

# Scaling-Up Liquid-Liquid Extraction Experiments with Deep Eutectic Solvents

Emad Ali, Sarwono Mulyono, Mohamed Hadj-Kali

**Abstract**—New generation of green solvents, known as Deep Eutectic Solvents, have emerged as potential alternatives to conventional solvents in many industrial applications. Among these applications, removing sulfuric compounds from fuel oil is receiving much interest because organic sulfides becoming a serious source of pollution. The separation of aromatic and aliphatic hydrocarbons having the same number of carbon atoms is also a challenging process especially at low aromatic concentration. Deep Eutectic Solvents were utilized for the separation of aromatics using liquid-liquid extraction method and both the distribution ratio and selectivity were higher than that for sulfolane which is the most used solvent in industry. Laboratory scale results demonstrated the benefits of DESs in this separation operation. In this work the use of a pilot plant scale centrifugal extraction multi-stage unit is studied for the separation of thiophene from a mixture of thiophene and heptane. The pilot plant is being used for the validation of previous laboratory scale results. This could constitute a very important step towards the implementation of this method in industrial scale.

**Keywords**— Liquid-Liquid Extraction, Deep Eutectic Solvents, Scale Up.

## I. Introduction

In recent years, many petrochemical transformation companies embarked in building refineries with special interests on aromatics production. In fact, these companies are investigating the possibility of adding aromatics as a key component in the existing refineries. The produced aromatics would be processed into downstream products, and then exported. In order to economically and technically utilize aromatics they must be separated from aliphatic compounds that are usually present in the refinery mixture.

The type of process used for the separation of aromatics from their mixture of corresponding aliphatic hydrocarbons depends on the concentration of the aromatic in the feed. For example, extraction is used when the concentration is in the range of 20–65 wt.%, while extractive distillation is used for the range of 65–90 wt.%. In addition, azeotropic distillation is used when the concentration of aromatics is higher than 90 wt.% [1,2]. However, when the concentration of aromatics is small, i.e. less than about 20 wt.%, there is no separation process that can be used efficiently and economically [3].

The difference in solubility of the components to be separated is the basis for the well known liquid-liquid extraction (LLE) process. In this case a solvent is added to original solution and the whole mixture is splitted into two immiscible phases. The added solvent should have the ability to extract the desired component from the original solution. Examples of solvents used in LLE include sulpholane, ethylene glycol, n-methyl pyrrolidone, and n-formylmorpholine. However, it was found that an additional step is needed to separate the solvent from both phases. This in turn will increase the cost of investments and the energy consumption [2]. The use of solvent especially ionic liquids (ILs) for LLE process has received attention due to its successful application in removal of sulfur-containing compounds in gasoline fuel. The technology is known as deep extractive desulfurization of fissile fuel which became an urgent object in refinery and petrochemical industries in order to meet the stringent regulations in Europe and USA [4,5]. Under this context, many researchers have been developing new innovative methods. Among all these new processes, extractive desulfurization appears to be especially promising because it is clean, cheap due to low energy demand, requires mild operation conditions and simplistic operation option. Hence, researching efforts over the last years are being focused on finding the most suitable solvent for deep desulfurization purposes [6].

Maria et al [7] reviewed the role of Ionic Liquids on desulfurization of fuel oils. Among these salts, the pyridiniums delivered the most promising results on sulfur reduction by simple liquid-liquid extraction. Liquid-liquid equilibrium data for ternary system was developed. The phase equilibrium can help to design and simulate multistage separation process. Chu et al. [8] studied the extraction of sulfur from diesel fuel using [BF<sub>4</sub>] based IL. They showed that the absorption capacity depends on the size and structure of the IL. They showed the best rate of desulfurization can reach up to around 40%. Wang et al. [9] tested several ILs from the removal of sulfur-containing compounds from gasoline at room temperature. They found that [BPy]BF<sub>4</sub> had the best selective extraction rate of 45.5% in one cycle and up to 96% in six cycles. They also reported that the anion, cation structure and size of IL are important factors affecting the recovery rate. Yi et al. [10] show that the alkylimidazole solvent and/or its mixture with an IL can be used as a potential extractant for the extractive desulfurization of fuel oils. The used S-containing solvent can be regenerated by a water diluting process followed by simple distillation. Luisa et al. [11] analyzed the use of IL [C8mim][BF<sub>4</sub>], as solvent for desulfurization of gasoline by liquid-liquid extraction. Results showed that solvent extraction of thiophene and dibenzothiophene is possible. After three stages the composition of thiophene is reduced by 79 wt % and that of dibenzothiophene is reduced by 87 wt %.

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Jiang and co-workers [12] demonstrated the effectiveness of few ILs on the removal of aromatic sulfur compounds in fuel oil. The results suggest that [EEIM][DEP] might be used as a promising solvent for the extractive desulfurization of fuel. The preference is based on its higher sulfur extractive ability, lower solubility for fuel and thus negligible influence on the constituent of fuel, and the ease of regeneration for the spent IL via water dilution process. Lusia et al. [13] tested the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate as solvent for the separation of thiophene from aliphatic hydrocarbons. The phase diagrams for the ternary mixtures including both the experimental and calculated tie-lines have been presented.

In the past decade, ILs analogues, called deep eutectic solvents (DESs), have emerged as alternatives to conventional solvents and ILs themselves [14-16]. A DES is a mixture of two or more components that has a melting point less than that of any of its components. DESs are usually composed of salts, a hydrogen-bond donor (HBD), or a complexing agent. DESs have many advantages over ILs. They are easily synthesized and thus the purity of the DES is not an issue. Their cost depends on the cost of used components. By a carefully choosing the components of the DES we can get non-toxic and biodegradable solvents. In addition, most DESs do not react with water. Some applications that used DESs as solvents include but are not limited to electrochemical processes, purification of palm [16], enzyme catalysis [17], and electrochemical applications [18].

Recently, we showed that low cost DESs can be used for the separation of aromatics using liquid-liquid extraction method. Both the distribution ratio and selectivity were higher than that for sulfolane which is the most used solvent in industry. The results were published in high esteemed journals [19-21]. Similarly, Changping et al. [22] investigated the use of DES in deep desulfurization of fuel. In optimal conditions, the extraction efficiency can reach as high as 82.83% for one cycle and 99.8% in five cycles. Despite, the solvent type, e.g. IL or Des, all previous research work focused on LLE at the lab scale. To our knowledge no effort, at least for the DES, of using extractive desulfurization on pilot plant scale was reported. In fact, in order to industrially implement the use of DES for LLE processes and particularly in deep desulfurization, pilot plant scale experiments must be conducted and the operational parameters should be optimized.

## II. Experimental Protocol

### A. Chemicals

Pure grade compounds thiophene, n-heptane, tetrabutylammonium bromide, choline chloride were purchased from Acros Organics (Belgium), ethylene glycol and pyridine from Panreac (Spain). All chemicals were of high purity (>99%) and used without any further purification. The DESs was prepared according to the method described by Abbott et al [14].

### B. Lab Scale Protocol

DES1 was prepared using tetrabutylammonium bromide salt and pyridine with a molar ratio of 1:8 while DES2 was prepared using choline chloride : ethylene glycol with a molar ratio of 1:4. The mixture was put in screw-capped bottles and then stirred in an incubating-shaker equipped with temperature ( $\pm 0.1$  °C) and speed control at a temperature of 100°C with a rotational speed of 200 rpm until a clear liquid was formed. In the other hand, feed mixture containing 10 wt% of thiophene in n-heptane was prepared by mixing weighed amounts of the chemicals using an analytical balance ( $\pm 0.0001$  g).

The feed was then mixed with the DESs in a mass ratio of 1:1. Each set of experiments was conducted at 25°C. The vials were placed in the incubator shaker. The shaking time was six hours followed by a settling time of about 12 hours to guarantee that the equilibrium state was completely attained. Samples were taken from the top and bottom layers and analyzed using a HPLC.

### C. Analysis

Samples from the top and bottom layers were withdrawn using a syringe and then diluted using 2-propanol. The samples were analyzed using a HPLC Agilent 1100 series with a zorbax eclipse xdb-c8 column. The temperature of the column oven was set to 30 °C. The mobile phase was acetonitrile and distilled water with a volume ratio of 3 : 1. The flow rate of the mobile phase was 1.4 ml min<sup>-1</sup> with a pressure of 120 bars. The uncertainty in the reported concentrations was estimated to be 0.001 wt% (10 ppm). The measured composition at equilibrium in both liquid phases is shown in Table 1 and the ternary phase diagram is given in Fig. 1. The reliability of the experimental data have been ascertained by using Othmer-Tobias and Hand correlations where the regression coefficients R<sup>2</sup> obtained was close to unity indicating the degree of consistency.

The distribution (D) and selectivity (S) of thiophene at equilibrium is given Table 2, which indicate that DES has higher selectivity at small thiophene mole fraction. Therefore, the solvent is more effective for fuel with traces of and/or diluted thiophene mixture.

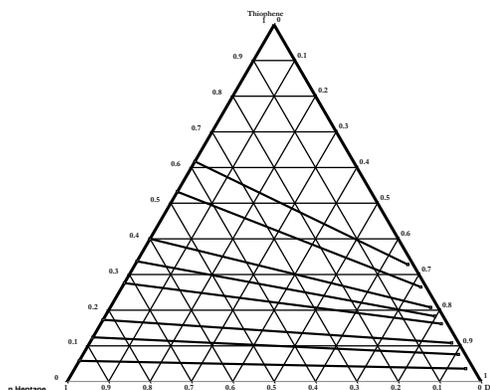


Figure 1: Ternary phase diagram for thiophene-DES-heptane system

TABLE 1: Composition of the experimental tie lines for the ternary system thiophene-DES-n-heptane

Feed			Top Layer			Bottom Layer			D	S
Thiophene	Heptane	DES	Thiophene	Heptane	DES	Thiophene	Heptane	DES		
0.050	0.452	0.498	0.058	0.942	0.000	0.036	0.019	0.945	0.625	30.660
0.103	0.399	0.498	0.124	0.876	0.000	0.076	0.017	0.907	0.619	32.580
0.152	0.349	0.500	0.173	0.827	0.000	0.108	0.017	0.875	0.622	29.772
0.205	0.299	0.496	0.276	0.724	0.000	0.162	0.015	0.823	0.587	28.287
0.252	0.252	0.496	0.337	0.663	0.000	0.183	0.020	0.797	0.544	18.287
0.300	0.202	0.499	0.400	0.600	0.000	0.208	0.018	0.774	0.519	16.832
0.349	0.151	0.500	0.532	0.468	0.000	0.265	0.014	0.722	0.497	16.755
0.402	0.100	0.498	0.617	0.383	0.000	0.328	0.013	0.659	0.531	15.597

### III. Pilot Plant Description and Methodology

#### A. Unit description and nomenclature

The pilot plant setup under consideration for the study of liquid-liquid extraction (LLE), is a 3-stage LLE unit (BP 17-3) designed and built in collaboration with SOLTEQ® (Malaysia). It is an intermediate size unit that is destined for research purposes and which may take up to 10liters of both heavy and light liquids.

The unit consists of mainly three sets of liquid-liquid centrifugal separators, two storage tanks for placing the heavy and light liquid phases, and a pumping and heating circuit (see Fig. 2 and the components nomenclature Table 2). The unit is also supplied with suitable instruments for process monitoring. A data acquisition system is furnished for automatic and continuous recording of operating parameters.

This pilot plant unit has been built after collaborative design work between university and an engineering constructor; it is intended for research work dealing with the optimization of the different operating process parameters such as flow rates, temperatures, number of stages, etc... It is the result of several years of research dealing with liquid-liquid extraction studies particularly with the use of deep eutectic solvents (DESs). As typical liquid-liquid extraction equipment, this pilot plant is schematically shown in Fig. 2 and described in Table 1. In addition, not shown in diagram, the unit contains Thermostat circuit for temperature control using a bath and 2 heat exchangers and an acquisition/control computerized system.

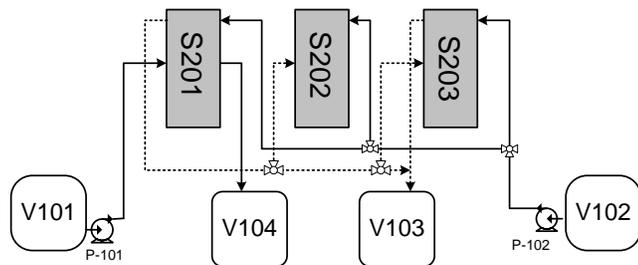


Figure 2: Simplified schematic of the pilot plant

TABLE 2: NOMENCLATURE OF PILOT PLANT UNIT

unit	Description
S-201	Stainless steel Motorized Centrifugal extractors :
S-202	Max flowrate 1.9Lpm; hold-up vol 0.2L; motor 1/8hp and
S-203	max 3450rpm
V-101	Light Phase Feed Tank : Stainless steel cylindrical vessel, max. capacity 10L
V-102	Heavy Phase Feed Tank : Stainless steel cylindrical vessel, max. capacity 10L
V-103	Light Phase Collection Tank : Stainless steel cylindrical vessel
V-104	Heavy Phase Collection Tank : Stainless steel cylindrical vessel
P-101	Light Phase Pump :Motor 0.05kW, capacity 2.5Lpm, 3bar
P-102	Heavy Phase Pump :Motor 0.15kW, capacity 2.5Lpm, 8bar

The pilot plant comprises a number of pumps and valves which allow circulating fluid phases through 1-, 2- or 3-stage scenarios. For instance, only S201 should be used for the 1-stage operation by setting valves directions in the correct manner (preventing flows through the S-202 and S-203 centrifugal extractors); also, the S-202 and S-203 may be included for 2- or 3- stage operation. To optimize the extraction operation, the centrifugal speed may be adjusted by acting on the motor controls via the acquisition/control system.

#### B. Experimental procedure

1. Set all valves on the correct directions (for the 1-, 2- or 3-stage operations)
2. Fill tank V101 with light phase, V102 with heavy phase
3. Turn on unit machine
4. Turn on computer and run the solteq software
5. Turn on extractors (S201, S202 and S203) depending on the flow scenario and set the speed
6. Turn on the pumps and set the speed
7. Let the operation run until the solutions are completely transferred from the supply tanks to the collection ones.
8. After stopping the pumping, turn off the solteq machine
9. Analysis the collected solutions in V103 for light phase and V104 for heavy phase
10. Save data temperatures and flow rate from the acquisition software.

### C. Experimental methodology

During this preliminary scale-up study, it is intended to reproduce previous typical laboratory scale results on much larger scale. Experiments were performed for a given DES with the same components molar ratio for three scales runs, i.e.:

- 10g,
- 100g, and
- 1000 ~2000g scales.

So, for the extraction experiments, the percentage recovery (i.e. extracted thiophene) is targeted in different scales studied. The pilot plant is operated at atmospheric pressure and room temperature. One stage is used with centrifugal pump runs at 3000rpm. The experiment lasted 30 minutes. At the end of the experiment, samples were taken from the heavy and light phase tanks and analyzed by HPLC, screen capture of the analysis is shown in Figs. 3 and 4. The peak corresponding to thiophene is zoomed inside each figure. The weight percentage of thiophene in both phases is determined by fitting its HPLC magnitude in the pre-designed calibration diagram. Consequently, the weight percent extraction of thiophene is calculated using the following correlation:

$$E\% = \frac{\text{thiophene wt\% in heavy phase}}{\text{thiophene wt\% in heavy phase} + \text{thiophene wt\% in light phase}}$$

### IV. Preliminary Scale-Up Results

Scale-up is an important stage for the passage from laboratory apparatus to industrial installation. Various process parameters and long term effects have to be investigated in order to optimize the operating condition. The preliminary runs performed concern the extraction of thiophene from heptane. This mixture mimics the gasoline fuel which usually contains thiophene, heptane and other heavy hydrocarbons. Starting from the same initial weight percent (10 wt%) and DES molar ratio (1:8), typical results are summarized in table 3. The first four runs in Table 3 are based on lab scale tests, among them three repeated ones at 10gm scale denoted as A, B, and C. The condition of the model oil and solvent is exactly the same for that used in the lab scale for fair comparison. The result of the pilot plant scale, which is also based on 1000g is listed at the bottom of the table. Shortage of raw materials availability limited the results at this initial stage of the study.

It can be seen from table 3, that the % extraction of thiophene from lab scale runs (triplicate values) had an average value of about 46 (with a standard deviation 1 %).

TABLE 3: SUMMARY OF LAB AND PILOT PLANT TESTS

Run No	System	% of thiophene extracted
1	DES1_10_A	47.5
2	DES1_10_B	47.6
3	DES1_10_C	45.2
4	DES1_100	53.7
5	Pilot plant DES1	41.1

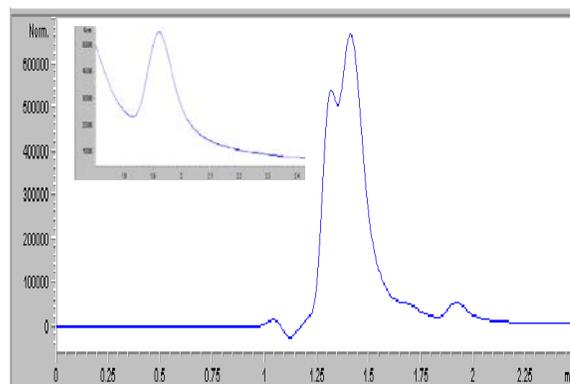


Figure 3: HPLC diagram for heavy phase showing DES and thiophene

The 100 g scale resulted in value of 54%, while that of the pilot scale was about 41%. The results show that thiophene recovery is increased as weight of solution is increased from 10 g to 100 g. Moreover, the pilot plant result confirms the percentage recovery obtained at lab scale.

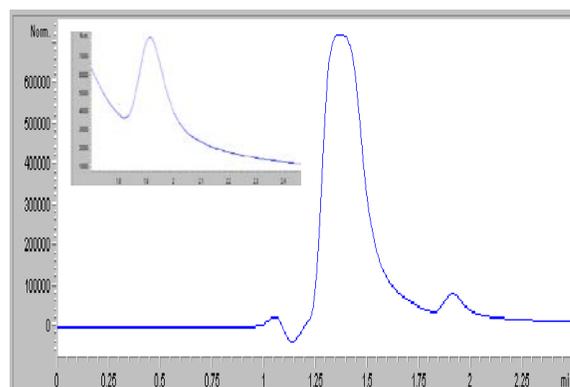


Figure 4: HPLC diagram for light phase showing DES and thiophene

Despite lack of repetitions for the last two scales, results are somewhat comparable and the same order of magnitude. Our extraction results are very comparable with those in the literature for them type of oil mixture. For example, Wang et al. [9] studied the extraction of thiophene from thiophene, n-heptane, xylol mixture. The reported sulfur removal percentage, with IL to oil mass ratio is 1:1, ranges from 21.8% to 45.5% depending on the type of IL used. This means the proposed DES in this work has slightly better extraction ability. However, we used binary oil mixture while ternary oil mixture is utilized in [9]. They have found that increasing the ratio of oil to IL, i.e. using less IL, the extracting ability reduces. Moreover, the extraction efficiency increases slightly with temperature. These parameter need to be assessed using pilot scale operations. Luisa et [11,13] showed that using [C8mim][BF4] IL, thiophene recovery can reach 79 wt% when three cycles are used. However, they used somehow different oil mixture. For example, they tested oil solution containing, thiophene in i-octane, in n-hexan, or in toluene. Changping et al. [22] has investigated the effect of the separation parameter such as temperature, extraction time,

phase ratio of model oil to DES, and initial concentration of sulfur compounds in the oil. However, the effect of parameters needs to be further assessed during upscale stage because continuous operation involve other factors such as feed flow rate, impurities, recycle, deactivation, etc. Therefore, in our next steps, more runs are scheduled for this scale up work during which optimization aforementioned parameters will be conducted.

## v. Conclusions

The use of Deep Eutectic Solvents for Liquid-Liquid Aromatic/Aliphatic Hydrocarbon using a pilot plant Separation has been tackled in this work. In particular, scale up from 10g to more than 1000g has been explored; preliminary results showed that extraction efficiencies (here %extraction of thiophene) are comparable between the different scale up magnitudes (10g, 100g, and 1000g, respectively). Despite lack of repetitions especially for the 100g and the pilot scales, results are encouraging. Nevertheless, DES used here is proven to be a good solvent to separate Hydrocarbon mixture that is difficult to separate using conventional methods such as distillation. More elaborate work is scheduled for the near future particularly for the optimization of process parameters which will enhance the liquid-liquid separation of Aromatic/Aliphatic Hydrocarbon.

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