Effect of Cosolvents And Surfactant in The Extraction of Aromatics from Kerosene

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Abstract. Extraction of aromatics from kerosene is very important to get clean fuel since the presence of aromatics prevents the production of ultra-low sulfur fuel and also for the important of these aromatics in an industry. In this study, lab-scale batch mixer-settler of 1-liter used to extract aromatic from hydrotreated kerosene by using mixture of solvents of (20wt% glycerol and 80wt%methanol) with the addition of 0.03wt% sodium thiosulfate surfactant were also best time of settling obtained at 80min. At these percent of solvent and surfactant the maximum removal percent obtained was 46.945%.

1. Introduction

Aromatic hydrocarbons are invariably present in different petroleum fractions obtained as refinery streams, for example naphtha, gasoline, kerosene, diesel and gas oil. From these petroleum fractions the aromatics are removed either for the production of aromatics like benzene, toluene, xylenes, naphthalenes and alkyl benzenes and alkyl naphthalenes or for refining these streams to improve their quality for a particular end use. The separation of aromatics from these feedstocks by simple distillation is not possible, as the nonaromatic hydrocarbons have very close boiling points. Moreover, they form azeotropes in between. Hydrotreatment and solvent extraction are the conventional processes used for dearomatization of kerosene fractions. Solvent extraction is an attractive route for dearomatization of high aromatics kerosene due to availability of more valuable aromatics extract as a by product [1]. The various solvents tried and those used in the industry for the separation of light aromatics from naphthas have been compiled and discussed in earlier publications [2], which give the basic considerations in the selection of solvents for the extraction of aromatics like benzene, toluene and xylenes (BTX), the total solvents tried so far for BTX extraction along with their physico-chemical characteristics and a number of model hydrocarbon-solvent systems for which liquid-liquid equilibrium data are available in the literature. In this article, an attempt has been made to use mixture of solvents. Kerosene is generally extracted with selective solvents to effect marked reduction in the concentration of aromatics, acidic sulphur, organometallic and nitrogen compounds and unstable materials. The resultant raffinate meet the product specifications which are becoming more and more stringent. Aromatics concentration in kerosene is reduced to produce jet fuels and/or illuminant. The aromatic extracts obtained from kerosenediesel/ gas oil fractions are used as feeds for hydrocracking or for carbon manufacture or as plasticizers for rubber, depending on their suitability. [3, 4]. stated that "only a very limited number of pure ILs have exhibited extractive and physical properties comparable to sulfolane values. For that reason, we have proposed the use of binary IL mixtures in order to obtain an IL-based solvent with intermediate extractive and physical properties between those of the ILs forming the mixture and comparable or higher than the sulfolane values [5]. It was establish that surfactant generally reduce the mass transfer coefficient, nevertheless rises the interfacial area [6].
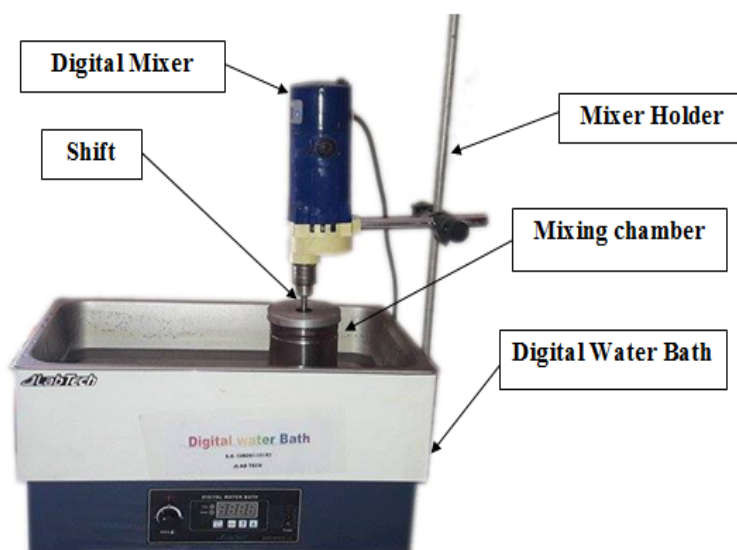
2. Experimental work

2.1 Material

Hydrotreated kerosene from AL-Dura Refinery used in current study as a feedstock in order to remove aromatics from it. The hydrotreated kerosene contains 21.02% aromatics according to the GC analysis of Minstery of Oil / Petroleum Research and Development Center (PRDC) in Waziriyah/Iraq. In addition, the physical properties of the hydrotreated kerosene listed in Table (1). Methanol from GCC with 99.8%purity for the extraction process was used. For the analysis step, methanol (HPLC grade) from Fluka with 99.9%was used. Glycerol from Fluka with 99was used.   Benzene (GCC) from GCC with >99% purity, Toluene from Merck with >99% purity, Xylene with >99%purity, Naphthalene with 99% purity and Sodium thiosulfate with 99.5% purity from (AnalaR) were used.

2.2 Extraction process apparatus

 In the present work, A Laboratory Batch Extraction Unit used. This laboratory unit consists of cylindrical reactor with baffles of 1cm, placed in digital water bath (1000-Watt capacity) to ensure temperature control at the specified value. Experimental set up and the details of mixer-settler geometry tabulated in (2). The agitator was located at 5cm from the bottom of the vessel. A digital mixer used with variable agitation speed. Experimental study carried out as shown in the photograph in Figure (1).

Table 1. Specification and geometrical characteristics of mixer-settler

Material of mixing unit	Stainless steel
Mixing chamber inside diameter (Diameter of cylinder D)	110mm
Cylinder height (L)	145mm
Impeller type	Six flat-blades turbine
Impeller diameter	40mm
Settling unit	Separator funnel made of glass (500ml and 1000ml capacity).

Figure 1. Photograph of single stage mixer, laboratory extraction unit

2.3 Experimental Procedure

In the experimental work we should mentioned that all the experimental work occurs at atmospheric pressure.

Here we specified the operating condition at (S/F=1(by weight), Temperature=40°C, time of mixing =30min, time of settling =1.5hr and agitation speed =1000 rpm) in order to study the effect in case of:

1) Extraction with single solvent either methanol or glycerol to check which one is the best for removing aromatics, this occurs by heating the solvent and the feed to the extraction temperature then mix the solvent (either methanol or glycerol) with the feed (kerosene) in a the mixer that placed in digital water bath (to control the temperature) by using mechanical stirring (digital mixer) at the operating condition mentioned above.

2) Extraction with mixture of solvents by mixing methanol and glycerol as co-solvent at different percentage of 10%, 20%, 30%… 90% with kerosene at the fixed operating condition and the procedure mentioned above in point (1).

3) Addition of surfactant. First, study the effect of the addition of either aniline or sodium thiosulfate surfactants on single solvent (methanol or glycerol) and then the mixture of solvents obtained from step (2). That accomplish by mixing the kerosene with the solvent with 0.01% weight percent of surfactant in the solvents mentioned above at the fixed operating condition and the same procedure as in point (1).

4) After mixing in the reactor for 30min, the mixture leave to settle by pouring it into 500ml separating funnel (make sure the stopcock is closed) for one and half hour at the extraction temperature.

5) The mixture then instantaneously starts to form two layers by settling, the upper layer is the raffinate layer (kerosene) and the bottom layer is the extracted layer (solvent rich phase) as shown in (2).

6) When pour the mixture in the separating funnel immediately two-layers start to form that look like an emulsion, the upper one start to decrease in height while the lower increase in height. The time of settling is when there is no change in the height of the two layer and the emulsion disappeared (the two layer become colorless with a boundary between them). It found that this achieved after 80 min of settling.

7) Then open the plug of the separating funnel then the stopcock, the bottom layer (extract) start to pour in the 500ml beaker and when completed close the stopcock, then open it to pour the remaining layer (raffinate) in another 200ml beaker.

8) The two layers weighted to ensure the balance.

9) The raffinate from each experiment then analysis by taking 0.1ml of the raffinate and diluted a hundred times using methanol (HPLC grade). Then, pour in a tightly sealed glass bottle and shake for at least two minute, and left overnight in order to dissolve a higher quantity of aromatics in the solvent for getting a better result.

10) The solution obtained from point (9) then analysis by using the Ultraviolet–Visible spectroscopy (UV- spectroscopy) device, and the concentration will estimate from the equation of the equilibrium curve of benzene, toluene, xylene and naphthalene.

3. Results and Discussion

In present study, extraction process performed at constant operating condition of 40°C temperature for methanol and 60°C for glycerol (because of it is high viscosity), solvent-feed ratio equal to (1) by weight, agitation speed of 1000 rpm, time of mixing of 30min and time of settling equal to 80 min under atmospheric pressure. We should mention that each experiment repeated at least twice to verify the validity of the results we obtained. At the mentioned operating condition above, the percent removal of aromatics is 31.07% by using methanol only and 9.23% for glycerol by increasing the temperature to 60°C (because of it is high viscosity) and all the other operating condition remaining constant. Figures (2&3) explained that the solubility of aromatics in methanol solvent alone higher than glycerol solvent alone for many reason, once, a good indicator of solvability is the dielectric

constant (ε) of the solvent. For glycerol ($\varepsilon = 44.4$), it is consider reasonably polar, so it is unlikely to be a good solvent for most aromatic hydrocarbons, which tend to have dielectric constants in the range (2.3 – 5), while methanol ($\varepsilon = 33$) has a lower dielectric constant than glycerol. Other reason as stated by [7] that methanol as a solvent is more effective according to kinetic, since the molecular weight of methanol is approximately one-third the molecular weight of glycerol. In addition, the surface tension of methanol is lower than that of glycerol; therefore methanol can penetrate easily in hydrocarbon to extract aromatic than glycerol. Another, methanol has a polar oxygen-hydrogen bond, which looks similar to what water has, but the other side have carbon-hydrogen bonds, which are very weakly polar since the electronegativity differences between carbon and hydrogen is quite small. We usually consider hydrocarbon chains non-polar when discussing solubility and so overall methanol is hybrids (have a polar group on one end and a non-polar group on the other while glycerol has three polar oxygen-hydrogen bonds but these attached to hydrocarbon chains, which are relatively non-polar. In another way using of glycerol alone is not economic, one reason that glycerol is vastly more expensive than methanol; and second glycerol has a very high boiling point, so it is need high temperature to decrease it is viscosity and get better percent removal during mixing that mean energy consumption. In addition, sodium thiosulfate (anionic surfactants) is more effective than aniline (cationic surfactants) because the use of solvents with high polarizability are often good solvators for anions which also possess high polarizability as stated by [8].

3.1 The effect of addition of surfactants to methanol solvent on removal percent
Figure (2) shows the effect of sodium thiosulfate (STS anionic surfactant) and aniline (cationic surfactant) on removal percent at the mentioned operating condition and methanol solvent. It was observed that the addition of 0.01%wt of surfactant in the methanol increases percent removal of aromatics especially PAHs, the percent removal increases from 31.07% using methanol only to 35.52% by the addition of 0.01%Aniline as cationic surfactant and to 37.34% by the addition of 0.01% STS as an ionic surfactant explained in figure (2).
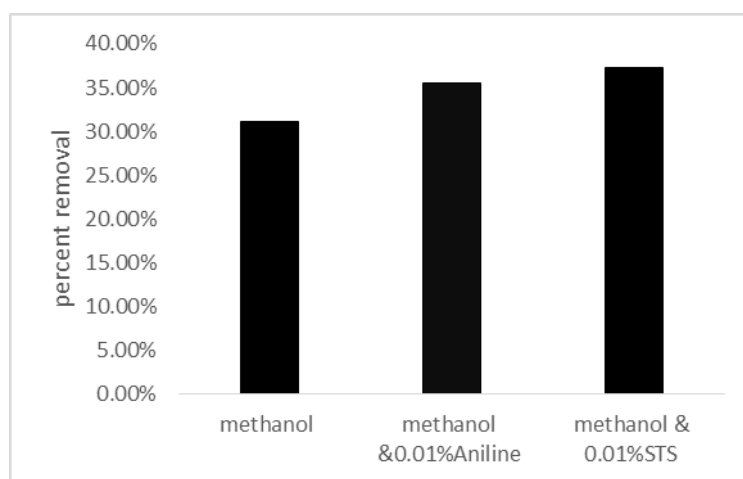
Figure 2. Effect of the addition of surfactant and type of surfactant in methanol on removal percent at (S/F =1, T=40°C, t_m=30min., t_s=80min)

3.2 The effect of addition of surfactants to glycerol solvent on removal percent
Figure (3) shows the effect of STS (anionic surfactant) and Aniline (cationic surfactant) on removal percent at the mentioned operating condition and glycerol solvent. The percent removal increases from 9.23% (S/F =1, T=60°C, t_m=30min., t_s=80min) to 12% by using aniline as cationic surfactant and 13.55% by using STS as cationic surfactant.
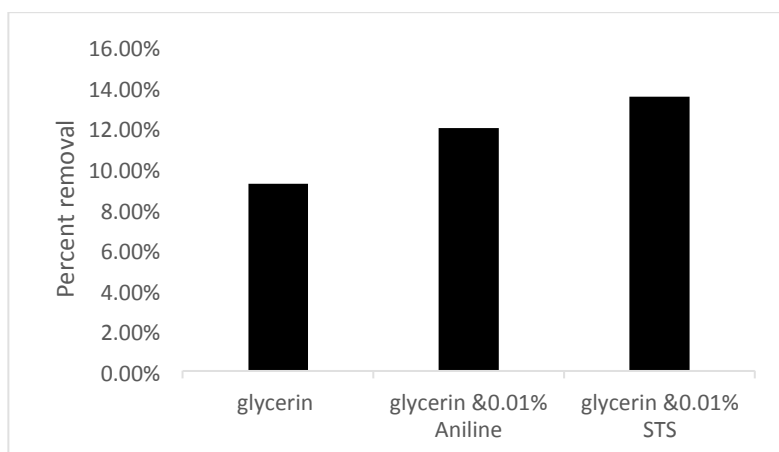
Figure 3. Effect of the addition of surfactant and type of surfactant in glycerol on removal percent.

*3.3 Effect of mixed solvent (co-solvent or anti solvent)*

The result obtained from the usage of mixed solvent shows that a maximum removal percent obtained at (20%wt. glycerol & 80%wt. methanol) explained in Figure (4) and that because glycerol has high selectivity as state by [9] and also high polarity (high dielectric constant) while methanol has low selectivity according to U.S. Patent [10]. Therefore polarity difference between the (methanol + co-solvent) molecules and the aromatic compound increases as the polarity of the co-solvent (glycerol) increases. So the addition of glycerol to 20% by weights in the solvent increase the polarity in the preferable difference then enhance extraction percent. Since at low polarity difference between the solvent and the aromatic compound results in attractive forces between the different molecules, and as a result the aromatic molecules are preferentially polarize then pulled toward the solvent that conclusion agree with [11]**.** Increasing the concentration of glycerol above 20%wt. lead to unfavorable polarity difference so the extraction percent decreased.
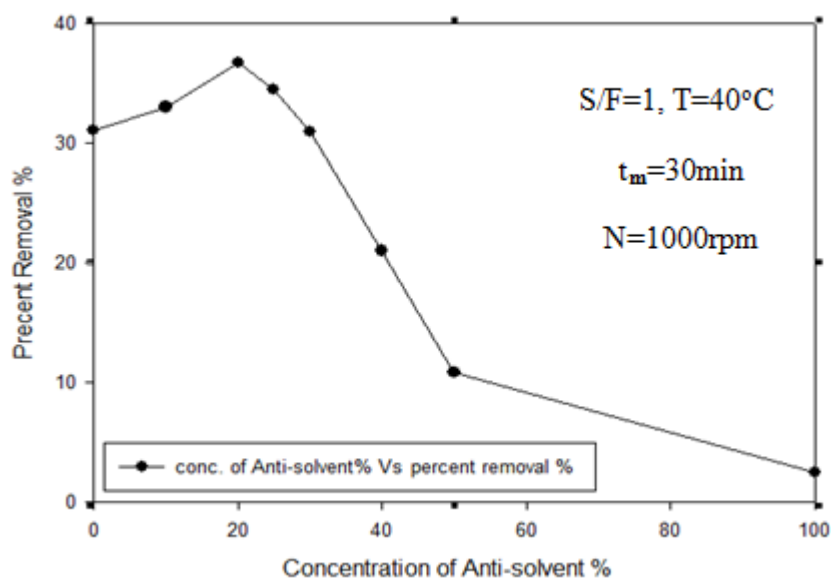
Figure 4. Shows the effect of glycerol as co-solvent (anti-solvent) on removal percent at (S/F =1, T=40°C, t_m=30min., t_s=80min, N=1000rpm).

3.4 Effect of increasing STS (sodium thiosulfate) concentration on mixed solvent

It was observed from Figure (5) that as the surfactant concentration increases, the removal percent increases in concentration range between 0.01wt.% and 0.03 wt.% of STS, because the interfacial tension diminishes considerably. However, at high STS concentrations, above 0.03wt.% that represent the CMC (Critical micelle concentration) the removal percent remained nearly constant and did not depend on STS concentration because of the formation of micelles as stated by [12, 13], the results obtained detailed in Figure (5).
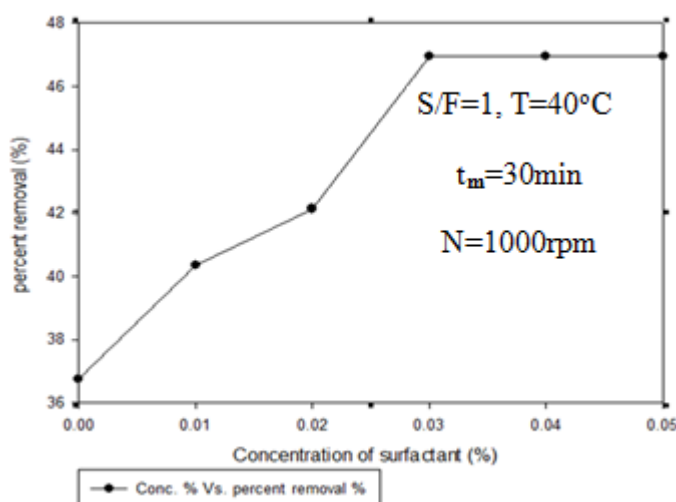
Figure 5. The effect of increasing surfactant concentration on removal percent

4. Conclusion:

The following conclusions obtained from the present work:

Lab-scale batch mixer-settler for removing aromatics successfully applied. Used of mixed solvents of (20%Glycerol and 80% methanol) more effective than the usage of methanol only and glycerol only. At operating condition of $40^{o}C$ temperature for methanol and $60^{o}C$ for glycerol, solvent-feed ratio equal to one, agitation speed of 1000 rpm and time of mixing of 30min under atmospheric pressure the removal percent for (20%glycerol, 80% methanol), methanol only, glycerol only is 36.74%, 31.07% and 9.23% respectively. The using of anionic surfactant (sodium thiosulfate STS) more effective than the use of cationic surfactant (aniline) in the extraction process. Increasing the concentration of anionic surfactant (0.01% - 0.03%) increases the removal percent form (40.35%-46.945%); any increment in the concentration above 0.03% is not effectible.

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