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SOLVENT EXTRACTION

George B. Arnold, Glenham, and Harold V. Atwell, Beacon, N. Y., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

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8 Claims. (Cl. 260-674)

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This invention relates to solvent extraction for the purpose of effecting fractional separation of a mixture of two or more liquid components by treatment with a solvent consisting mainly of water.

In accordance with the invention a liquid mixture containing two or more components such as a hydrocarbon mixture derived from petroleum is extracted with a solvent consisting mainly of water at elevated temperature and pressure so as to effect separation of the feed mixture into fractions differing in chemical constitution. More specifically, the extraction is effected at a temperature above the normal boiling point of the solvent and below the critical temperature of the solvent such that the solvent effects substantial selective action between constituents of different chemical constitution. The extraction is also effected under a pressure at least as high as the minimum pressure required to maintain in the liquid state at least the major portion of both the solvent and the soluble component of the feed mixture, and not more than about 200 pounds per square inch above this minimum pressure. Under these conditions there is formed a solvent phase comprising extract hydrocarbons dissolved in the main body of the solvent and a hydrocarbon phase comprising non-extract hydrocarbons.

The invention has particular application to the separation of aromatic hydrocarbons from hydrocarbon mixtures such as derived from petroleum and which contain aromatic and non-aromatic hydrocarbons including aliphatic and alicyclic hydrocarbons.

The present application is a continuation-in-part of Serial No. 458,092, filed September 12, 1942.

Serial No. 458,092 discloses extracting toluene from cracked naphtha or a hydrocarbon fraction rich in toluene with water in the proportion of about 1 part of hydrocarbon feed mixture to from about 5 to 20 parts of water. The extraction is effected under a temperature in the range about 400 to 600° F. and under pressures ranging from 1000 to 5500 pounds per square inch gauge. The resulting extract and raffinate phases are then separately discharged from the extraction zone and subjected to cooling so as to effect separation between hydrocarbons and water. Under these conditions water exerts a substantial solvent action for toluene and relatively low solvent action upon olefinic, naphthenic and paraffinic constituents of the feed mixture.

The parent application particularly contem-

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plated effecting the foregoing extraction of aromatics from a hydrocarbon mixture containing them under a pressure not more than about 200 pounds above the minimum required to maintain in the liquid state at least the major portion of both the solvent and the extract fraction of the hydrocarbon feed. When extracting with a solvent consisting essentially of water, the minimum pressure is about 1600 pounds for a naphtha charge so that the preferred extraction pressure is within the range about 1600 to 1800 pounds, and advantageously not substantially above about 1600 to 1700 pounds when extracting at a temperature of 550° F. It was found that by reducing the pressure to the foregoing minimum the amount of toluene contained in the extract reaches a maximum and the maximum recovery of toluene is thus realized. Upon reducing the pressure still lower a point is reached at which substantially all of the solvent is vaporized so that no extract phase is formed.

The present application is directed to using as the solvent, water containing from a fraction of a percent to about 25 percent by weight of a modifying substance selected from the group consisting of ammonia and water soluble aliphatic amines having from 1 to 5 amine residues such as methylamine, dimethylamine, trimethylamine, diethylamine, ethylenediamine, diethylenetriamine, and tetraethylenepentamine.

The minimum pressure employed when the water contains a modifying material such as anhydrous ammonia is less, and the extraction temperature is lower than the foregoing values disclosed for water alone as the solvent. Thus with water containing about 10 mol percent ammonia the minimum pressure will be about 850 pounds, while with water containing 20 mol percent ammonia the pressure will be about 1250 or not in excess of about 1300 pounds for extraction at 450° F.

Ammonia concentrations of not more than 10 to 20% are advantageous since higher concentrations reduce the density differential between extract and raffinate phases. A high density differential facilitates phase separation.

Temperatures of about 300 to 450° F. may be employed advantageously, particularly for extracting with water containing 10 to 20% ammonia, a feed consisting of a naphtha fraction boiling in the range about 190 to 250 and in which toluene is concentrated.

While the proportion of solvent to hydrocarbon feed employed in the extraction may be varied over a wide range nevertheless it is usually

sufficient when extracting toluene from a hydrocarbon mixture containing it to employ the solvent in the proportion of about 5 to 20 parts by volume of water to 1 part by volume of feed hydrocarbon mixture, the usual proportion being about 6 to 12 parts of solvent to 1 part of feed hydrocarbon.

Where it is desired to obtain toluene substantially free from olefins the extract hydrocarbons may be subjected to treatment with a suitable agent such as sulfuric acid for the purpose of removing the olefins. The acid treatment may also be employed for the purpose of removing sulfur compounds such as mercaptans as well as other impurities. Other reagents may be employed for this purpose including acid-treated clay, or strong caustic solutions employed under elevated temperatures and pressures.

In extracting aromatic hydrocarbons such as toluene from naphtha the naphtha fraction may be subjected to extraction with water followed by distillation of the resulting extract hydrocarbons to segregate a fraction rich in the desired aromatic constituents. As an alternative procedure the naphtha may be fractionated to segregate a fraction rich in the desired aromatic constituents, namely, toluene or consisting essentially of hydrocarbons having a boiling range of about 190 or 200° F. to 250° F. and this fraction then subjected to solvent extraction with water containing the modifying substance in order to separate the toluene. The raw naphtha may be extracted with a selective solvent such as furfural to obtain a fraction in which aromatics are concentrated and which concentrate may then be extracted with the water solvent of this invention.

If desired the feed naphtha or the portion thereof rich in aromatic hydrocarbons may be fractionally distilled into a plurality of narrow boiling range fractions, for example, fractions having a boiling range of about 10 to 50° F. These individual fractions may then be separately extracted and the resulting extracts subsequently blended to yield a wider boiling range aromatic material. In this way aromatic material of higher purity may be obtained with a lower solvent dosage.

It is contemplated that the naphtha or naphtha fraction rich in the desired aromatics may be subjected to preliminary treatment to remove gum-forming bodies and sulfur compounds prior to extraction. For example, the naphtha or suitable fraction thereof may be passed directly from the fractionating tower of the conversion unit in which the naphtha is produced to a conventional clay treating tower for removal of diolefins and gum-forming bodies. This clay treatment or a separate clay treatment may be carried out at temperatures sufficiently elevated to effect desulfurizing of the hydrocarbon mixture. Thereafter the treated hydrocarbon mixture is subjected to extraction to remove the aromatic constituents in a manner similar to that already described. The naphtha hydrocarbons from which the desired aromatics have been extracted can be run to gasoline or motor fuel production.

In addition to the foregoing, the process has application to the extraction of high antiknock aromatic blending stocks from wide boiling range naphthas or naphtha mixtures. It may also be applied to the treatment of high boiling petroleum fractions to obtain raffinates of desired properties, for example, Diesel fuel having a high cetane number, kerosene having superior burning properties or lubricating oils of high viscosity in-

dex. It is contemplated that it may be used for extractive separation of oils derived from other than petroleum sources, such as vegetable, animal and fish oils, rosin oils, etc., including fats, fatty acids and mixtures containing them.

Continuous countercurrent extraction has been mentioned and when operating in this manner the extraction may be carried out by passing the solvent and feed hydrocarbon mixture countercurrently through a packed tower. Advantageously the tower may have provision for recycling a portion of the raffinate and extract streams to the tower so as to improve its operating efficiency. For example, the feed hydrocarbon may enter at an intermediate portion of the tower while the solvent enters near the top. A portion of the extract phase after withdrawal from the bottom of the tower may be stripped to remove the solvent and the stripped extract material recycled to the tower at a point intermediate the point of feed hydrocarbon introduction and the point of extract phase withdrawal.

The solvent recovered from the withdrawn extract phase is advantageously recycled to the upper portion of the extraction tower together with the solvent separated from the discharged raffinate phase. If desired, the recovered solvent so recycled may be returned to the extraction tower a short distance above the point of feed hydrocarbon introduction and in which case makeup solvent is advantageously introduced to the upper portion of the tower. In this way the raffinate phase rising into the uppermost portion of the extraction tower is subjected to extraction with solvent which is substantially free from impurities or dissolved hydrocarbon matter. A further modification involves returning the solvent stripped from the discharged raffinate phase to the top of the tower while returning the solvent stripped from the extract phase to a somewhat lower point in the tower intermediate the top and the point of hydrocarbon feed introduction.

The extraction may be carried out in a single stage or a plurality of stages. Each stage may comprise a mixing unit and a settling unit.

It is also contemplated that concurrent extraction may be employed. For example, the feed hydrocarbon mixture and solvent may be passed through a mixing coil or other mixing device and raised to the desired elevated temperature under pressure and the resulting mixture then passed to a settling zone wherein extract and raffinate phases are formed and separately withdrawn. In such operation the feed hydrocarbon mixture may be raised to the desired extraction temperature merely by mixing with the solvent previously heated to a sufficiently high temperature so that upon mixing with the feed hydrocarbon, the resulting mixture is at approximately the desired extraction temperature.

If desired the extraction may be carried out in the presence of gaseous agents such as hydrogen, methane, ethane, carbon dioxide, etc. for the purpose of suppressing the solubility of non-aromatic hydrocarbons in the solvent.

In some instances, depending upon the nature of the oil undergoing treatment, extraction with the water solvent may be followed by extraction of the primary extract and raffinate fractions with other solvents such as furfural nitrobenzene, sulfur dioxide, and the like.

Reference will now be made to the accompanying drawing comprising a diagram of flow for a process wherein a toluene concentrate obtained as a fraction from hydroformed naphtha is sub-

jected to extraction with water containing about 20 weight per cent anhydrous ammonia for the purpose of recovering toluene. The toluene concentrate is characterized by the following:

Gravity A. P. I.....	49.4
Initial boiling point.....°F..	212
End boiling point.....°F..	242
Toluene content.....% by weight..	41.2

Referring to the drawing, the toluene concentrate is conducted through a pipe 1 from a source not shown to a heat exchanger 2 wherein it is heated to a temperature of about 425 to 450° F.

The heated feed is then conducted through a pipe 3 to the lower portion of an extraction tower 4.

The tower 4 may be packed with 1 inch Raschig rings. For example, the tower may have about five nests of rings, each nest being about 10 feet in depth and about 5 or 6 feet in diameter, the diameter depending on the charge capacity desired.

The feed is subjected to countercurrent contact with a body of solvent moving downwardly through the tower. This solvent is advantageously drawn through an exchanger or heater 5 and conducted through a pipe 6 to the upper portion of the tower. The stream of solvent may enter the tower at a temperature of about 425 to 450° F.

A pressure of about 1200 pounds per square inch gauge is maintained within the tower.

Under these conditions, extract and raffinate phases are formed. The raffinate phase comprising about 20-25% solvent and 75-80% hydrocarbons accumulates in the top of the tower 4 and is continuously withdrawn through a pipe 7.

The withdrawn raffinate phase, without substantial reduction in pressure, is conducted to exchanger 8 wherein the temperature is reduced to about 150° F. The cooled mixture is then conducted to a settler 9 wherein separation between hydrocarbons and solvent occurs under substantially the same pressure as in the tower 4. The settler is advantageously of sufficient capacity to permit a settling time of about 10 minutes or longer. The raffinate hydrocarbons are continuously drawn off from the upper portion of the settler through a pipe 10, while the solvent 50 is withdrawn through a pipe 11.

The extract phase accumulating in the bottom of the tower 4 comprises about 88-92% solvent and about 8-12% hydrocarbons, the toluene content of the extract hydrocarbons is about 99% by weight depending on the operation of the extraction tower.

The extract phase is continuously withdrawn through a pipe 12 to an exchanger 13 wherein it is reduced to a temperature of about 350° F. 60 to 250° F. also without substantial reduction in pressure.

The cooled extract phase mixture is then conducted to a settler 14, somewhat similar to the settler 9, wherein separation between solvent and extract hydrocarbons occurs. The solvent so separated is continuously drawn through a pipe 15 communicating with a pipe 16 through which the solvent is conducted to the previously mentioned exchanger 5 for return to the extraction tower. Solvent drawn off through the pipe 11 from the settler 9 also may be passed to the pipe 16 for return to the extraction tower.

Effecting phase separation, and separation of solvent from hydrocarbons without substantial

reduction in pressure is advantageous from the standpoint of recycling the recovered solvent to the extraction tower.

The extract hydrocarbons are continuously drawn off from the top of the separator 14 through a pipe 17, and a portion of the withdrawn extract is conducted through a branch pipe 18 communicating with an exchanger 19 wherein the hydrocarbons are heated to a temperature of about 425 to 450° F. The heated extract hydrocarbons are then conducted from the exchanger 19 through a pipe 20 communicating with the lower portion of the extraction tower 4. The recycled extract hydrocarbons are thus introduced to the extraction tower at a point substantially below the point of feed hydrocarbon introduction. The section of the tower below the point of feed hydrocarbon introduction thus provides a rectifying section.

The amount of extract hydrocarbons recycled may be in proportion of about one half volume of recycled hydrocarbons to one volume of feed hydrocarbons although either smaller or larger proportions may be recycled.

The rate of solvent introduced to the top of the tower through the pipe 6 is sufficient to maintain a solvent dosage of about 10-12 volumes of solvent per volume of feed hydrocarbon entering through the pipe 3.

If desired the extract toluene and the raffinate may be subjected to procedures such as water washing or acid washing, etc. to recover the small amount of residual ammonia left in the hydrocarbon phase from the settler. The recovered ammonia can then be used to supply the make-up solvent for the continuation of the extraction operation.

While specific operating conditions such as temperature, pressure and rates of flow have been referred to in connection with the foregoing method of flow, nevertheless it is contemplated that these conditions may be varied as desired depending upon the nature of the charge being extracted and the degree of toluene or other aromatic hydrocarbon recovery desired. For example, a temperature gradient may be maintained throughout the tower as by introducing the feed hydrocarbon at a temperature higher than that at which the solvent enters.

The total throughput of feed hydrocarbons, plus water, may be at the rate of about 1100-1200 gallons of liquid per square foot of tower cross-sectional area per hour or lower.

Obviously many modifications and variations of the invention, as hereinbefore 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 claims.

We claim:

1. A process for separating aromatic hydrocarbons from a naphtha hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons including olefins, paraffins and naphthenes which comprises extracting the naphtha with a solvent consisting of water containing from a fraction of a per cent up to not in excess of about 25% by weight of a compound selected from the group consisting of ammonia and water soluble aliphatic amines having from 1 to 5 amine residues, effecting the extraction at a temperature in the range about 300 to 450° F. and under an elevated pressure not in excess about 1300 pounds and sufficient to maintain the aromatic hydrocarbons in the liquid state at the extraction tem-

perature, forming a liquid solvent phase comprising aromatic hydrocarbons dissolved in the main body of solvent and a hydrocarbon phase comprising non-aromatic hydrocarbons mixed with some solvent, and separately removing said phases.

2. A process for separating toluene from a naphtha feed containing aromatic and non-aromatic hydrocarbons including olefins, paraffins, and naphthenes which comprises extracting said naphtha with a solvent consisting of water containing from a fraction of a per cent up to not in excess of about 25% by weight of a compound selected from the group consisting of ammonia and water soluble aliphatic amines having from 1 to 5 amine residues, effecting the extraction at an elevated temperature in the range about 300 to 450° F. and under a pressure of about 850 to 1300 pounds per square inch gauge, forming a solvent phase consisting essentially of solvent and toluene dissolved therein and a raffinate phase comprising a small amount of solvent mixed with insoluble hydrocarbons including non-aromatic hydrocarbons, separating said phases while still under elevated pressure and temperature, separately cooling the separated phases without substantial reduction in pressure to effect separation between hydrocarbons and solvent, and removing the hydrocarbons from the solvent.

3. A process for separating toluene from a naphtha feed containing aromatic and non-aromatic hydrocarbons including olefins, paraffins and naphthenes which comprises separating from said naphtha a hydrocarbon fraction boiling in the range about 190 to 250° F., extracting said fraction with a solvent consisting essentially of water containing from a fraction of a per cent up to not in excess of about 25% by weight of a compound selected from the group consisting of ammonia and water soluble amines having from 1 to 5 amine residues, effecting the extraction at a temperature in the range 300 to 450° F. and under an elevated pressure sufficient to maintain the solvent and hydrocarbon substantially in the liquid phase, forming a solvent phase consisting essentially of solvent and toluene dissolved therein, said solvent phase being substantially free from said non-aromatic hydrocarbons and a hydrocarbon phase comprising a small amount of solvent mixed with non-aromatic hydrocarbon, separating said phases while still under said elevated pressure and temperature, separately cooling the separated phases without substantial reduction in pressure to effect separation between hydrocarbons and solvent, and separately removing the hydrocarbons from the solvent.

4. The process according to claim 3 in which the extraction is effected with the solvent in the proportion of about 5 to 20 volumes of solvent per volume of naphtha fraction.

5. A process for separating toluene from a naphtha feed containing aromatic and non-aromatic hydrocarbons including olefins, paraffins and naphthenes which comprises separating from said naphtha a hydrocarbon fraction boiling in the range about 190 to 250° F., extracting said fraction with a solvent consisting essentially of water containing from a fraction of a per cent up to about 20% by weight of ammonia and in the proportion of about 5 to 20 volumes of solvent to 1 volume of naphtha, effecting the extraction at an elevated temperature in the range

about 300 to 450° F. and under a pressure of about 850 to 1300 pounds per square inch gauge, forming a solvent phase consisting essentially of solvent and toluene dissolved therein and a raffinate phase comprising a small amount of solvent mixed with insoluble hydrocarbons including non-aromatic hydrocarbons, separating said phases while still under elevated pressure and temperature, separately cooling the separated phases without substantial reduction in pressure to effect separation between hydrocarbons and solvent, and removing the hydrocarbons from the solvent.

6. A process for separating toluene from a naphtha feed containing aromatic and non-aromatic hydrocarbons including olefins, paraffins and naphthenes which comprises separating from hydroformed naphtha a toluene concentrate boiling in the range about 212 to 242° F., passing said concentrate in a continuous stream to the lower portion of an extraction tower, passing in a continuous stream to the upper portion of said tower a solvent consisting essentially of water containing about 20% ammonia in the proportion of about 5 to 20 volumes of solvent to 1 volume of naphtha, effecting countercurrent extraction of naphtha hydrocarbons in liquid phase with said solvent within the tower at a temperature of about 425 to 450° F. and under an elevated pressure not exceeding about 1300 pounds per square inch gauge, removing from the upper portion of said tower a raffinate phase comprising a small amount of solvent mixed with insoluble hydrocarbons including non-aromatic hydrocarbons, removing from the lower portion of said tower an extract phase consisting essentially of solvent and toluene dissolved therein, separately cooling the removed phases, and separately removing hydrocarbons from the cooled phases.

7. The process according to claim 6 in which the toluene content of the extract hydrocarbons in the extract phase is about 99% by weight.

8. A process for separating aromatic hydrocarbons from a naphtha hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons including olefins, paraffins and naphthenes which comprises passing said naphtha in a continuous stream to the lower portion of an extraction tower, passing in a continuous stream to the upper portion of said tower a solvent consisting essentially of water containing from a fraction of a per cent to about 20% by weight of ammonia and in the proportion of about 5 to 20 volumes of solvent to 1 volume of naphtha, effecting countercurrent extraction of naphtha hydrocarbons in liquid phase with said solvent within the tower at a temperature in the range of about 300 to 450° F. and under an elevated pressure in the range of about 850 to 1300 pounds per square inch gauge, maintaining a flow rate of feed hydrocarbons and water through the tower of about 1100 to 1200 gallons per square foot of tower cross-sectional area per hour, removing from the upper portion of the tower a raffinate phase comprising non-aromatic hydrocarbons mixed with some solvent, removing from the lower portion of the tower an extract phase comprising aromatic hydrocarbons dissolved in the main body of solvent, separately cooling the removed phases, and separating hydrocarbons from the removed and cooled phases.

GEORGE B. ARNOLD.
HAROLD V. ATWELL.