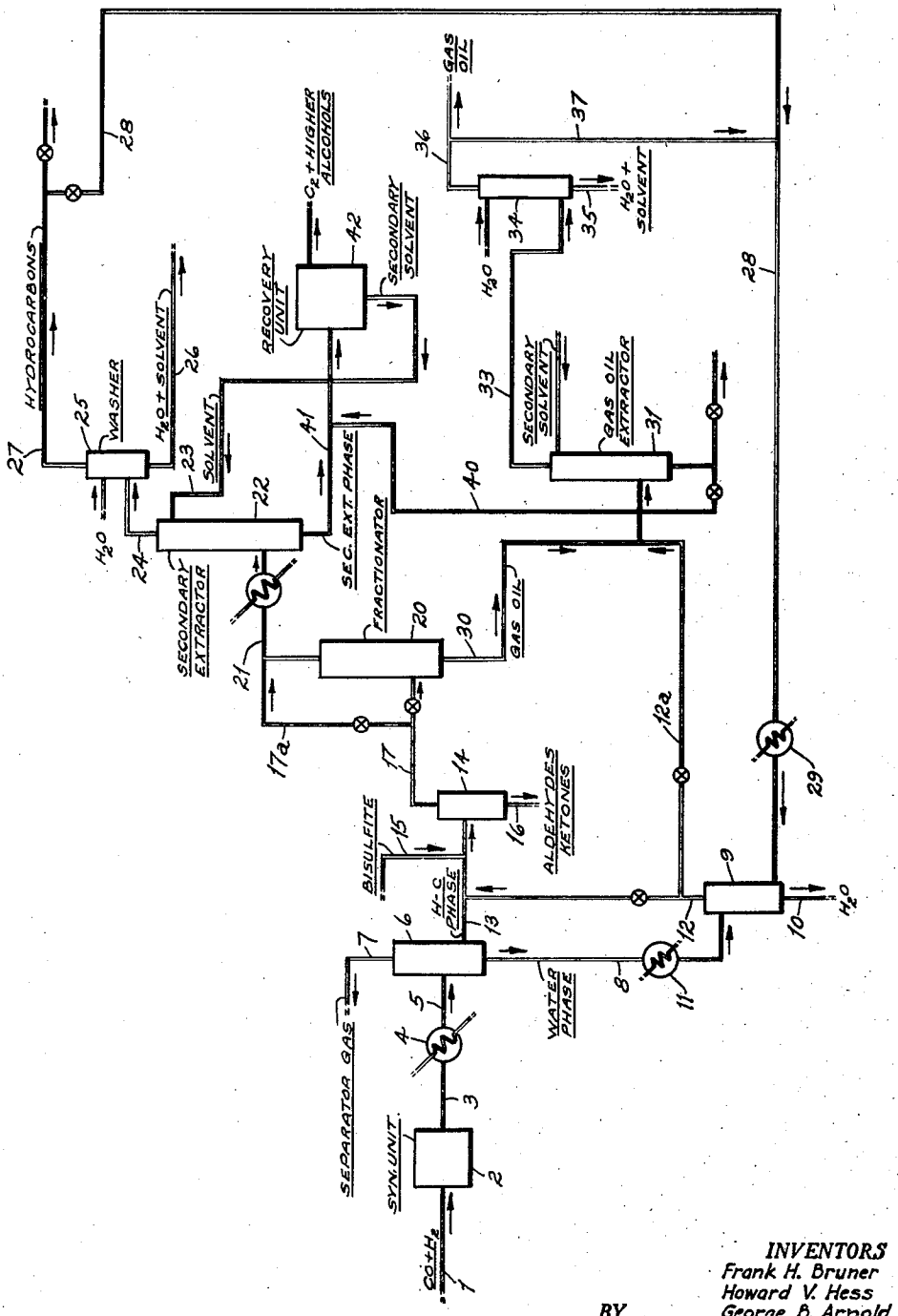
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SEPARATION OF OXYGEN-CONTAINING ORGANIC COMPOUNDS FROM AQUEOUS MIXTURES

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SEPARATION OF OXYGEN-CONTAINING ORGANIC COMPOUNDS FROM AQUEOUS MIXTURES

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1 Claim. (Cl. 260—450)

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This invention relates to the 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.

The invention broadly contemplates separating oxygen-containing compounds such as aliphatic alcohols from aqueous mixtures containing them by extraction with a hydrocarbon or hydrocarbon fraction such as naphtha at elevated temperature and preferably in the liquid phase such that the hydrocarbon exerts preferential solvent action upon such compounds. A 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, if present in the feed mixture, remain mainly in the water phase.

The solvent-rich phase is separated and subsequently treated with a secondary solvent, advantageously a solvent having substantially complete solvent action upon aliphatic alcohols and being substantially immiscible with hydrocarbons at ordinary temperatures, for example, in the range of 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 hydrocarbon-rich phase consisting essentially of hydrocarbons.

These secondary phases are removed. Alcohols may be removed from the separated solvent-rich phase by fractional distillation leaving secondary solvent for re-use. The 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 glycols and 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 naphtha and the normally liquid hydrocarbons including naphtha and higher boiling hydrocarbons produced in the synthesis of hydrocarbons from carbon monoxide and hydrogen. Synthesis naphtha which consists essentially of aliphatic hydrocarbons and which usually is substantially free from aromatic and naphthenic hydrocarbons has been found 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.

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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 naphtha in the proportion of about 1 to 2 volumes of naphtha 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 a small amount of organic acids. Upon cooling of the synthesis product, separation into a liquid hydrocarbon phase and a liquid water phase occurs. The water phase 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 is extracted with naphtha 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 organic acids. Small amounts of ketones and aldehydes may remain in the water phase. These phases are separated. The acids may

be recovered from the water if desired. The solvent-rich phase may be treated with sodium bisulfite solution or other chemical agent to effect removal of aldehydes and ketones therefrom. For example, treatment with a water solution of sodium bisulfite 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 solvent-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 alcohols dissolved in 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 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 alcohol solutions provides that required for azeotrope formation. 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. The distillate from the distillation will include methyl alcohol in azeotrope form if present in the secondary extract phase.

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 solid particles or powder. Advantageously the catalyst comprises iron, although other synthesis catalysts comprising cobalt or nickel may be used. The synthesis catalyst may comprise alkali metals or metal compounds and oxides of thorium, magnesium and aluminum 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 of synthesis reaction mixture is removed through a conduit 3 and passed through a cooler 4 wherein its temperature may be reduced to atmospheric or to about 100–150° F. without substantial reduction in pressure. The resulting cooled mixture is passed through a conduit 5 to a separating vessel 6. In the separator, three phases form: (1) a gas phase comprising unreacted gas, carbon dioxide and normally gaseous hydrocarbons such as methane, ethane, propane, butane, etc., (2) a hydrocarbon-rich phase containing some oxygenated compounds including aliphatic alcohols mainly of two or more carbon atoms per molecule, and (3) a water-rich phase comprising water, aliphatic alcohols, aldehydes, ketones and organic acids.

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 raise 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 under pressure in the range 100 to 300 pounds and sufficiently elevated to maintain liquid phase conditions within the extraction tower. The extraction pressure may be substantially the same as that prevailing in the synthesis unit.

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 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 in the range about 1 to 3% by weight basis the water phase flowing through the conduit 8. The solvent-rich phase removed from the top of the tower 9 comprising 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 hydrocarbon phase separating in the separator 6 is also conducted through the conduit 13 and passed to the vessel 14.

A water solution of sodium bisulfite may be introduced from a source not shown through a pipe 15 and thus commingled with the fluid stream flowing through the conduit 13. The bisulfite solution is added in sufficient amount and of 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 volume per cent of the combined water phase and hydrocarbon phase leaving the separator 6.

The alcohol-containing hydrocarbon-rich phase 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 bypassed, in which case, the total hydrocarbon-alcohol mixture flowing through the conduit 17 may be diverted through conduit 17*a*, 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 hydrocarbon-rich phase substantially free from oxygen-containing compounds and containing a relatively small amount of solvent. This 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 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 such as used in the extractor 22. Conditions of operation in the extractor 3 may be substantially similar to those in the extractor 22 such as to effect substantially complete removal of alcohols from the gas oil.

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 discharged 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 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 12*a* 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 feed 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)	0.63
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 pressures 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 pressures 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

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

We claim:

A process for separating non-acidic aliphatic water-soluble oxygenates containing up to about eight carbon atoms from acidic aliphatic water-soluble oxygenates, which comprises subjecting an aqueous solution containing said acidic and non-acidic oxygenates to countercurrent contact with a hydrocarbon solvent at a temperature of about 175 to 300° F. and under pressure sufficient to maintain substantially liquid phase conditions whereby there is obtained a hydrocarbon extract phase containing non-acidic oxygenates and a raffinate phase containing said acidic oxygenates.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,870,816	Lewis	Aug. 9, 1932
2,083,125	Scheuble	June 8, 1937
2,274,750	Soenksen et al.	Mar. 3, 1942
2,410,642	Farkas et al.	Nov. 5, 1946
2,446,231	Johnson	Aug. 3, 1948
2,476,788	White	July 19, 1949

OTHER REFERENCES

Fischer: Conversion of Coal into Oil, pub. by Ernest Benn Ltd., London (1925), 241–6.