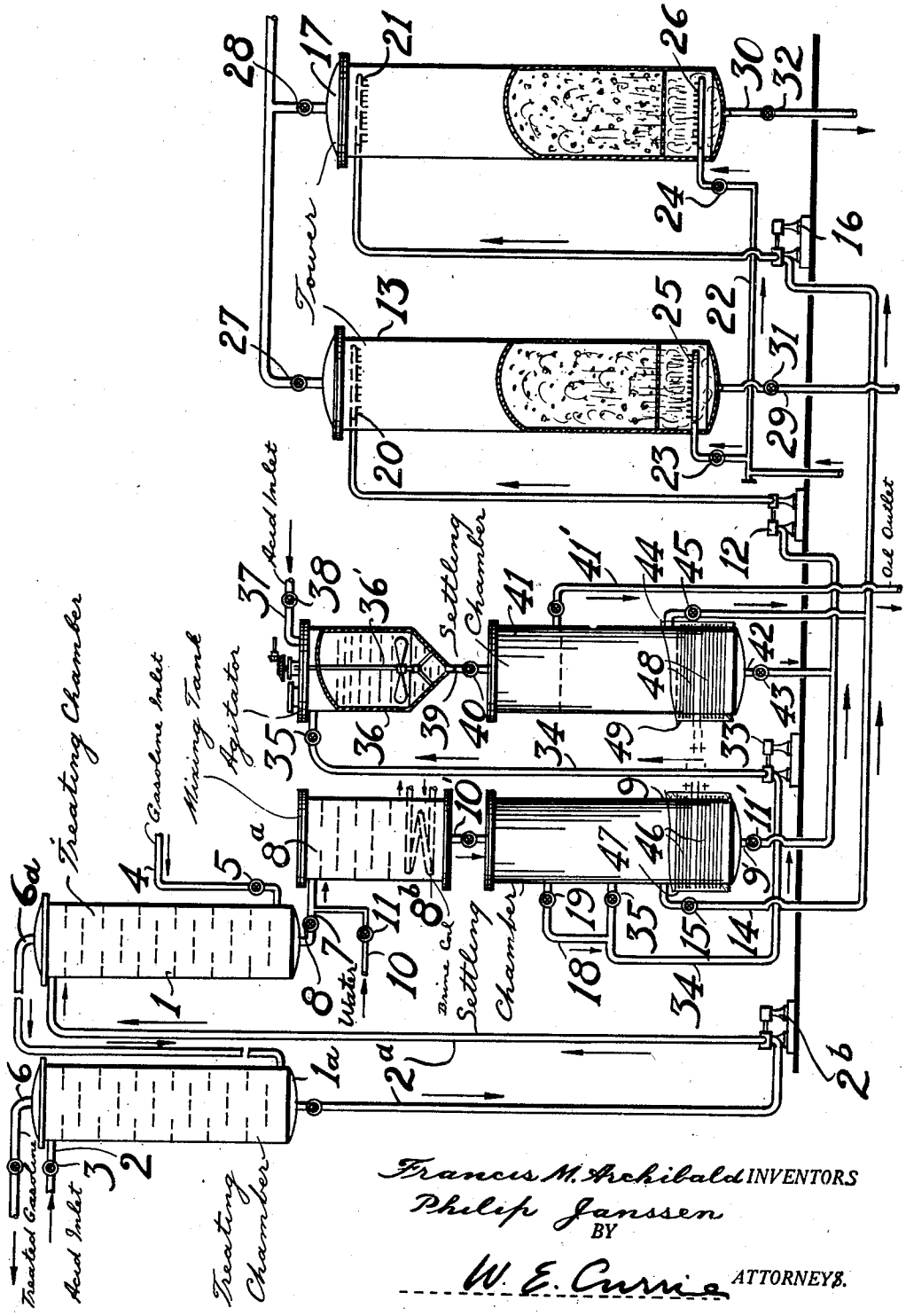
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RECOVERY OF ALCOHOLS FROM HYDROCARBONS

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RECOVERY OF ALCOHOLS FROM HYDROCARBONS

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This invention relates to improvements in methods of recovering alcohols from acid liquors containing alkyl sulfates formed by a treatment of hydrocarbons with sulfuric acid for the conversion of the unsaturated components thereof into their sulfated derivations.

In a treatment of hydrocarbons such as cracked gasoline or a fraction distilled from cracked gasoline, with sulfuric acid, the sulfuric acid solution containing alkyl esters and polymerized oils is separated, hydrolyzed by diluting with water and settled to separate the polymerized oils and the diluted acid containing the alcohols. The lower molecular weight alcohols such as isopropyl alcohol remain in solution in dilute sulfuric acid. The higher molecular weight alcohols such as butyl to heptyl alcohols do not remain wholly in solution in the diluted sulfuric acid but are found in solution in the polymerized oils. We have discovered that upon diluting sulfuric acid liquors containing the higher weight alkyl esters and maintaining the diluted acids at certain temperatures for certain concentrations of sulfuric acid, that more of the alkyl sulfates present are converted into alcohols. The alcohols are partly soluble in the polymerized oils. We have also discovered that if the temperatures are regulated according to the acid concentrations that the alcohol will remain in solution in the dilute sulfuric acid, from which the alcohols may be economically recovered.

An object of this invention is the separation of alcohols formed having four or more carbon atoms from the polymerized oils.

Another object of this invention is to separately recover from an acid liquor containing the alcohols formed, the high molecular weight alcohols having four or more carbon atoms, such as butyl, amyl, hexyl and heptyl alcohols.

Another object of this invention is to increase the yields of alcohols that are obtained from petroleum hydrocarbons.

Other objects and advantages will appear in the following illustration of our process in which:

The drawing is a diagrammatic view, illustrating an embodiment of our invention.

Referring to the drawing, numeral *1a* indicates a treating chamber into which sulfuric acid is passed through pipe 2 arranged with valve 3. The strength of the sulfuric acid generally used is about 90 percent. One or more additional treating chambers, such as *1* are preferably provided. Pipe 4 arranged with valve 5 is used to pass gasoline into the treating chamber *1*. The temperature at which the sulfuric acid and gasoline are brought into contact is best kept low, for example about 0° to 5° C. The gasoline described for illustration of this process is a distillate of cracked gasoline having a boiling range from 20° to 220° C. A pipe *2a* and pump *2b* conduct the acid liquid from chamber *1a* to the top of chamber *1*. Both chambers are provided with suitable contact means, such as baffle plates.

Pipe 6 is used to pass the treated gasoline from the treating chamber *1a*. The two chambers *1* and *1a* are connected by pipe *6a*. Sulfuric acid solution containing alkyl sulfates and polymerized oils is passed from the bottom of treating chamber *1* through pipe 7 arranged with valve 8 into the mixing chamber *8a*. Water is introduced into pipe 7 through pipe 10 arranged with valve 11. The water is mixed with the acid liquor in mixing chamber *8a* and passed through pipe 10' into settling chamber 9. The quantities of water and acid liquor passed into mixing chamber *8a* are regulated so that the resulting mixture is about 15 to 60% sulfuric acid strength. The acid and water on mixing generate heat and are cooled to a temperature of about 15° to 60° C. by means of temperature regulating coil *8b* through which a heat regulating solution such as brine is circulated.

The diluted acid liquor in settling chamber 9 is allowed to settle and it is desirable to have it separate into three phases. The mixture if maintained at a certain temperature according to the acid concentration separates into three phases; the bottom phase is found to be composed mainly of diluted sulfuric acid and about 3 to 5% of the alcohols present and a small percentage of hydrocarbons. Alkyl sulfates that have not been hydrolyzed into alcohols may also be present. The middle phase is composed of dilute acid and about 50 to 65% of the alcohols present. The upper phase is composed of mostly polymerized oils and about 2 to 15% of the alcohols present. The bottom phase is removed through pipe 9' fitted with valve 11 by means of pump 12 into tower 13. The middle phase is removed through pipe 14 arranged with valve 15 by means of pump 16 into tower 17. The top phase of polymerized oil is removed through pipe 18 arranged with valve 19 for further treatment as will be shown. The acid liquors passed to towers 13 and 17 are introduced into the upper parts by means of sprays 20 and 21. Towers 13 and 17 are here shown as packed towers. Other types of towers may be used such as bellcap towers. Steam line 22 arranged with valves 23 and 24 passes steam through sprays 25 and 26

into the bottom of towers 13 and 17. Acid liquor on coming in contact with live steam passing up through the towers is partially vaporized and alcohol vapors are separated and removed from the towers through vapor outlets 27 and 28. The acids separated from the alcohols in towers 13 and 17 are removed through pipes 29 and 30 arranged with valves 31 and 32 to storage (not shown). The alkyl sulfates that have not been hydrolyzed to alcohols are not all recovered as alcohols, as some are polymerized by the steam.

The above steps are suitable when the acid liquor separates into three phases, but the acid liquor upon being diluted with water does not always do so. We have discovered that only at certain temperatures and dilutions, (which are at times difficult to control) three phases are formed. Generally a two phase separation takes place. In the case of a two phase formation, one of diluted acid and the other of polymerized oil, an appreciable percentage of the alcohols is found to be in solution in the polymerized oil. The acid phase may be removed through pipe 9' to still 13 and subjected to steam distillation to recover the alcohols.

The separated polymerized oil which has in solution a part of the alcohols, is passed by means of pump 33 and line 34 arranged with valve 35 into mixing chamber 36. Sulfuric acid of a strength between 40 and 55% is passed into mixing chamber 36 through pipe 37 arranged with valve 38 and mixed with the polymerized oil by means of paddle 36'. The quantity of acid mixed with polymerized oil is about one volume of acid to one volume of oil. The temperature at which the polymerized oil and the acid are contacted is about 15° to 60° C. Heating means for controlling the temperatures in settling chambers 9 and 41 are provided. Electrical coils 46 and 48 in outside insulations 47 and 49 are used to maintain the desired temperatures. Other heat controlling means may be used.

The mixture of polymerized oil and acid is passed through pipe 39 arranged with valve 40 into settling chamber 41. The mixture is maintained at temperatures from 15° to 60° C. depending on the strength of the acid used and allowed to settle and is found to separate into three phases. The bottom phase is composed mostly of acid and a small percentage of alcohols. The middle phase is composed mostly of sulfuric acid, a greater part of the alcohols and a small percentage of hydrocarbons. The top phase is composed of polymerized oil and a small percentage of alcohols. The top phase of polymerized oil is passed by means of pipe 41' to storage (not shown) and may be used as a fuel. The two lower phases of sulfuric acid are passed separately into towers 13 and 21. The bottom phase is passed by means of pipe 42 arranged with valve 43 and pump 12 into the tower 13. The middle phase is passed through pipe 44 arranged with valve 45 and pump 16 into the upper part of tower 21. Steam is passed through sprays 25 and 26 into the bottom of towers 13 and 21. The acid liquor in passing through the tower is subjected to counter-current action of steam and the alcohols are recovered as vapors by means of vapor lines 27 and 28. The sulfuric acid remaining is removed from towers 13 and 21 by means of pipes 29 and 30 arranged with valves 31 and 32.

In an operation where a three phase separation takes place in the first settling tank 9, it may be desirable to further subject the layer of polymerized oil to further treatment to recover the alcohols. This is done by passing the polymerized oil through pipes 18 and 34 by means of pump 33 to mixing tank 36, mixing the polymerized oil with an equal quantity of 40 to 55% sulfuric acid in mixing chamber 36 and settling the mixture in settling tank 41, separating the phases and subjecting the two acid phases to separate distillation.

In the sulfation of the olefines having four or more carbon atoms, the corresponding alkyl sulfates are formed which are hydrolyzed to alcohol by the addition of water. These alcohols are soluble in polymerized oils as well as in aqueous acid solution and are difficult to separate from the polymerized oils upon diluting the sulfuric acid with water. We have discovered that upon regulating the strength of diluted acid to 15 to 60% and regulating the temperatures from 15° C. to 60° C. that the alcohols will go into solution with the sulfuric acid and that this sulfuric acid will further separate into two phases. One containing the major portion of the alcohols separates out as a middle phase over a lower phase of sulfuric acid containing a smaller quantity of the alcohols. For example, in the above process, the olefines are first treated with sulfuric acid. The sulfuric acid is diluted to about 15 to 60% sulfuric acid and cooled to 15 to 60° C. If a three-way separation results on settling, the bottom phase is one of diluted sulfuric acid containing a small portion of alcohols, the middle phase is one of diluted sulfuric acid and contains a major portion of alcohols and the top phase of polymerized oil contains a small portion of alcohols. The bottom phase and the middle phase are separately subjected to steam distillation to remove the alcohols from solution.

If, upon settling of the diluted acid liquor, a two-way separation results and the upper phase of polymerized oil is found to contain a considerable part of the alcohols, the polymerized oil may be further treated with a sulfuric acid solution of a strength of 40 to 70% and allowed to settle. In treating the separated polymerized oil, a stronger acid may be used up to 70%, as the tertiary alcohols that may be formed in the first acid treatment of the cracked gasoline had been removed in the separated sulfuric acid.

The following tables illustrate the separation of the alcohols that occurs upon settling various diluted acid liquors of different sulfuric acid strengths at different temperatures.

TABLE I

Percentage yield of alcohols in various phases based on dilute extract

Temperatures	20° C.	25° C.	35° C.	50° C.	60° C.
Upper phase	0.2	0.3	0.5	11.2	9.0
Middle phase	No phase	No phase	6.0	0.3	No phase
Lower phase	10.5	11.2	5.3	1.7	0.3

An acid liquor obtained by treating a cracked gasoline was taken and divided into five fractions. The different fractions were separately diluted to 33% sulfuric acid strength and allowed to settle separately at various temperatures. The different phases were separated and analyzed. The temperature found most suitable for recovering the alcohols was 35° C. as 11.3% of the alcohols were recovered. Analysis disclosed that on settling at 50° C. more alcohols as such were present but as the major part of the alcohols

were in solution in the upper phase of polymerized oil, it could only be economically recovered in a substantially pure state by re-extraction. The alkyl sulfates that are not hydrolyzed to alcohols on dilution are not all recovered as they tend to polymerize upon steam distillation.

TABLE II

Partition of alcohols between various layers

	Per cent	*Per cent*	*Per cent*
Acid strengths	30	42	53
Upper phase	90	5	1
Middle phase	No phase	85	0
Lower phase	10	10	99

A synthetic mixture of water white kerosene oil, and alcohols having more than four carbon atoms was prepared. The mixture was mixed first with an equal volume of 30% sulfuric acid and allowed to settle at 20° C. The mixture on settling separated into two phases. The upper phase of oil contained 90% of the alcohols and the lower phase of acid contained 10% of the alcohols. The mixture of oil, alcohols and sulfuric acid is further treated with strong sulfuric acid to bring the acid strength up to 43%. On settling at 20° C. a three phase separation takes place. The upper phase of oil was found to contain 5% of the alcohols, the middle phase 85% of the alcohols and the lower phase 10% of the alcohols. Upon further stirring with an addition of more strong sulfuric acid to bring the acid strength up to 53% and settling, a two phase separation takes place, the top phase of oil containing 1% of the alcohols and the lower phase of dilute sulfuric acid 99%. It was found that best separation of these alcohols from oil was made with a sulfuric acid of about 53% strength and at a temperature of about 20° C.

TABLE III

Approximate best settling temperatures for acids of different strengths recovered from a treatment of naphtha and diluted, yielding about 20% alcohols figured on the original acid liquor

Temperature	Acid strength	Upper phase	Middle phase	Lower phase
		Per cent	*Per cent*	*Per cent*
40	40	5	35	60
50	30	4	25	71
60	20	3	No phase	97

The table illustrates the different temperatures at which the different diluted acid liquors settle with the optimum yield of alcohols on steam distillation of the acid phases.

In treating a separated polymerized oil that has been recovered from a diluted acid liquor, sulfuric acids of 40% to 70% strength may be used. The stronger acids such as 70% do not tend to char or burn the alcohols as the tertiary alcohols have been removed in a previous step.

By the control of the dilution of the acid liquors and the settling temperatures, we have discovered that larger yields of alcohols may be obtained. The substantial conversion of all the alkyl esters to alcohols before steam distillation eliminates the resulting polymerization of the alkyl esters. In isolating the major portion of the alcohols in one phase, decomposition of the alcohols is substantially eliminated during distillation. The alcohols in solution in the polymerized oil are recovered.

The foregoing description is merely for illustration and various changes and alternative arrangements may be made within the scope of the appended claims in which it is our intention to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. An improvement in a process of manufacturing alcohols of more than three carbon atoms from a mixture of saturated and unsaturated hydrocarbons which comprises treating a mixture of saturated and unsaturated hydrocarbons of more than three carbon atoms with sulfuric acid under desirable sulfating conditions, and removing the sulfuric acid solution, diluting the acid solution with water to 15 to 50% sulfuric acid strength and settling the diluted acid at temperatures of 20° C. to 60° C. using the higher temperatures in settling the weaker diluted acid liquor and the lower temperatures in settling the stronger diluted acid liquor, separating the oil and subjecting the remaining diluted acid liquor to steam distillation to recover the alcohols.

2. An improved process of recovering alcohols from an acid liquor containing sulfated derivatives of olefines of more than three carbon atoms, said derivatives being primarily sulfates of butylene, hexylene and heptylene and substantially free from sulfated derivatives of propylene and lower olefines, which comprises contacting the higher boiling fractions of cracked naphtha with sulfuric acid of a strength of about 90%, while maintaining the temperature within limits at which fluid sulfated derivatives of unsaturated hydrocarbons are produced, removing the sulfuric acid solution so formed and diluting with water, settling the mixture into phases and separately withdrawing the phases, subjecting the separated phase of polymerized oil having in solution alcohols and sulfated derivatives of olefines having four or more carbon atoms to contact with a solution of sulfuric acid having a strength of 40 to 70%, settling the resulting mixture into phases, separately withdrawing the lower phases of sulfuric acid containing the alcohols and sulfated derivatives of olefines having four or more carbon atoms and subjecting the separated aqueous acid to steam distillation to recover the alcohols.

3. An improved process of separately recovering alcohols from an acid liquor produced by the reaction of sulfuric acid and cracked naphtha containing olefines having more than three carbon atoms which comprises contacting a cracked naphtha containing substantially no hydrocarbons having less than four carbon atoms with sulfuric acid under desirable sulfating conditions, removing the sulfuric acid solution, diluting the acid solution with water, settling the mixture, separating the separated polymerized oil and dilute acid, contacting the separated polymerized oil with sulfuric acid of a strength of 40 to 70%, settling the mixture, separately withdrawing the lower phase of sulfuric acid containing alcohol and the sulfated derivatives of olefines having four or more carbon atoms, and subjecting the separated dilute acid to steam distillation to recover alcohols.

4. An improvement in a process of manufacturing butyl, amyl, hexyl and heptyl alcohols, which comprises contacting a cracked petroleum hydrocarbon containing olefines having more than three carbon atoms with sulfuric acid having a strength of about 90%, under desirable sulfating conditions, removing the sulfuric acid so-

lution, diluting the acid solution with water, settling the diluted acid extract, separately withdrawing the polymerized oil and diluted acid, contacting the separated polymerized oil with sulfuric acid of a strength of 40 to 70%, settling the mixture, withdrawing the lower layer of sulfuric acid solution, subjecting the separated diluted sulfuric acid solutions to distillation and withdrawing butyl, amyl, hexyl, and heptyl alcohols as a distillate.

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