This invention relates to a petroleum treating process. More particularly, this invention relates to an improved petroleum treating process involving, in combination, catalytic reforming and solvent extraction for the upgrading of petroleum naphthas and the like.

For the upgrading of petroleum naphthas, such as a heavy straight run naphtha, catalytic reforming of the heavy straight run naphtha, followed by solvent extraction of the resulting reformate to yield a high octane, highly aromatic extract has been proposed. The production and recovery of substantially pure aromatic hydrocarbons or hydrocarbon fractions from a petroleum fraction by operations involving catalytic reforming and solvent extraction has also been proposed.

In these proposed operations there are produced an extract mix comprising aromatic hydrocarbons dissolved in the selective solvent and a raffinate mix comprising relatively non-aromatic hydrocarbons containing selective solvent dissolved therein. The selective solvent, having a boiling point substantially different, usually greater, than that of the accompanying aromatic hydrocarbons in the extract mix, is separated from the extract mix by fractional distillation. The relatively non-aromatic hydrocarbons or raffinate in the raffinate mix are separated from the selective solvent by suitable means, such as fractional distillation or by a secondary solvent extraction step.

In the aforesaid operations the complete recovery of the selective solvent by fractional distillation from the hydrocarbons in the extract mix and in the raffinate mix is a rather expensive operation and requires a substantial amount of heat energy.

Accordingly, it is an object of this invention to provide an improved process for the substantially complete recovery of selective solvent employed in a petroleum treating process involving catalytic reforming and solvent extraction of the resulting reformate.

Another object of this invention is to provide an improved process for the recovery of selective solvent from the raffinate mix produced in a petroleum treating operation wherein a catalytic reformate is treated with a selective solvent for aromatic hydrocarbons.

Still another object of this invention is to provide an improved method, involving catalytic reforming and selective solvent extraction, for the upgrading of petroleum naphtha fractions.

How these and other objects of this invention are accomplished will become apparent in the light of the accompanying disclosure made with reference to the accompanying drawing which schematically illustrates a process in accordance with the practice of this invention.

In accordance with this invention it has now been discovered that an improved petroleum treating process is obtainable by catalytically reforming a petroleum naphtha fraction, such as a naphtha fraction boiling in the range 150-450° F., more or less, to yield an aromatic reformate and subjecting the resulting reformate to solvent extraction by contact with a selective solvent which preferentially dissolves aromatic hydrocarbons to yield an extract mix comprising solvent and aromatic hydrocarbons dissolved therein and a raffinate mix comprising relatively non-aromatic hydrocarbons containing selective solvent dissolved therein and recovering the selective solvent dissolved in said raffinate mix by subjecting said raffinate mix to a secondary solvent extraction operation for the removal of selective solvent therefrom to yield a secondary extract mix followed by a tertiary solvent extraction wherein the selective solvent in the secondary extract mix is removed in said tertiary solvent extraction operation by contact with a liquid hydrocarbon fraction, such as said petroleum naphtha or catalytic reformate. Brieferly stated, in accordance with a specific embodiment of the practice of this invention the selective solvent is recovered from an aqueous solution containing the same, wherein said aqueous solution contains a minor amount, usually below about 25% by weight, selective solvent, by contacting said aqueous solution with a hydrocarbon fraction such as a petroleum naphtha fraction or reformate, especially a hydrocarbon fraction containing a substantial amount, about 30% by volume, preferably a major amount, about 50% by volume aromatic hydrocarbons.

The practice of this invention is particularly suitable for the upgrading of petroleum naphtha fractions, especially straight run petroleum naphthas. The petroleum fraction is first subjected to catalytic reforming to yield a catalytic reformate containing a substantial amount of aromatic hydrocarbons. Various catalytic reforming operations and processes are suitably employed in the practice of this invention. Suitable reforming processes may be sufficiently identified by the terms detailed and described in the art by merely mentioning their descriptive names. Accordingly catalytic reforming processes applicable in the practice of this invention include Platforming, Ultraforming, Houdrifoming, Catalytic Reforming, Catforming, Cycloversion, fixed bed Hydroforming, Fluid Hydroforming, Hydroforming, Thermofor Catalytic Reforming, and Sovaforming and the like. Generally, these catalytic reforming processes may be described as processes for upgrading relatively low octane naphthas or petroleum fractions in the gasoline boiling range to high octane motor gasolines, or for producing high octane motor fuel components from naphthas or catalytic petroleum fractions, or for producing high yields of aromatics or petrochemicals or high quality motor fuel components.

The catalytic reforming operation may be carried out by employing a fixed bed of catalyst, a moving bed of catalyst, or a fluidized catalyst, or any combination thereof, and may be operated at a temperature in the range 750-1000° F., more or less, and a pressure in the range 150-1000 p.s.i.g., more or less, depending upon the severity of reforming desired or the quality or composition of the petroleum fraction undergoing reforming. Various catalysts suitable for converting or reforming hydrocarbons may be employed, e.g., platinum, molybdena-alumina catalyst, chromium-alumina catalyst and cobalt molybdate catalyst. During the reforming operation the hydrocarbons in the petroleum fraction undergoing catalytic reforming are subjected to a number of catalytic reactions involving aromatization or dehydrocyclization, isomerization, desulfurization and even cracking depending upon the severity of the reforming operation and/or the charge stock therefor. All these reactions take place substantially simultaneously and in varying degree. Moreover, the naphthenic hydrocarbons in the petroleum naphtha feed are dehydrogenated to aromatic hydrocarbons and paraffinic hydrocarbons are isomerized to iso-paraffinic hydrocarbons and the iso-paraffinic hydrocarbons are isomerized and aromatized into the corresponding aromatic hydrocarbons. As a result of the catalytic reforming oper-
tion there is produced a catalytic reformate having a substantially increased aromatic hydrocarbon content, substantially greater than the aromatic hydrocarbon content of the petroleum naphtha feed thereto.

Subsequently to the catalytic reforming operation the resulting liquid reformate, in whole or in part, such as a heavy reformate fraction or an intermediate reformate fraction, e.g., a reformate fraction having a boiling range in the range 200–400°F, is subjected to liquid-liquid contact with a selective solvent which selectively dissolves aromatic hydrocarbons. As a result of this solvent extraction operation there are produced a raffinate extract comprising relatively less aromatic or paraffinic hydrocarbons containing a portion of the selective solvent dissolved therein and an extract mix comprising selective solvent containing aromatic hydrocarbons dissolved therein.

Selective solvents suitable for use in the practice of this invention include the well known selective solvents for aromatic hydrocarbons, e.g., diethylene glycol, triethylene glycol, tetrachloroethylene glycol, mono-, di- and tri-propylene glycols, mono- and di-butyleneglycols, and mixtures thereof and aqueous solutions thereof. Also suitable as selective solvents are the polyoxypropylyalkylene glycols, and glycol ethers, such as the Cellosolves series of compounds, alkyl ethers of ethylene glycol, including methyl-, ethyl-, propyl-, and butyl-Cellosolve. The so-called Carbitols are mixtures of dialkyl ethers of diethylene glycol, such as the methyl-, ethyl-, propyl-, and butyl-Carbitols, the glycol and polyoxypropylyalkylene glycol esters of low molecular weight organic acids such as the acetates and propionates, are also suitable. In the practice of this invention it is preferred to employ as a selective solvent a solvent having a relatively high boiling point and low vapor pressure as compared with the hydrocarbons, aromatic and/or non-aromatic hydrocarbons associated therewith and in the reformate undergoing solvent extraction. Other well known selective solvents for aromatic hydrocarbons, such as furfural, are also suitably employed in the practice of this invention.

Referring now to the accompanying drawing which schematically illustrates one embodiment of the practice of this invention a petroleum feed, such as crude oil or a petroleum naphtha, is introduced via line 10 into feed fractionator 11 wherein it is separated into an overhead fraction via line 12, a heavy naphtha fraction via line 14 and a bottoms fraction via line 15. The heavy naphtha fraction is introduced via line 14 into catalytic reformer 16 where it is subjected to contact with a suitable reforming catalyst, such as a platinum-containing catalyst, under reforming conditions of temperature and pressure.

A resulting catalytic reformate is recovered from catalytic reformer 16 via line 18 and introduced into reformate stabilizer 19. Within reformate stabilizer 19 hydrocarbons which are produced during the catalytic reforming operation is separated overhead via line 20 for recycle to catalytic reformer 16. There is also recovered overhead from stabilizer 19 via line 21 a normally gaseous hydrocarbon fraction comprising C₄-C₇ hydrocarbons which are suitably employed as fuel or recovered for the production of PCG. There is also shown recovered from stabilizer 19 via line 23 a normally gaseous hydrocarbon fraction having an end point of about 200–225°F. A heavy reformate fraction is also shown being recovered from stabilizer 19 via line 48. Desirably, in the practice of this invention substantially all of the reformate, after removal of the hydrogen and normally gaseous hydrocarbons via lines 20 and 21, respectively, or an intermediate fraction thereof, e.g., boiling in the range 200–400°F, is introduced via line 22 into reformate extractor 24 wherein it is subjected to liquid-liquid countercurrent contact with a selective solvent for aromatic hydrocarbons introduced into the upper portion of extractor 24 via line 30.

Any suitable selective solvent partially miscible with the reformate undergoing solvent extraction within extractor 24 and which preferentially dissolves aromatic hydrocarbons over non-aromatic hydrocarbons, may be employed in the practice of this invention. Suitable selective solvents include indicated aqueous solutions of diethyylene glycol, triethylene glycol, or mixtures thereof, particularly aqueous solutions thereof, such as aqueous solutions containing a substantial amount by volume, e.g., in the range 50–95% vol., of the glycol solvent. Extractor 24 is operated under suitable conditions such that the selective solvent, concentrated by the selecti

There is recovered overhead from extractor 24 via line 31 a raffinate reformate mix comprising hydrocarbons containing selective solvent therein. The raffinate reformate mix recovered overhead from extractor 24 via line 31 would include substantially all of the paraffinic and non-aromatic hydrocarbons present in the reformate introduced into extractor 24 via line 22. There is recovered from the lower end of extractor 24 via line 25 an extract reformate mix comprising selective solvent containing the more aromatic hydrocarbons dissolved therein. Substantially all of the aromatic hydrocarbons present in the reformate introduced into extractor 24 via line 22 are contained in the extract mix issuing from extractor 24 via line 25.

The extract mix issuing from extractor 24 via line 25 is then introduced into extract stripper 26 wherein it is subjected to fractional distillation to recover overhead an extract reformate comprising substantially only the more aromatic hydrocarbons. The extract reformate thus-recovered from extract stripper 26 via line 28 is particularly suitable as a high octane motor fuel component or blending agent and is characterized by a relatively high aromatic content, at least above about 60% by weight aromatic hydrocarbons, usually above about 75% by weight aromatic hydrocarbons.

There is recovered from the bottom of extract stripper 26 via line 29 the selective solvent substantially free of aromatic hydrocarbons. The selective solvent is then returned to extractor 24 via lines 29 and 30.

The raffinate mix issuing from the upper end of extractor 24 via line 31 is introduced into water wash tower 32 wherein it is subjected to contact, preferably countercurrent liquid-liquid contact, with a flowing stream of water, introduced into the upper portion of water wash tower 32 via line 34. Within water wash tower 32 the water contacts the raffinate mix to remove therefrom the glycol selective solvent. Following this operation there are issues from the upper end of water wash tower 32 via line 35 a raffinate comprising substantially only the less aromatic (paraffinic) hydrocarbons. The resulting water washed paraffinic raffinate may be recovered as product via line 38. Desirably, however, the paraffinic water washed raffinate, now substantially free of selective solvent, is returned via lines 39 and 44 to catalytic reformer 16 so that the major fraction, paraffinic hydrocarbons therein are subjected to additional catalytic reforming, including isomerization, dehydrocyclization.

The wash water issuing from the lower end of water wash tower 32 via line 36, now containing glycol selective solvent dissolved therein in a substantial amount, usually a minor amount in the range 2–40% by weight, is introduced into solvent recovery tower 40 wherein it
is subjected to countercurrent liquid-liquid contact with a petroleum naphtha, preferably additional reformate supplied from stabilizer 19 via lines 22 and 41. The petroleum naphtha fraction or reformate introduced into solvent recovery tower 40 via line 41 selectively removes the glycol solution from the wash water introduced into solvent recovery tower 40 via line 36. Accordingly, there is recovered from the upper end of solvent recovery tower 40 via line 42 the petroleum naphtha fraction or reformate now containing selective solvent dissolved therein. Desirably the reformate containing selective solvent in line 43 is introduced via line 22 into extractor 24. By operating in this manner the loss of selective solvent is maintained at a minimum.

The resulting wash water, now substantially solvent free, issuing from the bottom of solvent recovery tower 40 via line 43 may be recirculated via lines 44 and 34 to water wash tower 32 to recover selective solvent from additional reformate raffinate mix. Further, the solvent-free wash water in line 43 may be supplied via lines 45, 29 and 30 into extractor 24 to modify the selective solvent therein since it has been found that water modified selective solvents, particularly aqueous solutions of diethylene glycol and triethylene glycol, are particularly useful as selective solvents for aromatic hydrocarbons present in petroleum naphtha fractions such as catalytic reformates.

The following operations are exemplary of the practice of this invention. A heavy straight run petroleum naphtha was subjected to catalytic reforming (Platforming) to yield a resulting catalytic reformate having a 91 octane rating. This catalytic reformate was then subjected to fractionation to yield a relatively heavy catalytic reformate fraction boiling in the range 220–425° F. and comprising about 78% by volume of the original catalytic reformate. This heavy reformate was made up of 65% by volume aromatic hydrocarbons, 25% by volume olefinic hydrocarbons and 35% by volume saturated hydrocarbons.

In accordance with the practice of this invention this catalytic reformate fraction is subjected to solvent extraction by liquid-liquid contact with an aqueous solution of diethylene glycol for the removal of the aromatic hydrocarbons therefrom, followed by water washing of the resulting raffinate to remove the selective solvent therefrom. Following the raffinate water washing operation there is recovered a wash water containing a substantial amount of selective solvent, diethylene glycol, dissolved therein.

An aqueous solution of diethylene glycol, actually a 20% by volume aqueous solution of diethylene glycol comparable to the wash water recovered from the raffinate water washing operation was subjected to countercurrent liquid-liquid contact with a petroleum naphtha fraction, viz., heavy catalytic reformate described hereinafore. The contacting of the heavy catalytic reformate with the diethylene glycol solution was carried out at various temperatures. It was observed that during these operations the higher the contacting temperature the more effective was the selective solvent, diethylene glycol, extracted from the aqueous solution by the reformate. The results of these tests are set forth in the accompanying Table I.

Table I, and in accordance with the practice of this invention, recovery of selective solvent from the wash water is improved as the contacting temperature is increased and/or as the volume ratio of petroleum naphtha, catalytic reformate, to wash water is increased. Accordingly, in the practice of this invention it is preferred to carry out the extraction of selective solvent from the wash water at an elevated temperature above about 300° F., such as a temperature in the range 305–450° F., the pressure applied during this contacting operation being sufficient to maintain all the materials in the liquid phase. Further, it is preferred in the practice of this invention to employ a relatively large volume of petroleum naphtha, catalytic reformate, with respect to the volume of wash water undergoing treatment for the recovery of selective solvent therefrom. Accordingly, it is preferred that the volume of petroleum naphtha, catalytic reformate, employed be at least twice that of the wash water undergoing treatment, preferably in the range 3–10 times and more greater than the volume of wash water undergoing treatment.

As will be apparent to those skilled in the art many modifications, substitutions and alterations are possible without departing from the spirit or scope of this invention.

1. A petroleum treating process which comprises subjecting a petroleum naphtha to catalytic reforming to yield a reformate containing aromatic hydrocarbons and non-aromatic hydrocarbons, subjecting said reformate to contact with a selective solvent which selectively dissolves aromatic hydrocarbons to yield a raffinate mix comprising non-aromatic hydrocarbons and said selective solvent and an extract mix comprising aromatic hydrocarbons and said selective solvent, contacting said raffinate mix with water to remove said selective solvent therefrom to yield a raffinate phase comprising non-aromatic hydrocarbons and an extract phase comprising water and said selective solvent dissolved therein, subjecting said extract mix to fractional distillation to separate said aromatic hydrocarbons and said selective solvent, returning the selective solvent separated from said extract mix to contact additional reformate and recovering said selective solvent from said extract phase by contacting said extract phase in a liquid-liquid contacting operation with a portion of said reformate and returning the resulting reformate, now containing selective solvent dissolved therein, to the aforesaid operation wherein reformate is contacted with said selective solvent.

2. A process in accordance with claim 1 wherein said raffinate is recycled to the aforesaid catalytic reforming operation.

3. A process in accordance with claim 1 wherein said selective solvent is an aqueous glycol solution.

4. A process in accordance with claim 1 wherein said selective solvent is triethylene glycol.

5. A process in accordance with claim 1 wherein said selective solvent is diethylene glycol.

6. A petroleum treating process which comprises subjecting a petroleum naphtha having a boiling range in the range 200–450° F. to catalytic reforming to yield a reformate containing aromatic hydrocarbons and non-aromatic hydrocarbons, fractionating said reformate to separate therefrom an intermediate fraction having a boiling range in the range 200–400° F. and containing aromatic hydrocarbons and non-aromatic hydrocarbons, subjecting said fraction to contact with a selective solvent which selectively dissolves aromatic hydrocarbons to yield a raffinate mix comprising non-aromatic hydrocarbons and said selective solvent and an extract mix comprising aromatic hydrocarbons and said selective solvent, contacting said raffinate mix with water to remove said selective solvent therefrom and to yield a raffinate phase comprising non-aromatic hydrocarbons and an aqueous extract phase comprising water and said selective solvent.

<table>
<thead>
<tr>
<th>Temperature, °F.</th>
<th>Bath volume of reformate to volume 50% remaining diethylene glycol</th>
<th>Weight percent diethylene glycol in reformate extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>2/4</td>
<td>0.01%</td>
</tr>
<tr>
<td>100</td>
<td>2/4</td>
<td>0.08%</td>
</tr>
<tr>
<td>200</td>
<td>2/4</td>
<td>0.15%</td>
</tr>
<tr>
<td>300</td>
<td>2/4</td>
<td>0.45%</td>
</tr>
</tbody>
</table>

As indicated by the data set forth in accompanying
solvent dissolved therein, subjecting said extract mix to fractional distillation to separate said aromatic hydrocarbons and said selective solvent, returning the selective solvent separated from said extract mix to contact additional said intermediate fraction and recovering said selective solvent from said aqueous extract phase by contacting said extract phase in a liquid-liquid contacting operation with a portion of said intermediate fraction containing selective solvent dissolved therein, to the aforesaid operation wherein said fraction is contacted with said selective solvent.

7. A method in accordance with claim 6 wherein said selective solvent comprises an aqueous glycol solution.

8. A method in accordance with claim 6 wherein said solvent is aqueous triethylene glycol.

9. A method in accordance with claim 6 wherein said solvent is aqueous diethylene glycol.

10. A method in accordance with claim 6 wherein said raffinate phase after having been subjected to water washing to remove said selective solvent therefrom is returned to the aforesaid catalytic reforming operation.

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