PROCESS FOR EXTRACTION OF AROMATICS FROM PETROLEUM STREAMS

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The present invention provides a process for the extraction of aromatics from petroleum fractions i.e. naphtha, kerosene and gas oil, using re-extraction route for recovery of solvent.
PROCESS FOR EXTRACTION OF AROMATICS FROM PETROLEUM STREAMS

FIELD OF THE INVENTION

[0001] The present invention relates to an improved process for the extraction of aromatics from petroleum streams. The invention particularly relates to the extraction of aromatics from heavy naphtha, kerosene and gas oil range petroleum fractions with the aid of a suitable polar organic solvent and re-extracting the extract phase with a C<sub>6</sub>-C<sub>7</sub> paraffinic solvent.

BACKGROUND OF THE INVENTION

[0002] Different petroleum fractions obtained in crude distillation unit contain varying concentration of aromatics depending upon crude oil source. These aromatics are required to be removed to produce various end products meeting the specifications with respect to aromatics. For example, naphtha used as feedstock in petrochemical industry for the production of olefins should not contain more than 5% of aromatics due to refractory nature of aromatics. While in the case of fertiliser industry, limitation of aromatics (<10%) in naphtha feedstock is due to higher carbon to hydrogen ratio, which in turn affects hydrogen yield.

[0003] Refining of kerosene fractions is done in order to produce superior kerosene (SK) and aviation turbine fuel (ATF). These end products should meet BIS specification requirements in terms of smoke point, freezing point (for ATF) and aromatic content since the performance of these products depends on these specifications.

[0004] High aromatic content in gas oil fraction results in lowering of cetane number. In order to improve the cetane number the reduction of aromatics is essential. Hydrofining and solvent extraction are the conventional processes for de-aromatization. However, severe operating conditions such as high partial pressure of hydrogen and high hydrogen consumption are required for high aromatic feedstocks which make the process highly capital cost intensive compared to solvent extraction.

[0005] For example for de-aromatization of kerosene fractions from Assam crude oils, being rich in aromatics solvent extraction is employed. Presently, there are three refineries in the eastern part of our country. Where kerosene fractions are de-aromatized using liquid sulphur dioxide as the solvent (Edeleanu. L. British Patent 11.140 May 22, 1908). Considering present growth in technology development and environment awareness this is an obsolete process. It has several drawbacks of which the main drawbacks are:

[0006] (1) Liquid sulphur dioxide is highly corrosive in presence of traces of water, therefore, drying of feed and solvent is an important step.

[0007] (2) There is occasional failure of ATF produced by this process.

[0008] (3) The number of columns used for solvent recovery from raffinate and extract phases is too large.

[0009] (4) Extraction temperature is as low as -15° C. thus requires refrigeration

[0010] To overcome the above drawbacks, Indian Institute of Petroleum, Dehra Dun, Engineers India Limited, New Delhi and Hindustan Petroleum Corporation Limited, Mumbai have jointly developed a process for refining kerosene fraction (140-240° C.) which uses sulpholane as the solvent (Indian Patent No 170747, 23 March 1987) employing conventional attraction route. In this process scheme the recovery of solvent from extract phase is carried out by distillation. This approach is successful for systems consisting feed and solvents having wide difference of boiling points. However, this process consumes significant energy for the recovery of hydrocarbons, due to requirement of stringent operating conditions. Moreover, processing of feeds having wide boiling range e.g. naphtha to gas oil in the same unit using block out operations is not feasible due to over lapping of boiling points with the solvent. For such application solvent extraction in combination with re-extraction route for solvent recovery is feasible approach.

[0011] Re-extraction concept for the recovery of aromatics from extract phase is reported to have been used commercially e.g., for the production of pure benzene and toluene by Dimethyl sulfoxide (DMSO) process [Hydrocarbon Processing, 45 (5), 188, 1966]. Handling of low thermal stability solvent is the main drawback of this process. Improvement of cetane number of LCCO [Hydrocarbon Processing. 46, (9). 134, 1967] using Dimethyl formamide (DMF), production of high boiling aromatics by using N-Formyl Morpholine (NFM) [Hydrocarbon Processing, 51. (4), 141,1972] production of pure benzene and toluene from pyrolysis gasoline by using Tetraethylenglycol [DE 3.409.307 Sept 1983 and ISEC 1971] have also been tried. Re-extraction of aromatics from extract phase of kerosene fractions is also reported by Muller et al. at [DE 3.207.404: 4 Sept 1983] and Lobov Nauchn. Osn. Pererab. Negit Gaze Neftekhim. Tezésy Dokl. Vses. Knof. 234-5. 1977]. The solvent tried in the former work was N-Methyl pyrrolidinone (NMP) containing 6% water while the re-extraction was done by n-hexane, while in the latter work the feed used was kerosene fraction 200-270° C. and solvent used was DMF while the re-extraction solvent was n-heptane. In all these processes the lean solvent obtained from bottom of the re-extraction column is directly re-circulated back to the main extraction column without removing the re-extraction solvent.

[0012] Drawbacks of This Process Scheme Are:

[0013] Difficulty in maintaining the extraction solvent composition

[0014] Contamination of raffinate phase with re-extraction solvent

[0015] Requirement of additional fractionator for removal of re-extraction solvent from raffinate

[0016] Requirement of stringent operating conditions in water-solvent fractionator due to higher boiling point of solvents

[0017] Re-extraction solvent such as n-hexane & n-heptane being pure hydrocarbons are costly

OBJECTS OF THE INVENTION

[0018] The main object of the invention is to provide an improved process for the extraction of aromatics from petroleum streams, which obviates the drawbacks as detailed above.
Another object of the present invention is to provide process where solvent extraction of aromatics from aromatic rich petroleum fractions is done to obtain high octane aromatic extract for Motor Spirit pool, superior kerosene, high cetane gas oil and specialty solvents.

Yet another object of the invention is to provide a process wherein savings in capital cost are achieved by eliminating raffinate-re-extraction solvent fractionator.

Still another object of the invention is to reduce operating cost by saving in utilities by using heat integration of hot and cold stream.

Another object of the invention is to produce superior quality special boiling point solvents.

SUMMARY OF THE INVENTION

In the present work a modified process scheme has been developed for the extraction of aromatics from petroleum fractions i.e. naphtha, kerosene and gas oil, using re-extraction route for recovery of solvent.

Accordingly the present invention provides an improved process for the extraction of aromatics from petroleum feed streams which comprises:

a) contacting a petroleum feed with a polar organic solvent containing 2-20 wt % antisolvent in a extractor-A column to obtain an extract phase and a raffinate phase,

b) contacting extract phase obtained in step (a) with 1-6 vol % of a secondary solvent in the extractor B column to recover the extract hydrocarbons

c) distilling the bottom stream of extractor-B obtained in step (b) in column-F at reboiler temperature to recover the extraction solvent for further recycling

d) washing the top stream of extractor-B obtained in step (b) with water in column-C, followed by fractionation of the resultant hydrocarbons to obtain the extract hydrocarbons and secondary solvent and further recycling the secondary solvent to extractors,

e) washing raffinate phase obtained in step (a) in column-E to obtain raffinate hydrocarbons.

In one embodiment of the invention, step (a) is carried out at a temperature in the range of 20-80° C.

In another embodiment of the invention, step (b) is carried out at a temperature in the range of 20-60° C. to recover the extract hydrocarbons.

In yet another embodiment of the invention, the reboiler temperature in step (c) is in the range of 90-180° C.

In a further embodiment of the invention, washing of top stream of extractor-B obtained in step (b) with water in column-C, is done at temperature in range of 20-60° C., followed by fractionation of resultant hydrocarbons at temperature in the range of 100-400° C.

In another embodiment of the invention, the washing of the raffinate phase obtained in step (a) in Column E in step (c) is carried out at a temperature in the range of 20-60° C.

In another embodiment of the invention, the petroleum feed comprises an aromatic rich feed with a boiling temperature in the range of 90-360° C.

In another embodiment of the invention the selective solvent used is N-Methyl pyrrolidone admixed with 2.0 to 15 wt % water or sulpholane or glycol.

In yet another embodiment of the invention, ratio of solvent mixture to feed is in the range of 1:1 to 5:1 wt %.

In another embodiment of the invention feed and extraction solvent is contacted countercurrently in extractor-A at a temperature in the range of 30-80° C.

In another embodiment of the invention the recovery of aromatics from extract phase is effected countercurrently in extractor-B using a secondary solvent selected from C6-C7 petroleum fraction at a temperature in the range of 30-60° C.

In another embodiment of the invention the of secondary solvent to extract phase is in range of 1 to 4 by volume.

In another embodiment of the invention recover of solvent from top phase of extractor-B and raffinate phase is done by water washing at temperature in range of 30-40° C.

In another embodiment of the invention recovery of secondary solvent from top of extractor-B is done by distillation at atmospheric pressure at temperature in range of 110-300° C.

In another embodiment of the invention recovery of residual hydrocarbons in bottom phase of extractor-B is done by distillation at reboiler temperature in the range of 100-160° C.

In another embodiment of the invention, the petroleum feed is selected from the group consisting of heavy naphtha, kerosene and gas oil.

In another embodiment of the invention, the aromatics obtained are selected from the group consisting of high octane benzene free stock for gasoline pool, high Cetane Diesel, high aromatic solvent and feed-stock for needle coke production.

In another embodiment of the invention, refinery cut light naphtha cut is used as the re-extraction solvent.

FIG. 1 is a flow diagram of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the present work a modified process scheme has been developed for the extraction of aromatics from petroleum fractions i.e. naphtha, kerosene and gas oil, using re-extraction route for recovery of solvent. The novelty of the present invention lies in:

the process provides unique feasibility to deammatize three &d; stocks of different boiling range namely Heavy Naphtha, Kerosene and Gas Oil using an eco-friendly solvent such as NMP,
[0050] Single plant can be used in blocked our mode of operation to produce additional products such as high octane benzene free stock for gasoline pool, high Cetane Diesel, high aromatic solvent and feedstock for needle coke production. This is the unique feature of the invention as no such process has been reported so far to produce these value-added products from a single unit.

[0051] Use of refinery cut light naphtha cut as re-extraction solvent

[0052] The invention facilitates the controllability of the severity of extraction while in operation through manipulating anti-solvent composition depending upon feed characteristics and target product specification.

[0053] The invention allows production of de-aromatized raffinate free of re-extraction solvent.

[0054] In the present invention the aromatics are separated from non-aromatics from the feedstocks by extraction using polar organic solvents. The solvent used here is N-Methyl pyrrolidinone admixed with water, glycol, sulpholane etc. The petroleum fraction stream is introduced through line (1) and lean solvent is introduced via line (2) into the extractor-A where the two streams meet countercurrently. The extract phase, thus produced, is introduced via line (4) in the extractor-B, which meets the C6-C7 petroleum fraction (63-69°C cut) counter-currently entering via line (5). The raffinate phase produced is fed to raffinate wash column-E via line (3) where it is washed with water. The two contact zones may comprise either a packed or a sieve plate column.

[0055] The top phase which leaves the extractor-B via line (6) is water washed in extract wash column-C and then enters via line (8) in the distillation column-D where it is fractionated to yield aromatic extract which is collected via line (11) and C6-C7 petroleum fraction, which is re-circulated to extractor-B via line (5). The bottom of extractor-B enters to solvent recovery column-F via line (7). Hydrocarbons from the top of solvent recovery column (SRC) are routed to column-D via line (15). One part of water is recycled back to extract wash column-C via line (10). Another part of water is recycled back to raffinate wash column-E routed through water stripper-G via line (14). Washed raffinate is taken from line (12). The lean solvent from the bottom of solvent recovery column-F is re-circulated back to extractor-A via line (2). Water containing the solvent is fed to solvent recovery column-F via lines (9) and (13) used as stripping stream.

[0056] The process of the invention comprises extraction of aromatics from petroleum streams by first (a) contacting petroleum feed with a polar organic solvent containing 2-20 wt % antisolvent at a temperature in the range of 20-80°C in a extractor-A column to obtain a extract phase and a raffinate phase, (b) contacting the extract phase obtained in step (a) with 1-6 vol % of secondary solvent consisting of C6-C7 paraffinic petroleum fraction in the extractor-B column at temperature in the range of 20-60°C to recover extract hydrocarbons, (c) distilling bottom stream of extractor-B obtained in step (b) in column-F at reboiler temperature of 90-180°C to recover extraction solvent for further recycling; (d) washing top stream of extractor-B obtained in step (b) with water in column-C at a temperature in the range of 20-60°C, followed by fractionating the resultant hydrocarbons at a temperature in the range of 100-400°C to obtain the extract hydrocarbons and secondary solvent and further recycling the secondary solvent to extractor-B, and finally (e) washing the raffinate phase obtained from step (a) in column-E at a temperature in the range of 20-60°C by conventional method to obtain raffinate hydrocarbons.

[0057] The aromatic rich feed used is preferably a petroleum fraction having boiling temperature in the range of 90-360°C. The selective solvent used is N-Methyl pyrrolidinone admixed with 2.0 to 15 wt % water or sulpholane or glycol. The ratio of solvent mixture to feed is in the range of 1:1 to 5:1 wt %. The feed and extraction solvent are preferably contacted countercurrently in extractor-A at a temperature of 30-80°C. Recovery of aromatics from extract phase is affected countercurrently in an extractor-B using secondary solvent selected from C6-C7 petroleum fraction at a temperature of 30-60°C. Ratio of secondary solvent to extract phase is in range of 1 to 4 by volume. Recovery of solvent from top phase of extractor-B and raffinate phase is done by known method such as water washing at a temperature of 30-40°C. Recovery of secondary solvent from top of the extractor-B is effected by using conventional method such as distillation at atmospheric pressure at a temperature in the range of 110-300°C. Recovery of residual hydrocarbons in bottom phase of extractor-B is done by conventional methods such as distillation at reboiler temperature of 100-160°C.

[0058] The following examples are given by way of illustration and therefore should not be construed to limit the scope of the present invention.

**EXAMPLE 1**

[0059] For the extraction step the model mixture of propyl benzene-decane with 60 wt. % propyl benzene, was admixed with an equal weight of NMP (Pure) at 40°C. Two liquid phases under equilibrium were formed. Each phase was separated, made solvent-free and analysed. The extract phase contained 2.6 wt. % propyl benzene, while its concentration reduced to 4.1 wt. % in the raffinate phase with 89.0 wt. % yield.

**EXAMPLE 2**

[0060] For the extraction step the model mixture of propyl benzene-decane with 60 wt. % propyl benzene, was admixed with an equal weight of NMP at 20% sulpholane at 40°C. Two liquid phases under equilibrium were formed. Each phase, as separated, made solvent-free and analysed. The extract phase contained 2.2 wt % propyl benzene, while its concentration reduced to 4.8 wt. % in the raffinate phase with 94.5 wt. % yield.

**EXAMPLE 3**

[0061] 3.3 kgs/hr of heavy naphtha fraction (100-200°C) from Assam crude, containing 30.2 wt. % aromatic is fed to packed extractor-A. It is counter-currently contacted with the selective solvent (NMP+10% water) at 40°C. entering the column at a rate of 7.7 kgs/hr. The extract phase produced at a rate of about 8.6 kgs/hr. 4.1 kgs/hr of extract phase produced as above containing 0.54 kgs/hr of total hydrocarbons is fed to packed extractor-B and counter-currently contacted with C6-C7 paraffinic petroleum fraction.
entering at a rate of 6.1 kgs/hr. Phase produced at a rate of 7.0 kgs/hr from the top of extractor-B contains 0.49 kgs/hr of NMP. The phase is water washed and fractionated shielding 0.55 kgs/hr of naphtha extract containing 77.2 % of aromatics. The recovered $C_{8}-C_{12}$ paraffinic petroleum fraction is circulated back to extractor-B. The bottom of the extractors contains 3.15 kgs/hr of lean solvent and 0.011 kgs/hr of naphtha hydrocarbons. 2.3 kgs/hr of the raffinate phase produced from extractor-A contains about 0.133 kgs/hr of NMP was water washed in raffinate wash column-E yielding 2.16 kgs/hr of deamortized heavy naphtha with 7.8 wt. % aromatics.

EXAMPLE 4

[0062] 2.0 kgb/hr of gas oil fraction (240-400° C.) from Assam crude, containing 39.2 wt. % aromatic is fed to packed extractor-A. It was counter-currently contacted with the selective solvent (NMP+10% water) at 40° C, entering the column at a rate of 7.2 kgs/hr. The extract phase produced at a rate of about 8.2 kgs/hr. 4.7 kgs/hr of extract phase produced as above containing 0.377 kgs/hr of total hydrocarbons is fed to packed extractor-B and counter currently contacted with $C_{7}-C_{2}$ paraffinic petroleum fraction entering at a rate of 6.8 kgs/hr Phase produced at a rate of 7.6 kgs/hr from the top of extractor-B contains 0.56 kgs/hr of NMP. The phase is water washed and fractionated yielding 0.345 kgs/hr of gas oil extract containing 86.9 % of aromatics. The recovered $C_{8}-C_{12}$ paraffinic petroleum fraction is circulated back to extractor-B. The bottom of the extractor-B contains 4.07 kgs/hr of lean solvent and 0.02 kgs/hr of gas oil hydrocarbons. 1.38 kgs/hr of the raffinate phase produced from extractor-A contains about 0.059 kgs/hr of NMP was water washed in raffinate wash column-E, yielding 1.32 kgs/hr of deamortized gas oil with 16.2 wt. % aromatics.

[0063] The Main Advantages of the Present Invention are as Follows:

[0064] 1. Use of environmentally friendly solvent such as NMP in an admixture with anti solvents such as water, glycols, sulpholane etc. Use of conventional metallurgy such as carbon steel and simple and flexible flow sheet

[0065] 2. High capacity solvent like NMP in spite of its boiling point overlap with that of feed can be used since hydrocarbons are recovered from the extract phase by re-extraction route.

[0066] 3. Flexibility in handling wide range of petroleum fractions (naphtha to gas oil) in the same unit by using block out operation is possible

[0067] 4. Elimination of energy intensive distillation step of aromatic recovery from extract phase leading to considerable savings in utility and lower capital cost

[0068] 5. Operation of re-extraction column at ambient temperature results in requirement of lower utilities and minimize solvent degradation. This will also minimize the corrosion problem

[0069] 6. Production of good quality aromatic rich extract for various end uses e.g. gasoline blending, insecticide formulation

[0070] 7. Feasibility of producing superior quality specialty solvents by incorporating water stripper

[0071] 11. Availability of additional extraction column operating parameters (e.g. anti solvent composition and extraction temperature) due to incorporation of solvent recovery column

We claim:

1. A process for the extraction of aromatics from petroleum feed streams which comprises:

(a) contacting a petroleum feed with a polar organic solvent containing 2-20 wt % antisolvent in a extractor-A column to obtain a extract phase and a raffinate phase,

(b) contacting extract phase obtained in step (a) with 1-6 vol % of a secondary solvent in the extractor-B column to recover the extract hydrocarbons,

(c) distilling the bottom stream of extractor-B obtained in step (b) in column-F at reboiler temperature to recover the extraction solvent for further recycling

(d) washing the top stream of extractor-B obtained in step (b) with water in column-C, followed by fractionating the resultant hydrocarbons to obtain the extract hydrocarbons and secondary solvent and further recycling the secondary solvent to extractor-B,

(e) washing raffinate phase obtained in step (a) in column-E to obtain raffinate hydrocarbons.

2. A process as claimed in claim 1 wherein step (a) is carried out at a temperature in the range of 20-80° C.

3. A process as claimed in claim 1 wherein step (b) is carried out at a temperature in the range of 20-60° C. to recover the extract hydrocarbons.

4. A process as claimed in claim 1 wherein the reboiler temperature in step (c) is in the range of 90-180° C.

5. A process as claimed in claim 1 wherein flashing of top stream of extractor-B obtained in step (b) with water in column C. is done at temperature in range of 20-60° C., followed by fractionation of resultant hydrocarbons at temperature in the range of 100-400° C.

6. A process as claimed in claim 1 wherein the washing of the raffinate phase obtained in step (a) in Column E in step (e) is carried out at a temperature in the range of 20-60° C.

7. A process as claimed in claim 1 wherein the petroleum feed comprises an aromatic rich feed with a boiling temperature in the range of 90-360° C.

8. A process as claimed in claim 1 wherein the selective solvent used is N-Methyl pyrolidinone admixed with 2.0 to 15 wt. % water or sulpholane or glycol.

9. A process as claimed in claim 1 wherein the ratio of solvent mixture to feed is in the range of 1:1 to 5:1 wt %.

10. A process as claimed in claim 1 wherein the feed and extraction solvent is contacted countercurrently in extractor-A at a temperature in the range of 30-80° C.

11. A process as claimed in claim 1 wherein the recovery of aromatics from extract phase is effected countercurrently in extractor-B using a secondary solvent selected from $C_{6}-C_{7}$ petroleum fraction at a temperature in the range of 30-60° C.

12. A process as claimed in claim 1 wherein the ratio of secondary solvent to extract phase is in range of 1 to 4 by volume.
13. A process as claimed in claim 1 wherein recovery of solvent from top phase of extractor-B and raffinate phase is done by water washing at temperature in range of 30-40°C.

14. A process as claimed in claim 1 wherein recovery of secondary solvent from top of extractor-B is done by distillation at atmospheric pressure at a temperature in the range of 110-300°C.

15. A process as claimed in claim 1 wherein the recovery of residual hydrocarbons in the bottom phase of extractor-B is done by distillation at a reboiler temperature in the range of 100-160°C.

16. A process as claimed in claim 1 wherein the petroleum feed is selected from the group consisting of heavy naphtha, kerosene and gas oil.

17. A process as claimed in claim 1 wherein the aromatics obtained are selected from the group consisting of high octane benzene free stock for gasoline pool, high Cetane Diesel, high aromatic solvent and feed-stock for needle coke production.

18. A process as claimed in claim 1 wherein refinery cut light naphtha cut is used as the re-extraction solvent.