Extraction of Aromatics from 63-69°C Naphtha Fraction for Food Grade Hexane Production Using Sulpholane and NMP as Solvents

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The selective removal of aromatics from a narrow cut of naphtha, 63-69°C, by liquid-liquid extraction using sulpholane and N-methylpyrrolidone has been investigated. The experimental studies, carried out to generate design data, for the production of food grade hexane, were performed in a packed column under conditions to obtain a raffinate conforming to food grade hexane specifications and thereby verifying the viability of the separation technique even for a feed naphtha from Bombay High crude oil, unusually high in aromatics content. The experimental runs were simulated using a model in which both the dispersed and continuous phases were assumed to be axially mixed. The drop sizes, holdups, mass transfer coefficients and axial-mixing coefficients were estimated from literature correlations. The analytical solution to the axial dispersion model equations given by Miyauchi and Vermeulen for linearised equilibrium relationship was used to calculate the concentration profiles. The model predicted the aromatics concentration level in the raffinate reasonably well. It is concluded that food grade hexane can be conveniently made even from a cut containing 14% by weight aromatics using liquid extraction. The successful simulation of the packed column liquid extraction runs would suggest that scale-up to commercial units would be straightforward.

Hexane used as a solvent for oil seeds extraction has to conform to food grade specifications. For example, the Indian Standards Institution (ISI), stipulates a maximum in the aromatics content of 1% by volume (or 1.3% by wt) for this product[1]. The source for food grade hexane is straight run naphtha with a narrow 63-69°C cut. This cut, however, usually contains more than the specified concentration of aromatics, predominantly benzene. For example, the 63-69°C cuts from Iranian Light and Bombay High crude oils contain about 4% and 14% by weight of aromatics, respectively. Selective removal of aromatics from these naphtha cuts is therefore necessary. In principle both extractive distillation and liquid-liquid extraction with polar solvents can be employed for removing the aromatics to produce a raffinate conforming to food grade hexane specifications. Broughton and Asselin[2] have provided some data on the selectivities in extractive distillation and liquid-liquid extraction using sulpholane. Their data show that for the boiling range under consideration, 63-69°C, liquid-liquid extraction has higher selectivity than extractive distillation. Since the solvent recovery steps are identical in both cases, it is to be expected that liquid-liquid extraction would offer the more economic alternative for selective removal of aromatics from this stream.

Accordingly, this study concentrates on the liquid-liquid extraction concept.

To verify the technical feasibility of using liquid-liquid extraction for producing food grade hexane from Iranian Light and Bombay High naphtha cuts, experiments were carried out in a packed column. Two typical extraction solvents, sulpholane and N-methyl-pyrrolidone (NMP) were used. Experimentally measured equilibrium data with these solvent systems were used, along with literature correlations for hydrodynamics and mass transfer parameters, to simulate the packed column experiments with an axial dispersion model.

Experimental Procedure

The properties of the feed naphtha 63-69°C cuts used in these experiments are listed in Table 1. The sulpholane used had a boiling point of 287°C and refractive index of 1.4810 at 30°C and was supplied by M/s Shell Chemical Co., USA. NMP was supplied by M/s E. Merck, Schuncahardt, West Germany, and had a boiling point of 204°C and refractive index of 1.4684 at 20°C. Both solvents were vacuum distilled before use.

Generation of liquid-liquid equilibrium data—Liquid-liquid equilibrium measurements on the systems hexane-benzene-sulpholane containing 1.5% by weight water and hexane-benzene-NMP containing 10%

Table I	System Properties Used in Simulation of Experimental Runs at 30°C		
Liquid viscosity, mPa s			
Dispersed phase		9	2.475
Continuous phase		0.29	0.29
Diffusivity of aromatics, 10^{-9} m²s⁻¹			
Dispersed phase		0.214	0.66
Continuous phase		4.7	5.59
Property		System*	
		I	II
Liquid density, kg m⁻³			
Dispersed phase (solvent)		1261	1035
Continuous phase (feed)		669.5	669.5
Distribution coefficient		1.039	1.1325
Interfacial tension, mNm⁻¹		13	5

*System I: Extraction solvent sulpholane
System II: Extraction solvent NMP

by weight water were made in a glass-jacketed mixer-settler provided with a stirrer. The mixer-settler could be maintained to within ±0.05°C of the experimental temperature by circulation of thermostated water. A diagram of this unit is shown in Fig.1.

Solvent and hydrocarbon feed mixture of known composition and weight were taken in the mixer-settler and stirred for 25 min, which is a sufficient length of time as determined in trial experiments for establishment of equilibrium between phases. The equilibrium phases were then allowed to settle for 30 min, and were separately withdrawn and analysed.

Solvent was removed from the raffinate phase by water-washing and from the extract phase by azeotropic distillation with water. The aromatics content in the solvent-free extract and raffinate were determined by gas-liquid chromatography. The analytical technique has been standardised and reported elsewhere[3]. The solubility of hexane, relative to benzene, as determined from liquid-liquid equilibrium data on hexane-benzene-sulpholane compares well with that reported by Broughton and Asselin[2].

Packed extraction column experiments — The laboratory extraction column used in the studies was of Pyrex glass, jacketed, with provision for circulating thermostated water. It had an i.d. of 34 mm and was filled to a height of 1.5 m with metallic PROPAK packing (type 316-SS, size 4 mm×4 mm), supplied by M/s Scientific Development Co., USA. Settling zones of 0.15m were provided at the top and bottom of the column. The feed and solvent were pumped from separate tanks to the extraction column by metering pumps supplied by M/s Lewa, Himmelbauk, Tubingen, West Germany. The experiments were carried out at two temperatures, 30°C and 40°C, and the
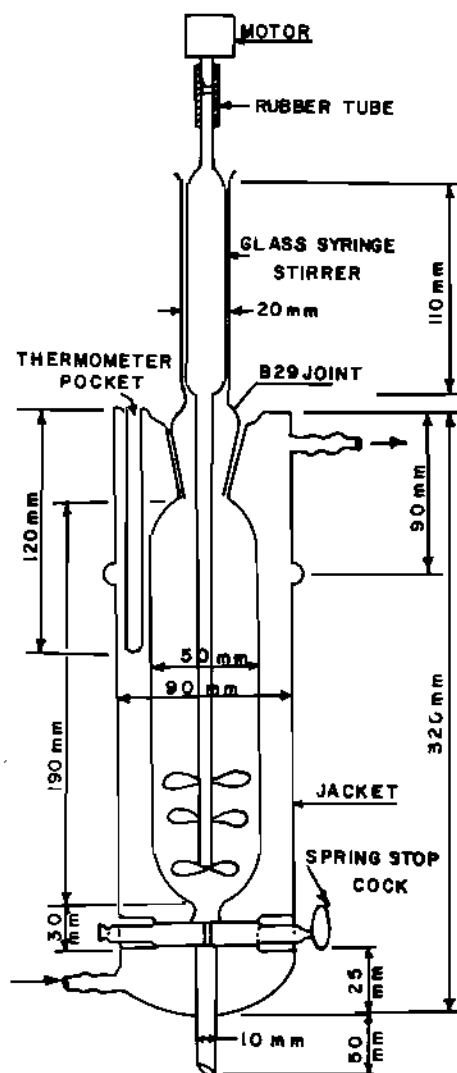

Fig.1   Diagram of mixer-settler used in liquid-liquid equilibrium measurements

column was operated with solvent (sulpholane containing 1.5% by weight water or NMP containing 10% by weight water) as the dispersed phase. A schematic diagram of the experimental set-up is given in Fig.2.

After steady-state had been achieved, samples of the raffinate and extract phases were collected and analysed as given above. Eight sets of experimental runs were carried out with both solvent systems and the results are summarized in Table 2.

The experimental results show that raffinate of food grade hexane specifications 1.3% by wt aromatics) can be produced using liquid-liquid extraction with these solvents. Sulpholane would require a higher solvent/feed ratio ($\cong$3.0 wt/wt) compared to NMP (1.0 wt/wt) at the same operating temperature with this column. The technical viability of the liquid-liquid extraction process has thus been established.
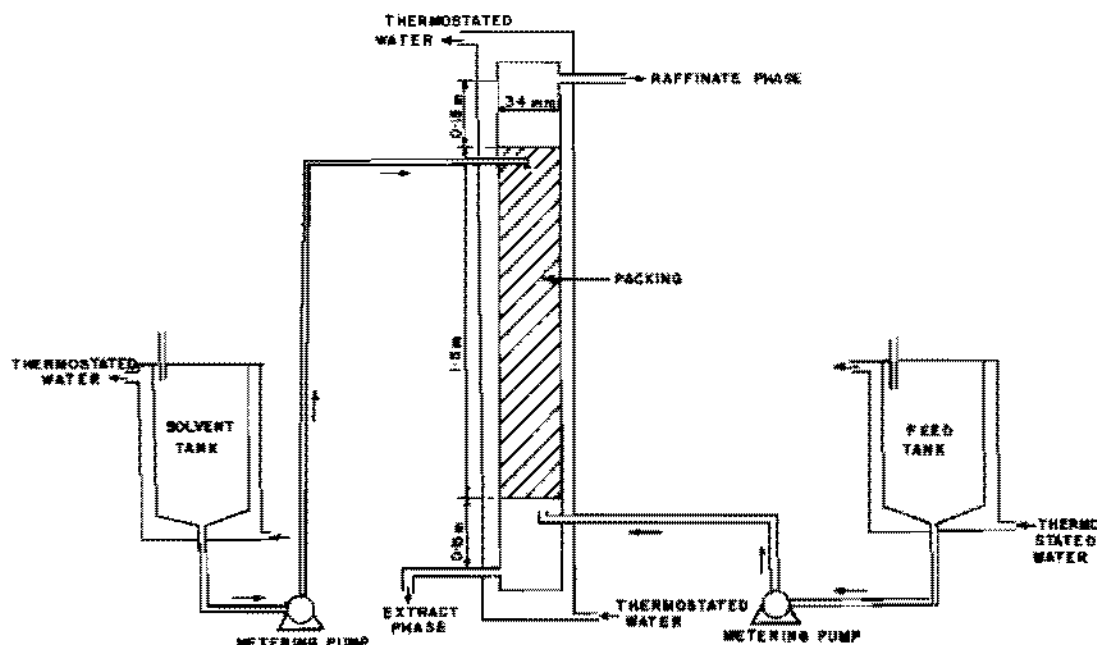
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Fig.2 Schematic diagram of laboratory-packed extraction column

Table 2 — Experimental Results Obtained in Packed Extraction Column

Packing size   = 4.06 mm
Packing void fraction   = 0.94
Interfacial area of packing   = 176 m⁻¹

Run No.	Solvent	Temp. °C	Wt% aromatics in feed	Phase flow rate Dispersed gs⁻¹	Phase flow rate Continuous gs⁻¹	Wt % aromatics in raffinate
1	Sulpholane	30	3.9	1.1076	1.0697	2.30
2	Sulpho-lane	30	3.9	1.6512	0.7910	1.40
3	Sulpho-lane	30	3.9	2.0483	0.5793	0.43
4	Sulpho-lane	40	3.9	1.1760	1.1367	2.10
5	NMP	30	3.9	0.7575	0.7532	1.20
6	NMP	30	3.9	1.4634	0.7419	0.20
7	NMP	40	3.9	0.7403	0.7082	0.95
8	NMP	40	14.6	0.9986	0.7380	0.80

For scale-up, it is necessary to simulate and model the experimental runs as discussed below.

Simulation of Experimental Results

A computer simulation exercise was undertaken to predict the aromatics content in the raffinate for the eight experimental runs reported in Table 2. The simulation required estimation of dispersed phase hold-up, drop diameter, mass transfer coefficients in dispersed and continuous phases and axial mixing

coefficients in the two phases. Literature correlations, as discussed below, were used to estimate the hydrodynamic and mass transfer parameters using the properties, either measured or estimated, as listed in Table 1.

The dispersed phase hold-up was calculated from an iterative solution of the slip velocity equation

$$V_s = \frac{V_d}{\varepsilon\phi} + \frac{V_c}{\varepsilon(1-\phi)} = V_0(1-\phi) \qquad \ldots(1)$$

Watson and McNeese[4] suggest that for low dispersed phase hold-up, the superficial slip velocity is a better correlating parameter for estimating hold-up than is the characteristic velocity. They have reported an average slip velocity of 0.02 ms⁻¹ for a packing of size 3mm. As the packing size is close to the one being used in the present study, a slip velocity of 0.02 ms⁻¹ was assumed in this case also.

The packing size being greater than the critical packing size for this system[5] the dispersed phase drop size could be calculated using the correlation due to Gayler and Pratt[5]

$$d_p = 1.42 \left[\frac{\mu_c^2}{\Delta\rho\sigma}\right]\left[\frac{\Delta\rho\sigma^3}{\mu_c^4 g}\right]^{0.475}\left[\frac{V_0\varepsilon\phi}{V_d}\right] \qquad \ldots(2)$$

On the basis of the calculated drop sizes it was determined that laminar circulation regime within the drop would prevail[7] and accordingly the dispersed phase mass transfer coefficients were estimated from the Kronig-Brink model[8]

$$k_d = \frac{17.7\ D_d}{d_p} \qquad \ldots(3)$$

The corresponding continuous phase mass transfer coefficients were calculated using the Ruby-Elgin correlation

$$k_c = 0.725 \left(\frac{d_p V_s \rho_c}{\mu_c}\right)^{-0.43} \left[\frac{\mu_c}{\rho_c D_c}\right]^{-0.58} V_s(1-\phi) \quad \ldots(4)$$

In using the correlations (3) and (4), the diffusivities of aromatics in the dispersed and continuous phases were estimated using the methods in Reid et al.[10] ; the values thus obtained are given in Table 1.

The experimentally measured liquid-liquid equilibrium data for the systems hexane-benzene-sulpholane (containing 1.5% by wt water) and hexane-benzene-NMP (containing 10% by wt water) indicate that in the region of interest the equilibrium relationship is linear as depicted in Fig. 3.

Linearised distribution coefficients were obtained from this data and were used to calculate the overall mass transfer coefficient based on the continuous phase, K_{oc} from the values of k_c and k_d determined by Eqs (3) and (4). The height of transfer unit was then calculated using

$$HTU_{oc} = \frac{V_c}{K_{oc}\ a}; \quad a = \frac{6\ \phi}{d_p} \qquad \ldots(5)$$

The "true" number of transfer units NTU_{oc} were next calculated from known column length, L, as

$$NTU_{oc} = \frac{L}{HTU_{oc}} \qquad \ldots(6)$$

The diffusion model equations have been used to account for axial dispersion in both phases. The Peclet number for the continuous phase was estimated using the correlation given by Wen and Fan[11] for various packing sizes and shapes
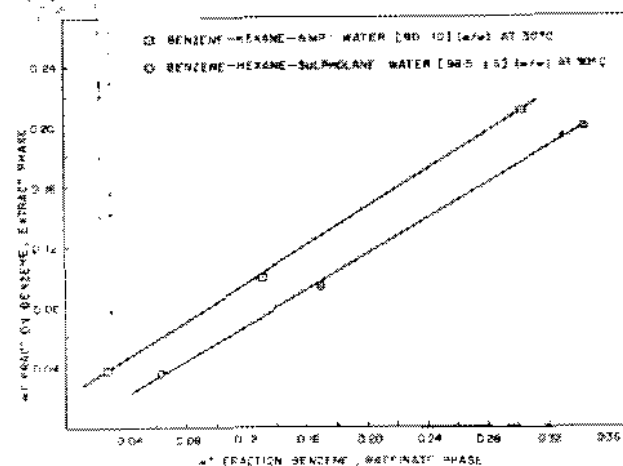

Fig.3   Liquid-liquid equilibrium distribution curve

$$Pe = \frac{1}{\varepsilon}[0.012\ Y^{-0.5} + 0.0078\ Y^{-0.7}] \qquad \ldots(7)$$

with

$$Y = \left[\frac{\psi\mu_c}{d_c V_c \rho_c}\right]^{0.5}\left[\frac{V_d}{V_c}\right] \qquad \ldots(8)$$

For the dispersed phase a constant value of 0.35 was assumed for the Peclet number as recommended by Jordan[12]. The general solutions of the diffusion model equations which have been given by Miyauchi and Vermeulen[13] have been used to calculate the concentration profile of aromatics in the raffinate phase as

$$X = A_1 + A_2\exp(\lambda_2 Z) + A_3\exp(\lambda_3 Z)$$
$$+ A_4\exp(\lambda_4 Z) \qquad \ldots(9)$$

where the λs are the roots of the characteristic equation and the coefficients A_i are functions of the λs and Peclet numbers[13]. The concentration of aromatics in the outgoing raffinate stream calculated using this equation is given in Table 3 for each run along with the corresponding experimentally observed values.

Results and Discussion

A comparison of the experimentally observed concentration of aromatics in the raffinate stream with that obtained from the computer simulation exercise, for each run as given in Table 3 indicates that there is a fairly close agreement between the two values with the deviations varying between −0.0044 and +0.0015. This agreement is especially gratifying in view of the large number of assumptions that are necessary in modelling the behaviour of the extraction column. The successful simulation of the packed column experiments with two different solvent systems under different conditions of feed composition, solvent/feed ratio and temperature substantiates the models used in describing the hydrodynamics, mass transfer and axial

Table 3   Comparison of Experimental and Predicted Aromatic Concentration in Raffinate

Run No.	Wt fraction aromatics in raffinate		
	Experimental	Predicted	Deviation
1	0.0230	0.0257	−0.0027
2	0.0140	0.0127	+0.0013
3	0.0043	0.0078	−0.0035
4	0.0210	0.0254	−0.0044
5	0.0120	0.0125	−0.0005
6	0.0020	0.0022	−0.0002
7	0.0095	0.0090	+0.0005
8	0.0080	0.0065	+0.0015

dispersion characteristics of packed column extractors as well as the basic data used in the simulations. The basic system properties and models may be used for design of a solvent extraction plant for production of food grade hexane from a 63-69°C naphtha fraction using these solvents.

Conclusion

Two extraction solvents, sulpholane and NMP have been investigated for selective removal of aromatics from a 63-69°C naphtha fraction to produce food grade hexane containing less than 1.3% by weight aromatics. The experiments indicate that this product can be conveniently made even from Bombay High naphtha cut containing 14% by weight aromatics. NMP would require a lower solvent/feed ratio at the same operating temperature. The experimental runs were simulated using a model in which both phases were assumed to be axially dispersed. The successful simulation of these runs substantiates the modelling and provides valuable design information for scale-up to industrial extraction plants.

Nomenclature

a	= interfacial area per unit volume of dispersion, m^{-1}
A_i	= coefficient in solution to diffusion model equation
C	= concentration, $kg\ m^{-3}$
d_p	= drop diameter, m
d_c	= packing size, m
D	= diffusivity of aromatic, $m^2 s^{-1}$
E	= extraction factor, Q_c/mQ_d
g	= acceleration due to gravity, $m\ s^{-2}$
HTU_{oc}	= height of transfer unit based on continuous phase, m
k	= individual mass transfer coefficient, $m\ s^{-1}$
K_{oc}	= overall mass transfer coefficient based on continuous phase, $m\ s^{-1}$
L	= length of extractor, m
m	= slope of equilibrium line, dC_d/dC^*_c
NTU_{oc}	= number of 'true' overall transfer units based on continuous phase

Pe	= Peclet number
Q	= volumetric flow rate of phase, $m^3 s^{-1}$
V	= velocity, $m\ s^{-1}$
V_o	= characteristic velocity, ms^{-1}
V_s	= slip velocity, ms^{-1}
X	= dimensionless aromatic concentration in feed phase
Y	= parameter defined in Eq. (8)
Z	= fractional length along extractor
ϕ	= hold-up
ϵ	= void fraction of packing
ρ	= density, $kg\ m^{-3}$
μ	= viscosity, mPa s
σ	= interfacial tension, $mN\ m^{-1}$
λ_i	= roots of characteristic equation [Ref. 13]
ψ	= sphericity of packing

Subscripts

c	= continuous phase (feed)
d	= dispersed phase (solvent)

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