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(54) METHOD OF SYNTHESIZING GASOLINE HYDROCARBONS

(54) METHODE DE SYNTHETISER DES HYDROCARBURES DE GASOLINE

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This invention relates to a method of synthesis gas conversion and more particularly to a method of catalytically converting synthesis gas in the presence of added aliphatic oxygen-containing organic compounds so that a greater portion of the product comprises liquid hydrocarbons in the gasoline boiling range.

In accordance with a preferred modification of the invention, synthesis gas comprising carbon monoxide and hydrogen is catalytically converted in a reaction zone to a product mixture comprising hydrocarbons, oxygen-containing compounds and water, which mixture is separated into a gas phase, a liquid hydrocarbon phase and a water phase, which latter two phases contain dissolved therein substantial quantities of oxygen-containing compounds. The gas phase containing normally gaseous products of conversion and unreacted carbon monoxide and hydrogen is recycled at least in part to said reaction zone. The aqueous phase containing dissolved therein mainly low molecular weight oxygen-containing compounds is subjected at elevated temperature and pressure to extraction with a hydrocarbon solvent so as to form a hydrocarbon-rich extract phase containing most of the non-acidic oxygen-containing compounds and a water-rich phase containing low molecular weight organic acids. The hydrocarbon-rich extract phase is combined with the liquid hydrocarbon phase which is initially separated from the products of conversion and which, in general, contains oxygen-containing compounds of higher molecular weight than the aqueous phase. Thereafter the combined phases are fractionated into two components, namely a low boiling fraction distilling below about 200 to 245°F. and a high boiling

fraction distilling above the specified temperature. A substantial portion of the low boiling fraction is recycled to the reaction zone so as to effect conversion of the low boiling oxygen-containing compounds contained therein to liquid hydrocarbons in the gasoline range.

The portion of the low boiling fraction which is not recycled to the synthesis unit is combined with the high boiling fraction and the composite is subjected to extraction with a hydrocarbon-immiscible solvent so as to extract oxygen-containing compounds from the hydrocarbon solution. As a result of the extraction, there are formed a hydrocarbon raffinate which is substantially free from oxygen-containing compounds and a solvent-rich extract phase containing extracted oxygen-containing compounds. The hydrocarbon raffinate is then subjected to such further treatment as will improve its quality in its intended use. Oxygen-containing compounds are separated from the extract phase.

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 hydrocarbons, the oxygen-containing organic compounds produced may amount to as much as 20 weight per cent of the total 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 oxygen-containing compounds produced. This invention provides a method of converting such low boiling oxygen-containing compounds, which are not as valuable economically as the higher boiling oxygen-containing compounds, into liquid hydrocarbons boiling in the gasoline range or higher boiling oxygen-containing compounds.

When the product of synthesis gas conversion is separated into a gas phase, a liquid hydrocarbons phase and an aqueous phase at atmospheric conditions, most of the low boiling oxygen-containing compounds, that is, compounds containing 4 or less carbon atoms, are present in the aqueous phase. This invention provides a method of transferring these low boiling oxygen-containing compounds to the hydrocarbon phase whence they may be recycled, together with a low boiling hydrocarbon fraction, to the synthesis unit.

The recycling of a part of the hydrocarbon fraction of the products which boils below about 200 to 245°F. and which contains substantially all of the non-acidic low boiling oxygen-containing compounds produced in the conversion, has a two-fold beneficial effect in increasing the yield of gasoline hydrocarbons produced by the synthesis reaction: first, the low boiling oxygen-containing compounds which comprise the alcohols produced in the conversion up to and including butyl alcohol, aldehydes up to and including pentanal and ketones up to and including methyl propyl ketone are converted into gasoline hydrocarbons; further, low boiling olefins such as propylenes, butylenes and amylenes which are present both in the recycle gas phase separated from the

products and in the recycle portion of the low boiling hydrocarbon fraction, are converted into compounds of higher molecular weight in the synthesis zone so that a higher ultimate yield of product boiling in the gasoline range is obtained. A further advantage resides in the fact that the presence of liquid hydrocarbons boiling up to about 245°F. absorbs a considerable portion of the liberated exothermic heat of reaction, thereby minimizing the problem of temperature control in the catalytic conversion of carbon monoxide and hydrogen. The method of the invention has an additional advantage when a fluid dense phase type of catalytic conversion is employed; the presence of a substantial quantity of recycle hydrocarbons can be used to offset at least to some extent the volume decrease accompanying the conversion of carbon monoxide and hydrogen into liquid hydrocarbons and the like.

In continuous operation, the product of synthesis gas conversion is initially separated into a gas phase, an aqueous phase and a liquid hydrocarbon phase at elevated temperature and pressure. The separation of the product into these phases at elevated temperature and pressure reduces the heat requirements of the process since it is not necessary to reheat the aqueous phase prior to extraction with a hydrocarbon solvent. Moreover, initial separation of the product at a temperature of about 200 to 300°F. and at a pressure of about 150 to 300 pounds per square inch displaces a portion of the lower boiling oxygen-containing compounds from the aqueous phase to the hydrocarbon phase, thus minimizing the burden in the solvent extraction of the

aqueous phase so that smaller solvent dosages and a smaller extraction tower may be employed.

In order that the invention may be more adequately described, reference will now be made to the accompanying Figure I in which a preferred modification of the process of the invention is presented in detail.

Carbon monoxide and hydrogen in a molecular ratio which is usually about 2 mols of hydrogen to 1 mol of carbon monoxide are obtained from a source not shown and introduced into a synthesis unit 2 through a pipe 1. In the synthesis unit 2, the reactants may be subjected to contact with a synthesis catalyst in the form of a fluidized mass of solid particles or powder. A catalyst having iron as its main constituent is advantageously used to effect this conversion although other synthesis catalysts containing cobalt or nickel may be employed. The synthesis catalyst may also comprise alkali metal compounds and the oxides of metals such as thorium, magnesium, aluminum, uranium and vanadium.

A catalyst having a composition of about 93-98 per cent iron, about 2-7 per cent alumina and about 0.1 to 3 per cent alkali expressed as potassium oxide has been found to be particularly effective for the conversion. The synthesis reaction with such a catalyst is usually carried out at a temperature of about 500 to 700°F. and under a pressure of about 150 to 300 pounds per square inch in order to yield liquid hydrocarbons boiling in the gasoline range as the primary product of conversion.

An effluent stream comprising the products of synthesis reaction and unreacted carbon monoxide and hydrogen leaves the synthesis unit 2 through a pipe 3 and is cooled

to a temperature of about 175 to 300°F. and preferably to about 200 to 225°F. in an exchanger 4. As has been indicated previously, the effluent may be cooled to about atmospheric temperature at this point but this not only places an added burden on the extraction of the aqueous phase, but also necessitates the reheating of the aqueous phase prior to its extraction with a liquid hydrocarbon fraction.

The total product is introduced through a pipe 5 into a separator 6 wherein the aqueous phase is separated from both the normally liquid hydrocarbon phase and the normally gaseous products of conversion. The separator 6 is maintained, for example, at a temperature of about 200°F. and at a pressure of about 150 to 300 pounds per square inch. The aqueous phase is withdrawn from the separator 6 through a conduit 7. Both the gas phase and the liquid hydrocarbon phase are removed from the upper portion of the separator 6 through a pipe 9 and are cooled to approximately atmospheric conditions in the exchanger 10 prior to introduction into a secondary separator 11 which is maintained at about atmospheric conditions of temperature and pressure. In the separator 11, the liquid hydrocarbon phase is separated from the gas phase. The liquid hydrocarbon phase is withdrawn from the separator 11 through a pipe 12 and its further treatment will be described more in detail later. The gas phase, containing unreacted synthesis gas and normally gaseous products of conversion, such as ethane, methane, carbon dioxide, etc., leave the separator 11 through a pipe 14. Some additional aqueous phase separates in a secondary atmospheric separator 11 and is withdrawn therefrom through a pipe 13.

The gas phase withdrawn from the separator 11 is recycled at least in part to the synthesis unit 2. The portion of the gas phase which is to be recycled proceeds along the pipe 14 and combines with the fresh feed to the synthesis unit 2 in the pipe 1. There may be employed recycle ratios of 0.25 to 4 wherein recycle ratio is expressed as moles of recycle gas per moles of fresh feed. A vent 15 serves as a means of withdrawing the non-recycled portion of the gas phase which portion may be treated so as to recover valuable constituents such as butanes therefrom.

The additional water phase which separates in the separator 11 flows through the pipe 13 into the conduit 7 wherein it combines with the aqueous phase initially separated from the products of conversion. Combined aqueous phases are then introduced into a primary extraction tower 20 which is maintained at a temperature of about 200°F. and at a pressure of about 200 to 250 pounds per square inch.

In the extraction tower 20, combined aqueous phases are subjected to countercurrent extraction with a hydrocarbon solvent such as naptha which is introduced therein through a pipe 22. Under the specified conditions of temperature and pressure prevailing within the extraction tower, the bulk of the non-acidic oxygen-containing organic compounds is substantially extracted from the water phase. As a result of the countercurrent extraction in the tower 20, there are formed a hydrocarbon-rich extract phase containing non-acidic oxygen-containing organic compounds and a water-rich phase containing low molecular weight organic acids.

The water-rich phase containing low molecular weight organic acids is withdrawn from the extraction tower 20

through a pipe 23 and the residual low boiling non-acidic oxygen-containing compounds which are predominantly ethyl alcohol may be removed as aqueous azeotropes by flashing in a flash tower 24. The aqueous azeotropes comprising mainly ethyl alcohol-water azeotrope which has a composition of about 95.5% alcohol and 4.5% water is recycled through a pipe 26 to the synthesis unit for conversion to hydrocarbons in the gasoline range.

Thereafter, the water-rich phase can be introduced through a pipe 25 into a fractionating tower, not shown, in which the water may be distilled from the organic acids by azeotropic distillation with a hydrocarbon fraction. The organic acids may then be separated into individual components by fractionation.

The hydrocarbon-rich extract phase containing extracted non-acidic oxygen-containing organic compounds leaves the extraction tower 20 through a pipe 27. This extract phase proceeds along the pipe 27 and combines in the pipe 12 with the hydrocarbon phase initially separated from the products of conversion. The combined mixture containing substantially all of the non-acidic oxygen-containing compounds produced in the conversion which includes aldehydes, ketones, alcohols and esters is introduced into a fractionating tower 28.

In the fractionating tower 28, the mixture of hydrocarbons and oxygen-containing compounds is divided into two fractions: a low boiling fraction distilling below a temperature which lies in the range of about 200 to 245°F. is taken off overhead through a pipe 29; the residual fraction, containing all the products of conversion distilling above the chosen temperature of division, is withdrawn from the lower portion of the fractionating tower 28 through a

pipe 30. If 245°F. is chosen as the temperature at which the mixture is split into fractions, the overhead fraction will contain hydrocarbons containing up to and including about 8 carbon atoms per molecule, alcohols up to and including butyl alcohol, aldehydes up to and including pentanal and ketones up to and including methyl propyl ketone.

The low boiling fraction which leaves the fractionating tower 28 through the pipe 29 is divided into two portions. The major portion is passed along the pipe 31 through which it is recycled to the synthesis unit 2. This major portion of the low boiling fraction of the products of conversion flows through the pipe 31 into the pipe 14 through which gaseous products of conversion are recycled to the synthesis unit 2. In the method of the invention, therefore, the total feed to the synthesis unit 2 comprises fresh synthesis gas, normally gaseous products of conversion comprising carbon dioxide, methane, ethane, etc., and the major portion of the hydrocarbons and oxygen-containing hydrocarbons distilling below about 200 to 245°F.

As has been indicated, the paramount beneficial effect accompanying the recycle of hydrocarbons and oxygen-containing products distilling below 200 to 245°F. is realized in the improved yield of liquid hydrocarbons distilling within the gasoline range thereby obtained. This invention provides a simple expedient of converting such oxygen-containing compounds to high-grade fuel. The yield of gasoline hydrocarbons may be increased as much as 10 per cent when low boiling hydrocarbons and oxygen-containing compounds are recycled to the synthesis unit as described in this invention; such an improvement is significant in a commercial unit

making about 5,000 barrels per day of gasoline hydrocarbons.

The minor portion of the low boiling hydrocarbon and oxygen-containing products of conversion is diverted from the pipe 29 through a pipe 34 and combines with the high boiling residual hydrocarbon and oxygen-containing products which were withdrawn from the fractionating tower 28 through a pipe 30 and thereafter cooled in the exchanger 35. The combined hydrocarbon phases are introduced through a pipe 36 into a secondary extraction tower 37 which is advantageously packed with contact material. Therein the combined hydrocarbon phases containing a minor portion of the oxygen-containing products of conversion distilling below 200 to 245°F. and substantially all of the oxygen-containing compounds distilling above 245°F. are subjected to extraction with a solvent for the oxygen-containing compounds which is immiscible with hydrocarbons under operating conditions which are usually atmospheric. A solvent such as ethylene glycol is introduced into the extraction tower 37 through a pipe 38 and therein is contacted countercurrently with the hydrocarbon solution of oxygen-containing compounds flowing upwardly therethrough. As a result of the secondary extraction, there are formed a hydrocarbon-rich raffinate which is substantially free from alcohols, aldehydes and ketones and a solvent-rich extract phase containing most of the unrecycled alcohols, aldehydes and ketones produced in the process, together with some of the ester products.

Ethylene glycol has proven to be an excellent solvent for effecting the extraction of aldehydes, ketones and alcohols from the hydrocarbon solution. However, it is

contemplated that other hydrocarbon-immiscible solvents such as polyolefin glycols, aldehydes such as furfural, ketones such as acetone and nitro hydrocarbons such as nitromethane may be employed for the solvent extraction of alcohols, aldehydes and ketones from the hydrocarbon solution. In further description of the invention, it will be assumed that ethylene glycol has been used to effect the extraction of the oxygen-containing compounds from the hydrocarbon phase.

The hydrocarbon-rich raffinate is withdrawn from the upper portion of the extraction tower 37 through a pipe 40 and is thereafter water-washed in a wash tower 41 for the removal of any residual glycols dissolved therein. To this end, water is introduced into the wash tower 41 through a pipe 42 in the ratio of about one volume of water to 10 volumes of hydrocarbon. The washed hydrocarbons are withdrawn from the upper portion of the wash tower 41 through a pipe 43. A portion of this hydrocarbon fraction, which is substantially free from oxygen-containing compounds, can be used to effect the extraction of non-acidic oxygen-containing compounds from the water phase in the primary extraction tower 20. Accordingly a portion of the washed hydrocarbon solution is diverted from the pipe 43 through a pipe 44 which latter pipe communicates with pump 45 and exchanger 46 wherein the hydrocarbon fraction is raised to a pressure of about 200 pounds per square inch and a temperature of about 200°F. The pipe 44 communicates with the pipe 22 and from there flows into the primary extraction tower 20.

The remainder of the washed hydrocarbons obtained from the wash tower 41 pass through a pipe 47 to a fractionating tower 48 wherein it is separated into a gasoline frac-

tion and a diesel fraction. The gasoline fraction is taken off overhead from the fractionating tower 48 through a pipe 49 and thereafter may be subjected to treatment with a material such as bauxite for the improvement of its octane rating. The diesel fraction is obtained from the fractionating tower 48 through a pipe 50 and may undergo treatment such as contacting with silica gel which will remove any residual high molecular weight oxygen-containing compounds still present therein. The diesel fraction may also be catalytically or thermally cracked to yield more gasoline hydrocarbons. The high boiling residuum is withdrawn from the fractionating tower 48 through a pipe 51.

Solvent-rich extract phase containing dissolved therein mainly alcohols, aldehydes and ketones is withdrawn from the lower section of the secondary extraction tower 37 through a pipe 55 and is introduced into a fractionating tower 56. Therein alcohols up to and including C_7 alcohols, aldehydes and ketones distilling below the boiling point of ethylene glycol, namely about 388°F., are separated by fractional distillation from the solvent and from the higher boiling oxygen-containing compounds. It should be noted that the process of the invention produces only a small quantity of such lower boiling alcohols, aldehydes and ketones because the major portion of the oxygen-containing products distilling below 245°F. are converted into hydrocarbons in the gasoline range by recycling them to the synthesis unit. The low boiling oxygen-containing compounds are removed as a distillate from the fractionating tower 56 through a pipe 57.

The glycol solution of high boiling oxygen-containing compounds is removed from the bottom portion of the fractionating tower 56 through a pipe 58 and introduced into a

distilling tower 59. The water from the wash tower 41 which contains ethylene glycol and oxygen-containing compounds which were washed from the hydrocarbon raffinate is also introduced into the distilling tower 59 through pipes 60 and 58. In the distilling tower 59, high boiling alcohols, aldehydes and ketones are steam distilled from the ethylene glycol solvent as water azeotropes which leave the tower 59 through a pipe 62 and flow into a settler 65 after condensation in an exchanger 63.

Glycol from which higher boiling oxygen-containing compounds have been steam-distilled is withdrawn from the distilling tower 59 through a pipe 64 and is therethrough recycled to the secondary extraction tower 37. The pipe 64 communicates with the pipe 38 which serves as the entry pipe for the hydrocarbon-immiscible solvent.

Since the high boiling oxygen-containing compounds are only sparingly soluble in water, they are readily separated from the condensate consisting of water and high boiling oxygen-containing compounds. Water is withdrawn from the lower portion of the settler 65 through a pipe 66. The higher boiling oxygen-containing compounds are withdrawn from the settler 65 through a pipe 68. The combined alcohols, aldehydes and ketones may be subjected to mild catalytic hydrogenation in order to convert aldehydes and ketones into alcohols. Since the oxygen-containing compounds are mainly in the form of alcohols as a result of this treatment, they are readily separated into individual compounds by close fractionation. Individual alcohols may be reoxidized to aldehydes and ketones if such compounds are desired.

In the description of the invention, the product of synthesis gas conversion is separated into a liquid hydrocarbon phase and an aqueous phase at elevated temperature and pressure which aqueous phase is then extracted with a hydrocarbon solvent at elevated temperature and pressure. It is contemplated that the initial separation of the products of conversion into an aqueous phase and a hydrocarbon phase at elevated temperature and pressure may effect such a displacement of low boiling oxygen-containing compounds from the aqueous phase to the liquid hydrocarbon phase that the subsequent step of separately extracting the aqueous phase with a hydrocarbon solvent may not be necessary. Consequently, the synthesis product may be separated at elevated temperature and pressure into an aqueous phase and a liquid hydrocarbon phase which is directly introduced into a fractionating tower for separation into a high-boiling fraction and a low boiling fraction, a portion of which is recycled to the synthesis unit. The extraction of the aqueous phase with a hydrocarbon solvent is eliminated in this instance.

It is contemplated that oxygen-containing compounds may be recycled to the synthesis reaction in the form of their aqueous azeotropes. In the detailed description of the invention, there is shown the recycle of ethyl alcohol to the synthesis unit in the form of its aqueous azeotrope. There is included within the scope of the invention the introduction of other low-boiling oxygen-containing compounds in the form of the aqueous azeotropes, in which form they are readily separated from the aqueous phase by distillation.

It is further contemplated that low-boiling oxygen-containing compounds can be recycled to the synthesis unit

without employing a hydrocarbon carrier. This can be accomplished by extracting the oxygen-containing compounds from the hydrocarbon phase of the synthesis product, then separating the oxygen-containing compounds from the extract phase and recycling a low boiling fraction of the oxygen-containing compounds to the synthesis unit.

Non-acidic oxygen-containing compounds distilling below 245°F. constitute by far the greater portion of the oxygen-containing organic compounds produced during the catalytic conversion of synthesis gas which is directed mainly towards the production of liquid hydrocarbons. Moreover, the most practical source of oxygen-containing organic compounds to be introduced into the conversion zone as part of the reactor feed is the synthesis reaction product itself. Thus, the addition of oxygen-containing compounds isolated in the synthesis product and distilling below 245°F. to the reaction feed mixture is the most feasible and practicable method of increasing the yield of liquid hydrocarbons and decreasing the yield of oxygen-containing compounds during catalytic conversion.

However, it is contemplated that oxygen-containing compounds which distill above 245°F. be added to the reaction feed mixture in order to decrease the yield of oxygen-containing compounds and increase the yield of liquid hydrocarbons produced during conversion of synthesis gas. Furthermore, the oxygen-containing organic compounds comprising organic acids, aldehydes, alcohols, ketones and esters of wide boiling point range and having up to about 20 carbon atoms per molecule may be derived from any source whatsoever. The oxygen-containing compounds which are incorporated in the reaction feed mixture can be obtained from the catalytic conversion of carbon monoxide and hydrogen which is directed

mainly towards the production of oxygen-containing compounds and commonly known as the Synol process. On a commercial scale, economic considerations will dictate the source from which should be obtained the oxygen-containing compounds which are to be introduced into the reaction zone as part of the reaction feed mixture and as a consequence the product mixture itself is generally the source of oxygen-containing compounds incorporated in the reaction feed.

It is also contemplated that one particular type of aliphatic oxygen-containing organic compound be incorporated in the reaction feed mixture. Since alcohols constitute the major component of the oxygen-containing organic compounds produced during the catalytic conversion of synthesis gas, it is within the realm of this invention that alcohols alone or even one particular alcohol, for example, ethyl alcohol, be incorporated in the reaction feed mixture. The production of oxygen-containing organic compounds is substantially decreased and the yield of liquid hydrocarbons is commensurately increased during conversion, even by the incorporation of one particular type of aliphatic oxygen-containing compound in the reaction feed mixture.

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.

Supplementary Disclosure

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.

This Supplementary Disclosure is part of our co-pending application, Serial No. 570,584, filed January 18, 1948, 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. This Supplementary Disclosure 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 hydrocarbons, 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_3+ 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 psi. 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 promotor, 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_3+ 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_2-CO synthesis gas mixtures. It had generally been recognized that the addition of water to operations employing 2 to 1 H_2-CO synthesis gas mixtures is harmful because it caused 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_2-CO synthesis gas. Indeed the substantial increase in the yield of C_3+ 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_2 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.

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_3+ 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_1 through C_4 alcohols, C_2 through C_4 aldehydes, C_3 and C_4 ketones and C_3 to C_4 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 II 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_1 and C_2 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 in suppressing oxygenate yield and increasing the yield of C_3+ 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 Gal-7

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_3+ 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_3+ 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 hydroxl, 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_3^+ 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.

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 for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F., to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said product mixture into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, separating from said hydrocarbon phase and said aqueous phase said oxygen-containing organic compounds distilling below about 245°F. and recycling at least a portion of said oxygen-containing compounds to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

2. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F. to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said product mixture into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase and recycling

a portion of said liquid hydrocarbon phase distilling below about 245°F. and containing low boiling oxygen-containing organic compounds to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

3. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F. to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said product mixture into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, recycling at least a portion of said gas phase to said conversion zone and recycling at least a portion of said liquid hydrocarbon phase distilling below about 245°F. and containing low boiling oxygen-containing organic compounds to said conversion zone so as to increase the yield of liquid hydrocarbons boiling in the gasoline range.

4. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F. to form a product comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said product mixture at elevated temperature between 175 and 300°F. and elevated pressure of about 150 to 300 pounds per square inch into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, recycling a major portion of said liquid hydrocarbon phase distilling below about 245°F. and containing low boiling oxygen-containing organic compounds to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

5. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F. to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said product mixture into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, fractionating said liquid hydrocarbon phase into a

fraction distilling below about 245°F. and containing low boiling oxygen-containing organic compounds and a fraction distilling above about 245°F. and recycling a portion of said low boiling fraction to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

6. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of 500 to 700°F. to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said product mixture at elevated temperature and elevated pressure into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, recycling at least a portion of said gas phase to said conversion zone, fractionating said liquid hydrocarbon phase at atmospheric pressure into a low boiling fraction distilling below about 245°F. and a high boiling fraction distilling above about 245°F. and recycling a major portion of said low boiling fraction to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

7. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone to form a product mixture comprising mainly hydrocarbons, oxygen-containing compounds and water, separating said product mixture into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, both of the latter two phases containing substantial quantities of oxygen-containing hydrocarbons recycling at least a portion of said gas phase to said conversion zone, subjecting said aqueous phase to extraction with a hydrocarbon solvent at elevated temperature and pressure so as to form a hydrocarbon-rich extract phase containing non-acidic oxygen-containing hydrocarbons and a water-rich phase containing organic acids, combining said extract phase with said liquid hydrocarbon phase which was initially separated from said product mixture, fractionating said combined phases at atmospheric pressure into a low boiling fraction distilling below about 245°F. and a high boiling fraction distilling above about 245°F. and recycling a portion of said low boiling fraction to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

8. In the catalytic conversion of carbon monoxide and hydrogen for the production of liquid hydrocarbons in the gasoline range, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone to form a product mixture comprising mainly hydrocarbons, oxygen-containing compounds and water, separating said product mixture at elevated temperature and elevated pressure into a gas phase comprising normally gaseous products of conversion and unreacted carbon monoxide and hydrogen, a liquid hydrocarbon phase and an aqueous phase, both of the two phases containing substantial quantities of oxygen-containing hydrocarbons, recycling at least a portion of said gas phase to said conversion zone, subjecting said aqueous phase to extraction with a aliphatic hydrocarbon solvent at elevated temperature and pressure so as to form a hydrocarbon-rich extract phase containing non-acidic oxygen-containing hydrocarbons and a water-rich phase containing organic acids, combining said extract phase with said liquid hydrocarbon phase which was initially separated from said product mixture, fractionating said combined phases into a low boiling fraction distilling below about 245°F. and a high boiling fraction distilling above about 245°F. and recycling a major portion of said low boiling fraction to said conversion zone so as to increase the yield of liquid hydrocarbons in the gasoline range.

9. The method according to claim 8 in which the separation of the product mixture and the extraction of the aqueous phase are effected at substantially equivalent conditions, namely about 175 to 300°F. and at about 150 to 300 pounds per square inch.

10. In the catalytic conversion of carbon monoxide and hydrogen to produce liquid hydrocarbons, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F. to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said oxygen-containing compounds from said hydrocarbon phase and said water phase, and recycling at least a portion of said oxygen-containing compounds which are vaporizable under reaction conditions to said conversion zone so as to increase the yield of liquid hydrocarbons.

11. In the catalytic conversion of carbon monoxide and hydrogen to produce liquid hydrocarbons, the method which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone in the vapor phase at a temperature of about 500 to 700°F. to form a product mixture comprising mainly hydrocarbons, water and oxygen-containing organic compounds comprising alcohols, aldehydes, ketones, esters and acids, separating said oxygen-containing compounds from said hydrocarbon phase and said water phase and recycling at least one of said oxygen-containing compounds which are vaporizable under reaction conditions in substantial amount to said conversion zone so as to increase the yield of liquid hydrocarbons.

Claims Supported By Supplementary Disclosure

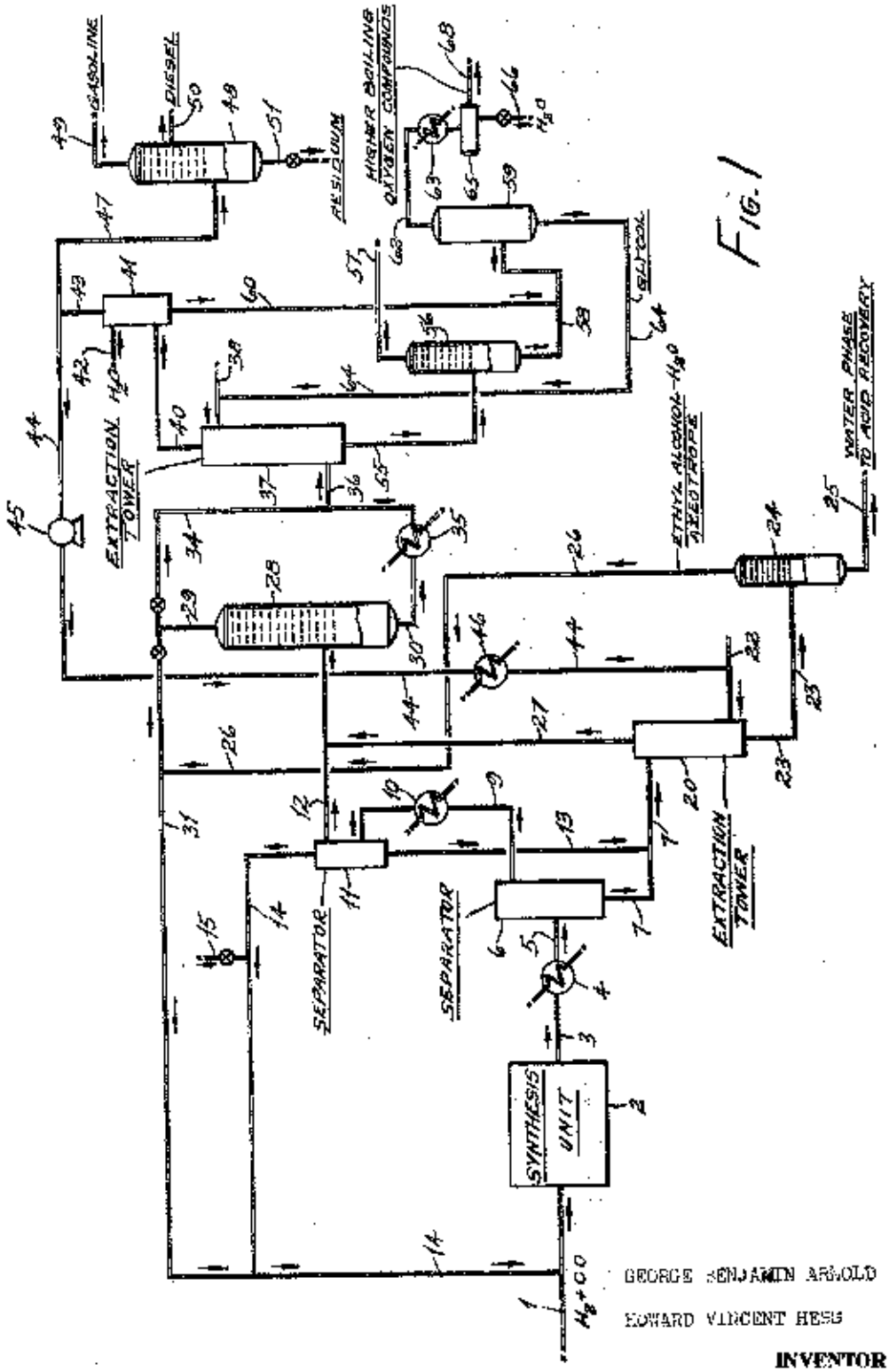
12. In the catalytic conversion of carbon monoxide and hydrogen to produce liquid hydrocarbons, a process which comprises catalytically reacting carbon monoxide and hydrogen in a conversion zone to form a product mixture comprising mainly hydrocarbons, water and oxygenates, separating said product mixture 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 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_{3+} hydrocarbons is increased.

13. 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.

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

15. 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.

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



F16. 1

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By-

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

Ottawa, Ontario, Canada, January 19th, ...19 48.

Smart & Biggar

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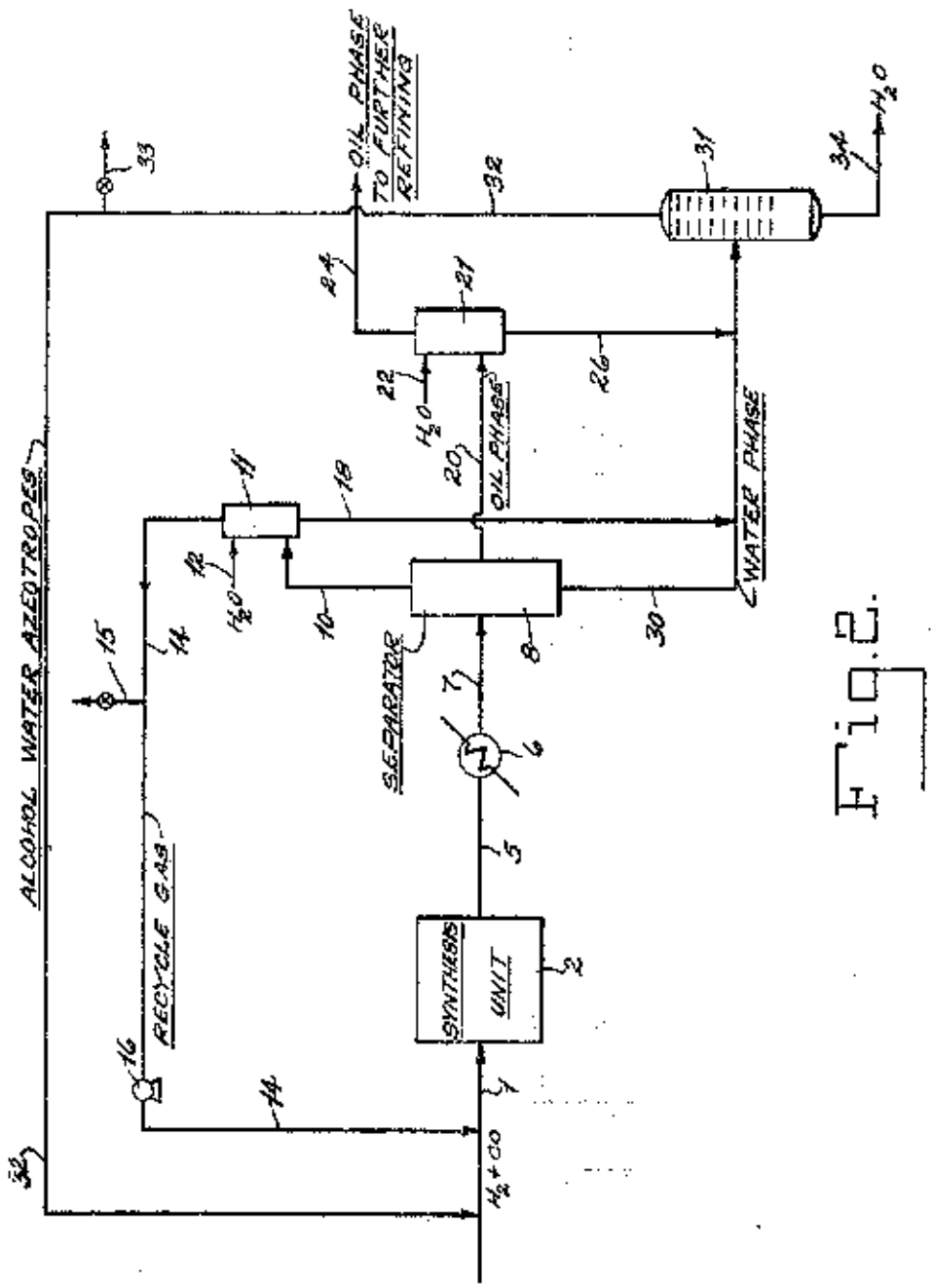

Fig. 2.

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