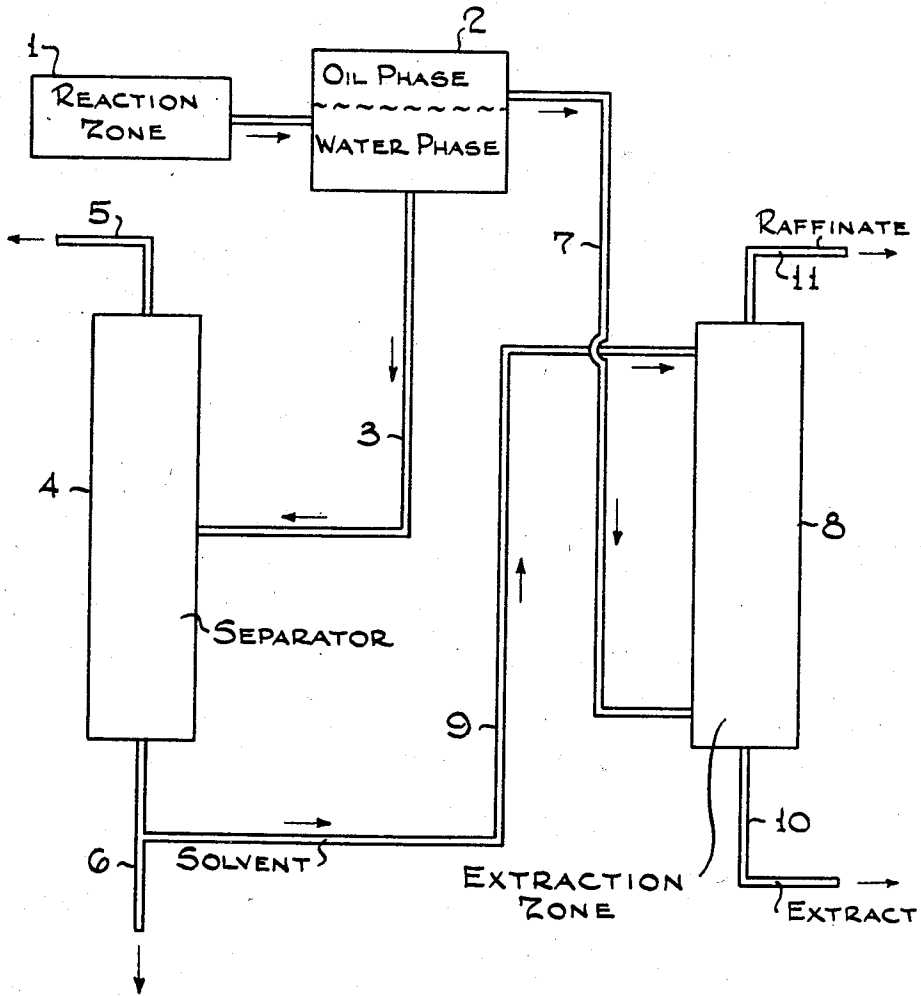


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RECOVERY OF OXYGENATED COMPOUNDS FROM HYDROCARBON OILS

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This invention relates to the recovery of the lower molecular weight oxygen-containing organic compounds both neutral and acidic from mixtures thereof with hydrocarbon oils by a process involving the extraction of such mixtures with dilute aqueous solutions of the water-soluble carboxylic acids i. e. C₁ through C₆ acids such as dilute aqueous acetic acid, dilute aqueous propionic acid, etc., or mixtures of the same.

Various processes are known to the art in which a mixture of hydrocarbons and organic oxygen-containing compounds are produced. Some of these processes are the low temperature carbonization of coal, peat and similar materials, the destructive hydrogenation and distillation of coals, wood, shales, etc. Numerous oxidation processes, particularly oxidation of petroleum oil fractions, such as is described in Ellis' Chemistry of Petroleum Derivatives, vol 1, chapter 36, pages 830 to 845, also yield mixtures of oxygenated compounds and hydrocarbons of substantially the same boiling range. This invention is particularly applicable to the hydrocarbon syntheses, such as the Fischer synthesis wherein oxides of carbon are reacted with hydrogen in the presence of catalysts to produce synthetic hydrocarbons, water and numerous organic oxygenated compounds, predominantly aliphatic. The oxygenated compounds produced in the synthesis operation may be a major product or a relatively small by-product depending upon the operating conditions. These oxygenated materials which are extremely valuable as chemicals, consist of a mixture of alcohols, acids, aldehydes, ketones and esters and are difficult to separate from the hydrocarbon oil because first, they are so numerous, secondly they boil within substantially the same range as the hydrocarbon oils and, thirdly, they often form azeotropes with each other and with the hydrocarbon oils.

Normally when the products of the above-described synthesis operation are condensed and allowed to settle, the condensate separates into a di-phase system, that is, an upper oil layer comprising substantially hydrocarbons and hydrocarbon-soluble oxygen-containing materials and a lower water phase comprising substantially water and water-soluble oxygen-containing materials. The oxygen-containing organic compounds formed in the synthesis operation range from very low molecular weight compounds to very high molecular weight compounds and therefore find themselves distributed throughout the oil phase and the water phase depending on their solubilities in these respective phases. In general, it can

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be said that the bulk of the organic oxygen-containing compounds of one of four carbon atoms will enter the aqueous phase while the bulk of the compounds containing five carbon atoms and more per molecule will be found in the oil layer, although it should be borne in mind that the separation of materials into their respective phases is oftentimes not clean-cut and depends to a large extent upon the conditions involved and the overall composition of the materials in the condensate from the synthesis reactor.

Processes have been developed for the separation and recovery of alcohols, ketones, aldehydes, etc. from the water layer. The starting point in many of such processes is a crude alcohol distillation in which the water layer is subjected to distillation to remove substantially all of the oxygenated compounds other than acids therefrom. Generally speaking, it is desired to leave the acids, such as acetic acid, propionic acid, etc., in the bottoms from which they are subsequently recovered.

It is an object of this invention to provide a method for the recovery of oxygenated compounds, particularly water-soluble oxygenated compounds from mixtures thereof with hydrocarbon oils.

It is an object of this invention to provide a method for the recovery of oxygenated compounds from the oil layer product of the hydrocarbon synthesis.

It is also an object of this invention to provide a method for the separation and recovery of organic oxygenated compounds both neutral and acidic from mixtures of both with hydrocarbon oils.

These and other objects of this invention are attained by carrying out the extraction of a mixture of neutral and acidic oxygenated organic compounds in hydrocarbon oils with a dilute aqueous solution of the water-soluble aliphatic carboxylic acids, such as acetic acid, propionic acid, etc., or mixtures of such carboxylic acids, at a temperature in the range of 125° C. to the critical temperature of the solvent, preferably 175-250° C. The critical temperature of the solvent will be in the neighborhood of 375° C. The acid bottoms obtained from the fractional distillation of the synthesis water layer is especially suitable for this extraction step as will be further explained below.

The material subjected to extraction, according to the terms of this invention, is complex in nature. It is composed of hydrocarbons including paraffins, olefins and in some cases, small amounts of aromatics. In addition, it contains

anywhere up to about 50% or more of oxygen-containing materials, particularly of high molecular weight such as those set out above. In cases where the material is derived from the hydrocarbon synthesis operation, the oil will have dissolved in it alcohols, acids, aldehydes, ketones and esters. Frequently, the esters predominate among the high boiling compounds, particularly that fraction boiling above 350° F. while carbonyl compounds, that is aldehydes and ketones, acids and alcohols, predominate among the oxygen-containing compounds boiling at temperatures up to about 350° F. Ordinarily the amounts of alcohols and acids found decrease with increasing analytical distillation temperatures due undoubtedly to the fact that they undergo esterification reactions during such distillation treatments. The oxygen content of the hydrocarbon oils resulting from the synthesis operation generally runs from one weight percent to ten weight percent.

It has been previously found, as described in our copending application Serial Number 792,802 filed December 19, 1947, that when such a mixture of hydrocarbon oils and oxygenated compounds is extracted at low temperatures, i. e. temperatures in the range of about 0° C. to 125° C., with a dilute aqueous solution of acetic acid with or without a small amount of its homologues, the lower molecular weight neutral oxygenated compounds present in the mixture are extracted therefrom by the acid solvent, leaving the lower molecular weight carboxylic acids contained in the mixture in the raffinate phase with the hydrocarbon oils. That is to say, the alcohols, esters, ketones, aldehydes, acetals, etc., through C₆ and some C₈, are dissolved by the dilute aqueous acetic acid and constitute the extract phase, while the acids present in the mixture are undissolved and together with the hydrocarbon oils in the mixture constitute the raffinate phase.

However, it has now been found that when the hydrocarbon oil-oxygenated compound mixture is extracted with dilute aqueous carboxylic acids at higher temperatures, i. e., in the range of 125° C. to the critical temperature of the solvent, both the neutral oxygenated compounds and the acidic oxygenated compounds are extracted, leaving the raffinate composed chiefly of hydrocarbons and the higher molecular weight oxygenated compounds. Another feature of the high temperature extraction with these acids is that at the higher temperatures, i. e., 125° C. to about 375° C., the esters present in the hydrocarbon mixture are substantially hydrolyzed thus producing larger amounts of alcohols and acids in the extract phase.

The dilute aqueous carboxylic acid solution employed as the selective solvent according to the terms of this invention should contain no more than 5 to 10 weight percent of the acid. The preferred range is 2 to 5 weight percent. The acid water bottoms previously described is an excellent solvent for the purpose of this invention.

The acid water bottoms obtained from the fractional distillation of the synthesis water layer contains about 95 weight percent water and a typical analysis is as follows:

	Weight percent
Water -----	95.50
Carboxylic acids (as acetic acid) -----	4.47
Other org. oxy. compds. (alcohol, esters, etc.) -----	0.03
	100.00

The 4.47 weight percent acid content is broken down into approximately 75 weight percent acetic acid, 20 weight percent propionic acid, and 5 weight percent butyric acid and higher acids. The small amount of other oxy-compounds present in the acid bottoms, i. e. the 0.03 weight percent alcohol, ester, etc., is not harmful to the material as a solvent.

In its simplest form this invention entails taking all or part of the aqueous acidic bottoms from the hydrocarbon synthesis water layer from which substantially all of the alcohols, ketones, aldehydes, etc., have been removed and contacting the oil layer resulting from the synthesis product condensation with the aqueous bottoms under extraction conditions. The total oil layer or appropriate fractions thereof may be so treated. In a number of cases these bottoms may be used as such for the extraction operation. This is especially true when it is desired to extract the oxygenated compounds from the lower boiling portions of the Fischer synthesis oil, say for instance the gasoline fraction (up to 400° F.), or some lower boiling portion of the gasoline fraction. This invention also includes an alternate possibility in which a lower alcohol such as methyl, ethyl or isopropyl or mixtures of these lower alcohols or mixtures of these with other neutral oxygenated compounds such as ketones are added to the aqueous acidic bottoms and this mixture employed as the extraction agent. For instance, if the entire Fischer synthesis oil is to be extracted or if only the higher boiling portions thereof are extracted, it is desirable that considerable amounts of the lower boiling oxygenated compounds be added to the aqueous bottoms in order to obtain a suitable solvent for the extraction. Preferably, however, the amount of alcohols or other low boiling oxygenated compounds combined with the aqueous bottoms is kept at the lowest value consistent with reasonable capacity and selectivity of the extraction agent for the oil-soluble oxygenated compounds. Best results have been obtained by the addition of at least 20 volume percent alcohol, particularly methanol.

The aqueous bottoms, either as such or after reinforcement with lower boiling oxygenated compounds as described above, may be contacted with the oil or suitable fractions thereof under a variety of conditions. For instance, the contacting may be carried out in a batch manner. Preferably, however, it is carried out using countercurrent flow of the extractant and the oil, either in counter-stage equipment or in a countercurrent packed or plate tower. The optimum solvent to oil ratio will vary over wide ranges depending upon the nature of the solvent, i. e. the acid and lower boiling oxygenated compound content thereof, the oxygenated compound content of the oil, the boiling range of the oil being extracted, and the temperature of the extraction. As the oxygenated compound content of the solvent is increased, the optimum solvent/oil ratio, in general, decreases. Also, the lower the oxygenated compound content of the oil feed, the lower are the solvent/oil ratio requirements. When extracting the higher boiling portions of the oil, either alone or in combination with the lower boiling portions thereof, in general, it is desirable to use a relatively high solvent/oil ratio since the solubility of the higher boiling oxygenated compounds in such aqueous solvents is lower than that of the lower boiling ones.

The temperature at which the extraction operation of this invention is carried out is important.

Temperatures which may be employed according to the terms of this invention are in the range of 125° C. to the critical temperature of the solvent which will be about 375° C. Temperatures lower than 125° C. are to be avoided when extracting the mixture of hydrocarbons and oxygenated compounds with the dilute aqueous acid solvents of this invention, due to the fact that at the lower temperatures, the acids contained in the mixture of hydrocarbons and oxygenated compounds are not extracted by the dilute aqueous acid solvents, but remain instead in the raffinate, thus making the separation of oxygenated compounds incomplete. The preferred extraction temperature range is 175° C. to 250° C.

The attached drawing represents a flow plan of one process and accompanying apparatus for carrying out this invention in its simplest embodiment.

Referring to the drawing, numeral 1 represents a reaction zone which produces a reaction product composed chiefly of hydrocarbons and oxygenated compounds, which when removed from the reaction and condensed, form in vessel 2 an upper hydrocarbon oil phase and a lower water phase, each phase containing dissolved therein varying amounts of organic oxygenated compounds such as alcohols, acids, ketones, aldehydes, etc., as explained previously. The water phase is removed via line 3 to zone 4 which may be a fractional distillation zone, an extractive distillation zone or a solvent extraction zone for separation of the water layer oxygenated compounds into the water soluble neutral oxygenated compounds taken overhead via line 5, and the dilute aqueous organic acids removed as bottoms via line 6. The oil phase from vessel 2 is removed via line 7 to extraction zone 8 entering at a point below the mid-section thereof. In extraction zone 8 the oil phase is countercurrently extracted with all or part of the dilute aqueous organic acid bottoms entering the extraction zone via line 9 at a point near the top thereof. During the extraction operation the lower molecular weight oxygenated compounds both neutral and acidic in the oil layer are extracted by the dilute aqueous acid and the resulting extract is removed for separation of solvent therefrom via line 10. A raffinate phase is removed overhead from the extraction zone by line 11.

The extract phase consists substantially of the lower molecular weight organic oxygenated compounds dissolved in the solvent. The oxygenated compounds can be removed from the solvent by any known means and this invention is not restricted to any method by which such removal is accomplished. For example, the oxygenated compounds may be recovered by submitting the extract phase to fractional distillation, extractive distillation, solvent extraction or other known methods of separation.

The raffinate phase from the extraction zone consists chiefly of hydrocarbon oils and the higher molecular weight oxygenated compounds. After separation of the solvent from the raffinate phase, the raffinate may be recovered for purification as gasoline, and/or further recovery of the higher molecular weight oxygenated compounds. However, any such treatment is not within the scope of this invention.

In order to visualize the amount of C₂-C₅ oxygenated compounds present in the synthesis oil layer, the following data are presented. In a certain hydrocarbon synthesis run the oxygenated compounds extracted by water from the oil layer represented the following approximate percentage

increases over the amounts obtained by processing the water layer from the same run.

	Percent increase
Propionic acid	15
Propyl alcohol	20
Butyric acid	100
Butyl and amyl alcohols	600

The following table contains examples to illustrate the process of this invention. In the examples cited the feed to the extraction process was a gasoline fraction, B. P. 35-200° C., recovered from a hydrocarbon synthesis unit. This gasoline contained the following amounts of oxygenated compounds expressed in milliequivalents per gram: acids 0.70; alcohols 0.57; esters 0.25 and carbonyls 0.65. The feed was extracted with the acid water bottoms recovered from the hydrocarbon synthesis water layer stripped to remove volatile neutral compounds therefrom. Analysis of the acid water bottoms revealed: acid content 4.2 weight percent as acetic acid; alcohol content 0.04 weight percent as ethyl alcohol. The runs at 250° C. are contrasted with those at room temperature.

Run #	Temp., ° C.	Solvent/oil Ratio	Mol Per Cent Extracted			
			Acids	Alcohols	Esters	Carbonyls
1	Room	0.07	1-6	12		
2	Room	0.50	1-4	37		
3	Room	1.00	1	42		
4	Room	2.00	1-1	51	9	34
5	250	0.50	13	26		
6	250	4.00	61	81		

¹ Denotes loss of acid to raffinate phase, i. e., denotes an increase in amount of acids present in oil phase following extraction.

It will be observed that the acids are not extracted by the acid water bottoms at room temperature, while at 250° C. the acid clean up is appreciable particularly at the higher solvent to oil ratio. Considerable increase in the amount of alcohols extracted is also noticeable and this is due in part to hydrolysis of esters at the higher extraction temperature aided no doubt by the acidic nature of the extraction solvent.

The solvent/feed ratios employed may be varied over a wide range and will be determined in any particular case by the extraction temperature, the equipment employed and desired clean-up of the extractable oxygenated compounds. For most purposes, the optimum range of solvent to feed ratio is from 2 to 5 to 1 although operation at from about 0.25 to 1 to as high as 10 to 1 may be carried out satisfactorily.

By the solvent extraction process as described in this invention all the oxygenated compounds containing up to and including five carbon atoms are quantitatively removed from the oil layer. The removal of esters of C₂ to C₅ is more complete at the higher extraction temperatures of this invention due to hydrolysis. In addition, incomplete removal of oxygenated compounds containing 6 carbon atoms and above is also effected. The higher molecular weight oxygenated compounds, i. e. those containing 6 carbon atoms and above, may be more completely removed from the hydrocarbon oil by other methods not a subject of this invention.

As previously stated the higher extraction temperatures are conducive to the substantial hydrolysis of esters present in the feed to the extraction step. When the feed is known to con-

tain appreciable quantities of esters whose hydrolysis to more valuable alcohol and acid products is desirable the hydrolysis may be accelerated by the addition of small quantities of catalysts such as mineral acids to the extraction solvent. The hydrolysis of esters is especially promoted by the presence of sulfuric acid or phosphoric acid in concentrations up to 10 weight per cent in the solvent.

Although the invention has been illustrated by the use of dilute aqueous acid bottoms recovered from the hydrocarbon synthesis water layer, the invention is by no means limited thereto. Dilute aqueous solutions of the water soluble aliphatic organic acids may be employed as well. In addition, the use of mixtures of the water-soluble aliphatic acids is also included within the scope of this invention. For example, a dilute aqueous solution containing equal or unequal proportions of acetic acid and propionic acid, or acetic acid and butyric acid may be employed.

Having fully described the invention in a manner such that it may be practiced by those skilled in the art,

What is claimed is:

1. An improved process for the recovery of aliphatic oxygenated compounds containing 1 to 6 carbon atoms per molecule from a mixture of such oxygenated compounds with hydrocarbons of substantially the same boiling range, said mixture resulting from the catalytic hydrogenation of oxides of carbon, which comprises selectively extracting the oxygenated compounds from the mixture in a liquid-liquid extraction by contact with a dilute aqueous solution of acetic acid, containing approximately 2 to 5 weight percentage of acetic acid, at a temperature in the range of 125° C. to 375° C., separating an extract phase comprising the oxygenated compounds and a raffinate phase comprising the hydrocarbons, and recovering the oxygenated compounds from the extract phase.

2. A process according to claim 1 in which the extraction is carried out at a temperature between 175° C. and 250° C.

3. A process according to claim 1 in which the ratio of solvent to feed extracted is between 0.25 to 1 and 10 to 1.

4. An improved process for the separation of aliphatic oxygenated compounds from hydrocarbon oil solutions containing them produced as reaction products in a hydrocarbon synthesis reaction whereby oxides of carbon are hydrogenated in the presence of a catalyst to yield a product which when condensed, separates into a hydrocarbon oil phase containing dissolved oxygenated compounds and an aqueous phase containing dissolved oxygenated compounds, which comprises separating the hydrocarbon oil phase from the aqueous phase, fractionally distilling the aqueous phase to produce an overhead product comprising essentially neutral oxygenated aliphatic compounds, and an aqueous bottoms containing 2 to 10 weight percent aliphatic carboxylic acids containing less than 5 carbon atoms per molecule, contacting the hydrocarbon oil phase at a temperature between 125° C. and 375° C. with said aqueous bottoms containing 2 to 10 weight percentage aliphatic carboxylic acids containing less than 5 carbon atoms per molecule, separating an extract phase comprising the oxygenated compounds, and a raffinate phase comprising the hydrocarbons, and recovering the aliphatic oxygenated compounds from the extract phase.

drocarbons, and recovering the aliphatic oxygenated compounds from the extract phase.

5. A process according to claim 4 in which the low molecular weight oxygenated compounds contain from 1 to 6 carbon atoms per molecule.

6. An improved process for the separation of neutral and acidic aliphatic oxygenated compounds from hydrocarbon oil solutions containing them produced as reaction products in a hydrocarbon synthesis reaction whereby oxides of carbon are hydrogenated in the presence of a catalyst to yield a product which when condensed separates into a hydrocarbon oil phase and an aqueous phase, which comprises separating the hydrocarbon oil phase from the aqueous phase, contacting the hydrocarbon oil phase in a liquid-liquid extraction at a temperature between 125° C. and 375° C. with a dilute aqueous carboxylic acid containing less than 5 carbon atoms per molecule and containing 2% to 10% by weight of acid, separating an extract phase comprising the neutral and acidic oxygenated compounds and a raffinate phase comprising the hydrocarbons, and recovering said oxygenated compounds from the extract phase.

7. An improved process for the separation and recovery of aliphatic oxygenated compounds comprising alcohols, aldehydes, ketones, esters, acetals, and acids from a mixture of such oxygenated compounds with hydrocarbons which comprises extracting the oxygenated compounds from the mixture in a liquid-liquid extraction by contact with a solvent comprising a dilute aqueous solution of an aliphatic carboxylic acid containing less than 5 carbon atoms per molecule and containing 2% to 10% by weight of acid, at a temperature between 125° C. and 375° C., separating an extract phase comprising the aliphatic oxygenated compounds and a raffinate phase comprising the hydrocarbons, and recovering the aliphatic oxygenated compounds from the extract phase.

8. A process according to claim 7 in which the oxygenated compounds are contained in a mixture with hydrocarbons of substantially the same boiling range.

9. A process according to claim 7 in which the aliphatic oxygenated compounds contain from 1 to 6 carbon atoms per molecule.

10. A process according to claim 7 in which the solvent is aqueous acid bottoms containing 2% to 10% by weight of acid recovered from the water layer of a hydrocarbon synthesis reaction product.

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