

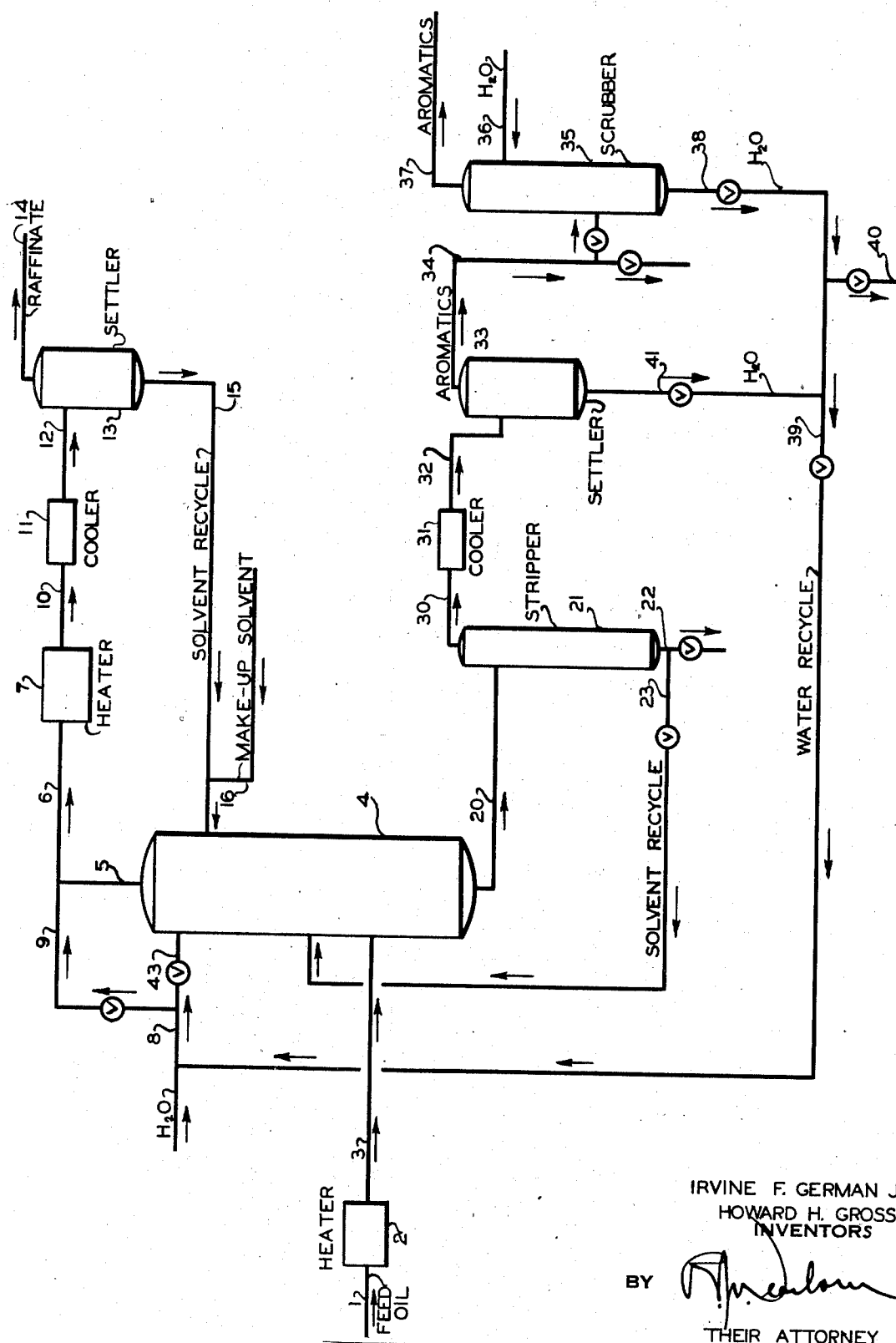
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EXTRACTION OF HYDROCARBONS

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EXTRACTION OF HYDROCARBONS

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This invention relates to the extraction of hydrocarbons and to the extraction of hydrocarbon mixtures with a solvent comprising a lactone-forming acid such as levulinic acid.

The invention contemplates extracting a hydrocarbon mixture with a lactone-forming acid such as levulinic acid in the presence of a modifying agent such as water in an amount sufficient so that a two-phase system exists when the solvent and hydrocarbon mixtures are in extractive contact within a predetermined temperature range. The resulting phases are separated and separately treated to remove the hydrocarbons and recover the acid solvent.

A lactone-forming acid such as levulinic acid tends to undergo decomposition to some extent when used as an extraction solvent at elevated temperatures, such decomposition involving lactone formation as evidenced by the presence of lactones in one of the liquid phases formed during the extraction.

In accordance with the present invention the liquid phase or hydrocarbon mixture containing lactones formed during the extraction is subsequently subjected to an elevated temperature in the presence of a substantial amount of added water so as to reconvert lactones present therein to the lactone-forming acid.

Thus, a mixture of aromatic and non-aromatic hydrocarbons may be extracted with a solvent comprising levulinic acid at a temperature in the range 150 to 225° F. for example to form extract and raffinate phases. The extract phase comprises aromatic hydrocarbons dissolved in the larger portion of the solvent while the raffinate phase comprises non-aromatic hydrocarbons mixed with a minor proportion of the solvent.

The raffinate phase will contain a small amount of lactones which are soluble in the raffinate hydrocarbons. Accordingly, the raffinate phase is withdrawn and commingled with a substantial amount of water, the water being present in an amount which is at least the molecular equivalent of the lactones present in the raffinate oil. The resulting mixture is then maintained at an elevated temperature in the range about 150 to 600° F. for a substantial period of time which may range from a few minutes to several hours or for an even longer period of time. As a result of this heat treatment the lactones are substantially all reconverted to levulinic acid.

The treated mixture is then cooled to effect separation between the hydrocarbons and the levulinic acid solution. The separated hydro-

carbons are discharged while the recovered acid is recycled to the extraction step.

In order to describe the invention in more detail reference will be made to the accompanying drawing comprising a flow diagram illustrating one method of practicing the process of the invention.

As indicated in the drawing, a mixture of aromatic and non-aromatic hydrocarbons is drawn from a source not shown and conducted through a pipe 1 to a heater 2 wherein it is raised to a temperature in the range about 200 to 250° F. The heated oil is then conducted through a pipe 3 to an intermediate portion of an extraction tower 4.

Within the extraction tower 4 the oil is brought into intimate contact with levulinic acid introduced to the upper portion of the tower at one or more points as described later. Advantageously the treatment within the tower 4 involves countercurrent flow of extraction solvent and oil undergoing treatment so that formation of extract and raffinate phases occurs.

The raffinate phase comprising non-aromatic hydrocarbons mixed with a minor proportion of solvent accumulates in the top of the tower and is continuously drawn therefrom through a pipe 5 communicating with a pipe 6 leading to a heater 7. This raffinate phase contains a small amount of lactones amounting to about 0.2 to 2.0% by weight of the raffinate oil.

A quantity of water introduced to the system through a pipe 8 is conducted through a branch pipe 9 communicating with the previously mentioned pipe 6 wherein the water so introduced is mixed with the raffinate phase. The amount of water so added to the raffinate phase is sufficient to provide a mixture in which the water present is at least the molecular equivalent of the lactones present in the raffinate oil. Advantageously the water is in substantial molar excess over the lactones and may amount to 20 mols per mol of lactone.

The resulting mixture is passed through the heater 7 wherein it is raised to a temperature within the range 150 to 600° F., preferably to a temperature of 250 to 300° F., and under sufficient pressure to maintain the system in a liquid state. The heated mixture is then drawn off through a pipe 10 to a cooler 11 although it will be understood that where it is desired to employ lower temperatures with a longer time of heating provision may be made for maintaining the heated mixture at the elevated temperature for a

substantial period of time ranging from 1 to 10 hours or more following which the mixture may be cooled.

The cooled mixture is conducted from the cooler 11 through a pipe 12 to a settling vessel 13 wherein the mixture is permitted to stand at a temperature corresponding to about room temperature so that separation of the aqueous acid mixture from the hydrocarbon occurs. The upper layer will comprise raffinate hydrocarbons which are drawn off through a pipe 14.

The aqueous layer, consisting mainly of levulinic acid, is drawn off through a pipe 15 through which it is returned to the upper portion of the extraction tower 4. Any make-up acid required can be added through a pipe 16.

The extract phase accumulating in the bottom portion of the extraction tower 4 is continuously drawn off through a pipe 20 to a stripper 21 wherein the aromatic hydrocarbons may be stripped from the acid solvent with the aid of steam under subatmospheric pressure, if desired.

Residual liquid, consisting of solvent from which the aromatic hydrocarbons have been stripped, is drawn off through a pipe 22 and recycled all or in part through the pipe 23 leading to the upper portion of the extraction tower 4. The acid solvent returned to the pipe 23 is of relatively high concentration and therefore may be introduced to the extraction tower 4 at a point intermediate between the point of feed oil introduction and the point of solvent return through the pipe 15.

The distillate removed in the stripper 21 is conducted through a pipe 30 to a cooler 31 wherein cooling and condensation is effected. The resulting condensate is conducted through a pipe 32 to a settler 33 wherein phase separation between aromatics and water occurs.

The separated aromatics which may still retain a small amount or trace of levulinic acid are conducted through a pipe 34 to a scrubber 35 wherein the aromatics may be subjected to countercurrent washing with a stream of water. The water may be introduced to the upper part of the scrubber through a pipe 36 in the proportion of about 1 volume of water to 1 volume of aromatics, so as to permit countercurrent contact between water and aromatics. The scrubbed aromatics are discharged from the top of the scrubber 35 through a pipe 37 while the wash water is removed from the bottom of the scrubber 35 through a pipe 38 communicating with a pipe 39. The pipe 39 communicates with the previously mentioned pipe 8 thereby providing means for recycling all or a portion of the water either to the top of the extraction tower 4 or for mixing with raffinate phase flowing through the pipe 6. The portion of water not recycled through the pipe 39 may be discharged from the system through a pipe 40. Likewise, water separated from the settler 33 is drawn through a pipe 41 which communicates with the previously mentioned pipe 39. This water also may be recycled through pipe 39 or removed from the system through pipe 40.

As previously mentioned, some water or recycled water containing a small amount of acid can be introduced to the upper portion of the extraction tower 4 through a pipe 43 which permits introducing the water at a point above that at which the solvent or more concentrated solvent solutions are introduced. In this way the raffinate phase is subjected to washing with

water as it rises towards the top of the extraction tower 4.

Moreover, by introducing water or substantially pure water at the top of the tower while introducing solvent of progressively increasing concentration at successive points in the tower toward the point of feed oil introduction a concentration gradient may be maintained throughout this portion of the extraction tower.

The method of flow thus illustrated is applicable to the treatment of naphtha or fractions of naphtha containing aromatic constituents. It has been found that levulinic acid of not in excess of about 97% concentration, that is, containing at least about 3% water by weight of the acid, is effective in extracting toluene of nitration grade from such hydrocarbon mixtures. The extraction may be effected in the presence of larger amounts of water, for example, using acid of about 75% concentration but under such conditions higher extraction temperatures are required since the solubility of toluene in the dilute acid is decreased thereby necessitating the employment of higher temperatures. For extracting benzene somewhat lower acid concentrations may be used, as low as about 60% acid.

More specifically, the invention concerns effecting the extraction of aromatics from hydrocarbon mixtures containing them by treating the mixtures with a levulinic acid-water solvent having a concentration within the range about 60 to 97% acid, based on the mixture of acid and water, or with anhydrous acid in the presence of 3 to 60% water by weight of the anhydrous acid. The ratio of acid-water solvent to feed oil may vary over a wide range, for example, from 1 or less to 10 or more volumes of solvent per volume of oil.

The extraction temperature employed may range from about 20 to 300° F. although the present invention is particularly concerned with operations employing extraction temperatures in the upper portion of this range, namely, in the neighborhood of 200° F. and above, at which temperatures levulinic acid undergoes some decomposition with formation of lactones.

The lactones so formed when extracting naphtha or naphtha hydrocarbon mixtures are usually found in the raffinate phase.

It has been found that by subjecting such lactones to elevated temperatures in the presence of a molar excess of water they are substantially completely reconverted to levulinic acid. For example, 1 mol of lactone is mixed with 1.32 mols of water. This mixture is maintained at a temperature of 300° F. for about 184 hours and then cooled to room temperature. The resulting product will comprise about 92.6% by weight of levulinic acid, 1.9% lactone and 5.5% water.

Consequently, and in accordance with the present invention, the raffinate phase containing a small amount of lactones is mixed with water and subjected to elevated temperature with continued agitation under conditions so as to effect substantial reversion of the lactones to the acid.

While mention has been made of applying the process to the treatment of naphtha hydrocarbons it is also contemplated that it may be applied to the treatment of other hydrocarbons or hydrocarbon mixtures derived from petroleum or some other source such as animal and vegetable oils.

Although the invention is particularly useful for the extraction of aromatic hydrocarbons from mixtures containing aromatic and non-aromatic hydrocarbons, it is contemplated that it may be

used in the treatment of other types of hydrocarbon mixtures as indicated above. It may be used to effect separation between olefinic and paraffinic hydrocarbons.

In connection with the extraction tower 4, provision may be made for the employment of extract recycle, raffinate recycle, temperature gradient throughout the extraction zone, etc. One or more towers may be employed or the process may be carried out in a stage system, each stage comprising mixing and settling zones.

While levulinic acid has been mentioned, it is contemplated that other gamma or delta keto or hydroxy acids which are useful as selective solvents for oil may be employed wherein the employment of such acids is accompanied by lactone formation.

While mention has been made of treating the raffinate phase so as to convert lactones to the acid form, nevertheless it is contemplated that the extract phase or any portion thereof likewise may be treated to effect conversion of lactones contained therein.

For example, provision may be made for diverting all or a portion of the liquid mixture flowing through pipe 30 to a conversion zone wherein it is maintained under suitable conditions such as employed in treating the raffinate phase to effect conversion of lactones to the corresponding acids. The so-treated mixture can then be cooled and subjected to settling so as to separate the solution of acid in water from the extract oil.

The separated solution may be recycled to the extraction tower 4 or otherwise disposed of. The extract oil can be removed or passed to the scrubber 35 to remove any retained acid.

While not shown, it is also contemplated that means may be provided for effecting thorough mixing of the heated lactone-containing mixture so as to facilitate the conversion to acid.

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 by the appended claims.

We claim:

1. A process for effecting separation between hydrocarbon bodies of different chemical constitution by solvent extraction which comprises extracting a mixture of hydrocarbons with relatively concentrated aqueous levulinic acid at a temperature in the range about 150 to 300° F., forming an extract phase comprising soluble hydrocarbons dissolved in a larger proportion of the acid and a raffinate phase comprising relatively insoluble hydrocarbons mixed with a minor proportion of the acid, said raffinate phase containing a small amount of lactones formed from the acid during said extraction, separating said phases, commingling the separated raffinate phase with water in substantial molar excess over the lactones present, maintaining the commingled mixture at a temperature in the range 150 to 600° F. for a substantial period of time such that lactones therein are converted to acid, separating the resulting acid from the raffinate hydrocarbons and returning the separated acid to the extraction step.

2. The method according to claim 1 in which the commingled mixture of water and raffinate phase is maintained at a temperature of about 250 to 300° F. for a substantial period of time such that lactones therein are converted to acid.

3. A process for effecting separation between

hydrocarbon bodies of different chemical constitution by solvent extraction which comprises extracting a mixture of hydrocarbons with relatively concentrated aqueous levulinic acid at a temperature in the range about 150 to 300° F., forming an extract phase comprising soluble hydrocarbons dissolved in a larger proportion of the acid and a raffinate phase comprising relatively insoluble hydrocarbons mixed with a minor proportion of the acid, said raffinate phase containing a small amount of lactones formed from the acid during said extraction, separating said phases, separating the bulk of the solvent from the extract phase, returning the separated solvent to the extraction step, washing the extract hydrocarbons from which the bulk of the solvent has been separated with water to remove residual solvent, commingling a portion of the wash water containing residual solvent with said separated raffinate phase in an amount such that the water is in substantial molar excess over the lactones present, maintaining the commingled mixture at a temperature in the range 150 to 600° F. for a substantial period of time such that lactones contained therein are converted to acid, separating the resulting acid from the raffinate hydrocarbons and returning the separated acid to the extraction step.

4. A process for effecting separation between oil constituents of different chemical constitution by solvent extraction which comprises extracting said oil with relatively concentrated aqueous levulinic acid at a temperature in the range 150 to 300° F., forming an extract phase comprising constituents of the oil soluble in the major portion of the acid and a raffinate phase comprising relatively insoluble constituents of the oil mixed with a minor portion of the acid, said raffinate phase containing a small amount of lactones formed from the acid during said extraction, separating said phases, commingling the separated raffinate phase with up to about 20 mols of water per mol of lactone, maintaining the commingled mixture at a temperature in the range about 250 to 300° F. for a substantial period of time such that lactones therein are converted to acid, separating the resulting acid from the raffinate hydrocarbons and returning the separated acid to the extraction step.

5. A process for effecting separation between oil constituents of different chemical constitution by solvent extraction which comprises extracting said oil with aqueous levulinic acid having a concentration of about 60 to 97 weight per cent acid at a temperature in the range about 150 to 300° F., forming an extract phase comprising constituents of the oil soluble in the major portion of the acid and a raffinate phase comprising relatively insoluble constituents of the oil mixed with a minor portion of the acid, said raffinate phase containing a small amount of lactones formed from the acid during said extraction, separating said phases, commingling the separated raffinate phase with up to about 20 mols of water per mol of lactone, maintaining the commingled mixture at a temperature in the range about 250 to 300° F. for a substantial period of time such that lactones therein are converted to acid, separating the resulting acid from the raffinate hydrocarbons and returning the separated acid to the extraction step.

6. A process for separating aromatic hydrocarbons from naphtha which comprises extracting the naphtha with aqueous levulinic acid having a concentration of about 60 to 97 weight per

cent acid at a temperature substantially above the melting point of anhydrous levulinic acid, forming an extract phase comprising aromatic hydrocarbons dissolved in a major portion of the acid and a raffinate phase comprising non-aromatic hydrocarbons mixed with a minor portion of the acid, said raffinate phase containing a small amount of lactones formed from the acid during said extraction, separating such phases, commingling the separated raffinate phase with up to about 20 mols of water per mol of lactone, maintaining the commingled mixture at a temperature of about 250 to 300° F. for a substantial period of time such that lactones therein are converted to acid, separating the resulting acid from the raffinate hydrocarbons and returning the separated acid to the extraction step.

7. A continuous process for effecting separation between oil constituents of different chemical constitution by solvent extraction which comprises introducing a stream of feed oil to an intermediate point of an extraction column maintained at an elevated temperature substantially above the melting point of anhydrous levulinic acid, introducing relatively concentrated aqueous levulinic acid to the upper portion of said column, effecting countercurrent contact between feed oil and acid within the column at said elevated temperature such that a raffinate phase comprising relatively insoluble constituents of feed oil mixed with a minor portion of acid and an extract phase comprising soluble constituents of the oil dissolved in a major portion of the acid are formed, continuously withdrawing extract phase from the lower portion of the column below the point of feed oil introduction, injecting water to the upper portion of said column above the point of acid introduction, subjecting raffinate phase rising therein to washing with said injected water, continuously withdrawing from the upper portion of the column above the point of water injection a stream of washed raffinate phase containing a small amount of lactones formed from the acid during said extraction, subjecting withdrawn raffinate phase containing water in substantial molar excess over the lactones present in the raffinate phase to an elevated temperature for a time sufficient to re-

convert lactones to acid, cooling the heated raffinate phase to a temperature sufficiently low to cause separation into an oil phase and an aqueous phase comprising acid, and recycling separated acid phase to the upper portion of said column substantially below the point of water injection.

8. A continuous process for extracting toluene from naphtha which comprises introducing a stream of naphtha hydrocarbons containing toluene to an intermediate point of an extraction column maintained at an elevated temperature in the range 150 to 225° F., introducing aqueous levulinic acid of about 97.0 concentration to the upper portion of said column, effecting countercurrent contact between feed naphtha and acid within the column at the aforesaid elevated temperature such that non-aromatic hydrocarbons mixed with a minor portion of the acid and an extract phase comprising aromatic hydrocarbons dissolved in a major portion of the acid are formed, withdrawing extract phase from the lower portion of the column below the point of naphtha introduction, injecting water to the upper portion of said column above the point of acid introduction, subjecting raffinate phase rising therein to washing with said injected water, withdrawing from the upper portion of the column above the point of water injection a stream of washed raffinate phase containing a small amount of lactones formed from the acid during said extraction, subjecting withdrawn raffinate phase containing water in substantial molar excess over the lactones present in the raffinate phase to a temperature in the range about 250 to 300° F. for a period of time sufficient to reconvert lactones to acids, cooling the heated raffinate phase mixture to about room temperature to form a hydrocarbon phase consisting essentially of nitration grade toluene and an aqueous phase comprising acid, separating said phases and recycling the separated acid phase to the upper portion of said column at a point substantially below the point of water injection.

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