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(12) **Patent:**

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(54) PRODUCTION OF HYDROCARBONS AND OXYGENATED COMPOUNDS

(54) PRODUCTION D'HYDROCARBURES ET DE COMPOSES OXYGENES

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*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This invention relates to the production of hydrocarbons and oxygenated compounds from carbon monoxide and hydrogen.

In accordance with the invention a synthesis gas containing carbon monoxide and hydrogen is reacted to produce a synthesis product mixture containing hydrocarbons, water and oxygenated compounds, the hydrocarbons and oxygenated compounds usually comprising compounds ranging from 1 to about 20 carbon atoms per molecule. The synthesis reaction is advantageously carried out with a synthesis catalyst of the iron type at a temperature in the range of about 500-700°F. and under super atmospheric pressure, for example, about 150-250 pounds per square inch gauge. Under these conditions, the synthesis product mixture may comprise about two liquid volumes of water and one volume of liquid organic compounds. The oxygenated organic compounds may amount to from 5 to 20 volume per cent of the total normally liquid synthesis product.

The synthesis mixture is partially cooled, preferably to about 200-300°F. without substantial reduction in pressure, so that two liquid phases form. One phase comprises a hydrocarbon-rich phase containing substantially all of the aliphatic alcohols of more than 2 carbon atoms per molecule, and a large proportion of the ethyl alcohol. The other liquid phase comprises a water-rich phase containing the remainder of the ethyl alcohol. Small amounts of ketones and aldehydes may be present in both phases, while the bulk of the acids will be present in the water phase.

A gas phase comprising unreacted carbon monoxide and hydrogen, carbon dioxide, and low boiling organic compounds, such as methane and acetaldehyde, may be separated from the synthesis mixture. Unreacted carbon monoxide and hydrogen as well as carbon dioxide may be removed from the gas phase and recycled to the synthesis reaction.

The aforementioned hydrocarbon-rich phase is subjected to solvent extraction with a water soluble solvent liquid, such as ethylene glycol, having substantially complete solvent action upon the alcohols and being substantially immiscible with hydrocarbons at ordinary temperatures, for example, in the range 70-150°F. As a result of the extraction, there is obtained a second hydrocarbon-rich phase consisting essentially of hydrocarbons, and a solvent-rich phase consisting essentially of alcohols dissolved in the solvent. These phases are separately removed for further treatment.

The second hydrocarbon-rich phase, with or without washing to remove traces of the solvent, can be subjected to contact with a catalyst such as bauxite, alumina, Fuller's earth, or other alumina or silica adsorptive materials at a temperature in the range of 700-900°F. so as to effect mainly isomerization of olefinic constituents of the hydrocarbon mixture and removal of impurities.

Preferably these hydrocarbons are fractionated to form a naphtha fraction and a diesel oil fraction. The naphtha fraction is then subjected to the catalytic treatment.

The solvent-rich phase is subjected to fractional distillation and other operations as will be described so as to effect separation of alcohols from the solvent, the latter being recycled to the extraction step.

The water phase initially separated from the synthesis water mixture containing the minor proportion of the total ethyl alcohol produced is advantageously subjected to distillation to recover the alcohol from the main body of water.

We have found that by effecting the initial separation of a water phase from the synthesis effluent at a temperature in the range of about 200-300°F. and without substantial reduction in pressure substantially all of the alcohols, and particularly the C_3 and higher, remain in the hydrocarbon phase and only a small amount, mainly ethyl alcohol, remains in the water phase. Thus, the water phase separated at a temperature of 200°F. contains of the order of 1.0-2.0% oxygenated compounds whereas that separated at room temperature contains at least about 6.8%. The water phase separated at temperatures above 200°F. contains still less of these oxygenated materials.

In order to describe the operation in more detail, reference will now be made to the accompanying drawing.

As indicated in the drawing, carbon monoxide and hydrogen usually in the proportion of about 2 mols of hydrogen to 1 mol of carbon monoxide are obtained from a source not shown and passed through a conduit 1 to a conventional synthesis unit 2. In the synthesis unit the reactants may be subjected to contact with a synthesis catalyst in the form of a fluidized mass of solid particles or powder. Preferably, the catalyst comprises iron, although other synthesis catalysts comprising cobalt or nickel may be used.

The synthesis reaction with an iron catalyst is usually carried out at a temperature of about 500-650°F. and under a pressure of about 200 pounds. An effective iron catalyst contains about 2-3% alumina and about 0.1-3% alkali metal expressed as potassium oxide.

An effluent stream of synthesis reaction mixture is continuously passed through a conduit 3 and a cooler 4 to a separator 5. The effluent stream is advantageously reduced to a temperature of about 200°F. without substantial reduction in pressure. In the separator, three phases form: (1) a gas phase comprising unreacted gas, carbon dioxide, and normally gaseous hydrocarbons such as methane, ethane, propane, butane, etc.; (2) a hydrocarbon-rich phase containing aliphatic alcohols containing 2 or more carbon atoms per molecule, and substantially free from fatty acids; and (3) a water-rich phase comprising water, a small amount of ethyl alcohol, and small amounts of fatty acids, etc. The synthesis product is substantially free from methyl alcohol.

These phases are separately withdrawn from the separator 5. As previously indicated, the gas phase may be treated to remove carbon monoxide, hydrogen and carbon dioxide for recycling to the synthesis unit 2.

The hydrocarbon phase containing about 70-90% of the oxygenated compounds, is drawn off through a pipe 7, cooled as desired and passed to an extraction unit 8 which advantageously comprises a vertical packed tower.

In the extraction unit 8 the hydrocarbon-rich phase is subjected to countercurrent contact with a stream of solvent liquid such as ethylene glycol at a temperature of about 70-100°F. and in the proportions of about one half to four volumes of solvent per volume of hydrocarbon phase.

A raffinate phase or insoluble phase consisting essentially of hydrocarbons retaining a small amount of solvent and alcohols is continuously drawn off through a pipe 10 and conducted to a wash tower 11 wherein the hydrocarbons are subjected to countercurrent washing with a stream of water introduced through a pipe 12 in the proportion of about 0.1

volume of water to 1.0 volume of hydrocarbons at atmospheric temperature. This washing effects substantially complete removal of residual solvent.

The washed hydrocarbons are passed through a pipe 13 to a fractionating tower 14 from which is produced a naphtha fraction and a diesel oil fraction. The latter is discharged through a pipe 15 while the naphtha fraction is passed to an isomerizing unit 16 wherein it is subjected to intimate contact with a solid finely-divided catalyst, such as alumina or bauxite at a temperature of about 800°F. so as to effect isomerization of olefinic constituents of the hydrocarbon feed thereby effecting octane improvement. If desired, the total hydrocarbon product from 11 may be passed through branch pipe 13a to unit 16 wherein it can undergo conversion into valuable gasoline hydrocarbons.

Removal of oxygenated compounds from the naphtha prior to treatment of the naphtha with bauxite results in some improvement in the yield without any loss in octane improvement.

The used wash water is continuously drawn off from the tower 11 through a pipe 17 leading to a still or evaporator 18 wherein water is distilled from the wash mixture to form a concentrate of solvent and alcohols. This concentrate is drawn off through a pipe 19 and may be recycled through pipe 20 to the top of the extraction tower 8.

The solvent or extract phase obtained in the extraction unit is continuously drawn off through a pipe 21 to a still or evaporator 22. This phase contains aliphatic alcohols ranging from 2 up through 8 to 12 or more carbon atoms per molecule.

In this still the alcohols more volatile than the solvent, and any water present, are removed as a distillate.

These alcohols comprise normal primary alcohols having from 2 to 7 carbon atoms per molecule.

The residual liquid drawn off from still 22 through pipe 23 comprises solvent and alcohols having about the same boiling temperature as the solvent as well as alcohols of even higher boiling range.

This residual stream may be passed through a pipe 24 into which water is introduced through a pipe 25.

The water is added in sufficient amount at atmospheric temperature so that upon introduction of the diluted mixture into a separator 26, dissolved alcohols are separated from the solvent, these alcohols comprising those having 8 or more carbon atoms per molecule as well as some C_7 alcohols.

The alcohols are withdrawn as indicated through a pipe 27 while the residual water and solvent, which may retain a small amount of alcohols, is advantageously passed through a pipe 28 to the previously mentioned separator 18.

A preferred method of treating the residual liquid from the still 22 is to pass it through a pipe 29 to a distilling column 30 wherein it is subjected to azeotropic distillation with the aid of steam introduced to the lower portion of the column through a pipe 31. As a result of this distillation there is obtained a distillate containing C_8 and higher alcohols in the form of azeotropes with water, which distillate is drawn off through a pipe 32, cooler 33 and passed to a separator 34 maintained at about atmospheric temperature. The distillate separates into two phases in the separator 34, namely, a phase comprising substantially anhydrous C_8 and higher alcohols, and an aqueous phase comprising mainly water containing a small amount of alcohol. The alcohols are discharged through a pipe 35, and the aqueous phase is discharged through pipe 36. The discharged aqueous phase is conducted through a heat exchanger 37 and from there passed to the lower portion of the column 30.

Solvent from which the alcohols have been distilled is drawn off through the bottom of the column 30 through a pipe 38 and recycled to the extractor 8.

The water phase initially separated from the synthesis product containing less than about 2% oxygenated compounds is drawn off through a pipe 40 at a temperature of about 200°F. to a still 41 wherein the pressure is reduced to atmospheric so that ethyl alcohol azeotrope is removed as distillate through a pipe 42 leaving a residual body of water which is discharged through pipe 43. By the aforesaid reduction in pressure advantage is taken of the sensible heat of the liquid flowing through pipe 40 to effect the distillation.

The alcohol distillate can be passed all or in part through the pipe 44 to the effluent from still 22 or may be discharged through pipe 45.

It is contemplated that the foregoing extractions and separations may be effected under super-atmospheric pressure, that is, at a pressure not substantially lower than that prevailing within the synthesis unit 2. If desired, the pressure can be reduced progressively in successive stages to avoid pumping.

Instead of ethylene glycol it is contemplated that other solvents which dissolve a substantial amount of water at atmospheric temperature may be employed for effecting liquid-liquid extraction of oxygenated compounds from the hydrocarbons, such other solvents including polyhydric alcohols, such as glycols and glycerols; ketones; aldehydes; acids such as levulinic; amines such as ethanolamines and ethylene diamine.

The synthesis reaction is advantageously effected with a fluidized mass of synthesis catalyst in solid particle form, although the catalyst may be used in the form of a stationary bed, or a moving bed, or a suspension in the reactants. While specific temperatures and pressures have been referred to, it is contemplated that these will vary depending on the catalyst used as well as upon the particular products desired. For example the synthesis temperatures may range from 300-700°F. and the pressure from atmospheric to several hundred pounds or more.

Obviously many modifications and variations of the invention as above 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.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the catalytic conversion of carbon monoxide and hydrogen into a product mixture comprising normally liquid hydrocarbons, water and oxygen-containing organic compounds including a mixture of aliphatic alcohols having from 2 to 20 carbon atoms per molecule, the improvement which comprises separating said product mixture into a liquid hydrocarbon-rich phase and a water-rich phase at an elevated temperature over 200°F. and at superatmospheric pressure sufficient to maintain said hydrocarbon-rich and said water-rich phases substantially in the liquid phase whereby normally water-soluble alcohols are concentrated in the hydrocarbon phase.

2. In the catalytic conversion of carbon monoxide and hydrogen into a product mixture comprising normally liquid hydrocarbons, water and oxygen-containing organic compounds including a mixture of aliphatic alcohols having from 2 to 20 carbon atoms per molecule, the improvement which comprises separating said product mixture into a liquid hydrocarbon-rich phase and a water-rich phase at an elevated temperature over 200°F. and at a pressure over about 100 pounds per square inch whereby normally water-soluble alcohols are concentrated in the hydrocarbon phase.

3. The method according to Claim 2 in which the separation is effected at a temperature of about 200 to 300°F. and at a pressure of 150 to 300 pounds per square inch.

4. In the catalytic conversion of carbon monoxide and hydrogen into a product mixture comprising normally liquid hydrocarbons, water and oxygen-containing organic compounds

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including a mixture of aliphatic alcohols having from 2 to 20 carbon atoms per molecule, the improvement which comprises separating said product mixture into a liquid hydrocarbon-rich phase and a water-rich phase at an elevated temperature over 200°F. and at a pressure of at least 100 pounds per square inch whereby substantially all of the C_3 and higher alcohols and a substantial portion of the C_2 alcohols are concentrated in the hydrocarbon phase and separately removing alcohols from said hydrocarbon and aqueous phases.

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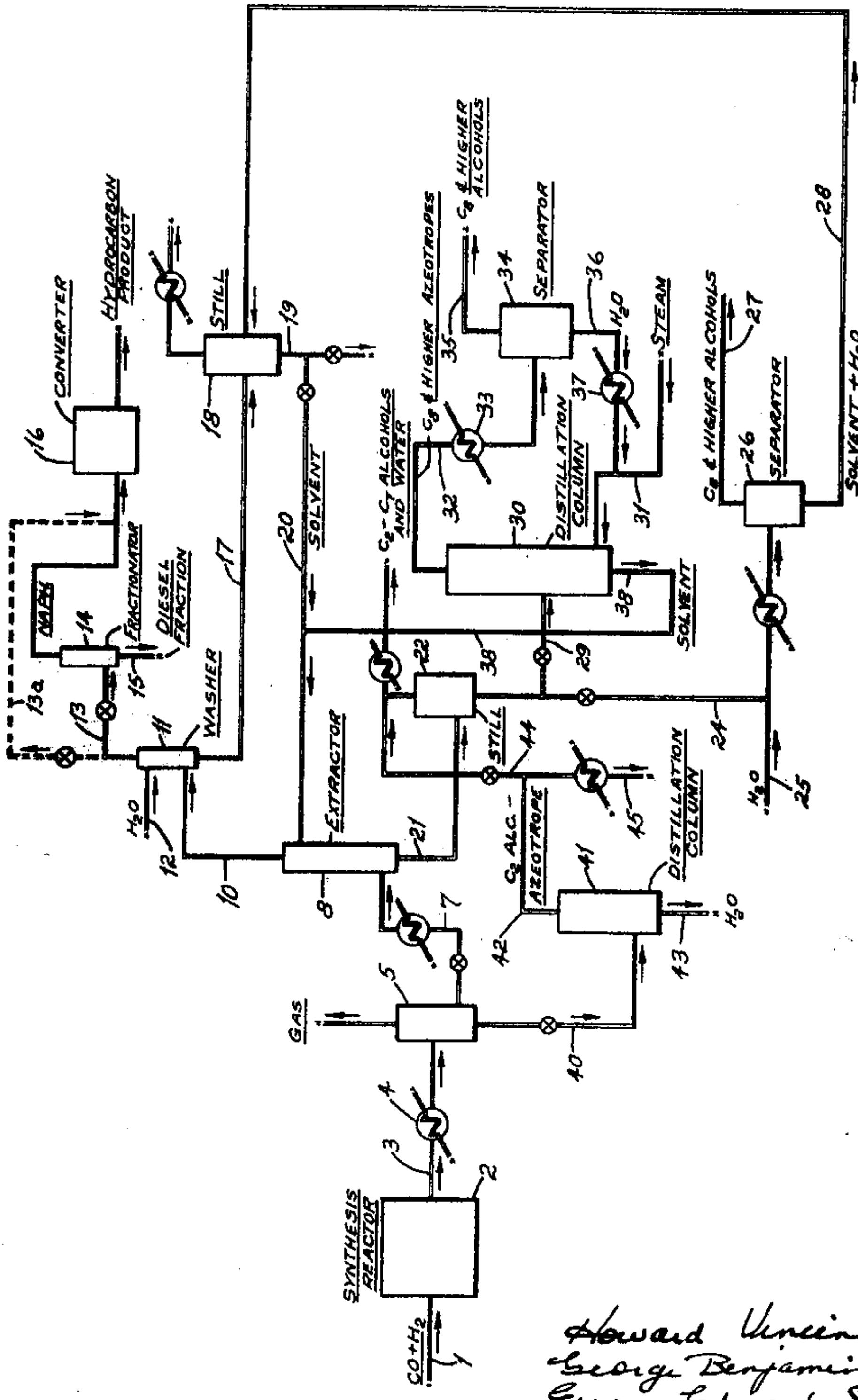

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Certified to be the drawings referred to in the specification hereunto annexed.

Ottawa, Canada, May 7th, 1947.

By
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