove water overhead. It is desirable that both the initial and the secondary distillation zones have an efficiency of about 20 to 40 plates and that the reflux ratio be in the range of about 5 to 10 volumes of reflux per volume of fresh feed.

The oxygen content of the oil initially separated from the water phase contained about 6% by weight of oxygen. This represents about 28 cc.'s per cubic meter of converted hydrogen and carbon monoxide consumed, calculated as 5 carbon atom compounds from the hydroxyl, carbonyl, carboxyl and ester oxygen contents.

In accordance with our process by treating the oil stream with about 8 volumes of water per volume of oil at least 75% of these oxygenated compounds are removed from the oil and their recovery effected. Thus, with an oil yield of 175 cc.'s per cubic meter of hydrogen and carbon monoxide consumed, the quantity of oxygenated product removed from the oil stream is about 21 cc.'s per cubic meter of hydrogen and carbon monoxide consumed. The oxygenated material present in the water layer is about 35 cc.'s per cubic meter of hydrogen and carbon monoxide consumed. Thus, the total production of oxygenated compounds is about 56 cc.'s per cubic meter of hydrogen and carbon monoxide consumed in the synthesis reaction. Thus, by scrubbing the oil phase an increase of 60% in the recovery of oxygenated compounds was secured.

As an illustration of the molecular weight and molecular type of the oxygenated products formed incidental to the hydrocarbon synthesis process, the following detailed analysis of the overhead fraction leaving the initial distillation zone is presented below:

ANALYSIS OF OXYGENATED PRODUCT FROM INITIAL DISTILLATION ZONE.

Type of Compound	Wt. % (Dry Basis)
Acetaldehyde	1.0
Acetone	2.0
Methanol	0.9
Methyl Ethyl Ketone	1.6
Ethanol	37.0
Isopropanol	3.6
n-Propanol	19.2
Sec.-Butanol	1.7
n-Butanol	15.5
Amyl + Higher Alcohols	10.6
Esters	1.0
Acids (Mainly Acetic)	5.0
Unknown	0.9
Total	100.0

It will be noted that ethyl alcohol is the predominant compound in the above group. The presence of alcohols up to and including the amyl alcohols in the overhead fraction from the initial distillation zone operating at 212° F. is the result of their coming over in the form of aqueous azeotropes which boil considerably below the boiling point of the pure compounds.

The oxygenated compounds removed from the second distillation zone are as follows:

ANALYSIS OF OXYGENATED PRODUCT FROM SECONDARY DISTILLATION ZONE.

Type of Oxygenated Compound	Volume % of Total
Alcohols	30%
Acids	20%
Aldehydes & Ketones	45%
Esters	5%

The oxygenated products removed from the secondary distillation zone are much higher boiling than those removed from the initial distillation zone and their boiling range is approximately 220° F. to 500° F.

The process of the invention is not to be limited by any theory as to mode of operation.

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 segregating oxygenated hydrocarbons from the vaporous products obtained by the hydrocarbon synthesis reaction of hydrogen with carbon monoxide, which comprises cooling said vaporous products at a temperature in the approximate range of 40° F. to 100° F. to condense therefrom an oil phase and an aqueous phase, separating from the oil phase the aqueous phase condensate which contains acids, esters, aldehydes, ketones and alcohols dissolved in water produced by the reaction, fractionally distilling from the separated aqueous phase condensate a light distillate fraction of oxygenated hydrocarbons boiling below approximately 212° F. and containing mainly ethyl, propyl, butyl and amyl alcohols with water which distills azeotropically therewith and recovering said light distillate and a bottoms fraction containing acids and residual undistilled water.

2. A process according to Claim 1, wherein said oil phase condensate is contacted with water, desirably in the form of a portion of the bottoms fraction of said distilled aqueous phase, to extract neutral oxygenated hydrocarbons therefrom.

3. A process according to Claim 2, wherein the product containing neutral oxygenated hydrocarbons extracted from the oil phase condensate is separated from the oil phase and admixed with the aqueous phase condensate undergoing distillation.

4. A process according to Claim 1, wherein the bottoms fraction of said distilled aqueous phase is passed to a secondary distillation zone from which a fraction containing higher boiling oxygenated hydrocarbons is recovered, the overhead fraction from said secondary distillation zone being contacted with said oil phase condensate to extract neutral oxygenated hydrocarbons therefrom.

5. A process according to Claim 4, wherein the overhead fraction from said secondary distillation zone containing neutral oxygenated hydrocarbons extracted from the oil phase condensate is separated from the oil phase and admixed with said aqueous phase condensate undergoing initial distillation.

6. A process according to Claim 4 or 5, wherein the secondary distillation zone is operated at substantially atmospheric pressure and the overhead fraction recovered therefrom boils in the range from 212° to 220° F.

7. A process according to any one of the preceding claims, wherein the initial distillation of said aqueous phase condensate is carried out at substantially atmospheric pressure and at a temperature of 208° F. or above.

8. An improved process for the segregation of oxygenated hydrocarbons from the vaporous reaction products obtained by the reaction of hydrogen and carbon monoxide, which comprises condensing said reaction products at temperatures in the approximate range of 40° F. to 100° F., separating an aqueous phase from a non-aqueous phase of the condensate thus formed, distilling said aqueous phase to separate at least two distillate fractions therefrom, the first of said fractions being a light distillate fraction containing neutral oxygenated hydrocarbons including C_2 through C_5 alcohols which distill azeotropically with water at temperatures below approximately 212° F., a second of said fractions being a heavy distillate fraction, rich in water, and containing higher boiling oxygenated hydrocarbons which is further distilled at temperatures between 212° F. and 220° F., to yield a residual fraction containing concentrated free fatty acids boiling above 220° F.

9. A process according to Claim 8, in which a portion of said heavy distillate fraction of the aqueous phase is used to extract oxygenated hydrocarbons from said non-aqueous phase.

Dated this 19th day of May, 1947.

D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2.
Agents for the Applicants.

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