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STUDIES ON PERMEATION OF HYDROCARBONS THROUGH LIQUID MEMBRANES IN A CONTINUOUS CONTACTOR

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Summary

This paper reports experimental studies, in a continuous cocurrent packed column, on the removal of aromatics from hydrocarbon streams by making use of selective transfer through aqueous surfactant membranes. Two types of feed mixtures were used: (i) benzene—heptane and (ii) straight run naphtha from Bombay High crude oil. The receiving phase in both cases was kerosene. The height of a mass transfer unit (HTU) was determined and found to largely lie in the range 2—2.5 m, irrespective of feed composition and solvent/feed ratio. The experimental study confirms the feasibility of a liquid membrane process for dearomatization and provides HTU data for further feasibility and scale-up studies.

Introduction

A novel separation technique called liquid membrane permeation (LMP), first developed by Li in 1968 [1] has been shown to have wide applicability in handling a variety of separation problems like hydrocarbon type separations [2—6], treatment of waste waters [7], hydrometallurgy [8] and medical technology [9]. The process details for carrying out a hydrocarbon type separation using this technique have been reported in several publications [2—6].

A number of continuous-scale processing schemes for liquid membrane separations of toluene—heptane mixtures were discussed by Cahn and Li [10]. Stelmaszek [11] studied the permeation of benzene—hexane mixtures in a column apparatus using single-droplet liquid membranes. Casamatta et al. [12] studied the permeation of toluene—heptane mixtures in a continuous-scale pulsed column and a spray column. The latter gave better results with toluene levels in the raffinate being brought down to 35 wt.% from 50 wt.% in the feed mixture.

In the present investigation we report data on the removal of aromatics both from (i) benzene—heptane mixtures taken to model straight run naphtha, and (ii) actual straight run naphtha from Bombay High crude oil, using emulsion liquid membranes in a continuous glass column packed with glass

Raschig rings. The continuous unit uses a cocurrent flow configuration; countercurrent operation leads to flooding. Assuming plug flow of both emulsion and hydrocarbon phases, the height of transfer unit for the interphase mass transfer process has been calculated.

Experimental

The benzene and n-heptane used were LR grade supplied by BDH India Ltd. n-Hexanol used as additive was from Riedel de Hanag Seelze, Hannover and was of 99% purity. The surfactant Hyoxyd X200 used as emulsifier was an ethoxylated alkylphenol supplied by HICO India Pvt. Ltd., having a cloud point >98°C and an HLB of 16.0.

Physico-chemical properties of straight run naphtha and straight run kerosene (used as solvent) are reported in Table 1.

In this work, n-hexanol was used at 2 wt.% concentration in the model hydrocarbon feed because it gave a better droplet size distribution of dispersed phase in the emulsion, as reported earlier [13], while at a concentration of 10—20 wt.% in kerosene solvent it aided phase separation [6]. The analytical techniques used for determining naphtha range hydrocarbon content in solvent and spent emulsion phases and their compositions have been described earlier [14].

Apparatus

The continuous-scale contactor used is shown in Fig. 1. The glass Raschig rings had a diameter of 5 mm and length equal to 5 mm. Feed emulsion and kerosene solvent were pumped into the column bottom with the help of LEWA metering pumps supplied by Himmelwerk AG, Tubingen, W. Germany, at flow rates measured volumetrically by on-line burettes (Fig. 1). The contactor had five outlets for withdrawing solvent and spent emulsion phases after cocurrent contact in the column. The phases were allowed to settle in an external settler. The settling periods were limited to 10 min for each run. Batch experimental data reported earlier [13] indicate that significant extraction does not occur during settling up to 25 min. By withdrawing

TABLE 1

Physico-chemical properties of straight run naphtha and kerosene from Bombay High crude oil

Property	Naphtha	Kerosene
Boiling range (°C)	IBP—115	180—240
Density, d_4^{20}	0.7280	0.7889
Refractive index, n_{20}^D	1.4120	1.4470
Aromatics content	26.0 (w/w)	28% (v/v)
Surface tension (dyn-cm^{-1} at 30°C)	21.5	25.0

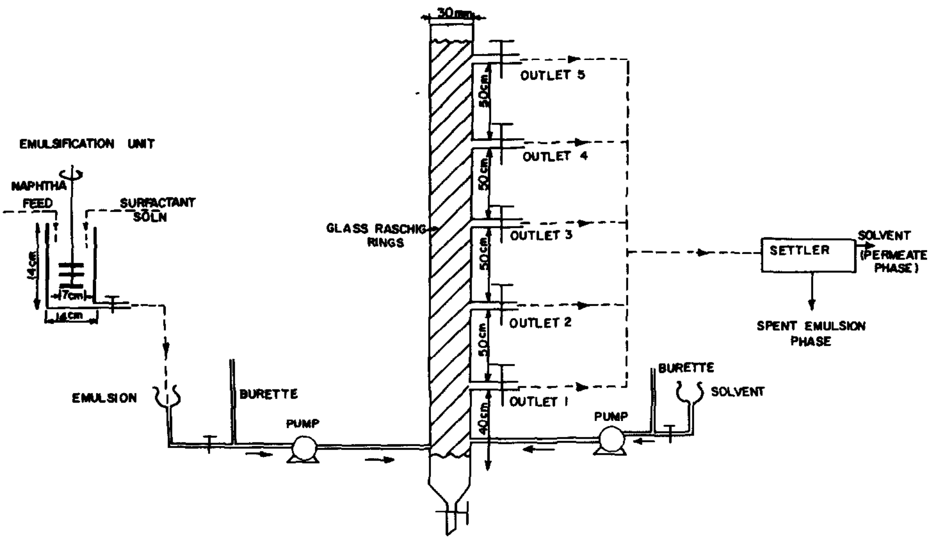

Fig. 1. Diagram of continuous permeator used at the Indian Institute of Petroleum for naphtha dearomatisation.

the emulsion and solvent phases successively through each outlet while keeping the other outlets closed, starting from the bottom outlet, the residence time available for phase contact could be varied.

The o/w emulsions of the hydrocarbon feed mixtures were prepared in 2 kg lots by agitating the hydrocarbon feed mixture with aqueous surfactant solution in a metallic mixer (Fig. 1) at 800 rpm. The hydrocarbon to water ratio in the emulsion was 0.92 (v/v) and the surfactant concentration used was 0.3 wt.%.

Discussion

Experimental results presented in Table 2 were obtained at two hydrocarbon feed/solvent ratios and varying concentrations of n-hexanol in kerosene. The flow rates of emulsion and solvent phases were 18×10^{-4} m^3/hr and 19.2×10^{-4} m^3/hr, respectively, at hydrocarbon feed/solvent ratio of 0.45, and 48×10^{-4} m^3/hr and 88.8×10^{-4} m^3/hr, respectively, at hydrocarbon feed/solvent ratio of 0.26. From a material balance of the feed mixture used it was seen that "solvent" kerosene does not permeate to any significant extent.

The mass transfer of a hydrocarbon permeant through an aqueous surfactant membrane is considered [5,15] to involve the following steps:

(1) Diffusion through the hydrocarbon feed phase.
(2) "Sorption" at the hydrocarbon feed/aqueous surfactant membrane interface.
(3) Diffusion through the liquid membrane.

TABLE 2

Experimental results on a continuous column using liquid surfactant membranes at 30°C

Run No.	Hydrocarbon feed used	Mass fraction aromatics in feed, x_0^R	Concentration of additive in kerosene solvent (wt.%)	Hydrocarbon feed to solvent ratio, R_0/S	Column height (m)	Mass fraction aromatics in raffinate x^R	HTU (m)
1	Model	0.5	20.0	0.45	0.4	0.446	2.41
					0.9	0.396	2.62
2	Model	0.5	10.0	0.26	0.4	0.426	1.75
					0.9	0.380	2.30
					1.4	0.300	1.90
					1.9	0.254	1.91
3	Model	0.5	7.0	0.26	0.4	0.390	1.13
					0.9	0.365	2.0
					1.4	0.336	2.46
					1.9	0.292	2.44
4	Bombay High naphtha (IBP—115°C)	0.26	10.0	0.26	0.4	0.220	2.03
					0.9	0.188	2.31
					1.4	0.150	2.05
					1.9	0.105	1.55

(4) Desorption at the aqueous surfactant membrane/solvent interface.
(5) Diffusion through the hydrocarbon solvent phase.

It may be assumed that equilibrium is attained rapidly at the two interfaces, so that the controlling resistances may be with any one of the above steps 1, 3, or 5. In the general case where each of the three constituent phases, the "feed", "aqueous" and "solvent" phases, in turn offer finite resistance the overall driving force can be shown to be the difference in mass fraction of the permeant (aromatic component) in the two bulk hydrocarbon phases, i.e.,

$$\Delta x = x^R - x^E \tag{1}$$

This expression for the overall driving force can be used for calculating the number of transfer units (NTU) in the packed column as [16]

$$\mathrm{NTU} = \int_{x^R}^{x_0^R} \frac{dx^R}{(1 - x^R) \ln [(1 - x^E)/(1 - x^R)]} \tag{2}$$

A permeant mass balance can be used to relate the mass fraction in the extract and raffinate phases at any height h above the inlet at the bottom; this gives

$$x^E = \frac{R_0}{E} x_0^R - \frac{R}{E} x^R \tag{3}$$

where we note that the fresh solvent contains no aromatic permeant, i.e., $x_0^E = 0$.

The flow rate of a non-permeating non-aromatic component entering with the feed mixture must remain constant, so

$$R_0(1 - x_0^R) = R(1 - x^R) \tag{4}$$

The total flow of the extract phase at any height h is

$$E = S + R_0 x_0^R - R x^R \tag{5}$$

where $S = E_0$ is the mass flow of fresh solvent entering the column.

With the above relations the expression for the NTU reduces to:

$$\mathrm{NTU} = \int_{x_h^R}^{x_0^R} \frac{\mathrm{d}x^R}{(1 - x^R)\ln\left[\dfrac{S/R_0}{x_0^R - x^R + (S/R_0)(1 - x^R)}\right]} \tag{6}$$

This expression was integrated between the limits of x_h^R, the mass fraction of permeant (aromatic) in the raffinate obtained at a particular column height h and x_0^R, the mass fraction of permeant in the feed.

The NTU value thus calculated was used in conjunction with distance between the inlet and outlet to evaluate the height of transfer unit (HTU). These values are reported in Table 2 for the four sets of experiments with model mixtures and straight run naphtha. The data indicate that HTU values fall largely within the range 2 to 2.5 metres and do not show a strong dependence on column height or operating conditions like throughput rates and feed to solvent ratios.

It is heartening to note from the table that the four sets of runs, with model compounds and with actual straight run naphtha, give almost the same values for HTU. This means that model compounds can be conveniently used in further scale-up studies.

Conclusion

Studies with model compounds and with actual straight run naphtha show that continuous-scale dearomatisation of these feed mixtures using liquid surfactant membranes is possible at 30°C. Low aromatic naphtha (~10% aromatics) produced is a suitable feedstock for fertilizer plants. The HTUs required are in the range 2—2.5 metres and these values can be used for preliminary design and for establishing the techno-economic feasibility of the process. Further scale-up studies may be required in larger-scale columns to firmly establish scale-up rules. Extension of the concept to dearomatisation of kerosene is in progress and the results will be reported in due course.

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List of symbols

R_0	mass flow of hydrocarbon feed at inlet to column
S	mass flow of solvent at inlet to column
R	mass flow of raffinate at height h
E	mass flow of extract at height h
x_0^{R}	mass fraction of aromatic in feed to column
x_0^{S}	mass fraction of aromatic in solvent
x^{R}	mass fraction of aromatic in raffinate at height h
x^{E}	mass fraction of aromatic in extract at height h
h	height along the column
H	total column height

Subscripts

1,2	denote upstream and downstream sides of the liquid membrane
h	at height h above bottom inlet

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