

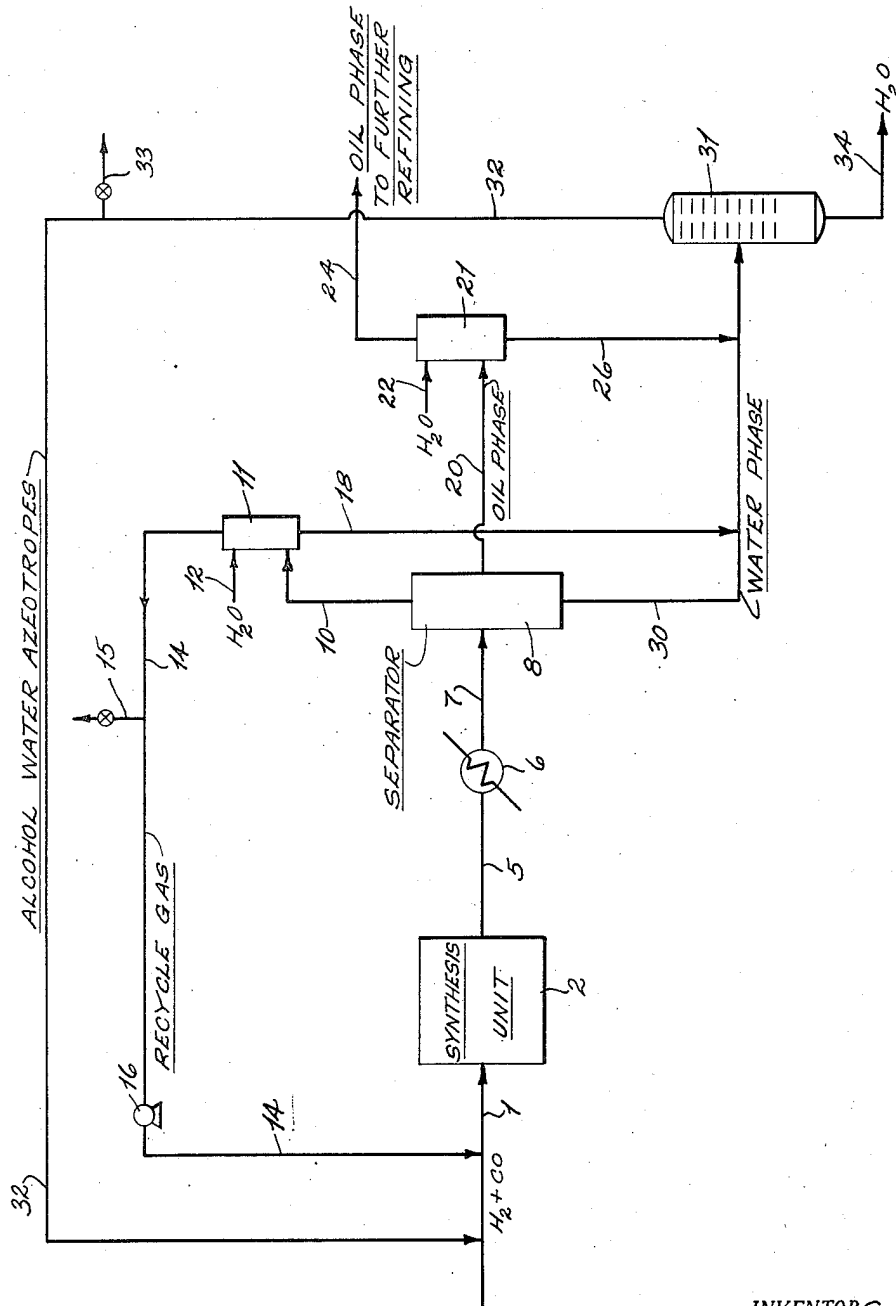
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METHOD OF SYNTHESIZING GASOLINE HYDROCARBONS

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## METHOD OF SYNTHESIZING GASOLINE HYDROCARBONS

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This invention relates to a method of synthesis gas conversion and more particularly to a method for catalytically converting synthesis gas so that a greater portion of the product comprises liquid hydrocarbons.

The present invention is a continuation-in-part of our co-pending application, Serial No. 725,836, filed February 1, 1947, which has issued as U. S. 2,568,841, wherein it is disclosed that the production of oxygenates in synthesis gas conversion is decreased and the yield of liquid hydrocarbons is increased by recycling liquid oxygenates to the reaction zone. The parent application involves the recycle of oxygenates separated from the reaction product to the reaction zone and is particularly concerned with the recycle of a hydrocarbon fraction containing oxygenates distilling below 245° F. to the reaction zone. The subject application is particularly directed to recycling an azeotrope fraction, comprising water and oxygenates and obtained by distillation of the aqueous phase, to the reaction zone. Oxygenate production is suppressed and the yield of liquid hydrocarbons is increased by recycle of an azeotropic distillate fraction to the reaction zone.

In accordance with the process of this invention, an improvement is wrought in the conversion of synthesis gas to liquid hydrocarbons by recycling to the conversion zone a fraction comprising an azeotropic mixture of water and water-soluble oxygenates obtained by distillation of the water phase separated from synthesis product. The recycling of an azeotropic distillate comprising water and water-soluble oxygenates increases the yield of liquid hydrocarbons obtained during conversion and substantially suppresses the formation of water-soluble oxygenates which accompanies the conversion of synthesis gas into liquid hydrocarbons. The distillate fraction recycled to the reaction zone comprises 10 to 40 per cent water and 60 to 90 per cent oxygenates.

Even when the catalytic conversion of carbon monoxide and hydrogen is directed mainly towards the production of liquid hydrocarbons in the gasoline range, the conversion is accompanied by the formation of considerable quantities of oxygen-containing organic compounds. These oxygen-containing organic compounds comprise alcohols, aldehydes, ketones, esters and organic acids, with the alcohols forming by far the greatest portion of the oxygen-containing organic by-products. In a typical synthesis operation directed towards the production of gasoline hydro-

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carbons, the oxygen-containing organic compounds produced may amount to as high as 20 weight per cent of the total organic compounds produced. Ordinarily, oxygenate production is approximately 5 to 20 weight per cent of the organic compounds produced. The lower boiling oxygen-containing organic compounds, such as, ethyl, propyl and butyl alcohols, together with low boiling aldehydes, such as ethanal, propanal and butanal, ordinarily comprise a large proportion of the total oxygenates and are found in the aqueous phase of synthesis product. This invention provides a method of suppressing production of low boiling water-soluble oxygen-containing compounds and effects a corresponding increase in the yield of C<sub>3</sub>+ hydrocarbons.

The oxygenates produced as a by-product of the conversion of synthesis gas to liquid hydrocarbons are valuable chemicals at the present time. The present invention anticipates the day when a plurality of synthesis plants will make by-product oxygenates a glut on the market, and provides a means for increasing the yield of liquid hydrocarbons for which there will always be a demand as fuel. Effecting the conversion in accordance with the process of this invention results in substantially complete suppression of water-soluble oxygenate production and approximately a 10 to 20 per cent increase in the yield of liquid hydrocarbons.

The process of this invention is particularly applicable to the production of synthetic hydrocarbons by the catalytic conversion of a synthesis gas mixture comprising approximately 2 parts of hydrogen and 1 part carbon monoxide by contact with an iron catalyst in a fluidized system at a temperature between 500 and 700° F. and a pressure of 100 to 500 p. s. i. Under these conditions it has been found possible to produce a high yield of liquid hydrocarbons which are highly olefinic in nature and which can be converted into high octane gasoline by a simple treating operation, such as vapor phase bauxite treating. The preferred catalyst for synthesis conversion of this type is an alkali-promoted iron catalyst comprising 90 to 99.5 per cent iron and 0.2 to 2 per cent alkali promoter, such as potassium oxide; small percentages of additives such as alumina or silica may be incorporated in the catalyst. The water phase of synthesis product obtained by conversion under the afore-described conditions contains approximately 20 to 30 grams of water-soluble oxygenates per cubic meter of fresh synthesis gas charged to the reaction zone. Recycle of an azeotropic distillate of water and

oxygenates to the reaction zone substantially suppresses formation of these water-soluble oxygenates and results in approximately a 20 per cent increase in yield of C<sub>3</sub>+ hydrocarbon fraction.

A surprising factor in the use of this invention is that the substantial water content of the recycle azeotrope fraction does not have a deleterious effect on synthesis gas conversions effected with 2 to 1 H<sub>2</sub>-CO synthesis gas mixtures. It had generally been recognized that the addition of water to operations employing 2 to 1 H<sub>2</sub>-CO synthesis gas mixtures is harmful because it causes loss of CO and production of carbon dioxide through the water gas shift reaction. The 10 to 40 weight per cent water content of the azeotropic fraction does not have a harmful effect on conversion with 2 to 1 H<sub>2</sub>-CO synthesis gas. Indeed the substantial increase in the yield of C<sub>3</sub>+ liquid hydrocarbon fraction is indicative of the fact that the loss of carbon monoxide to carbon dioxide is negligible when an aqueous azeotrope fraction is recycled to a conversion employing 2 to 1 synthesis gas.

Recycle of the azeotropic distillate fraction is also advantageous when operating with feed gas of other hydrogen to carbon monoxide ratios and particularly useful in operations employing 1 to 1 H<sub>2</sub> to CO synthesis gas and a fluidized catalyst. The water content of the recycle azeotrope fraction aids in keeping the fluidized catalyst free of carbonaceous and waxy deposits so that it is possible to maintain a fluidized catalyst system with 1 to 1 synthesis gas.

As disclosed in the parent application, the temperature at which synthesis product is separated has a substantial effect on the distribution of the oxygenates between the oil and water phases. When separation of synthesis product is effected at atmospheric conditions, most of the low boiling oxygenates containing 4 or less carbon atoms are present in the aqueous phase and higher boiling oxygenates containing 5 or more carbon atoms are present in the oil phase. However, when separation of synthesis product is effected at an elevated temperature of 200 to 300° F. and at a pressure of 150 to 300 pounds per square inch, a substantial number of low boiling oxygenates are displaced from the aqueous phase to the oil phase. In the practice of this invention, it is usually advantageous to effect separation of synthesis products at atmospheric conditions since thereby a greater percentage of oxygenates are present in the aqueous phase from which they can be separated as an azeotropic distillate which is recycled to the conversion zone.

A portion of the gas phase obtained on separation of synthesis product into gas, water and oil phases is also recycled to the reaction zone so that recycle ratios of 1 to 1 to 3 to 1 recycle gas to fresh feed are maintained. Advantageously, a recycle ratio of approximately 2 to 1 is employed with both 2 to 1 and 1 to 1 synthesis gas mixtures.

The oil phase separated from synthesis product is advantageously fractionated into gasoline and gas oil fractions. The octane rating of the gasoline fraction is substantially enhanced by vapor phase bauxite treating at an elevated temperature of 600 to 800° F.

The water phase is subjected to fractional distillation whereby there is obtained a distillate comprising an azeotropic mixture of water-soluble oxygenates and water. The composition of this mixture is determined by the end point of the distillation. The maximum distillation end point that should be employed in forming the recycle

azeotropic distillate is approximately 205° F. At this maximum end point there is produced an azeotropic distillate comprising approximately 40 per cent water and 60 per cent water-soluble oxygenates. The minimum end point that should be employed in this distillation is approximately 172° F.; distillation to this lower end point produces an azeotropic distillate comprising approximately 5 to 10 per cent water and 90 to 95 per cent water-soluble oxygenates.

It is advantageous to distill the aqueous phase to an end point of 195 to 205° F. because the azeotropic distillate obtained thereby contains a greater percentage of oxygenates and results in proportionately greater suppression of oxygenate production and increase in C<sub>3</sub>+ liquid hydrocarbon yield. Accordingly, the azeotropic distillate recycled to the reaction zone advantageously contains approximately 30 to 40 per cent water and 60 to 70 per cent oxygenates.

In the preferred modification involving recycling a distillate of end point of about 195 to 205° F. to the reaction zone, the recycled distillate contains C<sub>1</sub> through C<sub>4</sub> alcohols, C<sub>2</sub> through C<sub>4</sub> aldehydes, C<sub>3</sub> and C<sub>4</sub> ketones and C<sub>3</sub> to C<sub>4</sub> esters. When the fractional distillation is stopped at a lower end point, for example, at a temperature of about 185° F., the recycle azeotropic distillate contains mainly ethyl alcohol-water and propanol-water azeotropes.

In the accompanying figure there is diagrammatically illustrated the process of this invention.

A synthesis gas mixture advantageously comprising 2 parts of hydrogen and 1 part of carbon monoxide is introduced through a pipe 1 into a synthesis reactor 2 wherein it is converted into a product mixture comprising hydrocarbons, water and oxygenates. As has been indicated previously, the synthesis unit advantageously consists of a reactor adapted for conversion of synthesis gas by contact with an iron catalyst which is maintained in a fluidized state. Temperatures of 500 to 700° F. and pressures between 100 and 500 pounds per square inch are ordinarily maintained in the synthesis reactor 2. There is withdrawn from the reactor 2 through a pipe 5 a product mixture which is cooled in a heat exchanger 6 and is thereafter introduced through a pipe 7 into a separating vessel 8 wherein the product is separated into a gas phase, an oil phase and a water phase. The separator 8 is advantageously maintained at atmospheric temperature and pressure.

There is withdrawn from the upper portion of the separator 8 a gas phase comprising unreacted synthesis gas, carbon dioxide, C<sub>1</sub> and C<sub>2</sub> hydrocarbons and entrained oxygenates. This gas phase is introduced through a pipe 10 into a scrubbing tower 11 wherein it is water-washed to remove entrained oxygenates. Water is introduced to the tower 11 through a pipe 12. Water-washed gas phase is withdrawn from the tower 11 through a pipe 14 through which a portion thereof is recycled to combine with fresh feed so as to maintain a recycle ratio of 2 to 1. The recycle gas is raised to operating pressure in a compressor 16 in the line 14. Provision is made in the recycle line 14 for venting gas through the vent 15.

The water-wash obtained from washing the gas phase is withdrawn from the tower 11 through a pipe 18 and is combined with the water phase separated from synthesis product.

The oil phase containing dissolved oxygenates is withdrawn from the separator 8 through a pipe

20 and is introduced into a scrubbing tower 21 wherein it is scrubbed with water at atmospheric temperature to remove further quantities of water-soluble oxygenates therefrom. Water is introduced into the tower 21 through a pipe 22. The water-washed oil phase is withdrawn from the tower 21 through a pipe 24 through which it is conducted to further treating operations to improve its value as fuel.

The water wash obtained from scrubbing the oil phase is withdrawn from the tower 21 through a pipe 26 and also combines with the water phase separated from synthesis product.

There is withdrawn from the lower portion of the separator 8 through pipe 30 the water phase of synthesis product containing dissolved low boiling oxygenates. This water phase is combined with the water washes obtained from scrubbing the gas phase and the oil phase and is introduced into a fractionating tower 31 wherein it is subjected to fractional distillation. On fractional distillation of this water phase there is obtained a distillate comprising an azeotropic mixture of water-soluble oxygenates and water which is withdrawn from the upper portion of the fractionating tower 31 through a pipe 32 and is recycled therethrough to combine with recycle gas and fresh feed introduced into the synthesis reactor 2. Provision is made for withdrawing portions of this azeotropic distillate as desired through a draw-off pipe 33.

There is withdrawn from the lower portion of the fractionating tower 31 through a pipe 34 a distillation residue which contains approximately one-third of the synthesized water-soluble oxygenates; the oxygenates in the distillation residue are predominantly acids such as acetic and propionic acids. The distillation residue is substantially easier to convert to a rejectable water than is the aqueous phase obtained on initial separation of synthesis product. The fact that the aqueous residue obtained on formation of an azeotropic distillate is more readily converted to a rejectable water is an advantageous feature of the process of this invention. Moreover, a portion of this aqueous residue can be used in scrubbing the gas phase and the oil phase separated from the synthesis products.

The advantages of the process of this invention is suppressing oxygenate yield and increasing the yield of C<sub>3</sub>+ hydrocarbons are well illustrated in the following examples. Example I indicates normal operation wherein 2 to 1 synthesis gas is converted into liquid hydrocarbons by contact with a fluidized iron catalyst; Example II illustrates the results obtained when an oxygenate-water azeotropic fraction obtained by distillation of the aqueous phase is recycled to the reaction zone in accordance with the process of this invention.

#### Example I

A 2 to 1 hydrogen-carbon monoxide mixture is contacted with a fluidized alkali-promoted iron catalyst comprising approximately 100 parts of iron and 0.5 parts of potassium oxide, at a temperature of approximately 650° F. and at a pressure of approximately 200 pounds per square inch. A recycle ratio of recycle gas to fresh feed of approximately 2:1 is maintained during the conversion. The fresh feed is introduced into the reactor at a gravelocity of approximately 40 (standard cubic feet of reactants per pound of catalyst per hour). On separation of synthesis product at atmospheric conditions, 120 g. of C<sub>3</sub>+ hydrocarbons containing approximately 15 per

cent oxygenates and 230 g. of water containing approximately 13 per cent oxygenates are obtained per cubic meter of fresh feed charged. The production of water-soluble oxygenates amounts to approximately 29 g. per cubic meter of fresh feed.

#### Example II

Production of liquid hydrocarbons from synthesis gas is effected under the conditions set forth in Example I with the exception that an oxygenate-water azeotrope fraction obtained by distillation of the aqueous phase is recycled to the reaction zone. The aqueous phase is subjected to fractional distillation to a temperature of 203° F. whereby there is produced an oxygenate-water azeotrope fraction comprising approximately 63 per cent oxygenates and 37 per cent water. The total azeotrope fraction obtained in this manner is recycled to the reaction zone. Approximately 22 g. of oxygenates per cubic meter of fresh charge gas are recycled to the reaction zone in the oxygenate-water azeotrope fraction obtained as described above. The remaining oxygenate content of the water phase remains in the distillation residue obtained on fractional distillation to produce the oxygenate-water azeotrope fraction. After equilibrium is obtained, the yield of C<sub>3</sub>+ hydrocarbons amounts to approximately 140 g. per cubic meter of charged gas, an increase of approximately 20 g. Production of water-soluble oxygenates remains at approximately 29 g. per cubic meter of fresh charge gas indicating that recycle of the azeotropic fraction has resulted in substantially complete suppression of formation of water-soluble oxygenates. The yield of water on an oxygenate-free basis obtained is approximately 248 g. per cubic meter of synthesis gas charged; this increase is slightly greater than the amount of water charged in the recycle azeotropic fraction. It is also significant that there is no increase in production of higher molecular weight oxygenates which are soluble in the oil phase under the conditions of reaction. The distribution of the oxygenates among alcohols, acids and esters is substantially unchanged as the hydroxyl, saponification, and neutralization numbers of the oil phase oxygenates remain approximately constant.

The substantially complete suppression of water-soluble oxygenate production and the corresponding increase in C<sub>3</sub>+ hydrocarbons as a result of recycling the azeotropic fraction are apparent from the preceding examples. These effects of the recycle of an azeotropic distillate fraction comprising water and water-soluble oxygenates to the reaction zone make this invention of paramount importance in the future development of synthesis gasoline plants.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the catalytic conversion of carbon monoxide and hydrogen to produce liquid hydrocarbons, a process which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone to form a product mixture comprising mainly hydrocarbons, water and oxygenates, separating said product mixture at atmospheric temperature and pressure into a gas phase, a hydrocarbon phase and a water phase containing most of the low boiling oxygenates having four

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or less carbon atoms per molecule, directly subjecting said water phase to distillation to obtain an aqueous azeotropic distillate having an end boiling point not less than about 172° F. and not greater than about 205° F. and comprising 60-90 per cent water soluble oxygenates and 10-40 per cent water, and recycling at least a portion of said aqueous distillate to said conversion zone whereby production of water-soluble oxygenates is suppressed and yield of C<sub>3</sub>+ hydrocarbons is increased.

2. A process according to claim 1 in which carbon monoxide and hydrogen are reacted at a temperature of 500 to 700° F. and at a pressure of 200 to 400 pounds per square inch in the presence of an iron catalyst to produce the product mixture.

3. A process according to claim 1 in which a 2 to 1 hydrogen-carbon monoxide mixture is employed.

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4. A process according to claim 1 in which the aqueous distillate comprises 30 to 40 per cent water and 60 to 70 per cent oxygenates.

5. A process according to claim 1 in which a 1 to 1 hydrogen-carbon monoxide mixture is employed.

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