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Liquid Extraction of Aromatic Hydrocarbons by Tetrahydrofurfuryl Alcohol, An Environmentally Friendly Solvent

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Abstract: Commercial hexane (AW-406) produced in Iran is actually a blend of aliphatic compounds consisting: n-hexane, 3-methyl pentane and methyl cyclopentane. Benzene and toluene can be found in few percent quantities as contaminants in AW-406. A liquid-liquid extraction process was applied to separate aromatic contents of AW-406 solvent. Tetrahydrofurfuryl alcohol (THFA), a novel, naturally derived and environmentally friendly solvent was used in a bench-scale extractor and water was added as co-solvent. Liquid-liquid equilibrium data were generated experimentally. After eight stages, the yields of benzene and toluene removal were 70 and 60%, respectively. Design criteria of extraction column in a pilot scale have been obtained in regard to equilibrium calculations, number of equilibrium stages, flow rates and type of column.

Key words: Solvent extraction, tetrahydrofurfuryl alcohol, aromatic removal, equilibrium stages

INTRODUCTION

Aromatics can not be recovered from mixed hydrocarbon streams by conventional distillation because of the close boiling points and the azeotropes they form with some of the non-aromatics. Thus, solvent extraction processes are used for aromatic (Benzene, Toluene, Xylene; BTX) separation. The two primary commercial processes are liquid extraction and extractive distillation. Membrane separation of aromatics is an emerging technology (Matsumoto *et al.*, 2005; Schwarz and Malsch, 2005).

For many years a great deal of attention has been paid to the selective solvents for extracting aromatic compounds from hydrocarbon mixtures. Typical solvents used in commercial liquid extraction processes include sulfolane (Chen *et al.*, 2000; Choi *et al.*, 2002), furfural (De Lucas *et al.*, 1993; Espada *et al.*, 2007), N-Methyl Pyrrolidone (NMP) (Al-Jimaz *et al.*, 2007; Sankey, 1985), ethylene glycol and other glycol-based solvents (Sami *et al.*, 2003; Wang *et al.*, 1998), N-Formylmorpholine (NFM), Dimethylsulfoxide (DMSO) and others. These are highly polar solvents with certain qualitative similarities.

Food-grade hexane has been considered an excellent solvent for extraction of edible oil from oil seeds (Hamn and Hamilton, 2000). Oil-seed scum is also used as animal meal due to its nutritional properties. Benzene a light

hydrocarbon and suspected carcinogen and toluene can be found in few percentages (up to 7%) as contaminants in commercial hexanes. In the case of both meal and oil, the residual levels of hexane at time of consumption by animal or by humans have to be so low as to present no risk. This is provided that the hexane is of such a quality that aromatic contamination is sufficiently low to present no hazard (Guinn, 2002).

It is predicted that the production of oil seeds will increase to 2400 thousands tonnes in the next ten years in Iran. There are 19 vegetable oil production plants with large annual demand of extraction solvent. An industrial solvent produced in Iranian petroleum refineries, AW-406, is mostly contained C₆ components with the boiling point range 62-80°C. It can be a candidate for extraction solvent after removal of its aromatic components. AW-406 consists of 4-9% of aromatic compounds.

Liquid extraction processes using highly selective solvents are now widely used for the production of high-purity BTX aromatics (benzene, toluene and xylene), purification of lube oils, various petrochemicals and in the fertilizer, coal tar and metal recovery industries. Much research has been devoted to formulating improved liquid extraction solvents for aromatic removal. Also, global attempts aim at replacement of regular solvent by other environmentally friendly, biodegradable solvents in liquid extraction process. In recent years, various ionic liquids

have been widely proposed as solvent in separation of organic and biological compounds. Replacement of volatile solvents in the separation of aromatic and aliphatic hydrocarbons by non-volatile ionic liquids can offer environmental and process advantages (Li *et al.*, 2007; Meindersma *et al.*, 2006). The ionic liquid 1-ethyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl] amide has been shown that selectively remove benzene from its mixtures with hexane, suggesting that this ionic liquid can be used as an alternative solvent in liquid extraction processes for the removal of aromatic compounds from their mixtures with alkanes (Arce *et al.*, 2007). In spite of several advantages of these novel solvents, none of them have been commercialized due to many engineering problems (Domanska *et al.*, 2007). Thus, use of organic solvents is still more attractive than ionic liquids in extraction processes.

Tetrahydrofurfuryl Alcohol (THFA) has been recently recognized as a suitable substitute of the regular organic solvents. THFA, an environmentally friendly, naturally derived, biodegradable, water-miscible solvent, is a reasonable candidate for extraction solvent due to its physical characteristics i.e., low volatility (high boiling point) compared to aromatic components for economical solvent recovery; low freezing point for easy handling and less operational problems; good thermal stability for long, repeated use and EPA-approved biodegradable properties which is safe for environment.

The objective of this investigation was to study phase equilibrium behavior of THFA and AW-406 in liquid extraction of aromatics, in order to select process criteria for a liquid-liquid extraction pilot plant.

MATERIALS AND METHODS

AW-406, an industrial solvent produced by National Iranian Oil Production and Distribution Company (NIOPDC) was used as raw material (NIOPDC, 2006). The composition of AW-406 varies slightly in different refineries; the one used in this study was analyzed by gas chromatography and the resulted components are shown in Table 1. Other materials were of analytical grade.

Laboratory extraction method: The cross-current extraction experiments have been carried out in a batch mixer-settler for extracting aromatic components of AW-406 using fresh solvent at each stage. The schematic diagram of the experimental set up is shown in Fig. 1. The system consisted of an extraction column and a heating circulation system. The extractor was constructed with 8 cm ID and 50 cm height glass and total volume of the extractor was 2.5 L. The extractor was equipped with a

Table 1: Composition of AW-406 solvent

Components	wt. (%)
n-Hexane	38.16
2-Methyl pentane	22.90
3-Methyl pentane	17.60
Methyl cyclopentane	11.87
Benzene	7.00
Toluene	1.41
Others	1.06

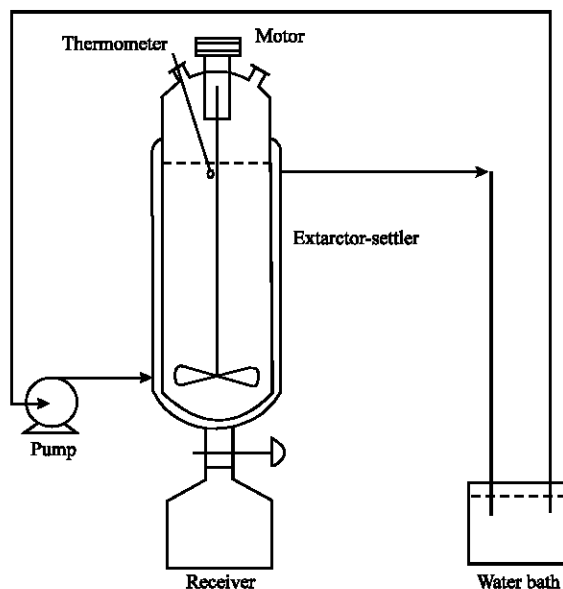


Fig. 1: Schematic diagram of laboratory liquid extraction set-up

variable speed stirrer. The applied extraction solvent was a mix of Tetrahydrofurfuryl Alcohol (THFA) and water, as co-solvent, since THFA and AW-406 are partially miscible. Volume percentages of THFA and water in the mix solvent were optimized as 85 and 15%, respectively. This volumetric ratio was successfully used for proper separation of extract and raffinate phases.

One hundred ninety five gram of AW-406 was fed to the extractor and mixed with 88.3 g of the mixed fresh solvent (85% THFA+ 15% H₂O) at each stage. Sufficient mixing was provided by a motor-driven teflon stirrer at 200 rpm. The temperature of the system was maintained at 25°C by circulating water through the jacket of the extractor. After attaining equilibrium (i.e., after 30 min) the co-existing phases, extract and raffinate, were allowed to be settled and subsequently separated. The co-existing phases were sampled and sent for analysis.

Analysis: The composition of the phases was determined by gas chromatography on a PHILIPS PU4500 chromatograph equipped with flame-ionization detector. The concentrations of the components were calculated with external standard method.

RESULTS AND DISCUSSION

Preliminary experimental studies in aromatics extraction of AW-406 using different organic solvents showed that the partition coefficient value of benzene in THFA is comparable with the most widely used solvents sulfolane and furfuryl alcohol, i.e., 0.96, 1.17 and 0.91, respectively. These results reveal that THFA may be used as a cost-effective solvent in aromatics extraction. The other engineering and economical aspects of the extraction process should be evaluated in pilot plant apparatus.

In the present study, liquid-liquid extraction of aromatics (i.e., benzene and toluene) from AW-406, a petroleum-derived solvent, with mix solvent (THFA+H₂O) was investigated in a bench-scale extraction set up at 25°C.

The cross-current extraction method was applied at eight stages and the extract and raffinate phases were analyzed after each stage to generate equilibrium data. The experimental data on the co-existing phase compositions is shown in Table 2.

Both of benzene and toluene were extracted simultaneously by the selected solvent. After eight stages of liquid extraction, the amount of benzene and toluene were decreased 70 and 60%, respectively.

In order to calculate the number of theoretical stages in a countercurrent extractor, liquid-liquid equilibrium data of extract and raffinate phases is calculated in Bancroft coordination system and plotted in Fig. 2 (Treybal, 1981).

Shortcut calculation method was applied in liquid extraction calculations by assuming linear operating line (constant operating line, F'/S'). By this method, the number of theoretical stages of a countercurrent liquid extraction unit can be calculated from Kremser equation (Eq. 2) when extraction factor is not equal to 1 (ε≠1) (Perry *et al.*, 1999).

The value of ε, the extraction factor, is calculated by dividing the slope of the equilibrium line m by the slope of the operating line F'/S' (Eq. 3).

The liquid-liquid equilibrium data points properly fit a line Eq. 1 with correlation coefficient of linear regression (R²) of 0.96 at the concentration ranges applied in the present study. The slope of the equilibrium line (m), equals to 0.555, has been used in calculation of theoretical stages of a countercurrent liquid extraction column.

$$Y = 0.555X - 0.0014 \quad (1)$$

$$N = \frac{\ln\left[\frac{X_f - Y_s/m}{X_i - Y_s/m}\right] \left(1 - \frac{1}{\epsilon}\right) + \frac{1}{\epsilon}}{\ln \epsilon} \quad (2)$$

Table 2: Composition of extract and raffinate phases in solvent extraction of AW-406 by mixed solvent (THFA+H₂O) at 25°C

Stage No.	Extract phase composition (wt.%)		Raffinate phase composition (wt.%)	
	Benzene	Toluene	Benzene	Toluene
1	2.16	0.45	6.39	1.35
2	2.94	0.49	5.55	1.31
3	2.34	0.28	4.30	1.25
4	2.15	0.36	3.60	1.26
5	1.46	0.29	2.79	0.96
6	1.49	0.30	2.90	0.83
7	1.02	0.28	2.40	0.73
8	0.92	0.26	1.90	0.55

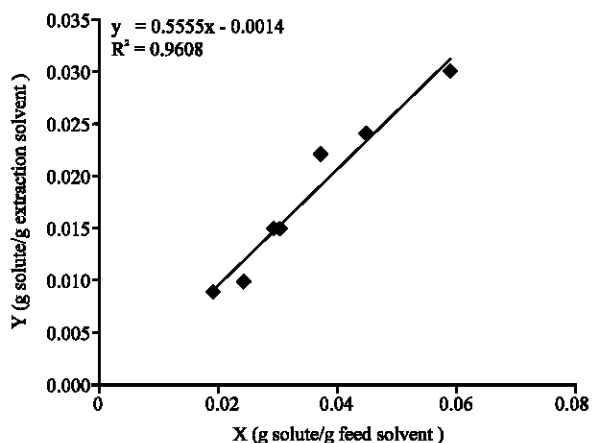


Fig. 2: Phase equilibrium diagram of benzene (solute)-AW-406 (feed solvent) and 0.85THFA+0.15 H₂O (solvent) at 25°C in Bancroft coordination system

$$\epsilon = \frac{mS'}{F'} \quad (3)$$

The weight ratio of solute of extraction solvent at the effluent of extractor (Y_s) is calculated from the overall extractor material balance (Eq. 4) (Perry *et al.*, 1999).

$$Y_s = \frac{F'X_f + S'Y_s - RX_i}{E'} \quad (4)$$

The main objective for calculating the theoretical stages (or mass transfer units) in the design of a countercurrent liquid-liquid extraction process is to evaluate the compromise between the size of the equipment and the ratio of extraction solvent to feed flow rates required to achieve the desired transfer of mass from one phase to the other. In any mass transfer process there can be an infinite number of combinations for flow rates, number of stages and degrees of solute transfer.

The feed flow rate to the extractor was assumed as 100 L day⁻¹ because of scale-up considerations.

Furthermore, this pilot size and capacity is comparable to the other solvent extraction pilot plants reported in the literature (Schweitzer, 1997; Walas, 1988).

The concentration of benzene at the effluent stream of the countercurrent extractor, X_r , was assumed to be 0.0005 (equivalent to 500 ppm) in the calculations.

By assuming the ratio of extraction solvent to feed solvent (S'/F') in the range of 1.0-4.0 and $X_r = 0.0005$, the number of theoretical countercurrent stages, extraction factor and weight ratio of benzene to extraction solvent at the effluent (Y_e) are calculated according to Eq. 2-4 and shown in Table 3.

One of the main objectives for calculating the number of countercurrent theoretical stages (or mass-transfer units) is to evaluate the performance of liquid-liquid extraction test equipment in a pilot plant or to evaluate production equipment in an industrial plant. There is a compromise between the size of the equipment and the ratio of extraction solvent to feed flow rates required to achieve the desired transfer of mass from one phase to the other. In any mass transfer process there can be an infinite number of combinations for flow rates, number of stages and degrees of solute transfer. Most liquid-liquid extraction equipment in common use can be designed to achieve the equivalent of 1 to 8 theoretical countercurrent stages, with some designed to achieve 10 to 12 stages (Perry *et al.*, 1999).

By increasing the amount of solvent extraction, the extraction factor increases and the number of theoretical stages decreases. However, a high solvent flow rate usually requires a high operating cost because of the solvent recovery costs. A high solvent flow rate should be carefully compared with an increase in capital cost for taller or more equipment to achieve more theoretical stages and reduce the required flow of solvent. Commercial solvent-to-feed ratios typically range from 2:1 to 4:1 (Perry *et al.*, 1999).

Comparing the results shown in Table 3 with those reported in the references, the number of stages of the pilot plant is selected as 11. Theoretically, the selected extraction column reduces benzene content from 70000 to 500 ppm, which should be tested by a pilot plant operation.

Based on the above calculations, the specifications of the countercurrent extractor in pilot scale are shown in Table 4.

Since the cost of solvent recovery is a major item, it may be advantageous to increase the number of contacting stages in order to minimize the amount of solvent to be treated.

Table 3: Calculations of the number of theoretical stages and benzene concentrations in effluent feed solvent stream (AW-406) in countercurrent liquid extraction column by varying solvent/feed solvent ratio

Solvent/feed solvent (S'/F') (wt. ratio)	Solvent flow rate (S') (kg h^{-1})	Extraction factor (ϵ)	No. of theoretical stages (N)	Benzene/ extraction solvent at effluent (Y_e) (wt. ratio)
1.0	93	0.556	∞	0.074
2.0	186	1.110	26.4	0.037
2.5	232	1.390	11.4	0.030
3.0	279	1.670	8.0	0.025
3.5	325	1.950	6.4	0.021
4.0	372	2.220	5.5	0.019

Table 4: General specifications of a pilot scale countercurrent extractor to remove benzene content of AW-406 solvent from 70000 to 500 ppm

Process parameters	Description
Solvent	0.85THFA+0.15H ₂ O
Continuous phase	Extract phase
Feed flow rate (L day^{-1})	100
Extraction solvent flow rate (L day^{-1})	230
No. of theoretical stages	11
Column diameter (in)	4

CONCLUSION

In this study, an environmentally friendly solvent, THFA, has been tested successfully to extract aromatic compounds from an industrial solvent (AW-406) to obtain a food grade solvent. The phase equilibrium data were taken from a bench-scale extractor.

Multistage countercurrent contacting column is designed at the present study to achieve high yield of aromatics removal. Since, there is a trade-off between the number of stages used and the relative amount of solvent necessary for a given degree of recovery, the solvent-to-feed ratio was selected as 2.5 and the theoretical stages as 11. Influence of the process parameters on extraction efficiency should be tested in a pilot plant apparatus.

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NOMENCLATURE

- E' : Flow rate of extract phase through extractor
- F' : Flow rate of feed solvent through extractor
- m : Slope of the equilibrium line
- N : Number of theoretical stages
- R' : Flow rate of raffinate phase through extractor
- S' : Flow rate of extraction solvent through extractor

- X_f : wt. ratio of solute to feed solvent in feed stream of the extractor
 X_r : wt. ratio of solute to feed solvent in effluent stream of the extractor
 Y_s : wt. ratio of solute to extraction solvent in feed stream of the extractor
 Y_e : wt. ratio of solute to extraction solvent in effluent stream of the extractor
 ϵ : Extraction factor

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