

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Sources of Aromatics

In Petroleum Refining, BTX aromatics can be extracted from several sources. Among these, petroleum cuts are considered as low aromatics-content sources and the rest are high content of aromatics as they are outputs of conversion units as follows:

##### 2.1.1 Petroleum Fractions

The fractions are indeed focused on naphtha fraction as the cut is made up of C<sub>5</sub>-C<sub>9</sub> hydrocarbons. The varied aromatics-content of naphtha is considered as marginal sources of aromatics especially when compared to the synthetic sources as the effluents of conversion units.

##### 2.1.2 Naphtha Catalytic Reforming Effluents

These sources actually are the converted naphtha where paraffins and naphthenes are catalytically converted to aromatics. The total amount of aromatics is up to 80-90% wt with over a half of these are xylene isomers.

##### 2.1.3 Fluid Catalytic Cracking Effluents

The effluents are the cracked products that much in gasoline range hydrocarbons with the moderate amount of aromatics.

##### 2.1.4 Steam Cracking Effluents

Unlike the catalytic-reforming-effluents, the steam cracking effluents provide more benzene than xylenes.

**Table 2.1** Composition of naphtha catalytic reforming effluents (Wauquier, 2000)

	<b>Component</b>	<b>Content in % wt</b>
Aromatics	Benzene	1 to 8
	Toluene	8 to 24
	Xylenes	30 to 50
	C <sub>9+</sub> (including mesitylene)	0.1 to 6
Paraffins	C <sub>5</sub>	0.6 to 6
	C <sub>6</sub>	1.5 to 11
	C <sub>7</sub>	1 to 7
	C <sub>8</sub>	0.5 to 2
	C <sub>9</sub>	0 to
Naphthenes + Olefins		0.5 to 2

**Table 2.2** Composition of steam cracking effluents (Wauquier, 2000)

	<b>Component</b>	<b>Content in % wt</b>
Aromatics	Benzene	25 to 50
	Toluene	14 to 23
	Xylenes	10 to 17
	C <sub>9+</sub> (including mesitylene)	0.1 to 6
Paraffins and naphthenes	C <sub>5</sub>	0.2 to 2
	C <sub>6</sub>	6 to 27
	C <sub>7</sub>	1 to 6
	C <sub>8</sub>	0.5 to 4
	C <sub>9</sub>	0 to 1

## 2.2 Aromatics Extraction

According to the prediction of phase equilibria of liquid mixtures where equilibrium data are not available, a UNIQUAC Functional-group Activity Coefficients (UNIFAC) model introduced by Fredenslund *et al.* (1975) has been used to estimate activity coefficients in mixtures of nonideal liquids. Combined data of the solution-of-functional-groups concept and the existing phase-equilibrium are utilized by the UNIFAC model to predict phase equilibria of the unknown systems. The model performed great agreement with the experimental data of wide range of binary and multicomponent mixtures; less than 20% deviation from measured values of activity coefficients at infinite dilution, in most cases was found.

Mukhopadhyay and Dongaonkar (1983) described that the UNIFAC method performs in good accuracy with the corresponding experimental liquid-liquid equilibrium data, with the exception of the plait-points regions, of three ternary systems for aromatics extraction: cyclohexane-benzene-sulfolane, N-hexane-benzene-sulfolane, and n-heptane-toluene-sulfolane at 298, 323, 348 and 373 K. In addition, the UNIQUAC and the Non-Random Two Liquids model (NRTL), which the experimental data on all possible binaries are required, were compared to the UNIFAC model. The predicted data from all three of those are in good agreement with the measured data but the UNIFAC model seems to be the only one to predict the data with the absence of the experimental data on all possible binaries of the system.

Furthermore, Mukhopadhyay and Pathak (1986) utilized the modified UNIFAC model based on replacing mutual solubility data evaluation with infinite dilution activity-coefficients evaluation. More accuracy on liquid-liquid equilibria was found in the same ternary systems as the earlier work although the data near the plait-point areas still deviated.

With a good commercial solvent for aromatics extraction, sulfolane, predicted phase-equilibrium data and the measured values of sulfolane and feed with 55% aromatics for aromatic extraction was studied by Hassan and Fahim (1988). The results are in good agreement but the deviations nearing the plait point of estimated values were observed. Effect of temperature on selectivity and distribution

coefficients is significant for the sulfolane-reformate system; selectivity increase with temperature.

Other solvents of interest for aromatic have also been studied. Tetraethylene glycol was investigated by Al-Sahhaf and Kapetanovic (1996). It was found that the critical solution temperature of tetraethylene glycol was not observed at the condition of the temperature upto around 343 K and the solvent-to-feed ratio was upto 10:1. The experimental work shows that the UNIFAC model can be used to estimate the liquid-liquid equilibrium data for aromatic extraction of naphtha reformate by using tetraethylene glycol as a solvent. The solvent capacity is not particularly high for aromatics.

Hamid and Ali (1996) presented the comparative study of several solvents: 3-methoxypropionitrile, ethylene glycol, dimethylsulfoxide, sulfolane, phenol, and nitrobenzene. Operating temperature (20-125 °C), solvent-to-feed ratio (1:1 to 3:1), selectivity, and solvent capacity of each solvent were evaluated. The extraction used Saudi Arabian light crude oil as feed. Among the selected solvents, sulfolane performed as the best solvent capacity and quite great selectivity and for aromatics extraction of Saudi Arabian light crude.

A combination of solvents, 1-cyclohexyl-2-pyrrolidone (CHP)/ ethylene carbonate (EC) mixed solvent, for aromatic extraction was studied by Radwan, Al-Muhtaseb, and Dowaidar (1997). The parameters varied were temperature, solvent composition, and solvent-to-feed ratio. The minimum energy of separation is determined as the optimum conditions. The optimum conditions were 65 wt % of EC and 35 wt % of CHP, 1.8 by volume of solvent-to-feed ratio, and temperature at 329 K.

A new UNIFAC group called TETRA was defined by Wang, Gou, and Zhu (1998). The experimental work of aromatics extraction with tetraethylene glycol was measured for 5 ternary and 2 multicomponent systems including cyclohexane, benzene, toluene, p-xylene, water, and tetraethylene glycol at 60 °C and 140 °C. The parameters required for TETRA group were determined by the experimental data and the parameters calculated were in good agreement with the experimental and literature data.

## 2.3 Solvent Properties

### 2.3.1 Selectivity

Since the feed of the extraction are made up of the desire solutes and impurities, this can show the efficiency of solvent as it should be selective to the desire solutes over the impurities.

$$\text{Selectivity} = \frac{(\text{wt. fraction aromatics in extract}) \times (\text{wt. fraction nonaromatics in raffinate})}{(\text{wt. fraction aromatics in raffinate}) \times (\text{wt. fraction nonaromatics in extract})} \quad \text{---- (2.1)}$$

### 2.3.2 Solvent Capacity

With preference to purity of desired extraction products, the quantity of the desire solutes dissolved in the solvent should be as high as possible. Furthermore, with high solvent capacity, it will require lower size of the equipment as there is less in volume of the solvent in the extraction circuit.

$$\text{Solvent capacity} = \frac{\text{wt. fraction aromatics in extract}}{\text{wt. fraction aromatics in raffinate}} \quad \text{---- (2.2)}$$

### 2.2.3 Specific Gravity

This can indicate how hard it is to separate the extract from the raffinate as they settle by gravity. For BTX aromatics extraction, the solvent specific gravity should be close to or greater than 1.1.

### 2.3.4 Boiling Temperature

After the extraction, the separation of solvent from the solutes is normally used by distillation because of ease of operation. So, the boiling point of the solvent should differ sufficiently to that of the solutes to ensure easier separation and regeneration of solute.

### 2.3.5 Viscosity

Since the extraction involved with mass transfer operation, the viscosity of the solvent will allow higher mass transfer rate to the extraction.

### 2.3.6 Others

In applications, to choose the solvent for the extraction, there are also other properties to consider. They are; thermal stability, chemical stability, toxicity, corrosiveness, and crystallization temperature.

## 2.4 Hydrocarbon System

The hydrocarbon system used in this experimental work was made up of one aromatic and one paraffinic component. The aromatics studied were benzene, toluene, and *p*-xylene. For the paraffinic hydrocarbons, as shown in Table 2.1 and Table 2.2, the typical *n*-hexane percentages in both naphtha catalytic reforming and steam cracking effluents are higher than that of *n*-heptane and *n*-octane. Thus *n*-hexane was selected as the representative component of the paraffinics. Table 2.3 shows the boiling point of hydrocarbon components used in the experiment.

**Table 2.3** Boiling point of hydrocarbons used in the experiment (Poling *et al.*, 2001)

Hydrocarbon	Boiling point (°C)
<i>n</i> -Hexane	68.73
Benzene	80.09
Toluene	110.64
<i>p</i> -Xylene	138.38