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Technologies for Aromatics Extraction and Production of Food Grade Hexane and Petrochemical Grade Hexane

Navneet Kumar [a], Shashank Sharma [b], S. K. Khanna [c]
[a] Department of Chemical Engineering, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh, India
[b] Department of Chemical Engineering, JMIETI, Radaur, Yamuna Nagar, Haryana, India
[3] Department of Chemical Engineering, Dev Bhoomi Group of Institutions, Dehradun, Uttarakhand, India

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Abstract

Solvent extraction is a versatile separation tool and used extensively in chemical processing industries including metallurgy, nuclear, petroleum, food, pharmaceutical and also for waste management. Generally it is used only second to distillation for the separation of close boiling components and azeotropic mixtures, since in these cases distillation either requires too many stages/too high reflux ratio or may not be feasible at all. For these applications solvent extraction is preferred route, as criteria for separation is based on chemical structure rather than boiling point.
In petroleum industry solvent extraction is used for , either to produce pure aromatics from reformate and hydrogenated pyrolysis gasoline and/or dearomatizing the straight run streams for the production of on spec products with respect to aromatic content for particular end uses. Typical applications are for the production of pure benzene and toluene, food grade hexane, special boiling point solvents, superior kerosene and aviation turbine fuel.

1. Introduction

Solvent extraction is a versatile separation tool and used extensively in chemical processing industries including metallurgy, nuclear, petroleum, food, pharmaceutical and also for waste management. Generally it is used only second to distillation for the separation of close boiling components and azeotropic mixtures, since in these cases distillation either requires too many stages/too high reflux ratio or may not be feasible at all. For these applications solvent extraction is preferred route, as criteria for separation is based on chemical structure rather than boiling point.

In petroleum industry solvent extraction is used for, either to produce pure aromatics from reformate and hydrogenated pyrolysis gasoline and/or dearomatizing the straight run streams for the production of on spec products with respect to aromatic content for particular end uses. Typical applications are for the production of pure benzene and toluene, food grade hexane, special boiling point solvents, superior kerosene and aviation turbine fuel. The present status of solvent extraction technologies in petroleum industry in India is given in following table.

Table: 1. Present Status of Solvent Extraction Technologies in Petroleum Industry in India

	Solvent	No. of Units	Location
Production of pure benzene & toluene	TEG/Tetra Sulpholane	1 4	Gujarat Refinery NOCIL, IPCL, BPCL, CRL
Production of Food Grade Hexane	Sulpholane NMP	2 1	BPCL, MRL HPCL, Bombay
Production of SK/ATF	Liquid SO_2	4	Digboi, Guwahati, Barauni, Bongaigaon

2. IIP-EIL Sulpholane Extraction Technology for Production Of Pure Benzene And Toluene

The typical sources of benzene and toluene in petroleum industry are catalytically reformed naptha and hyderogenated pyrolysis naptha. The composition of typical feed stocks is given in Table -1. The product specifications for benzene and toluene are indicated in Table -2. For the production of high purity light aromatics, the process using a combination of extraction and extractive distillation is widely practiced.

An ideal solvent should have good balance of solvency and selectivity to provide acceptable solvent circulation rate. Many solvents like triethyleneglycol, tetraethyleneglycol, N-methylpyrrolidone, N-formyl morpholine and sulpholane have been widely used. Sulpholane was used for this process as it had received wide acceptance.

3. Experimental Data Base

The design of extraction and extractive distillation steps requires detailed information on phase equilibria. As a result 700 ternary and multicomponent liquid-liquid equilibrium data and about 300 binary and ternary vapour-liquid equilibrium data points for solvent hydrocarbon systems were generated. The liquid-liquid equilibrium data were studied under atmospheric and moderate pressure conditions in the temperature range 25-1500 C, whereas vapour-liquid

Corresponding Author,
E-mail address: navkchem@gmail.com

equilibria were determined under atmospheric conditions. The mass transfer studies on hydrocarbon-solvent systems were carried out in laboratory continuous units.

Process Description

Simplified process flow sheet is given in Fig-1.

Extraction Section

The feed, entering the extractor midway moving upwards, comes in countercurrent contact with the descending solvent which selectively extracts the aromatics. Rich solvent from the extractor bottom is charged to extractive stripper. The steam consisting of aromatics and saturated hydrocarbons is taken from the top of the extractive stripper and is turned to the bottom of the extractor as backwash. Raffinate of low aromatic content is removed from the top of extractor and charged to the raffinate wash column (RWC) where water from solvent recovery column receiver removes the solvent from the raffinate. The water solution of solvent is returned to the recovery column.

Solvent Recovery Section

The extractive stripper bottoms are charged to the solvent recovery column (SRC) which produces the aromatic extract as solvent free top product and lean solvent for recycle. A small slip stream of the circulating solvent is sent to solvent regenerator where the degraded material is separated from the solvent.

Product Fractionator Section

The aromatic extract is sent to clay tower where unsaturates are absorbed enabling the products to meet the desired colour specifications, which is subsequently fractionated.

Commercial Status

First plan based on IIP-EIL sulpholane extraction technology for the production of benzene and toluene was commercialized at BPCL in 1985. This plant produces 98000-t/a benzene and 17000-t/a toluene. A second plant of similar capacity was subsequently commissioned at Cochin Refineries in 1990. The recovery and purity for benzene in these commercial units are >99.9% and 99.99% respectively. The technology has also been accepted by NOCIL for the expansion of capacity for aromatics extraction unit.

Production Of Food Grade & Petrochemical Grade Hexane

Low aromatic napthas meeting specific requirements are used for variety of industrial purposes e.g. food grade hexane (63-690C) for oil seed extraction, feed stock for petrochemical and fertilizer units and special boiling solvents (SSP) for specific applications.

The source of food grade hexane (FGH) is generally straight run 63-690C heart cut naptha. This cut however, usually contains more than specified concentration of benzene which being carcinogenic is required to be removed to very low level. This cut, however, usually contains 3-15% aromatics mainly benzene. For example, the 63-690C cuts from Iranian light and Bombay High crude oils contain about 4 and 14% by wt of benzene respectively. As benzene forms an azeotrope with hexane, its removal by fractional distillation is not possible and thus acid treatment or solvent extraction is required.

The present BIS specifications are given in Table-3. These specifications are going to be revised in near future. The proposed specifications are presented in Table-4.

Consumption

Vegetable oil industry is the main user of FGH, consuming around 90% of total hexane production in India. There are about 500 solvent extraction plants in the country. The total vegetable oil consumption in India was around 8 MMT/A for the 1996-97 and its expected to grow up to 9 MMT/A by 2000 AD. The food grade hexane consumption in india for the year 1996-97 was 125 TMT and expected to grow up to 150 TMT by 2000 AD. The consumption of vegetable oil and food grade hexane for the last few years, along with the projected figures for the year 2000 AD is presented in the following table:

Year	Vegetable Oil Consumption, TMT	Food Grade Hexane Consumption, TMT
1993-1994	5580	84
1994-95	6110	95
1995-96	6866	100
1996-97	8104	125
1999-2000*	9000	150

*Projected figures

Production

In India there are four refineries producing food grade hexane. The production capacity of these units is given in following table.

Refinery	Production capacity
BPCL, Bombay	25
MRL, Madras	25
HPCL, Bombay	70
IOCL, Koyali	35

Methods of production from raw hexane

1.Oleum Treatment

Oleum treatment was in use at HPCL for the production of FGH from 63-690C c crude cut of Iranian light oil.

Drawbacks of this technology are:

a) Oleum is highly corrosive.

b) Problems of disposal of acid sludge.

c) Acid sludge creates severe pollution.

d) Feed with high concentration of benzene cannot be treated.

f) Loss of benzene.

2. Extractive Distillation

Earlier used at BPCL, Bombay. A series of test runs on this unit and systematic laboratory studies revealed that it is not possible to produce hexane of anticipated future specifications even from feedstocks having 5 wt% benzene.

3. Liquid-liquid Extraction using Sulpholane as solvent

Liquid-liquid extraction has been found to be the best method to remove benzene and can produce hexane fraction having benzene as low as 1000 ppm. Indian institute of Petroleum, Dehradun earlier in collaboration with Engineers Indian Limited, New Delhi has developed solvent extraction technology for the production of food grade hexane/ SBP solvents using sulpholane as solvent which is successfully commercialized at Bharat Petroleum Corporation Limited, Bombay and Madras Refineries Limited, Madras. Each unit is producing 25,000 TPA of food grade hexane with maximum of 0.5 wt% of benzene.

With is technology deep extraction of aromatics particularly from low aromatic feedstocks (e.g. 63-690C/40-1200C straight run naptha cuts) requires very high solvent to feed ratios to meet the international specifications with reference to aromatics and benzene contents. At high solvent to feed ratio the capital as well as utility costs increase considerably. At the same time throughput is reduced significantly. This makes the process unattractive.

4. Liquid-liquid Extraction using NMP as solvent

The specifications with respect to benzene are contemplated to be changed to very low level (<0.2%). With this background, IIP have developed another technology for dearomatization of low aromatic straight run naptha cuts using NMP as solvent.

Amongst Sulpholane and N-Methyl Pyrrolidine (NMP) (both industrial solvents for aromatics extraction) it has been found that while sulpholane is the best solvent for production of pure aromatics (benzene and toluene), NMP (properties given in Table-5) is the best solvent for dearomatisation purposes particularly for low aromatic feedstocks (Typical compositions are given in Table 6 & 7). The advantages of NMP – water combination over sulpholane are low viscosity, high selectivity, high capacity, flexibility in operation with respect to feed quality and product specifications and easier recovery of hydrocarbons from extract phase. Pilot plant studies (Table-8) revealed that production of FGH meeting the international specifications is feasible by using NMP as solvent. The process flow sheet is same as that of sulpholane and as such sulpholane can be replaced by NMP in the existing units with minor changes.

The NMP extraction technology developed and licensed by IIP is most suited and economical for dearomatization and production of suitable naptha cuts meeting international specifications for different applications e.g. food grade hexane (63-690C cut), special boiling point solvents (55/1150C) etc. The simulated results for a typical commercial unit are presented in Table-9.

Salient Features Of The Process

- Use of Liquid-Liquid extraction approach instead of extractive distillation for effective removal of aromatics.
- Use of NMP which is the best solvent for dearomatization i.e. when raffinate is the product.
- Requirement of lower Solvent to Feed ratio i.e. higher throughput and lower utilities due to high capacity of NMP.
- Improved mass transfer efficiency due to low viscosity and interfacial tension of NMP.
- Easier recovery of hydrocarbons from extract phase.
- (At atmospheric pressure and at lower reboiler temperature compared to requirement of vacuum and high reboiler temperature in case of sulpholane).
- Lower thermal degradation of solvent due to its high thermal stability and lower reboiler temperature.
- Lower oxidative degradation as SRC operates at positive atmospheric pressure (1.3 kg/cm2).
- Lower solvent inventory and make-up solvent cost.
- Aromatic rich extract obtained as byproduct forms good feedstock for reformer.

Product Yield And Qualtiy

The yield of product raffinate is dependent upon the feed composition and the degree of quality improvement desired. The aromatics in the raffinate can be reduced to less than 0.5%. the benzene content in dearomatized food grade hexane and/or wide naptha cuts raffinate can be reduced to less than 1000 ppm.

Commercial Status

In November 1997 HPCL commercialized IIP-HPCL NMP based extraction technology for the production of food grade hexane. BPCL, Bombay has accepted IIP’s NMP based technology for the dearomatisation of naptha for the production of SBP and Food Grade Hexane for changeover from sulpholane to NMP in their existing hexane unit.

Process Description

Simplified process flow sheet is presented in figs. 2 and 3.

In the aromatization section the 63-690C hexane cut or typical naptha fraction say 40-1200C will be received in a feed surge drum (V-01). The feed is pumped (P-01) to the extraction column at the bottom plate. Lean solvent is introduced at the top of the extractor, which comes in contact with upcoming feed counter currently. The aromatic of naptha cut gets selectively extracted by solvent. The raffinate phase lean in aromatics is removed from the top and introduced at the bottom of raffinate wash column (RWC)(C-03) and brought in contact with water counter currently after being cooled in a raffinate cooler (E-01). Solvent present in the raffinate phase is carried over by water. The treated product (food grade hexane or dearomatized naptha) is taken from the top of the RWC and pumped (PO-2) to storage.

The aromatic rich solvent (extract phase) is withdrawn from the bottom of the extraction column and fed to solvent recovery column (SRC)(C-02) after getting preheated in lean solvent/rich solvent exchanger (E-02). The lean solvent from SRC reboiler (E-03) is pumped by solvent pump (P-03) to extraction column after giving heat in water heater (E-04), lean solvent/rich solvent exchanger and lean solvent trim cooler (E-05). Steam and/or water from water heater is introduced in the column to strip off the hydrocarbons from the solvent. The hydrocarbons along with the steam are condensed (E-06) and collected in the overhead vessel (V-02). Part of these hydrocarbons are sent to the column as reflux and remaining are pumped (P-09) to extract storage. The water phase from the overhead vessel is pumped (P-05) to RWC for washing the raffinate phase. A small strip stream of circulating solvent is sent to solvent regeneration column (C-04). Any degraded solvent is removed periodically from the bottom and solvent from the top is returned to solvent recycle stream. The respective dearomatized naptha cut goes to storage as a product or is further fractioned into desired fractions (Fig-3) in case of wide cut naptha.

Table: 1

Composition of typical feed stock for aromatic recovery

Components	Reformed Naphtha (Wt%)	Pyrolysis Naphtha(Wt%)
Paraffins		
C_4	0.53	-
C_5	8.55	-
C_6	10.37	18.78
C_7	5.39	12.35
C_8	0.90	0.08
Naphthenes		
C_5	-	1.07
C_6	0.77	12.95
C_7	1.03	0.55
C_8	0.65	-
C_9	0.13	-
Aeromatics		
C_6	60.70	54.12
C_7	10.96	0.10
C_8	-	-

Table: 2

Specifications for Nitration Grade Benzene and Toluene

Property	Benzene	Toluene
Specific gravity at 15 °C	0.882 to 0.886	0.869 to 0.873
Solidifying point	5.4 °C	Paraffin content to be less than 1.5 wt%
Total distillation range at 760mm Hg pressure	1 °C including temp. of 80 °C	1 °C including temp. of 110°C
Acid wash color	Not darker than a solution of 0.003 gm of $K_2Cr_2O_7$ in 1 lit. of water not darker than No.2 std.	Same as benzene
Acidity	No free acid	Same as benzene
Sulphur compounds	Free of H_2s & So_2	Free of H_2s & So_2
Copper strip corrosion	Copper strip shall not show iridescence neither grey nor black	Same as benzene

Table: 3

Specification of Food Grade Hexane (IS: 3470-1966)

S.No.	Characteristics	Requirement
1.	***Distillation*** IBP , °C, max Dry point, °C max Temperature range of final 10%,°C max	 63 70 2
2.	***Composition*** Aromatics, vol % max Saturates , vol %, min	 1.0 98.5
3.	Density at 25 °C, max	0.687
4.	Color (Saybolts), max	+30
5.	Sulphur, ppm, max	75
6.	Corrosion copper strip, 3hrs at 50 °C, max	1
7.	Doctor test	Negative
8.	Bromine no., max	1
9.	Non-volatile residue g/100 ml, max	0.001
10.	Lead, g/liter, max	0.0005
11.	Chloride, ppm, max	20

Table: 4

Specification of Food Grade Hexane

Characteristics	Specifications (Proposed)
Color (saybolt), min	30
Density at 15 °C, max	0.687
Refractive index n20	1.381-1.384
Distillation (a) IBP °C, min (b) Dry point °C, max (c) Temperature range of final 10%, °C, max	 63 70 2

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Non volatile residue g/100 ml, max	0.0005
Reaction of non volatile residue	Neutral to methyl orange pH indicator
Sulphur content, ppm, max	5
Lead as Pb, mg/kg, max	1
Aromatic hydrocarbon %, v/v , max	0.2
Polycyclin aromatic hydrocarbon UV absorbance per optical path length, max at wavelength (nm) 280 -289 290 -299 300 -359 360 -400	 0.15 0.13 0.08 0.02
Doctor test	Not included
Phosphate, ppm, max	Not included
Bromine no., max	Not included
Composition (a) Aromatics, % by vol, min (b) Saturates , % by vol, min	 Not included Not included
Corrosion, copper strip 3hrs. at 50 °C, max.	Not included
Chloride (as c1,ppm,max	Not included

Table: 5

Properties of N – Methyl-Pyrrolidone (NMP)

Formula	C_5H_9NO
Structure	
Molecular weight	99.1
Density at 25 °C, g/ml	1.027-1.028
Boiling point at 760 mm Hg, °C	203
Viscosity at 25°C, cp	1.65
Flash point, °C	91
Freezing point, °C	-24.4
Heat of vaporization, kcal/kg	117.8
Specific heat at 25°C, kcal/kg/°C	0.4
Stability	Excellent
Toxicity	Non toxic, prolong contact to skin should be avoided

Material for storage and handling 1020 carbon steel is satisfactory as a storage material. Rubber hose is unsuitable for handling. Standard carbon steel pipe is acceptable.

Table: 6

Typical feedstock characteristics

Feed	63-69°C straight run naphtha cut
Density at 20 °C, g/cc	0.6741
Composition analysis, Wt. %	
n-Pentane	0.2
2,2 Dimethyl Butane	0.2
Cyclopentane	1.0
2,3 Dimethyl Butane	2.3
2-Methyle pentane	18.1
3-Methyl pentane	15.4
n-Hexane	48.7
2,2-Dimethyl pentane	0.2
Methylcyclopentane	-
2,4-Dimethyle pantan	0.4
Benzene	3.9
Cyclohexane	1.8

NOTE: Feed stock having higher benzene /aromatic content can be processed easily.

Table: 7

PNA analysis of typical straight run Naphtha cut (40-120°C)

Hydrocarbon type	**Wt. %**
Total P	59.01
Total N	24.1
Total A	16.9
$P_3 – P_5$	20.1
P_6	25.6
P_7	9.7
P_8	3.6
P_9	0.0
P_{10+}	0.0
Total P	**59.0**
N_5	0.0
N_6	13.0
N_7	9.1
N_8	2.0
N_{9+}	0.0
Total N	**24.1**
A_6	11.9
A_7	4.7
A_8	0.3
Total A	**16.9**

Table: 8

Pilot Plant Studies at HPCL , Bombay

Feed: Raw hexane 63-69°C cut aromatics, wt% = 3.9

Solvent: NMP+Water

Characteristics	**Run No.**

Extractor temperature, °C **S/F ratio (w/w)** **Hydrocarbon ,wt. %** **Water .vol.%** **Raffinate –Benzene, Wt. %**	**1 2 3** **4 5 6** 40 40 33 50/31 40 40 1.05 1.89 1.89 1.05 1.05 2.6 Nil NilNilNilNilNil 6.2 10.6 11.6 10.0 10.6 15.0 0.23 0.04 0.03 0.25 0.33 0.10

Table: 9

Simulation if typical extraction unit

Extractor type		Sieve tray
Number of trays		68
Plate spacing		30 cm
Benzene content in feed		4.0 Wt.%
SULFONALE		**NMP + WATER**
Solvent rate	282(282.5)	282.5
Feed rate	84.2 (47)	94.0
S/F, w/w	3.335 (60)	3.0
Benzene conc. In raffinate	0.2 wt.% (100ppm)	100ppm

***30% saving on heat duty for NMP over sulfonale**