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COMPLETE SPECIFICATION

Improvements in or relating to Separation of Water-Soluble Oxygen-Containing Organic Compounds from a Mixture Containing Water

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ERRATA

SPECIFICATION No. 646,925.

Page 3, line 46, *for* "soild" *read* "solid"
Page 5, line 51, *for* "discarded" *read* "discharged"
Page 5, line 104, and page 5, line 115, *for* "pressure" *read* "pressures"

THE PATENT OFFICE,
12th March, 1951.

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resulting mixed product, including water, by cooling to substantially atmospheric temperature with or without reduction in pressure, in order to separate the product into aqueous and non-aqueous layers respectively. The resulting layers are then separated by decantation and separately treated, such treatment involving substantially conventional types of distillation, extraction, washing, or salting out, or a combination of any of these steps.

The invention broadly contemplates separating non-acidic water-soluble oxygen-containing compounds such as aliphatic alcohols from aqueous mixtures containing them by extraction with a normally liquid hydrocarbon or hydrocarbon fraction such as naphtha at elevated temperature and elevated pressure in the liquid phase such that the hydrocarbon exerts preferential solvent

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solvent is made under conditions so as to form a secondary extract or solvent-rich phase comprising oxygen-containing compounds dissolved in the secondary solvent and a secondary hydrocarbon-rich phase consisting essentially of hydrocarbons.

These secondary phases are removed. Alcohols and other oxygen-containing compounds may be removed from the separated solvent-rich phase by fractional distillation leaving secondary solvent for re-use. The secondary hydrocarbon-rich phase can be separately treated to remove small amounts of secondary solvent that may be associated with it after which the hydrocarbons or any portion thereof can be used for treating additional fresh feed mixture.

Ethylene glycol is an effective secondary solvent for effecting liquid-liquid extraction of oxygen-containing com-

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COMPLETE SPECIFICATION

Improvements in or relating to Separation of Water-Soluble Oxygen-Containing Organic Compounds from a Mixture Containing Water

We, TEXACO DEVELOPMENT CORPORATION, a Corporation organised under the laws of the State of Delaware, United States of America, of 135, East 42nd Street, New York, State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to separation of oxygen-containing organic compounds from aqueous mixtures containing them such as obtained from the conversion of carbon monoxide and hydrogen into hydrocarbons, oxygen-containing compounds and the like.

Heretofore, in the catalytic hydrogenation of carbon monoxide to produce hydrocarbons and oxygenated compounds, it has been customary to condense the resulting mixed product, including water, by cooling to substantially atmospheric temperature with or without reduction in pressure, in order to separate the product into aqueous and non-aqueous layers respectively. The resulting layers are then separated by decantation and separately treated, such treatment involving substantially conventional types of distillation, extraction, washing, or salting out, or a combination of any of these steps.

The invention broadly contemplates separating non-acidic water-soluble oxygen-containing compounds such as aliphatic alcohols from aqueous mixtures containing them by extraction with a normally liquid hydrocarbon or hydrocarbon fraction such as naphtha at elevated temperature and elevated pressure in the liquid phase such that the hydrocarbon exerts preferential solvent action upon such compounds. A hydrocarbon solvent-rich phase is obtained consisting essentially of hydrocarbon solvent and dissolved oxygen-containing compounds and a water phase consisting essentially of water. Organic acids present in the feed mixture are distributed between the hydrocarbon-rich phase and the water phase on the basis of their molecular weight, that is, low boiling organic acids up to C_4 acids are in the water phase and organic acids higher than C_4 acids are in the hydrocarbon-rich solvent phase.

The hydrocarbon-rich phase is separated and subsequently treated with a secondary solvent such as a glycol which advantageously has substantially complete solvent action upon oxygen-containing compounds which is substantially immiscible with hydrocarbons at ordinary temperatures, for example, between 70—150° F. The treatment with the secondary solvent is made under conditions so as to form a secondary extract or solvent-rich phase comprising oxygen-containing compounds dissolved in the secondary solvent and a secondary hydrocarbon-rich phase consisting essentially of hydrocarbons.

These secondary phases are removed. Alcohols and other oxygen-containing compounds may be removed from the separated solvent-rich phase by fractional distillation leaving secondary solvent for re-use. The secondary hydrocarbon-rich phase can be separately treated to remove small amounts of secondary solvent that may be associated with it after which the hydrocarbons or any portion thereof can be used for treating additional fresh feed mixture.

Ethylene glycol is an effective secondary solvent for effecting liquid-liquid extraction of oxygen-containing compounds from hydrocarbons, although other olefin glycols including polyolefin glycols may be used. Other useful solvents are polyhydric alcohols such as glycerols. Ketones and aldehydes may be used, as well as amine compounds such as ethanolamines and ethylene diamine.

An essential feature of the process of this invention is the extraction of oxygen-containing compounds such as aliphatic alcohols, aldehydes and ketones from aqueous mixtures with a hydrocarbon liquid such as petroleum naptha or the normally liquid hydrocarbons including naptha and higher boiling hydrocarbons produced in the synthesis of hydrocarbons from carbon monoxide and hydrogen. Synthesis naptha which consists essentially of aliphatic hydrocarbons and which usually is substantially free from aromatic and naphthenic hydrocarbons has been found particularly effective for this purpose. It is contemplated that synthesis hydrocarbons boiling in the range of gas oil are suitable as a solvent for this purpose.

Under liquid phase conditions and at a temperature in the range of about 200—300° F., naphtha hydrocarbons such as obtained from the synthesis reaction exert an unexpectedly high partition effect between water on the one hand and aliphatic alcohols, aldehydes and ketones on the other. For example, when countercurrently extracting an aqueous mixture containing about 7 or 8% by weight of primary aliphatic alcohols having from 2 to 8 or more carbon atoms per molecule at a temperature of 200° F. with naptha in the proportion of about 1 to 2 volumes of naptha per volume of aqueous mixture, substantially all of the alcohols are dissolved in the hydrocarbon solvent and can be removed from the extraction zone in the solvent phase, leaving a water phase consisting essentially of water.

The invention is particularly useful as applied to the treatment of aqueous mixtures obtained in the conversion of carbon monoxide and hydrogen by contact with a synthesis catalyst. The product of the synthesis reaction usually comprises hydrocarbons, oxygenated hydrocarbons and water. The oxygenated hydrocarbons include aliphatic alcohols, aldehydes, ketones and organic acids. Upon cooling of the synthesis product, separation into a liquid hydrocarbon phase and a liquid water phase occurs. The water phase separated at atmospheric conditions usually contains the foregoing oxygenated compounds in substantial amount, the compounds ranging mainly from 2 to 8 or more carbon atoms per molecule.

In accordance with this invention, the aforesaid water phase, obtained by cooling synthesis reaction products to about atmospheric temperature, is extracted with naptha at a temperature of about 200° F. and under a pressure of about 150 pounds or higher. As a result of this extraction there is obtained a solvent-rich phase comprising aliphatic alcohols, aldehydes, and ketones dissolved in naphtha, and a water phase consisting essentially of water and low boiling organic acids. The water phase also contains some low boiling oxygen-containing compounds such as ethyl and propyl alcohols, acetone, etc.

In the preferred mode of operation the initial phase separation of the hot synthesis reaction products is effected at a temperature in the range of about 175—300° F. and at a pressure of about 150—300 pounds per square inch, forming gaseous and liquid hydrocarbon phases as well as an aqueous phase. A substantial portion of the low boiling non-acidic oxygenated compounds which would otherwise be found in the aqueous phase if separation were effected at atmospheric conditions, migrates to the liquid hydrocarbon phase when high temperature-high pressure separation is employed. The aqueous phase so obtained is subjected to solvent extraction with naphtha or other hydrocarbon fraction whereby residual non-acidic oxygenated compounds are extracted therefrom. Effecting the initial separation at elevated temperature and pressure reduces the burden on the extraction step and allows the use of smaller solvent dosages, smaller extraction towers, etc., therein. In some instances displacement of the low boiling non-acidic compounds into the hydrocarbon phase is sufficiently large by initial high temperature-high pressure separation of the products that subsequent extraction of the resulting aqueous phase with a hydrocarbon solvent at high temperature and pressure may be eliminated.

After the water and hydrocarbon phases are initially separated, low boiling acids may be recovered from the water if desired. The hydrocarbon-rich phase may be treated with sodium bisulphite solution or other chemical agent to effect removal of aldehyde and ketones therefrom. For example, treatment with a water solution of sodium bisulphite results in the formation of addition compounds of ketones and aldehydes which can be separated from the so-treated solvent-rich phase.

Thereafter the treated hydrocarbon-rich phase is subjected to extraction with a secondary solvent as previously referred to so as to effect separation of the alcohols from the hydrocarbon solvent. The secondary extract phase comprising mainly alcohols dissolved in the secondary solvent can be then subjected to fractional distillation or such other treatment as necessary in order to recover the individual alcohols therefrom.

For example, this secondary extract phase may be passed to a distilling column or columns wherein it is subjected to fractional distillation to produce therefrom C_2 and C_3 alcohols in the form of their azeotropes with water, and C_4—C_6 alcohols in substantially anhydrous form. Residual water retained in the alcohols solutions provides that required for azeotrope formation. The distillate from this fractional distillation will include methyl alcohol in azeotrope form if such is present in the secondary extract phase.

The residual fraction containing C_7 and higher molecular weight alcohols as well as secondary solvent can be subjected to separate steam distillation so as to separate these higher alcohols from the solvent which latter can be recycled to the secondary solvent extraction step.

Reference will now be made to the accompanying drawing comprising a flow diagram illustrating the application of the process of the invention to the treatment of an aqueous mixture obtained from the conversion of carbon monoxide and hydrogen.

As indicated in the drawing, carbon monoxide and hydrogen in the proportion for example, of 2 mols of hydrogen to 1 mol of carbon monoxide and obtained from a source not shown are passed through a conduit 1 to a conventional synthesis unit 2. In the synthesis unit the reactants may be subjected to contact with a synthesis catalyst in the form of a fluidized mass of soild particles or powder. Advantageously the catalyst comprises iron, although other synthesis catalysts comprising cobalt or nickel may be used. The synthesies catalyst may comprise alkali metals or metal compounds and oxides of thorium, magnesium and aluminium as promoters.

For example, an effective iron catalyst contains about 2 to 3% alumina and about 0.1 to 3.0% alkali (expressed as potassium oxide). The synthesis reaction with such a catalyst, operating for the production of hydrocarbons mainly, is usually carried out at a temperature of about 500—650° F. and under a pressure of about 200 pounds.

An effluent stream comprising unreacted synthesis gas, products of synthesis reaction, the organic portion of which comprises mainly compounds having from 1 to 20 carbon atoms per molecule, leaves the synthesis unit 2 through a pipe 3 and is cooled to a temperature of about 175—300° F. and preferably to about 200—225° F. in an exchanger 4. The effluent may be cooled to about atmospheric at this point but this involves less economical operation. The total product is introduced through a conduit 5 to 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 100—300 pounds per square inch which advantageously is approximately equivalent to that existing in the synthesis unit 2.

In the separator 6, three phases are formed, namely, (1) a gas phase comprising unreacted gas, carbon dioxide and normally gaseous hydrocarbon such as methane, ethane, propane, butane, etc., (2) an initial hydrocarbon phase containing the major portion of the oxygenated compounds produced in the conversion, and (3) a water-rich phase comprising low boiling organic acids and low boiling aliphatic alcohols, aldehydes and ketones such as ethyl alcohol, propyl alcohol, acetone, acetaldehyde, etc.

These phases are separately withdrawn from the separator 6. The gas phase may be discharged through conduit 7 and may be recycled in part to the synthesis unit 2. This gas phase may also be treated to remove carbon monoxide, hydrogen and carbon dioxide for recycling to the synthesis unit.

The water phase is continuously removed from the separator 6 through a conduit 8 to an extraction tower 9. A heat exchanger 11, inserted in the conduit 8, serves to adjust the water phase to a temperature of about 200 to 300° F. prior to its introduction into the extraction tower 9. In the extraction tower 9 it is subjected to countercurrent contact with naphtha or higher boiling hydrocarbons obtained in a subsequent step of the process. When naphtha is used as the extracting medium, the extraction is carried out at a temperature of about 200—300° F. Slightly lower temperature may be used, as for example 175° F., when gas oil is used as the extracting medium. This extraction is carried out at a pressure approximately that employed for the initial separation of the product which is sufficiently elevated to maintain liquid phase conditions within the extraction tower.

The hydrocarbon solvent is introduced

to the lower portion of the tower and rises therethrough countercurrently, to the downwardly flowing feed mixture. As a result of the extractive treatment, a stream of water substantially free from alcohols, aldehydes and ketones is discharged from the bottom of the tower through a conduit 10. This water will retain at least the bulk of the low boiling acids present in the water phase stream flowing through the conduit 8. Thus, the organic acids in this water stream, taken as acetic acid, may be about 1 to 3% by weight based on the water phase flowing through the conduit 8. The hydrocarbon-rich phase removed from the top of the tower 9 comprising mainly alcohols, and a relatively small proportion of aldehydes and ketones dissolved in naphtha is conducted through a conduit 12 and may be passed therefrom into a conduit 13 leading from the previously mentioned separator 6 to a vessel 14. The initial hydrocarbon phase separating in the separator 6 is also conducted through the conduit 13 and passed to the vessel 14.

It is feasible to effect separation of the synthesis product and the extraction of the aqueous phase in a single vessel. To this end, the synthesis product at a temperature of about 200 to 225° F. and at a pressure of about 100 to 300 pounds per square inch is introduced into the middle portion of an elongated column as vessel 6 wherein the synthesis product separates into a gas phase, a hydrocarbon phase and an aqueous phase. As the aqueous phase settles to the lower portion of the column, it is subjected to countercurrent contact with a hydrocarbon fraction relatively lean in oxygen-containing compounds under similar conditions of temperature and pressure so as to extract further portions of oxygen-containing compounds from the aqueous phase. The lower portion of such column thus performs the function of the tower 9.

A water solution of sodium bisulphite may be introduced from a source not shown through a pipe 15 and thus commingled with the hydrocarbon phase flowing through the conduit 13 into the vessel 14. The bisulphite solution is added in sufficient amount and in suitable concentration to react with aldehydes and ketones present in the mixture flowing through the conduit 13 and form addition compounds. The resulting mixture containing addition compounds flows into the vessel 14 wherein the addition compounds separate as an aqueous layer. This aqueous layer is drawn off through a pipe 16 and subjected to such further treatment as may be desired in order to recover the aldehydes and ketones. These aldehydes and ketones may amount to about 1½ to 2 volumes per cent. of the combined water phase and hydrocarbon phase leaving the separator 6.

The hydrocarbon-rich phase containing alcohols forming in the vessel 14 is continuously drawn off through the conduit 17 and if desired passed to a fractionator 20 wherein the mixture may be separated into a distillate fraction boiling within the range of naphtha, for example up to about 400° F., and a residual fraction comprising higher boiling material. Both fractions will thus comprise mixtures of hydrocarbons and alcohols

A distillate fraction is removed from the fractionator through conduit 21 and passed to a secondary extractor 22.

As indicated the fractionator 20 may be by-passed, in which case, the total hydrocarbon-alcohol mixture flowing through the conduit 17 may be diverted through conduit 17a, communicating with conduit 21 and thus passing directly to the secondary extractor 22.

In the secondary extractor the entering mixture of hydrocarbons and alcohols is subjected to countercurrent contact with a solvent liquid such as ethylene glycol. The solvent is introduced to the top of the extractor through conduit 23 to which reference will be made later. Conditions are maintained within the extractor so that the solvent exerts substantially complete solvent action upon the alcohols and substantially, no, or only very little, solvent action upon the hydrocarbons.

The secondary solvent may be charged at the rate of about 1 to 1½ volumes per volume of feed mixture entering through the conduit 21. The extraction may be effected at a temperature in the range of 70—150° F. As a result, there is obtained from the top of the extractor, a secondary hydrocarbon-rich phase substantially free from oxygen-containing compounds and containing a relatively small amount of solvent. This secondary hydrocarbon-rich phase is continuously removed through a conduit 24 to a washing tower 25 wherein it is scrubbed with water so as to extract residual solvent therefrom. The residual solvent dissolved in water is removed through conduit 26 and may be passed to a distilling means or other recovery means adapted to recover the solvent from the water.

The washed or scrubbed hydrocarbons are removed and conducted through conduit 27. A portion thereof is diverted through conduit 28 and used as the solvent in the aforementioned extraction tower 9. The hydrocarbons are raised to a temperature of about 200 to 300° F. in a heat exchanger 29, situated in the conduit 28, prior to their use in the extraction tower 9. The portion not so recycled is passed to a product recovery or product treating system not shown. For example, this portion may be subjected to treatment with clay, bauxite or other contact material for the purpose of converting it into products of desired characteristics including gasoline of high antiknock.

Referring again to the fractionator 20, the gas oil fraction removed therefrom as a residual fraction is conducted through a conduit 30 and may be passed to an extractor 31 similar to the extractor 22. In this extractor the mixture of oil and alcohols is likewise extracted with a selective solvent. Conditions of operation in the extractor 8 may be substantially similar to those in the extractor 22 such as to effect substantially complete removal of alcohols from the gas oil.

To effect extraction of the higher boiling oxygenated compounds such as C_9 to C_{20} alcohols, from the gas oil fraction, a solvent is chosen which has substantially complete solvent action upon these higher boiling oxygenated compounds and which is also substantially immisicible with the gas oil hydrocarbons at ordinary temperature. The boiling point of this selective solvent is advantageously lower than the temperature which constitutes the point of demarcation between the gasoline and gas oil fractions. Examples of selective solvents which have the desired properties are nitro-methane, nitroethane, methylethyl ketone, furfural, ethyl alcohol, propyl alcohol, or a mixture of ethyl and *n*-propyl alcohols obtained from the extract phase of the gasoline extraction.

A gas oil stream substantially free from oxygen-containing compounds and containing a relatively small amount of solvent is removed from the top of the extractor 31 through a conduit 33 to a scrubber 34 wherein it may be washed with water to remove the residual solvent therefrom, the residual solvent and water being discarded through a pipe 35.

The washed gas oil stream is discharged through a pipe 36. In the event that gas oil is being used as the solvent in the extractor 9, a portion of the gas oil flowing through pipe 36 may be diverted through pipe 37, communicating with the previously mentioned pipe 28 by which the hydrocarbon solvent is conducted to the tower 9. In this event, the stream leaving the top of the tower 9 through pipe 12 is diverted through pipe 12a to the extractor 31.

From the bottom of both extractors 22 and 31 are withdrawn extract phase mixtures comprising alcohols dissolved in the secondary solvent. The secondary extract phase from the tower 31 may be separately treated or may be conducted through a conduit 40, communicating with a conduit 41 through which the secondary extract phase from the extractor 22 is withdrawn. Both streams then pass to an alcohol recovery unit 42.

The recovery unit 42 may comprise a plurality of distilling columns and auxiliary apparatus adapted to effect separation of the individual alcohols from the secondary solvent-alcohol mixture.

For example, there may be obtained from the recovery unit 42, the following products, the per cent. yield being on the basis of total hydrocarbon phase and water phase leaving the separator 6:—

	Volume per cent.
Ethyl alcohol-water azeotrope	10
N-propyl alcohol-water azeotrope - - - - - - - -	2.6
N-butyl alcohol (anhydrous) -	0.87
N-amyl alcohol (anhydrous) -	0.80
N-hexyl alcohol (anhydrous) -	0.68
N-heptyl alcohol (anhydrous) -	0.55
Higher alcohols (anhydrous) -	0.63

While not specifically mentioned, it is contemplated that the countercurrent extraction operations carried out in the extractors 9, 22 and 31 may involve employment of suitable temperature gradients through the extraction towers and extract recycle. The solvent dosages may vary from those mentioned. Temperatures may vary from those mentioned while the pressure are maintained sufficient for liquid phase operations.

While the foregoing synthesis reaction has been described with reference to the production of hydrocarbons as well as oxygen-containing compounds, it is contemplated that the synthesis operation may be carried out under conditions adapted mainly for the production of oxygen-containing compounds. Synthesis reaction temperatures may range from 200—700° F. and pressure from atmospheric to several hundred pounds or more. Moreover the synthesis reaction is not necessarily confined to the employment of a fluidized mass of synthesis catalyst. In other words, the synthesis catalyst may be used in other forms, as for example in the form of a stationary bed, a moving bed or a suspension in the reactants.

Moreover, the extracting operations of the present invention are not limited to the treatment of alcohol-water mixtures obtained from the conversion of carbon monoxide and hydrogen but may be employed to treat mixtures derived from other sources.

While ethylene glycol has been mentioned as a suitable secondary extraction solvent, it is contemplated that other solvents may be used including high molecular weight compounds such as those which may be produced in the synthesis unit and may be recovered from the recovery unit 42.

It is contemplated that the solvent-rich phase leaving the top of the extraction tower 9 can be separately extracted with secondary solvent instead of being mixed with the hydrocarbon phase mixture leaving the separator 6. Such separate treatment would be in order where the mixture of water and oxygen-containing compounds is obtained from an extraneous source. For example, when the solvent-rich phase from the extraction tower 9 is separately treated with a secondary solvent, and the resulting secondary extract phase passed to a recovery unit such as the recovery unit 42, the following yields may be obtained basis feed mixture to extractor 9:—

	Volume per cent.
Ethyl alcohol-water azeotrope	10
N-propyl alcohol-water azeotrope - - - - - - -	3
N-butyl alcohol-water azeotrope - - - - - - -	1
Higher molecular weight alcohols (anhydrous) - - -	5

It is further contemplated that the bisulphite treatment in the vessel 14 may be omitted and aldehydes and ketones produced in the conversion be separated from the hydrocarbon fraction together with alcohols by the glycol extraction. In such event the mixture of alcohols, aldehydes and ketones separated from the hydrocarbon fraction may be subjected to mild catalytic hydrogenation in order to convert the aldehydes and ketones to alcohols. A portion of the gas phase separated from the synthesis products may be used as the source of hydrogen in effecting the catalytic conversion of aldehydes and ketones into alcohols. Further, the gaseous effluent from the catalytic hydrogenation can be recycled to the synthesis unit. In the absence of bisulphite treatment to separate aldehydes and ketones, the hydrogenation of the separated oxygen-containing compounds so as to convert aldehydes and ketones into alcohols expedites the separation of the oxygen-containing compounds into individual components by minimizing azeotrope formation.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the separation of non-acidic water-soluble oxygen-containing organic compounds, and more particularly compounds obtained from the synthesis of carbon monoxide and hydrogen, from a mixture of said compounds with water, which comprises contacting the aqueous mixture with a normally liquid hydrocarbon solvent, subjecting the mixture of water and solvent to elevated temperature and elevated pressure sufficient to maintain substantially liquid phase conditions within the extraction zone and to effect a displacement of said compounds from the water to the solvent and thereby forming a hydrocarbon-rich phase and a water phase and separating organic compounds from said hydrocarbon-rich phase.

2. A process according to claim 1 in which the solvent consists essentially of normally liquid aliphatic hydrocarbons.

3. A process according to any one of the preceding claims, wherein said extraction is effected at a temperature between 175—300° F. and under a pressure of about 100—300 pounds per square inch gauge.

4. A process for manufacturing hydrocarbons and oxygen-containing organic compounds by the catalytic conversion of carbon monoxide and hydrogen which comprises forming a mixture comprising hydrocarbons, oxygen-containing compounds, including aliphatic alcohols, and water by the catalytic conversion of carbon monoxide and hydrogen, separating from said mixture an initial hydrocarbon phase containing some oxygen-containing compounde and a water phase containing remaining oxygen-containing compounds, removing separated water phase, extracting oxygen-containing constituents from said removed water phase in accordance with the process according to either one of claims 1 or 2, separating said hydrocarbon-rich phase from said water phase, subjecting both said hydrocarbon-rich phase and said initial hydrocarbon phase to extractive contact with a secondary solvent liquid, effecting said contact at a temperature such that the secondary solvent has a relatively high solvent action on said oxygen-containing compounds and a relatively low solvent action on hydrocarbons forming a secondary extract phase comprising oxygen-containing compounds dissolved in secondary solvent and a non-extract phase consisting mainly of hydrocarbons, separating secondary extract and non-extract phases and removing oxygen-containing compounds from separated secondary extract phase.

5. A process according to claim 4, in which the initial phase separation is made at a temperature between about 175—300° F. and at a pressure of 100 to 300 pounds per square inch.

6. A process according to claim 1 in which the hydrocarbon solvent is the hydrocarbon phase of synthesis product and the aqueous mixture of oxygen-containing compounds is the aqueous phase of a synthesis product, which is extracted at elevated temperature and pressure by cooling said synthesis product after it issues from the synthesis reactor to a temperature between about 200 and 300° F. and elevated pressure whereby there is formed a water phase and a hydrocarbon phase containing substantially all of C_4 and higher oxygen-containing compounds, which phases are separated for removing all oxygen-containing compounds from each of said phases separately.

7. A process according to claim 6, wherein said conversion of carbon monoxide and hydrogen takes place under super-atmospheric pressure and at an elevated temperature between 200—700° F.

8. A process according to either of claims 7 or 8, wherein the carbon monoxide and hydrogen are converted into a mixture comprising hydrocarbons, water and oxygen-containing compounds and said mixture is separated into a water phase and a hydrocarbon phase at a temperature of 175—350° F. and under a pressure sufficient to maintain liquid phase conditions, said water phase containing a minor percentage of the oxygen-containing compounds produced in the conversion, said hydrocarbon phase thereafter being separated into two fractions, one of said fractions comprising essentially gasoline hydrocarbons, the other said fraction comprising essentially gas oil hydrocarbons and each of said hydrocarbon fractions being separately treated so as to remove oxygen-containing compounds therefrom.

9. A process for manufacturing hydrocarbons and oxygen-containing compounds, which comprises forming by conversion of carbon monoxide and hydrogen a synthesis product mixture comprising hydrocarbons, oxygen-containing compounds including aliphatic alcohols, aldehydes, ketones, organic acids and water, said synthesis product mixture being passed into the intermediate portion of a separating column maintained at a temperature between 175—300° F. and under pressure sufficient to maintain substantially liquid phase conditions forming in the lower portion of said column a water phase containing a residual portion of said oxygen-containing compounds, introducing to the lower portion of said column a distinct hydrocarbon fraction lean in oxygen-containing compounds, passing said distinct hydrocarbon fraction in contact with said water phase, effecting solution of residual oxygen-containing compounds in said distinct hydrocarbon fraction, discharging from the lower portion of said column water substantially free from non-acidic oxygen-containing compounds and containing low boiling organic acids, forming in the upper portion of said column a hydrocarbon-rich phase containing dissolved oxygen-containing compounds and comprising said distinct hydrocarbon fraction and hydrocarbons initially separating from the entering feed mixture, separately discharging said hydrocarbon-rich phase from the upper portion of said column and recovering dissolved oxygen-containing compounds therefrom.

10. A process for the catalytic conversion of carbon monoxide and hydrogen into a mixture of hydrocarbons, oxygen-containing organic compounds, water and the like, which comprises effecting conversion of carbon monoxide and hydrogen in a reaction zone into a product mixture comprising aforesaid substances including some aldehydes and ketones at elevated temperature and pressure, separating said product mixture into an aqueous phase, a liquid hydrocarbon phase and gas phase, subjecting said aqueous phase containing a substantial portion of said oxygen-containing compounds to solvent extraction with a hydrocarbon solvent in an extraction zone at elevated temperature and at elevated pressure sufficient to maintain substantially liquid phase conditions, thereby forming a hydrocarbon-rich extract phase containing non-acidic oxygen-containing organic compounds and a water-rich phase containing low boiling organic acids, separating said last two mentioned phases, combining said hydrocarbon-rich extract phase with said liquid hydrocarbon phase initially separated from said product mixture, subjecting said combined hydrocarbon phases to solvent extraction with a solvent immiscible with hydrocarbons at extraction conditions, forming a solvent-rich extract phase containing non-acidic oxygen-containing compounds produced in the conversion and a hydrocarbon-rich raffinate which is substantially free from oxygen-containing compounds, separating said oxygen-containing compounds from said solvent-rich extract phase, subjecting said separated oxygen-containing compounds

to catalytic hydrogenation so as to convert aldehydes and ketones to alcohols and thereby forming a hydrogenated product comprising essentially alcohols.

11. A process according to claim 10, wherein said separation into an aqueous phase, a liquid hydrocarbon phase and a gas phase is effected at elevated temperature and pressure and wherein the individual alcohols formed by the catalytic hydrogenation are recovered by fractionation of said hydrogenated product.

12. The process of separating oxygen-containing organic compounds from aqueous mixtures, substantially as hereinbefore described.

Dated the 27th day of May, 1947.
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