

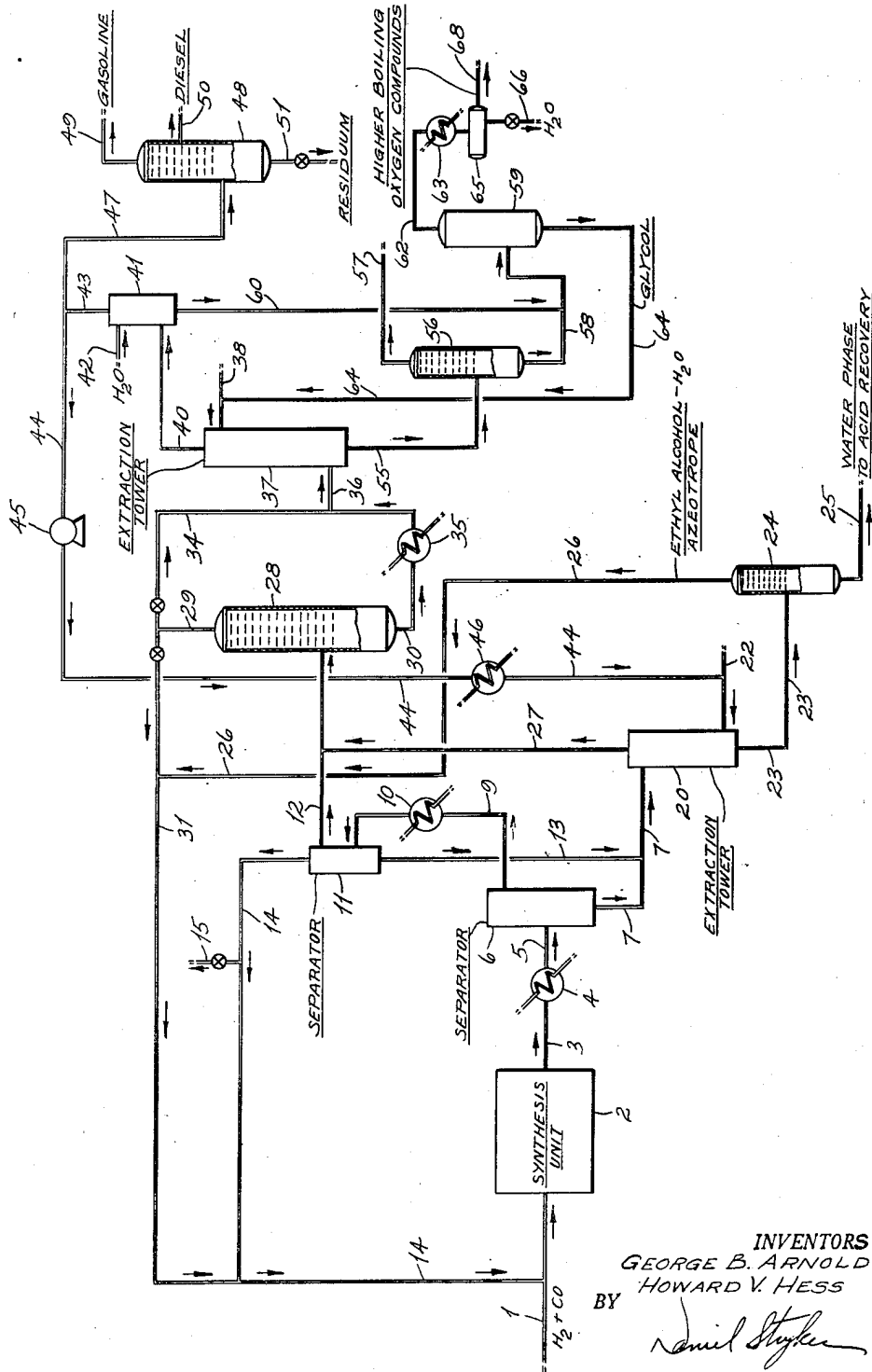
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G. B. ARNOLD ET AL

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METHOD OF SYNTHESIZING GASOLINE HYDROCARBONS

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INVENTORS
 GEORGE B. ARNOLD
 HOWARD V. HESS
 BY *Amiel Stykes*
 ATTORNEY

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METHOD OF SYNTHESIZING GASOLINE HYDROCARBONS

George B. Arnold, Glenham, N. Y., and Howard
V. Hess, Charleston, W. Va., assignors to The
Texas Company, New York, N. Y., a corporation
of Delaware

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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 so that a greater portion of the product comprises liquid hydrocarbons in the gasoline boiling range.

In accordance with 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.

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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

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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 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

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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 8 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 naphtha 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 are 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

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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 con-

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version 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 fraction 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

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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 C₇ 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 re-oxidized to aldehydes and ketones if such compounds are desired.

In the description of the invention, the product of synthesis gas conversion is separated into

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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.

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 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 con-

taining 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

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of said gas phase to said conversion zone, subjecting said aqueous phase to extraction with an 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 por-

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tion 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.

GEORGE B. ARNOLD.
HOWARD V. HESS.

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