Separation of Cyclopentane from close boiling paraffins using selective solvents in extractive distillation step

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ABSTRACT: Light petroleum fraction like naphtha and natural gas liquid (NGL) contain valuable naphthenic products such as cyclopentane and Cyclopehexane. Cyclopentane has emerged as the best alternative to CFCs, HCFCs and HFCs for blowing polyurethane for insulation in refrigeration industries. The reasons of this choice of cyclopentane includes; zero ozone depleting potential, environmental acceptance, reasonably low initial thermal conductivity, appropriate boiling point and proven availability. These factors outweighed the disadvantage of CP flammability.
The separation of cyclopentane from their appropriate boiling range cuts is considered to be difficult separation step. Such appropriate cuts are generally required first to be made aromatic free before separation of these naphthenes from their corresponding boiling range paraffins. Simple distillation cannot be used as the boiling points overlap. Moreover, these components form azeotropes in between. The present study emphasis on direct separation of CP from the appropriate light naphtha cuts using extractive distillation approach.

Key words: Extractive distillation, selectivity, capacity, NMP, light naphtha, NGL

INTRODUCTION

Cyclopentane has emerged as the best alternative to CFCs, HCFCs and HFCs for blowing polyurethane fro insulation in refrigeration industries and has been successfully used by refrigerator manufactures worldwide. The reasons for this choice of CP includes, zero ozone depleting potential, environmental acceptance, reasonably low initial thermal conductivity, appropriate boiling point and proven availability. These factors outweighed the disadvantage of CP flammability. The extractive distillation technique for separation of pure hydrocarbons from petroleum was first applied for the manufacture of toluene (1&2). The principle behind extractive distillation is the introduction of a selective solvent that interacts differently with each of the components of the original mixture and which generally shows a strong affinity with one of the key components (3). The thermodynamic advantages of extractive distillation over conventional distillation, which result in lower energy requirements, have long been known (4). A process for cyclohexane through extractive distillation has been developed by Humble Oil and Refining Company (5). A similar approach to the production of pure cyclohexane from light petroleum distillate by extractive distillation technique was adopted from Nettensheim (6). Phillips Petroleum Co. developed and commercialized as extractive distillation process that uses a mixed solvent to purify cyclohexane from its heptanes isomer (7&8). Separation of benzene and cyclohexane with mixed solvent (diethyl glycol, dimethylsulfoxide, N-methylformamide) using extractive distillation were studied (9). A new extractive distillation solvent has been developed for recovering high purity (99.9%) cyclohexane from pyrolysis gasoline fractions with 97% yield using phenoxyethanol as a solvent (10). The cyclohexane concentrate was subjected to extractive distillation with aniline as solvent in continuous pilot unit and 99% pure cyclohexane recovered from the extract solution in the solvent recovery unit. 77-81% cyclohexane concentrate from 60-90°C cut of Ankleshwar crude has also been tried as feed stock (11).

Other solvents tried through extractive distillation approach for separation of cyclohexane/cyclopentane from paraffins includes N-alkyl-2-pyridones (methyl-, ethyl-, and isopropyl) (12), NMP and NMP with water (13). N-mercaptoethyl-2-pyrrolidone and cyclohexanol (14), a mixture of NMP and ethylene glycol or tetra ethylene glycol (15), N-mthyl-2-thiopyrrolidone (I), I+Tetra EG, N-(β-mercaptoethyl)-2-pyrrolidone+I and I+sulpholane (16).

MATERIALS AND METHODS

The separation of cyclopentane from their appropriate boiling range cuts is considered to be a difficult separation step. Such appropriate cuts are generally required first to be made aromatic free before separation of these naphthenes from their corresponding boiling range paraffins. Simple distillation cannot be used as the boiling points overlap. Moreover, these components form azeotropes in between. Fractional distillation with large number of trays may be successful route to some extent but nearly similar boiling components like 2,3-dimethyl pantane and 3,3,3,-trimethyl butane remain with product as impurity and hence product purity is affected. Extractive distillation is another successful technique for the separation of naphthene from the mixture.

The first criteria in the selection of solvents for the extractive distillation is their physicochemical characteristics based on which either they are rejected or considered for further screening through measurements of selectivity and solvent power (17). Based on this some potential solvents have been selected for the present study and procured.

NGL and stripper top stream of extraction unit have been chosen as potential feedstocks in the first instance and procured from ONGC, Hazira and BPCL, Mumbai respectively. Cyclopentane and n-pentane were procured from Fluka, Switzerland of 99.9% purity. NMP of 99.5% purity was procured from BASF, GDR. The purities of chemicals used in the study was checked by Gas Chromatography and by measuring the refractive indices (RI) at 20°C by Abbe's refractrometer with the precision of +0.0002 units.

Cyclohexane-hepatne and cyclohexane-hexane were chosen as model hydrocarbons to present the heartcut for cyclohexane and cyclopenatne-n-pentane as model hydrocarbon to present cyclopenatne cut. The liquid-liquid equilibrium (LLE) studies on these models were carried out with N-methyl pyrollidone (NMP), N-formyl morpholine (NFM), Tetrahydrofurfural alcohol (THFA) and dimethyl formamide (DMF). Water was used as antisolvent. Analysis method was used for determination of these compositions of equilibrium phases. In order to get the tie-lines, single stage batch equilibrium runs were carried out in a jacketed mixer-settler of about 200 ml capacities. The mixer-settler was provided with a thermometer pocket and a syringe stirrer and was maintained at the run temperature within $+0.05^{o}C$ with the help of a thermostatic bath. The solvent and the hydrocarbon feed mixture of known composition and weights were taken in the

mixer-settler and stirred well. The stirring was done for 10 minutes, which is sufficient time for the establishment of equilibria in the present set-up. After mixing, the phases were allowed to settle for about the same time, at the same time temperature and then withdrawn separately, weighed and analysed.

Synthetic model hydrocarbon mixture of cyclopenatne-n-pantane, and heartcut prepared from NGL have been studies on the continuous Oldershaw column unit having 50 plates. The heart cut was made benzene free before use. NMP and NMP + 5% water were used as solvent. Bottom temperature and solvent to feed (S/F) ratio were studied as variables. The feed entry temperature and location were fixed. Under steady state conditions the column top and bottom samples were collected for analysis. Analysis was carried out by GC.

RESULTS AND DISCUSSION

Extractive distillation experiments using NMP (pure) and NMP + 5% water as solvents was carried out with model mixture of n-pentane-cyclopenatne and $45-52^{o}C$ heart cut. Some of the typical results along with operating conditions are provided in Table-1 and 2. Results in Table-1 indicate the bottom hydrocarbons (cyclopentane fraction) yield is around 21% with cyclopenatne purity of about 66% for NMP (pure) solvent, whereas for NMP+5% water cyclopetane fraction yield is about 12% with cyclopentane as 95.3%. Further from the results in Table-2 it is clear that higher boiling components like 2,3-dimethyl butane, 2-methyl pentane, 3-methyl pentane and hexane present in heart cuts are difficult to separate overhead in the extractive distillation column fro cyclopentane and as a result desired purity of cyclopentane is hindered. Fractional distillation (simulated) for optimum pentane cut (Table-2) was carried out in same Oldershaw distillation column (50 plates) as in extractive distillation approaches. In the simulation pentane fraction i.e. IBP-$36^{o}C$ from IBP-$55^{o}C$ cut of NGL, Hazira was used. The results show that it is possible to produce cyclopentane in about 79% purity by fractional distillation whereas the purity is improved to 95.8% in extractive distillation step using NMP+water.

Enhancement of purity of cyclopentane in the extractive distillation step is expected due to solvent effect which increase the volatility difference between close oiling 2,2-dimethyl butane and cyclopentane as is clear from α-value presented in Table-3. The recovery varies from 98 for extractive distillation and 99% for the simple distillation case (Table-2). Comparison of α with and without solvent indicates that presence of solvent enhance α for the most close oiling 2,2-dimthyl butane from 0.98 to 1.12. This will help in separation of 2,2-dimethyl butane from cyclopentane by using extractive distillation which otherwise would not be possible by simple distillation.

Prefractionator is essential to produce pentane fraction for maximum cyclopentane recovery and purity for NGL. For this purpose based on probe experiments prefractionator has been designed/simulated. For the pentane fraction, cyclopentane may be produced either by simple distillation or by extractive distillation depending upon the purity levels of cylcopentane required. With simple distillation a cyclopentane purity of about 79% may be achieved whereas the purity increases to about 95% by extractive distillation step. The recovery is almost same in two cases. Thus, it is clear that extractive distillation is an alternative approach to produce higher purity.

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Table-1
RESULTS OF EXTRACTIVE DISTILLATION RUN ON SYNTHETIC FEED
(n-Pentane-Cyclopentane)

Oldershaw Column: 50 Plates   **Solvent Entry**: 40 Plates

Feed Entry: 10 Plates   **Solvent**: NMP (Pure) & NMP + 5% Water

S.No.	Operating Characteristics	NMP (Pure)	NMP + 5% Water
1.	Cyclopentane in Feed, wt%	14.0	14.0
2.	Solvent to Feed Ratio (w/w)	5.4	5.99
3.	Feed inlet temperature, ^{o}C	40.0	40.0
4.	Reboiler temperature, ^{o}C	140.0	130.0
5.	Top temperature, ^{o}C	33.0	33.0
6.	**Flow rates (Kg/hr)**		
	Solvent	872.76	939.78
	Feed	161.54	156.79
	Distillate Phase	127.06	138.29
	Bottom Phase	907.23	958.27
	Bottom Hydrocarbons	34.47	18.49
7.	**Distillate Composition, Wt %**		
	Distillate Yield, wt%	78.66	88.20
	RI at 20°C	1.3587	1.3585
	i-Pentane	2.5	2.0
	n-Pentane	97.5	94.7
	2,2-dimethylbutane		0.4
	Cyclopentane		2.9
8.	**Bottom Phase Composition, Wt%**		
	Solvent	96.15	98.07
	Hydrocarbons (HC's)	3.85	1.93
9.	**Bottom HC's Composition (Solvent free)**		
	RI at 20°C	1.3910	1.4069
	Extract yield, wt%	21.34	11.80
	i-Pentane	Trace	Trace
	n-Pentane	33.1	0.4
	2,2-dimethyl butane	0.9	0.3
	Cyclopentane	65.6	97.0
	2,3-dimethylbutane	0.2	1.2
	2-mthylpentane	0.2	0.2
	3-methylpentane	-	0.8
	n-Hexane	-	0.1

Table-2

SIMULATED RESULTS OF EXTRACTIVE DISTILLATION AND FRACTIONAL

DISTILLATION FOR THE PRODUCTION OF CYCLOPENTANE

Feed: Pentane Fraction   **Solvent**: NMP (Pure) & NMP + 5% Water

Number of Theoretical Plates: 50   **Solvent Entry**: 10th Stage from top

Feed Entry: 40th Stage from top (20th for Fractional Distillation)

S.No.	Operating Characteristics	NMP (Pure)	NMP + 5% Water	Fractional Distillation
1.	Reflux Ratio	1:1	1:1	6.9:1
2.	Cyclopentane in Feed, wt%	33.6	3.5	3.5
3.	Solvent to Feed Ratio (w/w)	7.0	7.1	-
4.	Feed inlet temperature, ^{o}C	40.0	40.0	40.0
5.	Reboiler temperature, ^{o}C	110.7	144.9	80.0
6.	Top temperature, ^{o}C	36.9	36.2	29.4
7.	**Feed Composition, wt%**			
	Butane	-	11.0	11.0
	i-Pentane	-	41.8	41.8
	n-Pentane	-	42.8	42.8
	2,2-dimethylbutane	-	0.9	0.9
	Cyclopentane	33.6	3.5	3.5
	2-methylpentane	-	-	-
	3-methylpentane	-	-	-
	n-Hexane	-	-	-
8.	**Flow rates (Kg/hr)**			
	Solvent	7930.0	56000.00	-
	Feed	1130.0	7871.18	7871.18
	Distillate Phase	500.0	7671.18	7528.18
	Bottom Phase	8560.0	56195.0	343.0
	Bottom Hydrocarbons	630.82	279.19	343.0
9.	**Distillate Composition (Top) (Solvent free), wt% (Pentane rich stream)**			
	Butane	-	11.3	11.6
	i-Pentane	9.8	43.0	43.7
	n-Pentane	70.1	43.9	44.7
	2,2-dimethylbutane	9.1	0.7	-
	Cyclopentane	10.2	-	-
	2-methylpentane	0.6	-	-
	3-methylpentane	0.046	-	-
	n-Hexane	-	-	-
10.	**Bottom Phase Composition, wt%**			
	Solvent	92.6	94.7	-
	Water	-	4.8	-
	Hydrocarbons	7.4	0.5	-
11.	**Bottom Hydrocarbon**			

Composition (Solvent free) wt.% (CP Stream)			
i-Pentane	0.0458	-	-
n-Pentane	1.0	-	0.8
2,2-dimethylbutane	6.7	3.7	19.5
2,3-dimethylbutane	-	0.3	0.2
Cyclopentane	52.0	95.8	79.3
2-methylpentane	31.3	0.1	-
3-methylpentane	8.9	-	-
Recovery of Cyclopentane	**86.6**	**98.0**	**99.38**

Table-3

TYPICAL RELATIVE VOLATILITIES VALUES (α) FOR THE MODEL HYDROCARBONS WITH RESPECT TO CYCLOPENTANE

Composition	α Values	
	Without Solvent	**With NMP + 5% Water**
2,2-dimethylbutane	0.98	1.12
2,3-dimethylbutane	0.77	0.86
2-methylpentane	0.69	0.78
3-methylpentane	0.62	0.71