Fuel 234 (2018) 1388–1400

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Optimisation of extractive desulfurization using Choline Chloride-based deep eutectic solvents

Khalid Hussein Almashjary[a], Mohammad Khalid[b,*], Swapnil Dharaskar[c], Priyanka Jagadish[b], Rashmi Walvekar[d], Thummalapalli Chandra Sekhara Manikyam Gupta[e]

[a] Department of Chemical & Environmental Engineering, Faculty of Engineering, University of Nottingham, Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor, Malaysia
[b] Graphene & Advanced 2D Materials Research Group (GAMRG), School of Science and Technology, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, 47500 Subang Jaya, Selangor, Malaysia
[c] Department of Chemical Engineering, School of Technology, Pandit Deendayal Petroleum University, Raisan, Gandhinagar, Gujarat 382007, India
[d] School of Engineering, Taylor's University, Lakeside Campus, 47500 Subang Jaya, Selangor, Malaysia
[e] Apar Industries Limited, Chembur, Mumbai 400071, India

ARTICLE INFO

Keywords:
Deep eutectic solvents
Desulfurization
Response surface methodology
Dibenzothiophene
Extraction
Optimisation

ABSTRACT

Sulfur in fuels is one of the main sources of pollution. Thus, the desulfurization of fuel (gasoline and diesel) is demanding for effective and alternative solutions. Deep eutectic solvents (DES) are gaining rapid interest in extraction processes due to their excellent properties as a solvent. In this study, extractive desulfurization (EDS) of model oil containing dibenzothiophene (DBT) as an organo-sulfur compound was carried using Choline Chloride acting as Hydrogen bond acceptor (HBA) and Propionic acid (Pr) as Hydrogen bond donor (HBD), respectively. Experiments are performed to study the effect of DES molar ratio, temperature and sonication time on DBT removal efficiency with molar ratios of 1:2 and 1:3 (HBA:HBD) using response surface methodology (RSM). DBT is quantitatively analysed using high-performance liquid chromatogram (HPLC) and Fourier transform infrared spectroscopy (FTIR) studies. The results showed high removal efficiency of 64.9% at a temperature of 37 °C, 10 min sonication; 1:3 ratio of ChCl/Pr and at a treat ratio of 1:3 model oil in a single stage extraction. This study will provide an alternative green solution which requires shorter reaction time and lower operating temperature as compared to conventional method i.e. hydrodesulfurization (HDS).

1. Introduction

Over the years, crude oil has been the leading source of energy in the world, contributing to 41% of the total energy needs [1]. Crude oil contains sulfur as one of its common impurities which results in harmful emissions during fuel combustion process. The crude oil properties are mainly influenced by sulfur content and the American Petroleum Institute (API) gravity. Sulfur exists mainly as mercaptans, sulphides, disulphides and thiophenes [3] that defines the crude oil as either sour or sweet based on its quantity. Sweet crude contains sulfur content of < 0.42% sulfur by weight and it varies 0.1% to values more than 5% by weight [2]. The presence of sulfur compounds lead to processing difficulties such as inhibition of catalysts, corrosion of equipment and pipeline systems, release of harmful gases such as sulfur oxide (SO_X) gases during combustion, etc [4].

Strict regulations have been put forward by most countries in relation to sulfur removal so as to reduce pollution to the environment from combustion engines. In the European Union, the "Euro IV" standard which has been applied since 2005 specifies a maximum of 50 ppm of sulfur in diesel for most highway vehicles: ultra-low-sulfur diesel (ULSD) with a maximum of 10 ppm of sulfur must "be available" from 2005 and was widely available as of 2008. A final target (to be confirmed by the European Commission) of 2009 for the final reduction of sulfur to 10 ppm, which will be considered the entry into force of the Euro V fuel standard.

HDS is the most common and current industrial process technology that has been used to remove sulfur from fuels. This technology faces a setback due to aromatic sulfur compounds such as DBT and their alkyl derivatives since they have high stability of the conjugated structure [3]. Other non-HDS technologies that are suitable to remove sulfur include bio-desulfurization, adsorptive desulfurization, oxidative desulfurization and EDS [5–7,16]. EDS has advantages such as application

---

* Corresponding author.
E-mail address: khalids@sunway.edu.my (M. Khalid).

https://doi.org/10.1016/j.fuel.2018.08.005
Received 23 May 2016; Received in revised form 25 April 2018; Accepted 1 August 2018

Table 1
Desulfurization methods summary.

Method of desulfurization	Advantages	Disadvantages
Hydrodesulfurization	• Mechanism well known. • H_2 feasibly applied for desulfurization in light fractions.	• Uses high temperature and pressure [3]. • Expensive catalyst. • Cannot be used to remove 4,6-dimethyldibenzothiophene (4,6-DMDBT) [3].
Bio-desulfurization	• Moderate operating conditions i.e. low temperature and pressure. • Eco-friendly with minimal green house emission as compared to HDS.	• Not commercially employed due to sanitation, storage and handling. • Lowers fuel value. • Expensive and difficult to incorporate with existing operation [5–6].
Adsorptive desulfurization	• Moderate operating conditions i.e. low temperature and pressure. • Easy to incorporate in an operation and less complex.	• Selectivity of sorbent employed to remove sulfur is a limitation. • Surface reaction requires high amount of sorbent [5–6].
Oxidative desulfurization	• Non catalytic method. • Cheap raw materials. • Mechanism is well studied for light fractions. • Rate of reaction is higher as compared to HDS. • H_2 is not required for desulfurization.	• Strong oxidative agents eg H_2O_2 is expensive for large scale application. • No extensive research on heavy fractions eg. bitumen. • For deep desulfurization catalyst is a requirement. • Further reaction on oxidation may lead to formation of non-required products especially when sulfuric acid is used [5–6].
Extractive desulfurization(Ionic Liquids)	• Low operating conditions i.e. low temperature and pressure. • Easy to incorporate in a refinery process. • Feedstock is not affected. • Solvents such as ionic liquids can be recycled as well as phase separation can be done by mere settling.	• Solubility of sulfur in solvents is a limitation hence proper choice of solvent [7]. • Higher efficiency is achieved with oxidation of sulfur. • ILs can be toxic [7].

Table 2
Molar ratio calculations for different DES.

	Molar Ratio of Salt to HBD	Mole % of Salt	Mole % of HBD
DES 2	1:2	0.33	0.67
DES 3	1:3	0.25	0.75

Table 3
List of variables in the process.

Parameter	Range
DES Ratio	1:2–1:3
Synthesis temperature for DES	80–130 °C
Model oil ratio	1:1–1:3(by volume)
Extraction temperature	25–70 °C
Extraction time	10–60 min

Table 4
HPLC experimental conditions.

HPLC	Specification
Equipment model	Agilent (1260 Infinity Series)
Column	Reversed-phase ZORBAX extended C18, 4.6 × 150 mm, 5 µm
Detector	Variable wavelength detector (VWD)
Pump	Quaternary pump
Autosampler	Equipped
Experimental conditions	Mobile phase combination: Methanol and water (90/10) @ 1 mL/min Injection volume: 1 µL [18] Column temperature: 35 °C Detection wavelength: 234 nm [15] R^2 (DBT): 0.9995

of low temperature and pressure, less energy input and process simplicity [18]. However, challenges lies in the solvents used that are toxic and volatile that have serious environmental threat [5,7]. Reasonably, there is a dire need to develop a green and effective solvent to solve this issue. Table 1 presents a summary of available desulfurization methods.

Currently, green solvents are being researched in hope for greener process. Environmental impacts resulting from toxic organic solvents can be eliminated by the use of DESs. DESs are analogues of ionic liquids (ILs) that are composed of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) formed from a eutectic mixture [8]. They are capable of selectively removing sulfur organic compounds from crude oil to achieve deep desulfurization with low melting point and vapour pressure [9]. In addition, several successful applications of DES in various fields have been reported [11,12]. DESs have shown potential for deep desulfurization efficiency and easily synthesised. Research has provided evidence with sulfur reduction by using DES to values < 8.5 ppm liquid fractions using ammonium-based DES with five cycles of extraction [10]. The hydrogen bonds that are formed when DES and DBT resulting to removal of sulfur compounds account for better deep desulfurization and better efficiency. Green extractions of sulfur from crude oil possess a great significance in terms of environmental pollution [10].

Table 5
Independent variables, codes and design coordinates.

Coded Name	Parameter Name	Units	Minimum	Maximum	− 1 Actual	+ 1 Actual
A	Extraction Time	Min	10	60	10	60
B	Synthesis Temperature	°C	80	130	80	130
C	Model Oil Ratio		1	3	1	3
D	Extraction Temperature	°C	25	70	25	70
E	DES ratio		2	3	–	–

DESs have been reported as solvents for EDS of petroleum fractions. Moreover, recent studies that have been conducted show great potential [10,15]. Research works on choline-based DES have also been done with the aim to attain deep desulfurization using magnetic stirrer instead of ultrasound to enhance mixing but achieved efficiencies below 40% [10]. This call for more research to raise the low efficiencies to higher ones so as to get to the objective of deep desulfurization. Water bath sonicator was incorporated to boost mixing during desulfurization as opposed to magnetic stirrer with a frequency of 35 kHz. Sonication has exhibited higher sulfur removal efficiencies as magnetic stirrer with Imidazolium ionic liquid; as well as energy saving [17]. In process engineering, design of experiment (DOE) is a statistical tool that has the ability to model the process operation, analyse as well as incorporate several variables that affect the process output. Response surface

Table 6

CCD experimental design along with experimental and predicted values of percentage removal of DBT.

Run	Extraction Time (A)	Synthesis Temperature (B)	Model Oil Ratio (C)	Extraction Temperature (D)	DES Ratio (D)	Percentage Removal DBT (%)	
						Experimental	Predicted
1	10.00	80.00	3.00	70.00	3	63.41	62.76
2	35.00	105.00	2.00	47.50	2	64.65	64.43
3	60.00	130.00	1.00	25.00	2	64.15	63.65
4	10.00	130.00	3.00	25.00	3	61.16	61.47
5	35.00	105.00	2.00	70.00	3	61.58	63.41
6	60.00	105.00	2.00	47.50	2	63.04	65.07
7	10.00	80.00	3.00	25.00	3	61.85	62.35
8	60.00	80.00	1.00	25.00	3	66.48	66.60
9	35.00	130.00	2.00	47.50	3	64.10	65.74
10	60.00	130.00	1.00	70.00	2	64.41	64.07
11	35.00	105.00	2.00	47.50	2	64.65	64.43
12	35.00	105.00	2.00	47.50	2	64.65	64.43
13	60.00	80.00	3.00	25.00	2	60.64	61.53
14	10.00	80.00	1.00	25.00	3	66.83	66.16
15	35.00	105.00	2.00	25.00	2	61.54	61.52
16	35.00	105.00	1.00	47.50	2	63.70	65.85
17	10.00	80.00	1.00	70.00	2	63.70	63.82
18	35.00	105.00	2.00	47.50	2	64.65	64.43
19	60.00	80.00	3.00	70.00	2	62.75	62.12
20	35.00	105.00	2.00	70.00	2	61.58	62.04
21	10.00	105.00	2.00	47.50	2	64.65	65.21
22	60.00	80.00	1.00	25.00	2	65.10	64.00
23	10.00	130.00	3.00	70.00	2	61.83	62.20
24	10.00	105.00	2.00	47.50	3	65.71	66.45
25	35.00	105.00	2.00	47.50	2	64.65	64.43
26	35.00	105.00	2.00	47.50	3	66.71	65.90
27	35.00	80.00	2.00	47.50	3	65.36	66.35
28	35.00	105.00	2.00	47.50	3	66.71	65.90
29	60.00	80.00	1.00	70.00	3	66.52	66.13
30	35.00	105.00	2.00	47.50	3	66.71	65.90
31	35.00	105.00	2.00	47.50	3	66.71	65.90
32	10.00	130.00	3.00	25.00	2	61.16	60.89
33	10.00	80.00	3.00	25.00	2	61.39	61.13
34	60.00	80.00	3.00	25.00	3	62.13	63.22
35	60.00	130.00	1.00	25.00	3	65.58	65.60
36	35.00	130.00	2.00	47.50	2	65.10	64.59
37	60.00	130.00	3.00	25.00	2	60.03	60.67
38	35.00	105.00	2.00	47.50	2	64.65	64.43
39	60.00	80.00	3.00	70.00	3	63.47	63.58
40	60.00	130.00	3.00	70.00	3	62.22	62.75
41	60.00	130.00	3.00	70.00	2	62.15	61.93
42	60.00	130.00	1.00	70.00	3	65.58	65.80
43	60.00	130.00	3.00	25.00	3	62.42	61.72
44	10.00	130.00	1.00	25.00	2	63.99	64.29
45	35.00	105.00	2.00	47.50	3	66.71	65.90
46	60.00	105.00	2.00	47.50	3	68.32	66.78
47	10.00	80.00	3.00	70.00	2	61.20	61.76
48	10.00	80.00	1.00	25.00	2	64.23	64.02
49	10.00	130.00	1.00	25.00	3	65.43	65.77
50	35.00	80.00	2.00	47.50	2	64.88	64.55
51	10.00	130.00	1.00	70.00	2	65.39	64.76
52	10.00	130.00	3.00	70.00	3	61.81	62.54
53	35.00	105.00	3.00	47.50	3	65.84	64.35
54	60.00	80.00	1.00	70.00	2	63.98	63.76
55	10.00	130.00	1.00	70.00	3	67.93	66.01
56	10.00	80.00	1.00	70.00	3	65.67	65.73
57	35.00	105.00	3.00	47.50	2	64.85	63.33
58	35.00	105.00	1.00	47.50	3	65.12	67.77
59	35.00	105.00	2.00	25.00	3	63.58	63.10

methodology (RSM) has been previously used in modeling and optimisation successfully in various process operations [12–14]. Same technique has also been applied for the liquid-liquid EDS of fuels [15]. In this research, ChCl/Pr DES was used for desulfurization of model oil that contains DBT and further experiments were conducted to study extraction efficiency. Since the process operation had multiple variables, the RSM technique was used to model and optimise the extraction process by relating to the operating conditions.

2. Materials and methods

The chemicals used for the synthesis of DES such Choline Chloride (ChCl) and Propionic acid (Pr) (purity > 99%) were purchased from Merck Sdn. Bhd. and Sigma Aldrich Sdn, Bhd. Malaysia respectively. For model oil preparation, dibenzothiophene (purity > 98%) and n-Octane (purity > 99%) were procured from Merck Sdn. Bhd. and Sigma Aldrich Sdn, Bhd. Malaysia. All chemicals were analytical grades and were used as received without any further modification.

Table 7
ANOVA analysis for percentage removal of DBT.

Source	Sum of Squares	Degree of Freedom df	Mean Square	F Value	p-value (prob > F)
Model	176.99	19	9.32	7.72	< 0.0001[a]
A-Extraction Time	0.074	1	0.074	0.061	0.8060[b]
B-Synthesis Temperature	0.74	1	0.74	0.61	0.4393[b]
C-Model Oil Ratio	79.45	1	79.45	65.85	< 0.0001[a]
D-Extraction Temperature	1.56	1	1.56	1.29	0.2627[b]
E-DES ratio	32.01	1	32.01	26.53	< 0.0001[a]
AB	0.77	1	0.77	0.63	0.4305[a]
AC	0.35	1	0.35	0.29	0.5907[a]
AD	3.828E-003	1	3.828E-003	3.173E-003	0.9554 [a]
AE	0.49	1	0.49	0.41	0.5267[a]
BC	0.50	1	0.50	0.42	0.5225[a]
BD	0.89	1	0.89	0.74	0.3945[a]
BE	0.94	1	0.94	0.78	0.3818[a]
CD	1.39	1	1.39	1.15	0.2897[a]
CE	1.86	1	1.86	1.54	0.2220[a]
DE	0.11	1	0.11	0.095	0.7597[a]
A^2	2.61	1	2.61	2.17	0.1492[a]
B^2	0.10	1	0.10	0.085	0.7728[a]
C^2	0.13	1	0.13	0.11	0.7454[a]
D^2	36.34	1	36.34	30.12	< 0.0001[b]
Residual	47.06	39	1.21		
Lack of Fit	47.06	30	1.57		
Pure Error	0.000	9	0.000		
Cor Total	224.05	58			
Std. Dev.	1.10		R-Squared	0.7900	
Mean	64.15		Adj R-Squared	0.6877	
C.V. %	1.71		Pred R-Squared	0.5206	
PRESS	107.40		Adeq Precision	11.102	

[a] Significant at “Prob > F” less than 0.05.
[b] Insignificant at “Prob > F” more than 0.05.

2.1. Preparation of DES

Two different DESs were synthesised by mixing Choline Chloride (ChCl) and Propionic acid (Pr) in a ratio (HBA:HBD) of 1:2 and 1:3, respectively as shown in Table 2. The mixture was heated at 80–120 °C for 3 h using hot plate stirrer until a clear solution was obtained.

All the DESs were prepared in an air-tight Schott bottles to prevent moisture and contamination.

2.2. Model oil configuration

In order to determine the degree of desulfurization, model oil was prepared using dibenzothiophene (DBT) as an organosulfur compound. DBT contains 17.4% sulfur, therefore to mimic real fuel with sulfur content of 1600 ppm, 2.35 g of DBT was diluted in 250 mL with n-Octane as initial sulfur content.

2.3. Extraction process

EDS experiments are carried out in a 20 mL glass vials. To maintained the mass ratio (1:1), 10 mL of DES and 10 mL of model oil was used [17]. The desulfurization temperature used in this study was varied from 25 to 70 °C similar to the earlier reported literatures [15]. Water bath sonicator was used for mixing at 35 kHz with a variable temperature from 25 to 70 °C and time for sonication was set from 10 to 60 min. Before to start sonication, foil test was done to detect the area with highest performance. This was necessary so as to have effective sonication. After sonication, the vials were left for a period of 24 h to allow phase separation. The upper layer i.e. raffinate is the model oil and the bottom layer i.e. extract is the DES. For further analysis, the raffinate phase was drawn after each extraction experiment. The parameters for optimisation such as mixing ratios of DES with model oil, temperature and reaction time are summarised in Table 3. The sequence of experiments is represented in a chronological and systematic way defining the experimental conditions and the parameters clearly.

2.4. Analytical methods

DBT concentration in the raffinate was determined using HPLC (Agilent 1260 infinite series) and FTIR spectrometer (Perkin Elmer Spectrum RX I) using KBr as pelletizing matrix. HPLC details with experimental conditions are presented in Table 4.

The efficiencies of the DESs after EDS were determined using equation (1),

$$Efficiency\ (\%) = \frac{IDBT - FDBT}{IDBT} \times 100\% \tag{1}$$

where IDBT = initial concentration of DBT in the model oil (i.e. 1600 ppm); FDBT = final DBT concentration after EDS in the raffinate.

2.5. Experimental design

Since this process operation is a multivariable process, hence, it was important to incorporate factors that influence extractive desulfurization. However, it was impractical to consider all factors such as frequency and amplitude of sonication. For the purpose of this research, factors such as agitation speed, sonication frequency and amplitude was fixed. Central composite design (CCD) under RSM in Design ExpertV9 (Stat-Ease Inc. Minneapolis, USA) will be used to optimise the experimental factors. The experimental factors that will be optimised in this study are extraction time (A), synthesis temperature (B), model oil ratio (C), extraction temperature (D) and DES ratio (E). Percentage removal of DBT based on Eq. (1) will be the response used in CCD, to optimise the EDS parameters. The experiments were carried out in a random manner to minimize errors in response. CCD forms the design space with the axial spacing (α) of 1 with face centered. The CCD model under RSM was used to investigate the effects of five different experimental parameters in EDS on one response output (i.e., percentage removal of DBT) based on 59 sets of experiments. Parameters A to D are numeric factors and parameter E is a categoric (nominal) factor are varied according to the ranges mentioned in Table 5.

Regression analyses were applied on the experimental results using Design Expert V9 (Stat-Ease Inc. Minneapolis, USA). The effect of extractive parameters (A, B, C, D and E) was calculated both mutually and individually by Design Expert. The five experimental parameters (A, B, C, D and E) and one response output (i.e., percentage removal of DBT) is fitted together in quadratic polynomial model as shown in Eq. (2):

$$Y = B_0 + \sum B_i X_i + \sum B_{ij} X_i X_j + \sum B_{ii} X_i^2 \tag{2}$$

where Y is the response output, B_0 is independent constant effect, B_i is the linear/individual effect, X_i are the independent experimental parameters (i = A,B,C,D,E), B_{ij} is the interaction effect (i = A,B,C,D,E and j = A,B,C,D,E), B_{ii} is the squared effect. The data collected was analysed using multiple regressions to fit the quadratic model through Analysis of Variance (ANOVA) to study the significance of each experimental parameter and their interactions during the EDS process. The response surface models developed were then optimised to determine the required conditions for energy efficient EDS process.

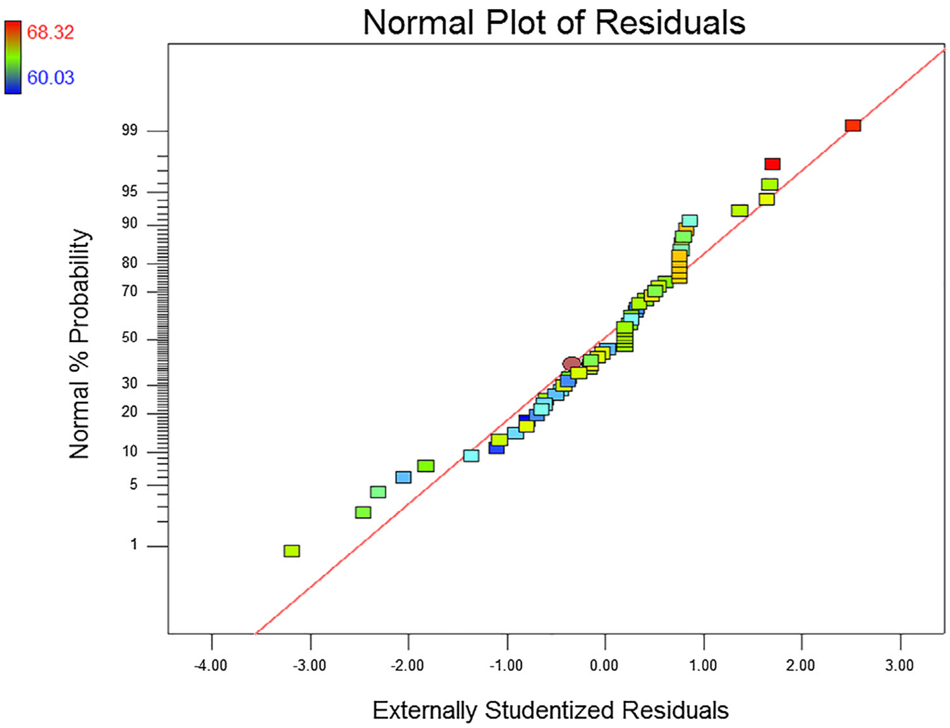

Fig. 1. Normal probability plot of residuals.

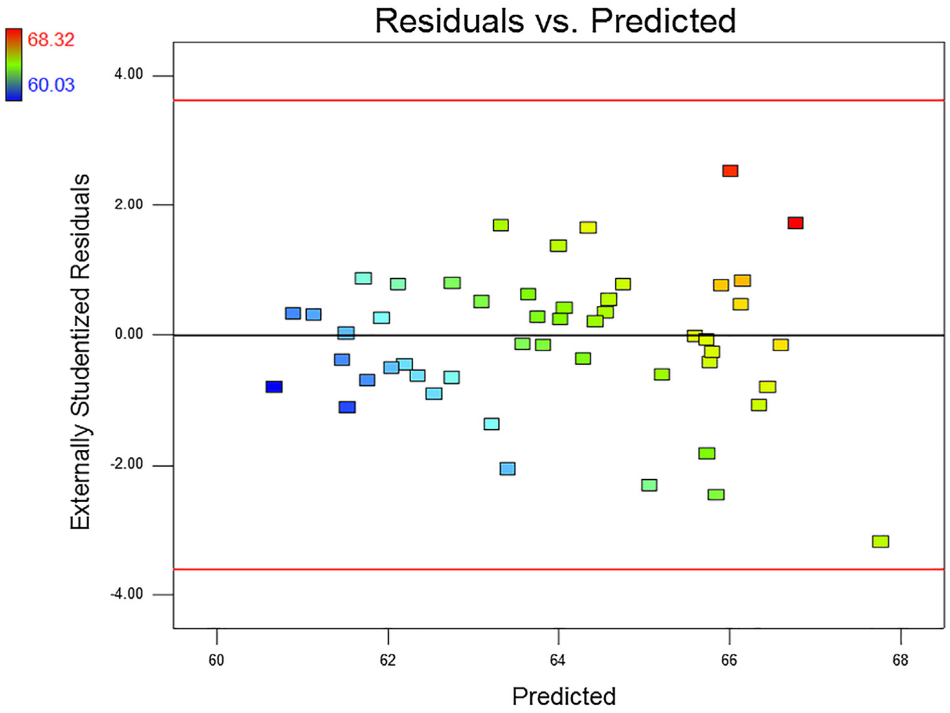

Fig. 2. Plot of residuals versus predicted.

3. Results and discussion

3.1. Model fitting and analysis of variance (ANOVA)

The 59 experimental runs generated by CCD with varying extractive parameters along with experimental and predicted values of percentage removal of DBT are as shown in Table 6.

The effect of each experimental parameter and the correlation with other parameters based on the response above are fitted to the following second order polynomial Eq. (3):

$$Y = +65.17 + 0.045A - 0.14B - 1.49C + 0.21D + 0.74E - 0.15AB + 0.11AC - 0.011AD + 0.12AE - 0.13BC + 0.17BD - 0.16BE + 0.21CD - 0.23CE - 0.056DE + 0.71A^2 + 0.14B^2 + 0.16C^2 - 2.65D^2 \quad (3)$$

where Y is the percentage DBT removal (%); A, B, C, D and E are extraction time, temperature, model oil ratio, extraction temperature and DES ratio respectively. The F-statistic test in ANOVA is used to analyse the statistical significance of the model. The ANOVA results for this

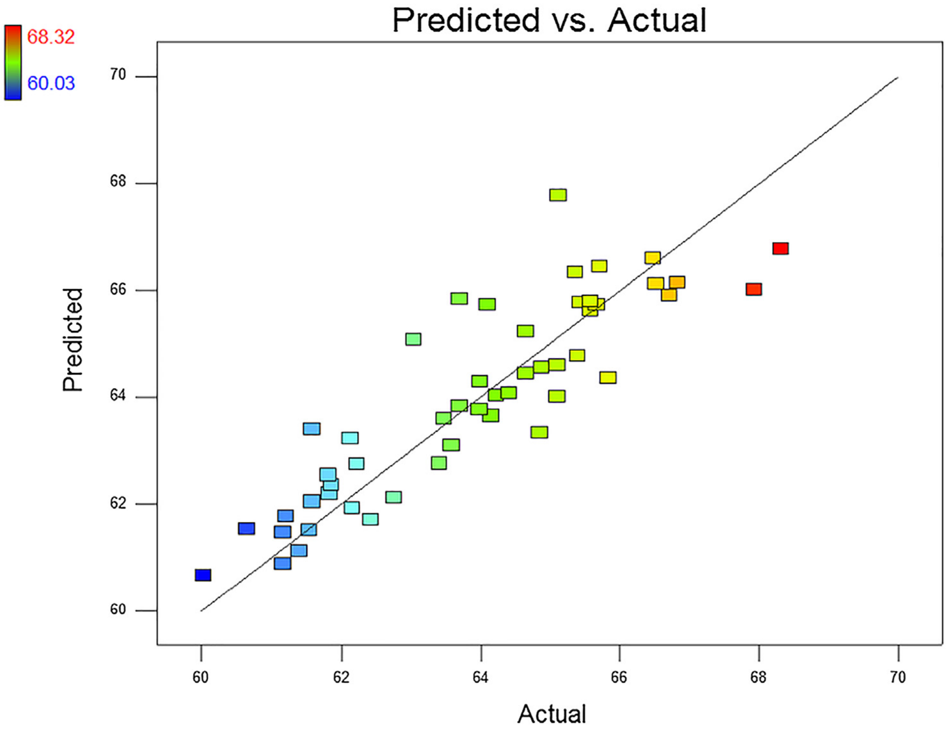

Fig. 3. Predicted against actual values of percentage removal of DBT.

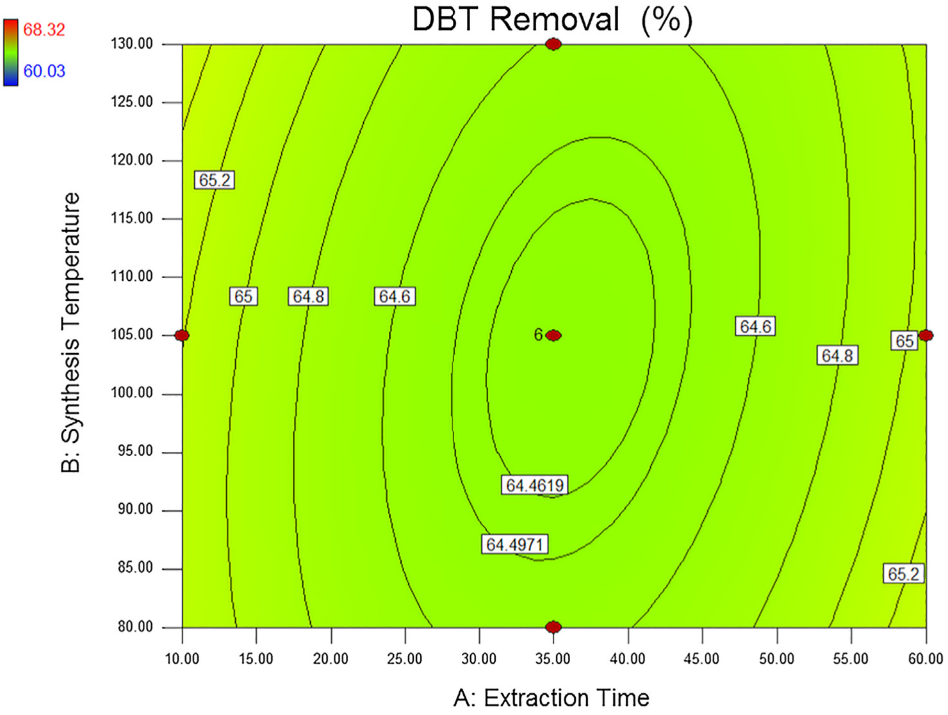

Fig. 4. Contour plots of synthesis temperature and extraction time on percentage DBT removal for DES2.

study is as shown in Table 7. Significance of model terms can be explained by probability (P) > F values. If probability (P) > F values smaller than 0.05 less, it can be said that model terms are significant. Whereas if values greater than 0.1000, the model terms are not significant.

Table 7 shows that the chosen quadratic model is significant as it has a Prob > F of < 0.0001. The significant extractive parameters are C, E and D^2, as they have (Prob > F) value of < 0.05, which shows 95% of confidence level. The adjusted and predicted R-squared are also in reasonable agreement with difference < 0.2, ensuring the model provides good predictions for the outcomes.

Fig. 1 shows the normal plot of residuals, all data seem to follow a normal distribution indicating no abnormality in data. Fig. 2 shows the residuals vs predicted values, as it is randomly scattered across plot it indicates constant variance in the data set. Fig. 3 shows the predicted versus actual value of percentage removal of DBT, which shows that they are in good agreement.

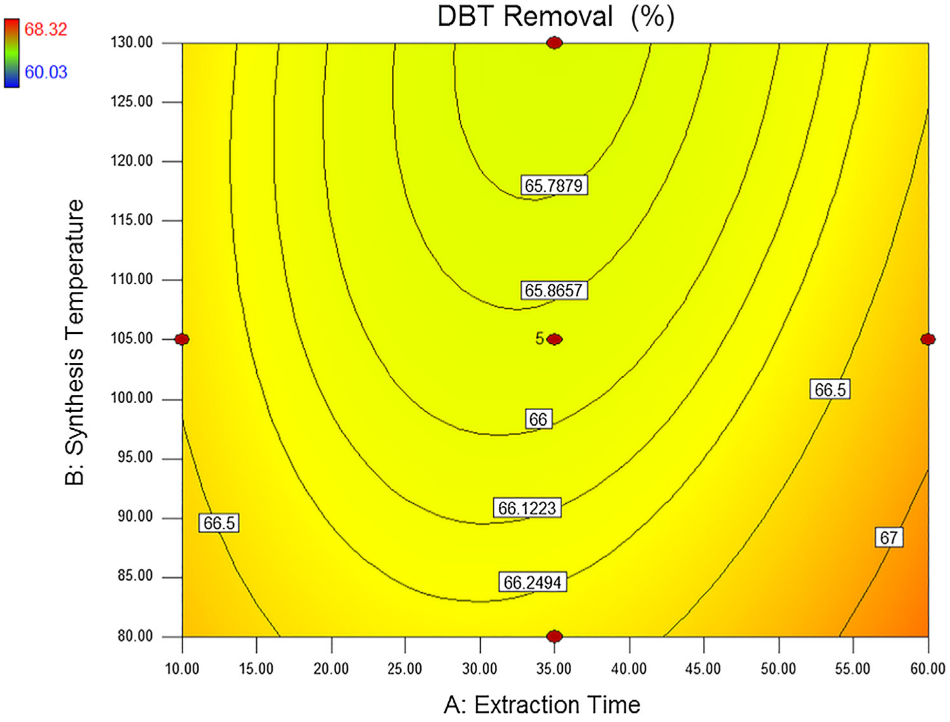

Fig. 5. Contour plots of synthesis temperature and extraction time on percentage DBT removal for DES3.

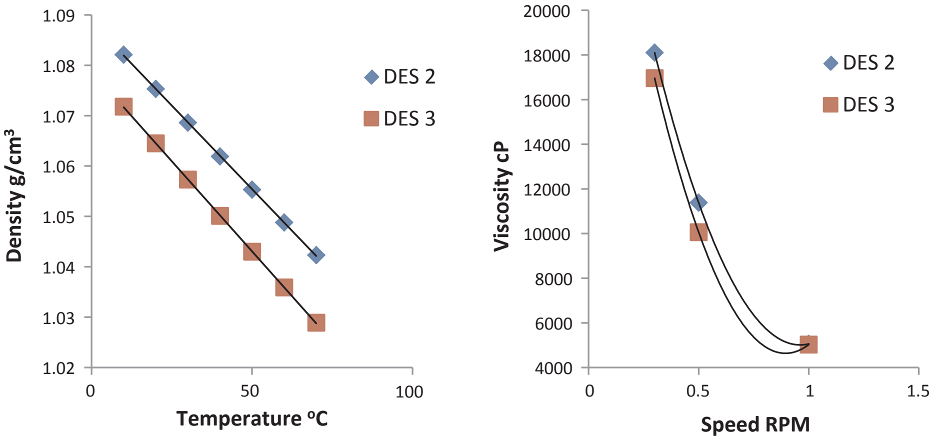

Fig. 6. Effect of temperature speed on density and viscosity on DESs.

3.1.1. *Effect of extraction parameters on DES efficiency in desulfurization*

In order to note the effect of the extraction variables, three dimensional response were plotted that showed several trends in response to the studied variables in relation to DBT removal. Synthesis temperature and extraction time showed no notable change in DBT removal efficiency for DES 2 as shown in Fig. 4. The percentage DBT removal was insignificant from 64.6% to 65.2% throughout the entire range that was investigated. A similar result was also observed for DES3 in Fig. 5, there was no significant change in percentage DBT removal with a change in synthesis temperature and extraction time.

Effect of DES ratio revealed that higher composition of HBD resulted in higher desulfurization i.e. DES 3 was more efficient than DES 2. However, both DESs showed efficiencies of above 60% average. The mixing ratios of model oil showed significant trend i.e. at higher model oil ratios removal efficiencies of both DESs were low. Extraction temperature revealed that at lower temperatures high desulfurization was achieved. An increase in temperature lowered the performance of both DESs. These results and trends are similar to other DESs and ILs from several literatures [10,15,17,19].

3.2. *Effect of DES on deep desulfurization with model oil*

3.2.1. *Analysis of physical properties of DES*

Fig. 6 shows Choline-based eutectic solvents physico-chemical properties and similar literatures have produced similar trends on densities and viscosities [20–23]. This phenomenon would probably have resulted due to low viscosity of DES 3 compared to DES 2 hence short time was required to reach equilibrium. Furthermore, these results are preferable for industrial application since shorter reaction times are desired during processing. Heating of DESs causes the ions to vibrate which results to molecular rearrangement in their weak ion-ion interaction and thus reduces the density and viscosity [24].

3.2.2. *Effect of temperature and extraction time on DBT removal*

The temperature is important if the extraction technology is to be applied in industrial situation. In this study, temperature did not have a profound effect on the percentage DBT removal, as observed in the contour plots of Figs. 4 and 5. In most scenarios, higher temperatures do not mean higher extraction possibility. Higher temperatures will

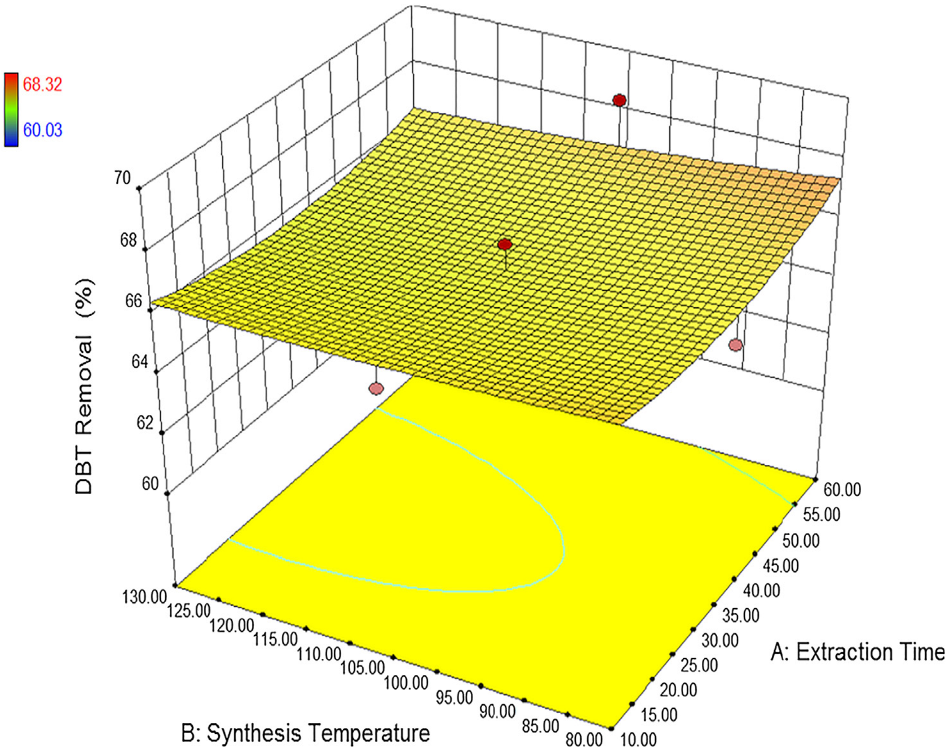

Fig. 7. 3D Response surface plot illustrating the effect of synthesis temperature and extraction time on percentage DBT removal.

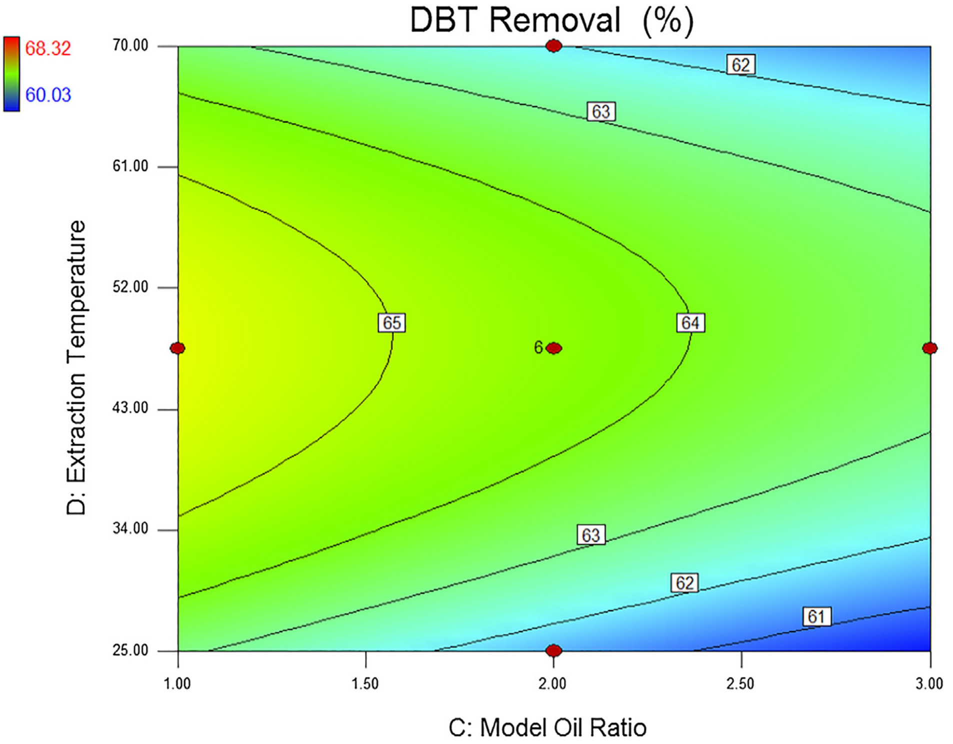

Fig. 8. Contour plot of extraction temperature and model oil ratio at DES = 2 on percentage DBT removal.

account for higher energy costs. With this aspect, it's therefore necessary to choose lower temperatures of 80 °C for synthesis. This result will be of great importance during application in large scale in future. In this study, to observe the extraction effect minimum 10 min and a maximum of 60 min extraction time was selected. Similar to that of temperature, extraction time seem to have no significant effect on the percentage DBT removal as shown in Figs. 4 and 5. This implies that DBT removal could be achieved at a shorter time of 10 min. A combined effect of both extraction time and temperature on percentage DBT removal, showed no significant effect on the percentage DBT removal as shown in Fig. 7. It is also important to mention that DBT removal with time increases steeply initially then a further increase has no significant effect. Similar results were observed by Tang et al. [19] and Li et al. [10] using different DESs. Based on these observations, it can be

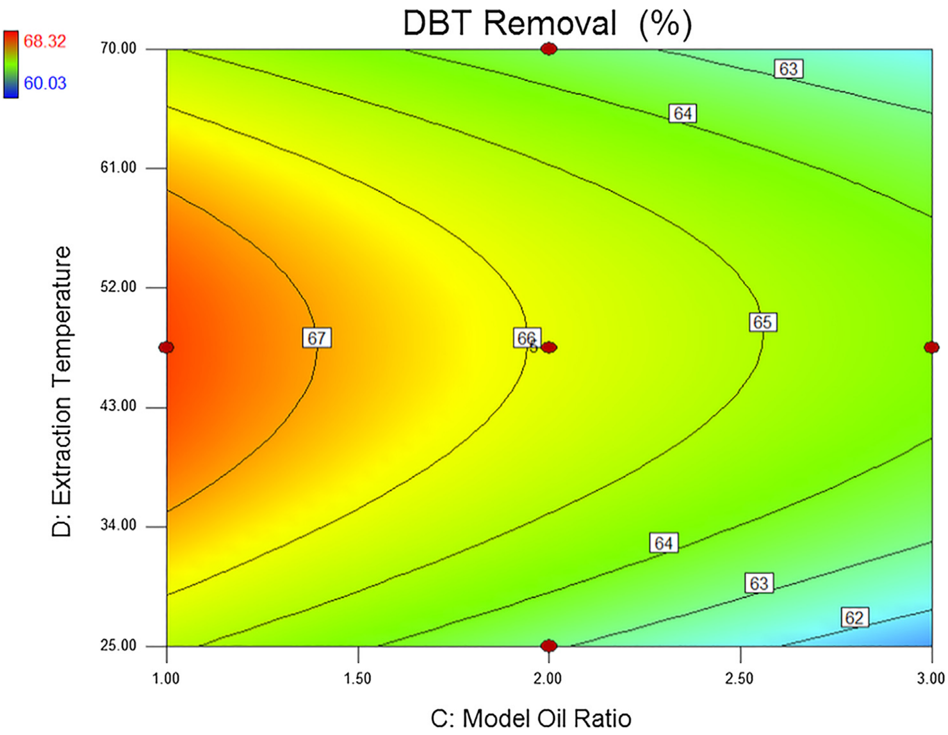

Fig. 9. Contour plot of extraction temperature and model oil ratio at DES = 3 on percentage DBT removal.

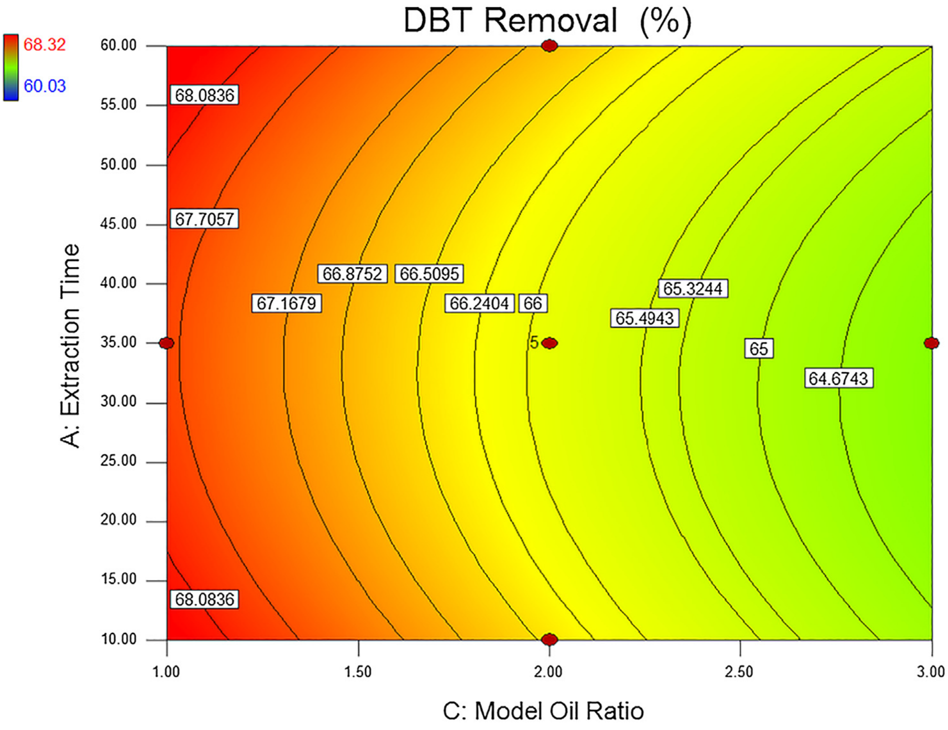

Fig. 10. Contour plot of extraction time and model oil ratio at DES = 3 on percentage DBT removal.

concluded that the extraction equilibrium was reached in 10 min with efficiency up to 68% for DES 3.

3.2.3. *Effect of DES ratio on extraction*

Selection of a suitable DES is also part of this study and also an important factor for desulfurization. From the experimental findings, the amount of HBD i.e. propionic acid has significant influence in the extraction process. This influence is clearly evident through the contour plots in Fig. 8 (for DES 2) and Fig. 9 (DES 3). From Figs. 8 and 9, it can be seen that the percentage DBT removal increased from 65% (DES 2) to 67% (DES 3).

A similar increase in removal efficiency owing to DES ratio was also reported earlier using $FeCl_3$ based eutectic solvents [15]. It is also important to explain that with increase in HBD the carbon atom chains also increases which in turn decreases the hydrogen bond interactions due to steric hindrance [23]. Increasing HBD also lowers density as

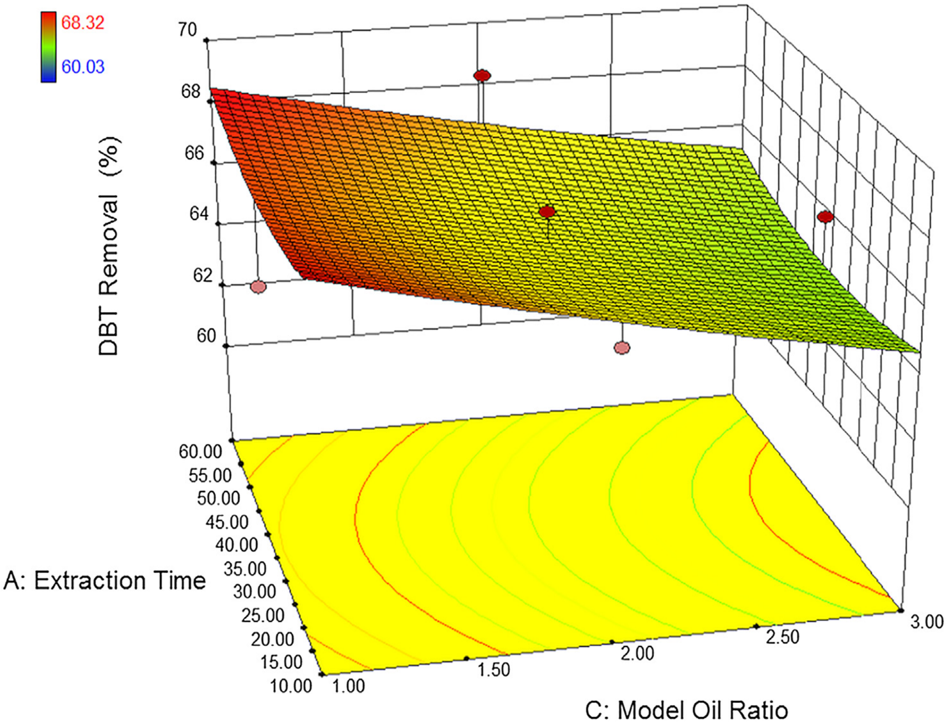

Fig. 11. 3D Response surface plot illustrating the effect of extraction time and model oil ratio on percentage DBT removal.

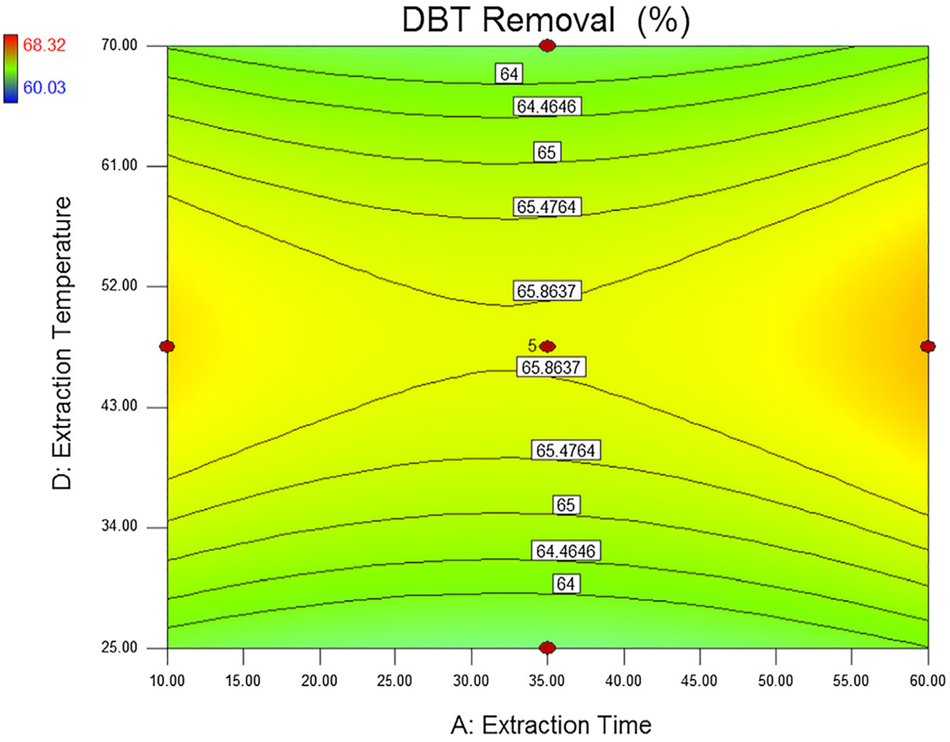

Fig. 12. Contour plot of extraction temperature and extraction time for DES2 on percentage DBT removal.

explained earlier. The HBD wraps around Cl^- anion thus affecting packing structure and provides more active hydrogen for DBT removal. The mechanism of Sulfur removal will be explained in the later section. Similar effect of higher HBD percentage in DES was also reported elsewhere [10,15].

3.2.4. Effect of model oil ratio in desulfurization

Quaternary ammonium-based DESs are less toxic and cheaper in terms of material cost as well as synthesis. It is beneficial that less amount of DES to be used from an industrial point of view to curb cost and attain high extraction. In relation to this, the DES ratio was maintained at 1 while the model oil varied.

Although at minimal ratio of 1:1 with DES 3 showed higher extraction of up to 68% as compared to 1:3 which produced an extraction of 64.6% as observed from Fig. 10. A 3D response surface plot as in Fig. 11, also shows the significant effect of model oil ratio. This means

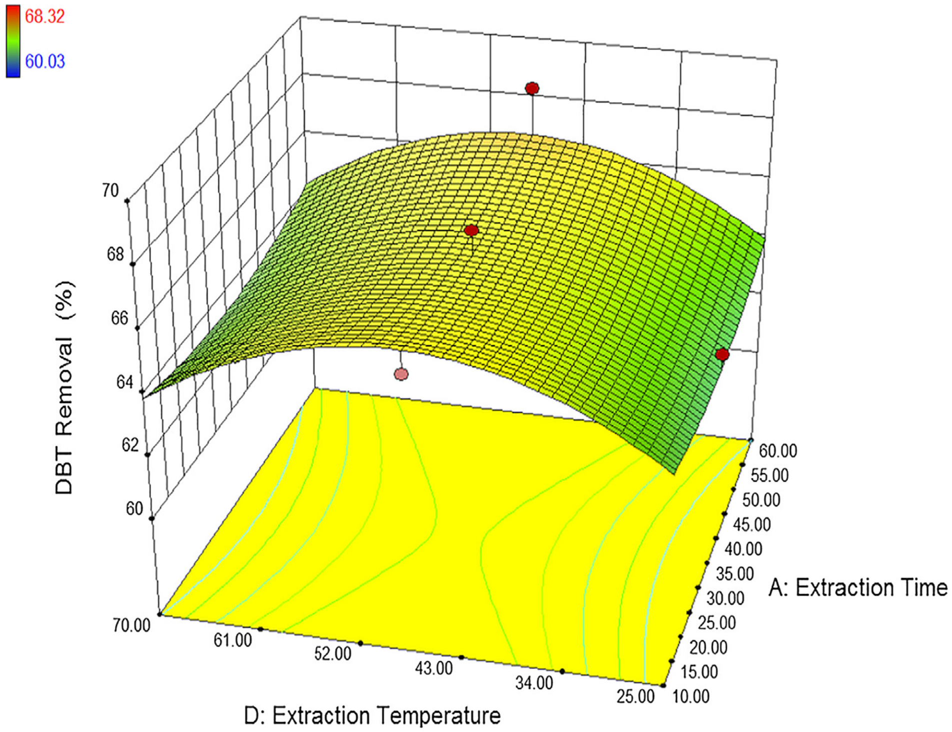

Fig. 13. 3D Response surface plot illustrating the effect of extraction temperature and extraction time at DES3 on percentage DBT removal.

Table 8
Parameters yielding the highest percentage removal of DBT at optimum conditions.

Extraction Time (mins)	10
Synthesis Temperature (°C)	80
Model oil Ratio	1:3
Extraction Temperature (°C)	37
DES Ratio	3

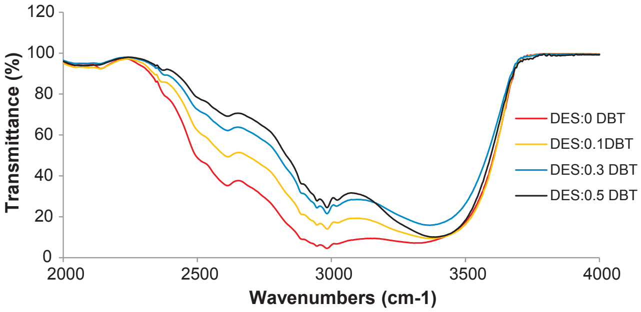

Fig. 14. FTIR of different molar ratio.

increase in amount of DES in extraction has direct influence on DBT removal. However, for economic purpose a ratio of 1:3 would be suitable and excess amount of DES would lead to increase in extraction and recovery process costs. Effect of DES to model has revealed that increase in model oil ratio yielded low DBT extraction as evident from both Figs. 10 and 11. This finding is in agreement with results reported earlier in the literatures [10,14,15,17,18]. The ratio of active hydrogen for desulfurization to amount of model oil could lead to this effect. This best explains as to why higher model oil resulted in low desulfurization.

3.2.5. Effect of extraction temperature on desulfurization

Temperature is one of the main parameters during desulfurization process even with traditional methods i.e. HDS. In order to optimise the process both DES 2 and DES 3 were used at similar conditions but varying temperatures. EDS was conducted from 25 °C to 70 °C to monitor the influence of temperature.

Figs. 12 and 13 shows a stable trend on the effect of temperature during EDS with DES, there is an increase in DBT removal percentage from 64% to 65.8% when temperature is varied from 25 °C to 47 °C. However, with further increase in temperature there was a decrease in percentage DBT removal. The decrease in efficiency was probably due to evaporation of n-Octane at higher temperatures and thus not favourable for EDS. Therefore, lower extraction temperature was suitable since the DES could achieve highest desulfurization. This response can be further attributed to the exothermic nature of acid-base complexation and thus higher temperatures lowered extraction efficiency [25]. In relation to exothermic phenomenon, increasing temperature speeds up electrophilic substitution reaction on the DBT aromatic ring [19]. This indicates that the process could be operated at room temperature as compared to the traditional HDS method that requires up to 350 °C. These results also correspond to similar trends obtained with ILs and DESs from previous published works [10,17,19].

3.2.6. Extraction parameters optimisation

In order to maximize sulfur removal and minimise the resources the conditions for optimisation were set to minimum extraction time, minimum synthesis temperature, minimum extraction temperature, maximum model oil to DES ratio and a range between DES 2 and DES 3. The DOE software was set at these conditions and with the aid of the desirability function optimised solutions were generated. 100 solutions were generated and the one with the highest desirability was selected. The optimised conditions that led to a high percentage DBT removal at approximately 64.9% are as shown in Table 8.

3.2.7. Validation

From the optimised conditions, a validated run was carried out to verify the prediction. An extraction efficiency of 64.9% was achieved with DES 3 at 10 min sonication, 37 °C extraction temperature, synthesis temperature of 80 °C and model oil ratio of 1:3. This experimental result showed similar values as the ones predicted by DOE i.e. 64.07%.

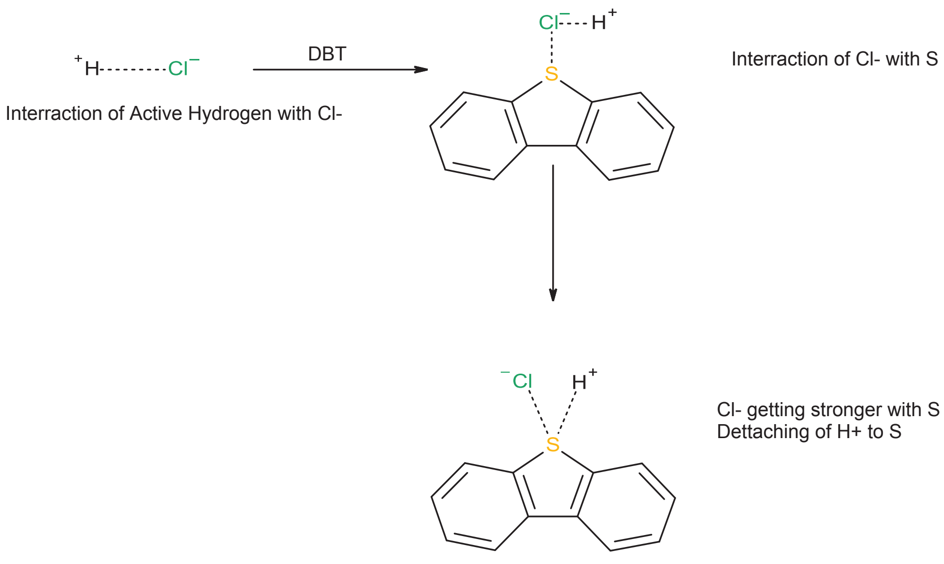

Fig. 15. DBT Extraction mechanism.

Table 9
Recycling of DES without regeneration.

No of Cycle	DESs Used	Sulfur Concentration (ppm)	Sulfur removal (%)
1	DES 3	561.6	64.9
2		635.2	60.3
3		702.4	56.1
4		776	51.5

Temperature = 37 °C; Molar Ratio of Salt to HBD = 1:3; Sonication time = 10 min; Initial Sulfur concentration = 1600 ppm.

The difference between the predicted and the actual result had an error of 0.4% which is allowable. This implies that the model was correct and the solution generated was optimal.

3.3. Extraction mechanism of DBT removal with DES

It is important to understand the extraction mechanism of EDS using DESs. This will be significant for improving the extraction process by enhanced molecule design and development. From the HPLC results it is evident that DBT is removed but it does not tell the effects on the molecular basis. Therefore, FTIR analyses were conducted to study the mechanism.

From Fig. 14, the peak of the carboxyl group gets narrower and narrower with increase in DBT concentration. This could be a result the hydrogen bond in DES that is formed between the Cl^- and active hydrogen H^+, has been destroyed with addition of DBT. This could be resulted by the interaction of H^+ of the DES and the sulfur atom in DBT. Also it can be argued that the interaction of Cl^- with DBT gets stronger and thus destroyed the hydrogen bond in DES itself i.e. interaction with propionic gets weaker. In conclusion, from the above observation that the hydrogen formed between the active hydrogen of DES and the sulfur atom of DBT leads to desulfurization. Fig. 15 explains the chain mechanism suggested elaborating the EDS.

The extractive mechanism has also been suggested by several literatures [10,19].

4. Recycling of spent DESs without regeneration

For industrialization and from the environmental point of view, DES recycling and regeneration are very much needed. Thus, sulfur extraction performance of DESs without regeneration was investigated and the results are presented in Table 9. It is observed that the desulpurisation efficiency of DESs without regeneration was reused up to four cycles. It was seen that the spent DESs was able to remove DBT from fuel even without regeneration, nevertheless, at a lower efficiency of 51.5% from 64.9%, with ratios as 1:3 with spent DESs. Reduction in sulfur removal might be recognized of DBT which dissolved in DESs and decreased the DESs extraction performance. The results indicated that after DESs was recycled four times, the rate of sulfur removal decreases slightly [17]. Therefore, after four cycles it's become nearly saturated and loss sulfur extraction ability and needs to be regenerated.

5. Conclusion

Choline Chloride: Propionic acid DES was used to remove DBT from model fuel oil. The process was successfully modeled and optimised using Design Expert software with RSM technique. The model was tested for validity of prediction and quadratic model was observed to work for the response. It was observed that an extraction sonication time of 10 min, DES synthesis temperature of 80 °C, extraction temperature of 37 °C and molar ratio of 3 was optimum to attain ~65% desulfurization efficiency in one cycle. EDS has a huge potential in pre-refining or post-refining of mid-stream cuts from crude oil distillation. This is going to limit the use of higher operating conditions that are required to attain higher desulfurization by the HDS unit. On other hand, incorporating ultrasound as a means of assisting extraction has shown safe and cheap cost of operation with higher desulfurization rates.

References

[1] US-EIA, Annual Energy Review 2011; 2012.
[2] Gary J, Handwerk G. Petroleum refining : technology and economics. 2nd ed. New York: Marcel Dekker; 1984.
[3] Simanzhenkov V, Idem R. Crude oil. Chemistry 2003.
[4] Kazerooni Mohammad Reza Memar, Farahbod Farshad. Experimental investigation of sulphur removal from LPG: new aspect. J Environ Sci Technol 2016;9:164–9.
[5] Atlas R, Deever R, Us TX, Axel R, Rd B. Method for removing organic sulfur from heterocyclic sulfur-containing organic compounds. US H1986 H; 2001.
[6] Javadli R, Klerk A. Desulfurization of heavy oil. Appl Petrochem Res. 2012;1:3–19.
[7] Kerton F. Alternative solvents for green chemistry vol. 20. The Royal Society of Chemistry; 2009.
[8] Maugeri Z, Domínguez de María P. Novel choline-chloride-based deep-eutectic-solvents with renewable hydrogen bond donors: levulinic acid and sugar-based polyols. RSC Adv. 2012;vol. 2:421. Table 1.
[9] Abinaya K, Sivalingam A, Kannadasan T. Desulfurization of liquid fuels by selective extraction method: a review. Int J Sci Res 2013;2277. 0–3.
[10] Li C, Li D, Zou S, Li Z, Yin J, Wang A, Cui Y, Yao Z, Zhao Q. Extraction desulfurization process of fuels with ammonium-based deep eutectic solvents. Green Chem 2013;15:2793.

[11] Zhang Q, De Oliveira Vigier K, Royer S, Jérôme F. Deep eutectic solvents: syntheses, properties and applications. Chem Soc Rev 2012;41:7108.

[12] Arami-Niya A, Wan Daud WMA, Mjalli FS, Abnisa F, Shafeeyan MS. Production of microporous palm shell based activated carbon for methane adsorption: modeling and optimization using response surface methodology. Chem Eng Res Des 2012;90(6):776–84.

[13] Azargohar R, Dalai AK. Production of activated carbon from Luscar char: experimental and modeling studies. Microporous Mesoporous Mater 2005;85:219–25.

[14] Mokhtar WNAW, Bakar WAWA, Ali R, Kadir AAA. Deep desulfurization of model diesel by extraction with N, N-dimethylformamide: optimization by Box-Behnken design. J Taiwan Inst Chem Eng 2014;45(4):1542–8.

[15] Gano ZS, Mjalli FS, Al-Wahaibi T, Al-Wahaibi Y, AlNashef IM. Extractive desulfurization of liquid fuel with FeCl3-based deep eutectic solvents: experimental design and optimization by central-composite design. Chem Eng Process Process Intensif 2015;93:10–20.

[16] Zhu W, Wang C, Li H, Wu P, Xun S, Jiang W, et al. One-pot extraction combined with metal-free photochemical aerobic oxidative desulfurization in deep eutectic solvent. Green Chem 2015;Il:2464–72.

[17] Dharaskar SA, Wasewar KL, Varma MN, Shende DZ. Imidazolium ionic liquid as energy efficient solvent for desulfurization of liquid fuel. Sep Purif Technol 2015;155:101–9.

[18] Wilfred CD, Kiat CF, Man Z, Bustam MA, Mutalib MIM, Phak CZ. Extraction of dibenzothiophene from dodecane using ionic liquids. Fuel Process Technol 2012;93(1):85–9.

[19] Tang X, Zhang Y, Li J, Zhu Y, Qing D, Deng Y. Deep extractive desulfurization with arenium ion deep eutectic solvents. Ind Eng Chem Res 2015;54:4625–32.

[20] Ciocirlan O, Iulian O, Croitoru O. Effect of temperature on the physico-chemical properties of three ionic liquids containing choline chloride. Rev Chim 2010;61:721–3.

[21] Perkins SL, Painter P, Colina CM. Experimental and computational studies of choline chloride-based deep eutectic solvents; 2014.

[22] Mjalli FS, Naser J. Viscosity model for choline chloride-based deep eutectic solvents. ASIA-PACIFIC J Chem Eng 2015;10:273–81.

[23] Yusof R, Abdulmalek E, Sirat K, Rahman MBA. Tetrabutylammonium bromide (TBABr)-based deep eutectic solvents (DESs) and their physical properties. Molecules 2014;19:8011–26.

[24] Verduzco LF. Density and viscosity of biodiesel as a function of temperature: empirical models. Renewable Sustainable Energy Rev 2013;19:652–65.

[25] Tang X-L, Shi L. Study of the adsorption reactions of thiophene on Cu(I)/HY-Al2O3 by Fourier transform infrared and temperature-programmed desorption: adsorption, desorption, and sorbent regeneration mechanisms. Langmuir 2011;27(I):11999–2007.