Materials Physics and Chemistry (2019) Volume 1, No 1
doi:10.18282/mpc.v1i2.573

Original Research Article

Desulfurization of the dibenzothiophene (DBT) using imidazolium-based ionic liquids (ILs)

Bilal Kazmi[1], Dr. Awan Zahoor[1], Dr. Hashmi Saud[2], Dr. Zafar Khan Ghouri[3]*

1 Department of Chemical Engineering, N.E.D. University of Engineering and Technology, Karachi, Pakistan
2 Department of Polymer & Petrochemical Engineering, N.E.D. University of Engineering and Technology, Karachi, Pakistan
3 Central Laboratories Unit, Qatar University, P.O. Box: 2713, Doha, Qatar
**Correspondence: zafarkhan.ghouri@qu.edu.qa*

ABSTRACT

In this work we examined the industrial scale extraction process of ultra-low sulfur diesel with the help of simulation software ASPEN Plus®. This work focuses on the [Cnmim] [BF_4] (imidazolium-based) ionic liquid and employed it in the extractive desulfurization of the dibenzothiophene (DBT) from the model diesel fuel under a very mild process condition. UNIFAC (uniquasi functional activity) was chosen as the thermodynamic method to model the ionic liquid on ASPEN Plus® and different physical and chemical properties were then taken from the literature to be incorporated in the simulation model. Different parametric analysis was studied for the removal of thiophene-based compounds from the model diesel. The results acquired shows the significance of imidazolium-based ionic liquids (ILs) for the extraction of S-contents from the liquid fuels at an optimal process conditions of 40 °C and 2 bar pressure with the 2.8: 1 ratio of ionic liquid and model diesel which validates the experimental results obtained previously in the literature.

Keywords: *desulphurization; ionic liquids; catalyst; dibenzothiophene; diesel*

Received: Mar 5, 2019 **Accepted:** May 10, 2019 **Online:** May 27, 2019

1. Introduction

During the past few years scientists have started to work more towards the environmental issues and bringing alternatives to control the emissions from the fuel products. These measures were taken in light of the new world environmental policies regarding the reduction of the sulfur-containing compounds from the fuel products [1]. Therefore a number of countries have developed a very stringent policy in this regard in recent past the environmental protection agency in the united states of America has set the limit of 15 ppm of sulfur content in the diesel used by the vehicles [2–4]. The European union has also applied a very stringent policy in 2005 which stated that the sulfur content in the diesel fuel to be around 50 ppm [5,6].The main reason for adopting this strict rules is because of the fact that sulfur emissions from different fuel products affects human health and also have a great impact on the overall environmental conditions as well [12]. The release of these sulfur content causes acid rains, ozone depletion and affects the human respiratory system [8]. Sulfur present in these liquid fuels inhibits the pollution-controlling equipment in vehicles (i.e. deactivation of the automotive catalyst converter) which leads to the release of the toxic and volatile organic compounds into the atmosphere [8,9]. Taking these factors into account refining needs to work more towards the sulfur content removal from the fuel products in the view of the environmental protection agency policies [10].

Currently the most classical technology used by the refineries for the sulfur removal is the hydrodesulfurization (HDS) technology. This technology utilizes the hydrogenation treatment of the aromatic compounds (such as benzothiophene, dibenzothiophene, thiophene, 2-butylbenzothiophene and their derivatives) since they are the ones which are present at the highest concentration in the refinery streams compared to the aliphatic compounds [7,12,29,30]. Nowadays the conditions employed by the refineries for sulfur content removal are processed under the extreme temperature and pressure conditions, large volumes for the reactor and with the help of an active catalyst [33,34]. The purpose of HDS is to convert the sulfur compounds to H_2S and hydrocarbons. But some alkylated derivatives of thiophene are quite resis-

Copyright © 2019 Bilal Kazmi *et al*. This is an Open Access article distributed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International License (http://creativecommons.org/licenses/by-nc/4.0/), permitting all non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

tant to hydrotreatment and difficult to remove by the HDS. So the removal of theses sulfur contents from the fuel amounting is increasing the cost of processing and also attributes in the high amount of energy and consumes a large amount of hydrogen. Sulfur removal by HDS currently requires upgradation to the present technology existing. Various new options have been considered for the deep desulfurization of the fuels such as reactive distillation, oxidative desulfurization, adsorption, absorption, biodesulfurization (using bacteria), extraction, membrane separation among others [8,9,15,16,30].

Among them, extractive desulfurization is considered to be as the most studied technique used in the recent past [32]. This technology utilizes the contact between the solvent and the sulfur compound by the liquid- liquid extraction phenomena. Besides the traditional volatile organic solvents, the use of ionic liquids (ILs) to extract sulfur contents out of these fuels products is the most discussed topics in the recent years due to their fascinating properties. The use of ionic liquids for the extractive desulfurization of the fuels was first investigated by Wasser Scheid [31,32].

The ILs are generally termed as the “green solvents”. This name was given due to their unique ability both physically and chemically. ILs are the heterocyclic compounds belong to the molten salt group and mostly they are composed of asymmetric and bulky cations (organic) and anions (organic/inorganic) [16]. They generally have the unique property of nonflammability which makes them non-hazardous for the industrial scale. Generally, most of their ionic liquids exhibit negligible vapor pressure under common process conditions thus they can be easily regenerated and negligible loss to the environment so fewer pollution hazards. Most of the ILs are thermostable and chemically stable as well. They are generally in the liquid state over the wide temperature range [11,14,16,32]. They have the solvation capacity for organics and inorganics types of compounds, also with the proper selection of cation and anion for the IL synthesis, this unique feature can allow the scientists and engineers to tailored their solvation ability for the number of solutes [14,16].

Undoubtedly in future, the desulfurization technology will be performed with the help of ILs [32,34]. It may be the industrially favorable process because of favorable conditions of low temperature and pressure and low cost as well, Scientists and engineers have been working in the advancement and preparation of ILs to be used on a wide industrial scale. So the potential of IL brings about a new chapter in the advancement of chemical technology in different application areas. Therefore to support the thermodynamics study and a comprehensive simulation study has been performed to validate the experimental results for the extractive solvent and achieve the targeted separation [32]. The ILs chosen for this study are imidazolium-based IL 1-alkyl-3-nethylimidazolium tetrafluoroborate [$C_n$mim] [BF_4]. The Table 1 illustrates the structural model of the selected ionic liquid. They are selected because they capable of efficiently extract the sulphur contents like dibenzothiophene (DBT) from fuel oils because during the extraction of DBT using imidazolium based ionic ILs it forms the interaction between the aromatic and the thiophene ring of the sulfur containing compound [37–42].1-butyl-3-methylimidazolium tetra fluoroborate [BMIM][BF_4] performs efficiently for the extraction of DBT and it enhance the interaction. Since the cation group in the [BMIM][BF_4] anion may interact with the DBT [41,42].

So the mechanism for the extraction of sulfur contents using ionic liquid are based on the liquid clathrates between the unsaturated bonds of aromatic ring of thiophene based impurities and ionic liquid [44]. The conjugated ring of sulfur or the alkyl substitutes becomes larger which results in the increase in polarity and dispersive energy of the electron ring resulting in a stronger interaction between the aromatic ring of sulfur and the imidazole ring in the ionic liquid [44]. The potential of the ILs has been studied extensively in the present times with the help of experimental results but to employ it on the industrial scale. Therefore, one needs to recognize its technical feasibility with the help of simulation platform. For this simulation study requires predictive model and thermodynamic properties of the components [21,32,34]. Since these incorporates well into the simulation. ILs are still not included in the data bank of the simulator (Aspen plus®). It is due to the less availability of their physical and chemical properties prediction correlation also lack experimental thermodynamic data. Therefore it is needed to develop a comprehensive database for the simulator for the prediction of the physical and chemical parameters for the correlative physical and thermodynamics models within the

ASPEN Plus. So envisaged highly on relating the experimental data with the adequate thermodynamic model to extract their thermodynamic behavior and physical properties of the ionic liquid and their mixtures. Several property models have been used in the literature recently for the prediction of critical scalar and temperature dependent properties. various correlative models such as UNIQUAC, NRTL, UNIFAC, Modified UNIFAC, etc. can be employed for the equilibrium based binary interaction parameter calculations[28].

So the focus of this work is to utilize a predictive model for the simulation of the extractive desulfurization of fuels using different types of ionic liquids(ILs) for the development of the industrial scale process of desulfurization of the diesel based on the previous thermodynamics studies of the potential capability of ionic liquids(ILs).this will help to make the technology of desulfurization beneficial both in terms of economic as well as operational aspects [34-36].

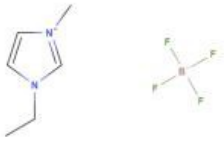
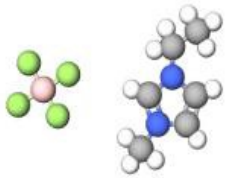
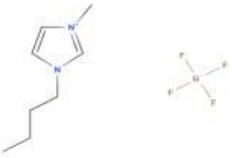
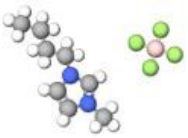
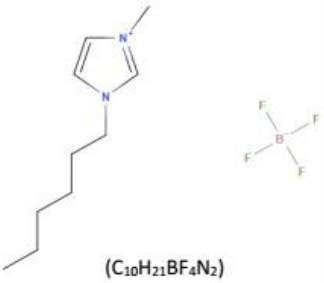
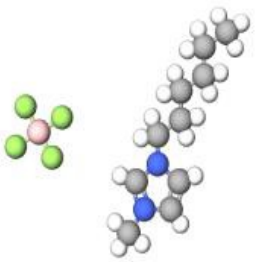
COMPOUND NAME	STRUCTURAL FORMULA	
1-ethyl-3-methylimidazolium tetrafluoroborate	 $(C_6H_{11}BF_4N_2)$	 [EMIM][BF_4]
1-butyl-3-methylimidazolium tetrafluoroborate	 $(C_8H_{15}BF_4N_2)$	 [BMIM][BF_4]
1-hexyl-3-methylimidazolium tetrafluoroborate	 $(C_{10}H_{21}BF_4N_2)$	 [HMIM][BF_4]

Table1. Name of ionic liquid and structural formula

2. Predictive thermodynamic model

Predictive thermodynamic models have been playing a vital role in the separation process. These models are typically chosen to predict the phase equilibria [19,20]. These models are quite helpful in predicting the possible results of the ILs, but in this case successful binary interaction parameters of all the types of components should be known [26]. The COSMO-RS (conductor like screening functional-group activity coefficient) model is the most effective method for the calculation of the thermophysical properties. It is based on the quantum chemistry and uses only atomic specific parameter for the prediction of the thermodynamic property of the liquid system, but the COSMO-RS parameters required by the ASPEN plus® are not widely available in the literature [19,20,26,28].

UNIFAC also known as the UNIQUAC model which is used for the calculation of the nonelectrolyte activity in the nonideal mixture [19–21]. UNIFAC combines the concept of the functional group contribution and the UNIQUAC

model for the estimation of the binary interaction parameters [21]. UNIFAC also gives us the understanding of the size and surface area of the individual functional group present which is obtained from the data related to the molecular structure of the components. The predicted activity coefficients can be used to generate binary interaction parameters in any excess Gibbs energy model. In addition to this, UNIFAC parameters are available for the most of the functional groups in the mixtures so it can be selected over the COSMO-RS model as it has better results and the model can easily be linked with the ASPEN plus® [21].

UNIFAC model consists of two parts, the first is known as the combinational part $\ln \gamma_i^c$ which is used for the determination of the size and shape of the molecule since each molecule has a different molecule [19]. The second part is known as the residual part $\ln \gamma_i^R$ which is used essentially for the determination of the energetic energy interaction between the molecules [19,20,26,27]. So the activity coefficient model in the UNIFAC model can be represented as:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R$$

The combinational part is calculated with the help of the surface and volume parameters using the following equations [19,20,26,28,42]:

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i x[1 - (V_i/F_i) + \ln(V_i/F_i)]$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \qquad V_i = \frac{r_i}{\sum_j r_j x_j} \qquad r_i = \sum V_k^{(i)} R_k \qquad q_i = \sum V_k^{(i)} Q_k$$

The residual part of the activity coefficient model can be calculated from the following equation:

$$\ln \gamma_i^R = \sum V_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}$$

Where,

Γ_k= residual activity coefficient

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing only molecules of type i.

3. Ionic liquid representation in UNIFAC model

Since the predictive thermodynamic model is using UNIFAC for our simulation study so for that we need to decompose our IL as proposed by Kim *et al* [19,43].There are several approaches for the choice of the UNIFAC functional group [20,28].one of the approach is to decompose cation and anion are divided into several groups i.e. 1-butyl-3-methylimidazolium tetrafluoroborate[BMIM] [BF_4] is decomposed into 1 CH_3 group, 3 CH_2 group and one [MIM][BF_4] group as shown in the **Figure 1** [19,28,45]. The reason behind this is that the ionic pair has strong electrostatic interaction so it is better to treat the ionic liquid in terms of electrically neutral groups [19,20]. **Table 2** illustrates the decomposition of the different components used in the study according to the various functional groups among them.

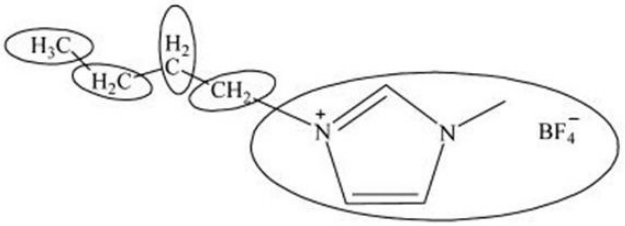


Figure1. Decomposition of ionic liquid using UNIFAC functional groups

Table 2. Types of functional groups present in ionic liquids

Component	[MIN][BF_4]	CH_2	CH_3	ACH	C_4H_4S
1-buty-3-methyl-imidazolium	1	3	1	-	-
Dibenzothiophene	-	-	-	8	1
Hexane	-	4	2	-	-
Hexadecane	-	14	2	-	-

4. Surface area and volume parameter

Calculation of the surface and volume parameters requires the concept of the equilibrium geometry of the molecule in the ideal phase from molecular energy minimization [26]. Quantum chemical calculations have been used as a predictive tool for the determination of these values. The surface area parameter and volume parameter for the UNIFAC group can be calculated using the following equations [19,20].

$R_k = (V \times N_A)/V_{VW}$ $Q_K = (A \times N_A)/A_{VW}$

where

V = group volume using COSMO calculation; A = group area using COSMO calculation;

N_A = Avagadro's number (6.023×10^{23} mol^{-1}) V_{VW} = (15.17 cm^3/mol) segment volume as stated by Bondi [25]

A_{VW} = (2.5×10^9 cm^2/mol) segment area as stated by Bondi [25]

Table 3 illustrates the values of the volume and the surface area parameters of different functional groups present [19,20,28].

Table 3. Surface and volume parameters based on UNIFAC

Group	Volume parameter (R_k)	Surface area parameter (Q_k)
[MIN][BF_4]	6.5669	4.005
CH_2	0.6744	0.540
CH_3	0.9011	0.848
ACH	0.5313	0.400
C_4H_4S	2.8569	2.140

5. Binary interaction parameter

Interaction parameter (a_{mn}, a_{nm}) has been calculated by fitting the solubility data in ILs to calculate the residual part by corelating the activity coefficient at infinite dilution. So the interaction parameter extracted from various literatures are illustrated in the Table 4 [27–29]. The unique advantage of UNIFAC parameters are they can be incorporated in to the famous process design and optimization software and also parameters are calculated very fast using UNIFAC model.

Table 4. Group interaction parameter of the groups involved based on UNIFAC model

m	n	a_{mn}	a_{nm}
[MIN][BF_4]	CH_2	588.74	1108.51
ACH	[MIN][BF_4]	1494.39	85.64
ACH	C_4H_4S	-39.16	23.93
ACH	CH_2	-11.12	61.13
C_4H_4S	[MIN][BF_4]	673.31	-42.93

6. Simulation details

It has been extensively reported in the previous results that for the removal of sulfur impurities from the liquid fuels IL correlates well with the type of aromatics impurities found in the fuels and help achieve the targeted separation of the ultra-low sulfur diesel [21]. The main focus of this simulation study is to study the effect of using IL for the removal of sulfur impurities using ASPEN PLUS® extensively and to use the results obtained from the simulation at different parameter conditions. A step by step guide for setting up ASPEN PLUS® for the simulation involving IL will also be included in the detail report. Highlighting how to model IL using thermodynamic method and using its property parameters and thermodynamics constraints for creating a user defined component in the ASPEN plus® environment. The major reason for this rigorous component defining in the software environment is generally the need to be considering because ILs are not included in the data base of the ASPEN plus® [21]. So user need to thoroughly define the IL to incorporate it into the simulation.

Certain properties and physical parameters are required for the component to carry out any process simulation in the ASPEN plus® which includes critical and scalar parameters and temperature dependent properties as well e.g. ideal gas heat capacity, the heat of vaporization, molar volume, etc. These properties can be acquired from the National institute

of standards and technology (NIST) database and literature as well.

The selection of the appropriate thermodynamic model is also essential to the link the properties to the modeled process. UNIFAC is considered as the suitable predictive model to be utilized in to the simulation as the main modeled method for solving and calculating the different simulation aspects. Simulation covers both aspects of the process i.e. the extraction and the Ionic liquid regeneration using the rigorous counter current liquid-liquid extraction model.

There are several types of hydrocarbon compounds present in the diesel feed from C_8 to $C_{21}$and various other species as well. But we are limited to certain compounds this is because of the availability of the interaction parameters. It has been reported in the literature that hexadecane resembles in the various properties with diesel both physical and chemical properties **Table 6**. So based on this hexadecane was chosen to model the diesel stream in the simulation [21].

For the case of sulphur impurities there are several types of sulfur components can be found in the typical diesel stream as shown in Table 5 but we have chosen dibenzothiophene as our main impurity out of the various impurities present within the untreated diesel as the main impurity for the separation using IL to simplify the process.

Table 5. Composition of Sulfur Components in typical diesel feed

Diesel feed components	S ppm
DBT	120
Thiophene	1099
2-Butyl-benzothiophene	5781
Total PPM (Weight)	7000

Table 6. Hexadecane properties

Property	Hexadecane
Molecular formula	C_{16}
Boiling point	287 °C
Molecular weight	226 g/mol
Density	0.88 g/ml

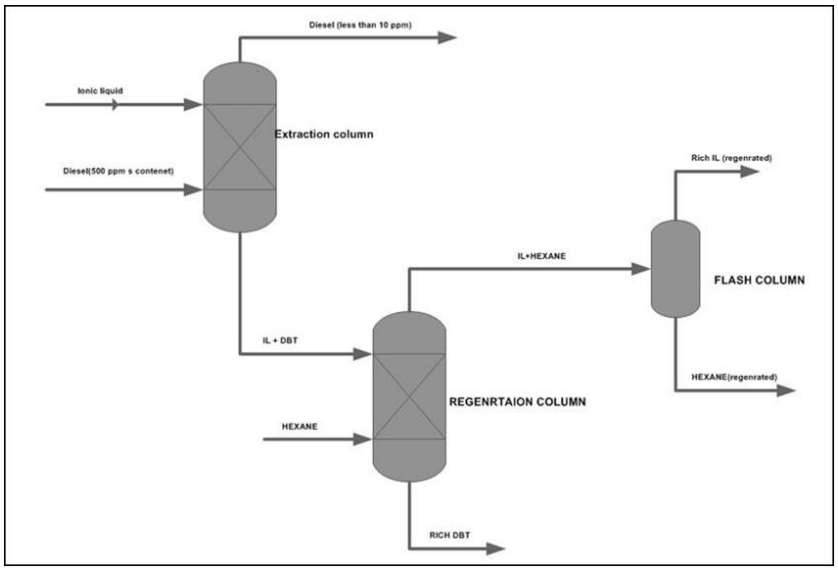


Figure 2. Process flow diagram of the extraction of thiophene based impurities using ionic liquid

7. Results and discussion

7.1 Effect of equilibrium stages and feed rates

During the designing of any process we need to determine the optimal process parameters to achieve the desired results. But the process would only be feasible if it is cost effective so besides selecting optimal parameters, economic considerations should also be kept in mind for the system design. To reduce the S-content in the diesel raffinate to be ~10 ppm, we need to investigate the effect of the ionic liquid to diesel ratio and select an optimal column stages for the effective extraction of the S-contents.

We have selected a model diesel feed containing 500 ppm of S-content for the simulation. The results obtained shows

that to achieve >10 ppm concentration we required to select a higher number of column stages and also the higher flow of ionic liquid compared to diesel. So based on the results >10ppm concentration can be achieved effectively with an optimal stages in the column to be (10) and ratio of the ionic liquid to diesel to be 3:1. Increasing number of stages further would increase the extraction but that would require a higher capital cost. So the selected parameters will result in the most efficient removal of S-content as evident shown in the figure below.

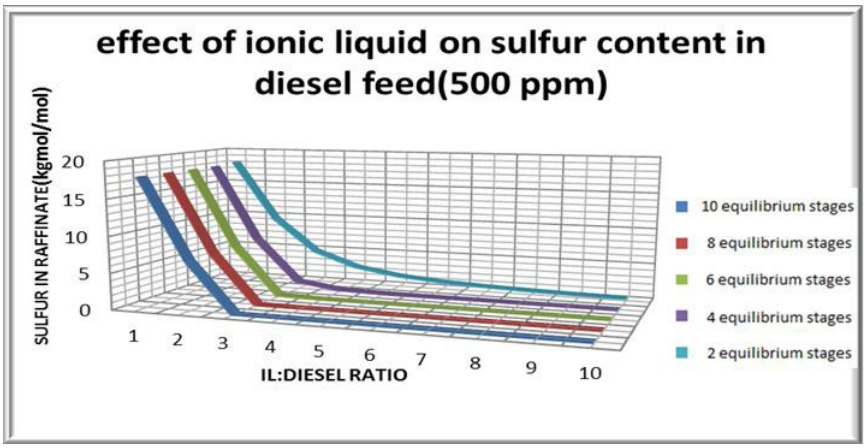


Figure 3. Effect of ionic liquid on the sulphur content of diesel at different theoretical stages at 40 °C and 2 bar column pressure

7.1 Operating condition of temperature and pressure

The selection of an optimal condition for the process is quite an important task specially while working on the simulation. So keeping this point of view into consideration we need to check the effect of temperature and pressure on the system. So we have checked the effect of temperature on the Sulfur content in the diesel raffinate. It has been observed that as we increase the temperature it in turn increases the content of Sulfur in the raffinate diesel stream so that would be considered as the negative impact. Since the main objective of the simulation is to reduce the sulfur content below 10 ppm and also make the process feasible on operational basis so the optimal temperature range for the removal of sulfur contents would be to around 40 °C.

But working on higher temperature has some positive points as well as the temperature rises it inversely decreases the viscosity of the ionic liquid which results in an improved extraction and that would allow us to reduce the actual stages required for the column that would benefit us economically [21,41]. But due to the fact that the major objective is to keep the sulfur content in the diesel below 10 ppm the ideal condition or the optimal temperature range is on lower temperature range. So based on the discussion the optimal temperature range would be 30-50 °C which corresponds well with the results published in literature earlier [21,41]. So selection of the optimal temperature range is highly important for the effective removal of the sulfur content by ionic liquid. So [BMIM][BF_4] selected ionic liquid has performed best in these conditions for the removal of DBT from the model diesel fuel.

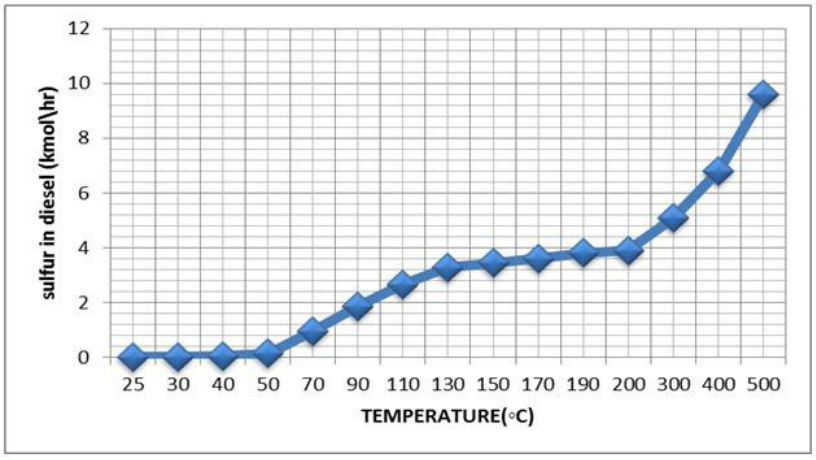


Figure 4. Effect of temperature on the sulfur content

7.3 Regeneration column for ionic liquid

In evaluation of the process it is also important to take into consideration the operating cost and different economic parameters into consideration for the solvents involved in the process. Since the market cost of ionic liquids are quite high. So it is critically important to minimize the loss of ionic liquid in the main extraction column and reutilized the sulfur rich ionic liquid so it could be recycled in the process. In this way process would become effective. It is also important to take into consideration the amount of ionic liquid lost due to miscibility.

From the simulation results shown in **Figure 5** it is observed that ionic liquid removes almost all the thiophene based sulfur compounds from the diesel feed stream. As the process continues the extraction ability of the ionic liquid lower due to the fact that DBT dissolves in to the ionic liquid and reduces its ability for the extraction of sulfur compounds. So in order to recycle this ionic liquid back into the system we need to regenerate it into the regeneration column with the help of organic solvent which essentially eliminates almost all of the sulfur based compounds from the ionic liquid stream it also ensures the efficient extract ant performance with negligible miscibility of organic solvent into ionic liquid [21]. So it is quite critical to study the flow of hexane as a regenerator and also the equilibrium stages for the regeneration column and its repulsive impact on the sulfur content in the sulfur rich ionic liquid feed to the regenerator.

So for the main extraction column operating at 2 bar and 40 ℃ the loss of ionic liquid is almost negligible to the amount fed into the column. With stream rich in thiophene based sulfur impurities and ionic liquid mixture. So a study was conducted using different rate of hexane to ionic liquid and also impact of organic solvent to ionic liquid at different equilibrium stages on the sulfur content removal as shown in the figure. So based on the results it's quite obvious that with a flow ratio of (0.5-0.6) between hexane and ionic liquid and an optimal number of theoretical stages of around (5-6) for the regenerator column operating at 2 bar and 40 ℃ should be selected that would result in a very minimal amount of ionic liquid lost to the amount fed.

These values are based on the calculation performed using UNIFAC as the predictive method. So according to the results there is a minimal loss due to miscibility although these higher flow rates involved these results would become significant. So clearly it is quite an important task to use a minimal ratio of the organic solvent (hexane) against the ionic liquid to cut down the economic cost and also the loss of ionic liquid.

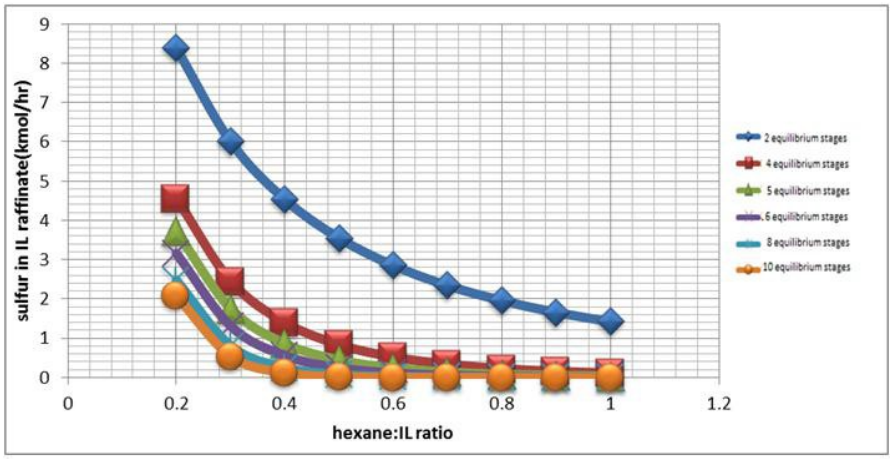


Figure 5. Hexane to ionic liquid ratio at different equilibrium stages for the regeneration of ionic liquid

7.3 Effect of cations on the extraction

Since the UNIFAC data was available, so simulating other members of the ionic liquid having same anion $[BF_4]^-$ and different hydrocarbon chain lengths of the imidazolium-based cations. The performance of the [EMIM][BF_4] compared to the [HMIM][BF_4] to examine the effect of changing cations on the process efficiency. It can be seen that although the performance of the [HMIM][BF_4] was better than the [EMIM][BF_4] but [EMIM][BF_4] requires more flow of ionic liquid as compare to the [HMIM][BF_4]. Also, the amount of hexane required for the regeneration of [HMIM][BF_4] was lower than [EMIM][BF_4]. So based on this it can be concluded that as the alkyl chain length of the cation increases the

sulfur removal ability also increases but as we increase the length of the carbon chain it also results in increasing the cost, viscosity and also results in the less selectivity for the thiophene based impurities [46,47]. So based on this [BMIM][BF_4] can be used because it's both physical and chemical properties are available. Hence for this study [BMIM][BF_4] is considered to be as the most optimum extract ant for the removal of sulfur-based impurities both economically and process wise as well.

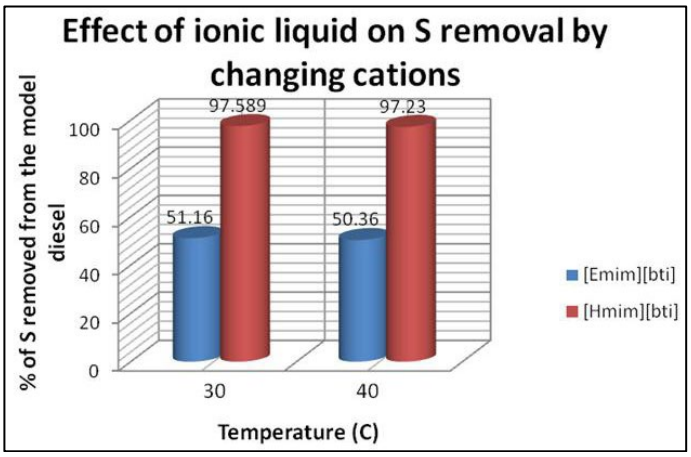


Figure 6. Comparison between the performance of the [EMIM][BF4] and [HMIM][BF4] at a condition of 30 and 40 °C at 2bar

8. Conclusion

The results indicate that by using UNIFAC as the thermodynamic method for the simulation of desulfurization of model diesel fuel we can get the best results with the help of the suitable thermodynamic parameters on ASPEN Plus®. The use of ionic liquid belong to family of imidazolium shows its greater ability for the removal of the sulfur contents from the diesel at the optimal process conditions of 40 °C and 1 bar with a mass ratio of 3:1 between the ionic liquid and the fuel. The results validate the experimental results previously published and also have provided us the insight on the capability of imidazolium based ionic liquid as the suitable candidate for the extractive desulfurization of the fuels. Currently the ionic liquid prices are high but with further research on the regeneration process of the ionic liquid we can see the extractive desulfurization of the fuel oils as the most feasible both on the operational and environmental aspects.

References

1. Directive of the European Parliament and of the Council 2003/17/EC.
2. Regulatory Impact Analysis of the United States Environmental Protection Agency EPA420-R00-026
3. Planeta J, Kara´sek P, Roth M. Distribution of sulfur-containing aromatics between [HMIM][Tf2N] and supercritical CO_2: A case study for deep desulfurization of oil refinery streams by extraction with ionic liquids. Green Chemistry, 2006, 8(1): 70–77.
4. Regulatory Announcement: Heavy-duty engine and vehicle standards and highway diesel Fuel sulfur control requirements, United States Environmental Protection Agency, Air and Radiation, EPA420-F-00-057, Washington (DC).
5. EU-Directives: 1998/70/EC, OJ L 350, 28.12.1998, p. 58 (Directives amended by Commission Directive 2000/71/EC OJ L 287, 14.11.2000, p. 46), and 2003/17/EC OJ L 76, 22.3.2003, p. 10.
6. Chan K, Lee J J, Bae J S, *et al*. Hydrodesulfurization of DBT, 4-MDBT, and 4,6-DMDBT on fluorinated CoMoS/Al2O3 catalysts. Applied Catalysis A General, 2000, 200(1–2): 233–242.
7. Babich I V, Moulin J A. Science and Technology of Novel Processes for Deep Desulfurization of Oil Refinery Streams: A Review. Fuel, 2003; 82: 607–631
8. Song C. An Overview of New Approaches to Deep Desulfurization for Ultra-clean Gasoline, Diesel Fuel and Jet Fuel. Catalyst Today, 2003; 86: 211–263.
9. Srivastava V C. An Evaluation of Desulfurization Technologies for Sulfur Removal from Liquid Fuels. Royal Society of Chemistry, 2012; 2: 759–783
10. Huang C, Chen B, Zhang J, *et al*. Desulfurization of Gasoline by Extraction with New Ionic Liquids. Energy & Fuels, 2004, 18(6): 1862–1864.
11. Dharaskar S A, Wasewara K L, Varmaa M N, *et al*. Deep removal of sulfur from model liquid fuels using 1-butyl-3-methylimidazolium chloride. Procedia Engineering, 2013, 51: 416–422.
12. Brunet S, May D, Perrot G, *et al*. On the hydrodesulfurization of FCC gasoline: A review. Applied Catalysis A General, 2005, 278(2): 143–172

13. Rodríguez-Cabo B, Rodriguez H, Rodil E, *et al*. Extractive and oxidative-extractive desulfurization of fuels with ionic liquids. Fuel, 2014, 117(1): 882–889
14. Werner S, Haumann M, Wasserscheid P. Ionic liquids in chemical engineering. Annual Review of Chemical & Biomolecular Engineering, 2010, 1(1): 203–230.
15. Dharaskara S A, Wasewara K L, Varmaa M N, *et al*. Ionic liquids: The novel solvent for removal of dibenzothiophene rom liquid fuel. Procedia Engineering, 2013, 51: 314–317.
16. Ferreira A R , Freire M G, Ribeiro J C, *et al*. Ionic liquids for thiols desulfurization: Experimental liquid–liquid equilibrium and COSMO-RS description. Fuel, 2014, 128(14): 314–329.
17. Viveros-Garcı´a T, Ochoa-Tapia J A, Lobo-Oehmichen R, *et al*. Conceptual design of a reactive distillation process for ultra-low sulfur diesel production. Chemical Engineering Journal, 2005, 106(2): 119–131.
18. Yazu K, Yamamoto Y, Furuya T, *et al*. Oxidation of dibenzothiophenes in an organic biphasic system and its application to oxidative desulfurization of light oil energy. Fuels, 2001, 15, 1535–1536
19. Lei Z, Zhang J, Li Q, *et al*. UNIFAC model for ionic liquids. Ind. Eng. Chem. Res. 2009, 48, 2697–2704
20. Lei Z, Dai C, Liu X, *et al*. Extension of the UNIFAC model for ionic liquids. Industrial & Engineering Chemistry Research, 2012, 51(37): 12135–12144.
21. Nancarrow P, Mustafa N, Shahid A, *et al*. Technical evaluation of ionic liquid-extractive processing of ultra-low sulfur diesel fuel. Industrial & Engineering Chemistry Research, 2015, 54: 10843−10853
22. Bezzo F, Bernardi R, Cremonese G, *et al*. Using process simulators for steady-state and dynamic plant analysis: An industrial case study. Chemical Engineering Research & Design, 2004, 82: 499.
23. Valderrama J O, Robles P A. Critical Properties, Normal boiling temperatures, and acentric factors of fifty ionic liquids. Industrial & Engineering Chemistry Research, 2007, 46(18): 6063−6064.
24. Bondi A. Van der waals volumes and radii. Journal of Physical Chemistry, 1964, 68(3): 441−451
25. Santiagoa R S, Santosb G R, Aznara M. UNIQUAC correlation of liquid–liquid equilibrium in systems involving ionic liquids: The DFT–PCM approach. Fluid Phase Equilibria, 2009, 278(1): 54−61.
26. Han J, Lei Z, Dong Y, *et al*. Process intensification on the separation of benzene and thiophene by extractive distillation. Aiche Journal, 2015, 61(12).
27. Gmehling J, Rasmussen P, Fredenslund A. Vapor-liquid equilibriaby UNIFAC group contribution. 2. Revision and extension. Industrial & Engineering Chemistry Process Development, 1982; 21: 118–127.
28. Dai C, Dong Y, Han J, Lei Z. Separation of benzene and thiophene with a mixture of N-methyl-2-pyrrolidinone (NMP) and ionic liquid as the entrainer. Fluid Phase Equilibrium. 2015; 388: 142–150.
29. Lin L, Zhang Y, Kong Y. Recent advances in sulfur removal from gasoline by pervaporation. Fuel 2009; 88: 1799–809.
30. Kulkarni PS, Afonso CAM. Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges. Green Chemistry, 2010; 12: 1139–1149.
31. Bösmann A, Datsevich L, Jess A, *et al*. Deep desulfurization of diesel fuel by extraction with ionic liquids. Chemical Communications, 2001; 23: 2494–2495.
32. Rodríguez-Cabo B, Rodríguez H, Rodil E, *et al*. Extractive and oxidative-extractive desulfurization of fuels with ionic liquids. Fuel, 2014, 117(2014): 882–889
33. Te M, Fairbridge C, Ring Z. General, oxidation reactivities of dibenzothiophenes in polyoxometalate/H_2O_2 and formic acid/H_2O_2 systems. Applied Catalysis A General, 2001, 219: 267–270.
34. Domanska U, Wlazło M. Effect of the cation and anion of the ionic liquid on desulfurization of model fuels. Fuel, 2014, 134(9): 114–125.
35. Meindersma G W, de Haan A B. Conceptual process design for aromatic/ aliphatic separation with ionic liquids. Chemical Engineering Research & Design, 2008, 86(7): 745–752.
36. Hansmeir AR, Meindersma G W, de Haan A B. Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids. Green Chemistry, 2011, 13: 1907–1913
37. Asumana C, Yu G, Li X, *et al*. Extractive desulfurization of fuel oils with low viscosity dicynamide based ionic liquids. Green Chemistry, 2010, 12(11): 2030.
38. Yu G, Zhao J, Song D, *et al*. Deep oxidative desulfurization of diesel fuels by acidic ionic liquids. Industrial & Engineering Chemistry Research, 2011, 50(20): 11690–11697.
39. Nie Y, Li C, Wang Z.. Extractive desulfurization of fuel oil using alkyl-imidazole solvent and its mixture with dialkylphosphate ionic liquids. Industrial & Engineering Chemistry Research, 2007, 46: 5108.
40. MuMurry, J., 1992. Organic Chemistry, 3rd edition. Brooks/Cole Publishing Company, Belmont
41. Dharaskar S A, Wasewar K L, Varma M N, *et al*. Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel. Environmental Science & Pollution Research, 2013, 9(4): 578–587.
42. Banerjee T, Singh M K, Sahoo R K, *et al*. Volume, surface and UNIQUAC interaction parameters for imidazolium based Ionic liquids via polarizable continuum model. Fluid Phase Equilib, 2005, 234: 64−76.
43. Kim Y S, Choi W Y, Jang J H, *et al*. Solubility measurement and prediction of carbon dioxide in ionic liquids. Fluid Phase Equilib, 2005, 228–229(3): 439–445.
44. FarzinNejad N, Shams E, Adibi M, *et al*. Desulfurization from model of gasoline by extraction with synthesized [BF4]- and [PF6]-based ionic liquids. Petroleum Science and Technology, 2012, 30(15): 1619–1628.
45. Lei Z, Dai C, Chen B. Gas solubility in ionic liquids. Chemical Reviews, 2014, 114(2): 1289–1326.
46. Koswari E. Recent advances in the science and technology of desulfurization of diesel fuel using ionic liquids. In Ionic Liquids−New Aspects for the Future
47. Al-Ghouti M A, Al-Degs Y S. A novel desulfurization practice based on diesel acidification prior to activated carbon adsorption. Korean Journal of Chemical Engineering, 2014, 32(4): 1–9.