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Extractive desulfurization of dibenzothiophene by mixed extractant of N,N-dimethylacetamide, N,N-dimethylformamide and tetramethylene sulfone: Optimization by Box–Behnken design

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Abstract

In this paper, the performance of extractive desulfurization (EDS) from gasoline was studied using a mixed solvent, which consisted of N,N-dimethylacetamide (DMAC), N,N-dimethylformamide (DMF) and tetramethylenesulfone (TMS). The effects of relevant parameters on EDS including volume ratio of DMAC/DMF/TMS, extraction temperature, extraction time, stirring speed, volume ratio of extractant and gasoline and initial concentration were investigated. The extraction removal of dibenzothiophene (DBT) and the residual sulfur content reached 99.1% and 9.5 ppm, respectively, at an optimal extractive condition of volume ratio of DMAC/DMF/TMS of 3:1:1 and volume ratio of extractant to gasoline of 1:5 at a stirring speed of 100 rpm over 10 min for extraction at 30°C (ambient temperature) with five extraction stages. The DMAC/DMF/TMS extractant could be reused several cycles while maintaining high sulfur removal before being regenerated through adsorption. The impacts of three individual process variables such as, extraction time, extraction temperature and volume ratio of extractant to gasoline were investigated using Box–Behnken experimental design and their optimum values were found to be 15 min, 37°C and 0.5, respectively. These results can be referred for sulfur removal from gasoline in industrial applications.

Keywords: Extractive desulfurization; Mixed solvent; N,N-dimethylacetamide; N,N-dimethylformamide; Tetramethylene sulfone; Dibenzothiophene

1. Introduction

The deep removal of sulfur-containing compounds from fuel oils has attracted wide interests due to the stringent environmental regulations imposed on sulfur level in gasoline. The sulfur compounds in petroleum can be converted to sulfur oxide (SO_x) and airborne particulate emissions which would lead to serious environmental pollution [1]. Sulfur could also affect the catalytic converter of vehicles and shorten the life span of the internal combustion engine [2, 3]. Therefore, demand for ultra-low-sulfur gasoline is currently huge [4, 5].

Sulfur-containing compounds in petroleum include polysulfides, mercaptans, disulfides, thiophene (TH), dibenzothiophene, benzothiophene (BT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and their alkylated derivatives. These compounds are very difficult to be removed from fuel. As a traditional desulfurization technology which has been applied conventionally in industry, hydrodesulfurization (HDS) is facing a huge challenge in meeting new stringent regulations and legislations [2, 6]. This classical process consumes hydrogen, and must be operated at high temperature and pressure [7, 8]. Therefore, it is highly desired to develop non-HDS methods to produce clean diesel containing extremely low concentration of sulfur under mild conditions and also with low cost. Among ways that has been investigated, EDS has received much attention due to its advantages such as mild operating conditions and no consumption of H_2 [6, 9]. EDS is principally based on better solubility of sulfur compounds and aromatic hydrocarbons compared with nonaromatics in appropriate polar solvent [10, 11]. Also, it does not change the chemical structure of the compounds and consequently has no effect on the quality of liquid fuels [9]. Importantly, EDS performs high desulfurization efficiency [12]. In the field of oil recovery, Hu et al. [13] reported that the solvent extraction as a part of key technology performed good result.

Organic solvents have attracted much attention in the field of extractive desulfurization, because of their low viscosity, unique physical chemical properties and high regeneration efficiency. Different organic solvents, such as dimethyl sulfoxide (DMSO), acetonitrile and 1-methyl-2-pyrrolidinone (NMP) have been used as extractive solvents in desulfurization [11]. Nevertheless, the commonly used solvents are of high toxicity, expensive, ineffective and they have serious consequences for the environment. Therefore, it can be of great significance to explore new cheap, effective and recyclable solvents to improve the extractive desulfurization process.

N,N-Dimethylacetamide (DMAC) is a colorless and transparent nonproton solvent with high polarity [14]. It has an applicability over a wide temperature range owing to its high boiling point (>160°C). It has been widely used in industries because of its numerous excellent properties, such as good solubility, high hydrothermal stability, difficult hydrolysis, and so on [14]. Another extractant of N, N-dimethylformamide (DMF), is an aprotic solvent and the boiling point is 153°C. Pioneer works reported DMF solvent as an excellent polar solvent for various classes of compounds, the dissolution being favored by interactions of the substrate with DMF [15-17]. Mokhtar et al. [6] found that the utilization of DMF for the desulfurization of DBT achieved a good result. Tetramethylene sulfone (TMS) is a polar solvent with rather good selectivity and the high boiling point of 285°C makes it better thermal stability.

Generally, the multi-extraction system of EDS performs a better desulfurization at a shorter extraction time, lower stirring speed, and especially higher sulfur extraction efficiency than single extraction. An explanation for this is the cooperative formation mechanism among extractants. Hassan et al. [18] claimed that DMF exhibited more efficient extraction solvent characteristics in the addition of ethylene glycol.

In this study, the extractive desulfurization was developed, which was conducted by

DMAC, DMF and TMS. Their mixture was treated to be the primary extractant. Our study provided an example of the mixed solvent, of which we particularly focus on the positive effect in the extractive desulfurization. Effects of some important paramet rs on desulfurization were investigated. A Box–Behnken design was applied to determine the optimum S-extraction efficiency and yield rate, and also to explain the relations between sulfur removal and three pertinent parameters, namely, extraction time, temperature and solvent/model gasoline volume ratio.

2. Experimental

2.1. Materials

All the chemicals were of analytical grade and used as received. DBT (>98%) was the product of Beijing Bailingwei Technology Co. Ltd. (China); BT (>98%) was the product of Beijing Bailingwei Technology Co. Ltd (China); n-octane was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (China); DMAC was purchased from Tianjin Fuyu Fine Chemistry Co. Ltd. (China); DMF was purchased from Sinopharm Group Chemical Reagent Co. Ltd. (China); TMS was obtained from Shanghai Crystal Pure Reagent Co. Ltd. (China).

2.2. Procedures

The model gasoline was prepared by dissolving certain amount of DBT in n-octane to obtain a solution with initial sulfur concentration of 1000 ppm, and then the solution was submitted to the extractive conditions, as described below. The mixed extractant was prepared by DMAC, DMF and TMS with the volume rate of 3:1:1.

The extractive experiments were carried out at atmospheric pressure, at a constant temperature (between 30 and 60^{o}C), in an Erlenmeyer flask (100 ml). Then the reactor was placed in a stirred thermostatted shaker. The typical extraction procedure was as follows: 10 mL of model gasoline and the calculated volume of mixed extractant were mixed together in different volume ratios of mixed extractant and gasoline (0.5-2.5). Following this, the binary mixture was stirred at 100 rpm, stopped at desired time intervals and sampling was conducted for further quantification. The extraction time ranged from 2 min to 20 min, then held for 15 min.

To achieve ultra-deep desulfurization, same process could be repeated several times with the total amount of extractant remaining unchanged. This experimental procedure consisted of extraction and separation, which was modified from the procedure established by Mokhtar et al [6]. The used extractant was reused several cycles for fresh gasoline and then regenerated by a simple adsorption method. All experiments were repeated three times to secure reproducibility of results.

2.3. Analysis

DBT and BT concentration in samples were analyzed using gas chromatography (GC) (Agilent 6890 N, USA) equipped with a flame ionization detector (FID, HP6890). A HP-5 capillary column (30 m×0.32 mm×0.25 μm film thickness) was used for separation. Highly purified nitrogen (mass concentration≥99.9999%) was used as carrier gas.

The sulfur removal was calculated to evaluate the activity of the ternary extraction system. Reaction rates equations for extractive desulfurization was calculated using Eq. (1), where η is the extraction rate, and C_0 and C_t represent the initial and final sulfur content in model gasoline, respectively.

$$\eta = \left[\left(C_0 - C_t \right) / C_0 \right] \times 100\% \tag{1}$$

Yield rate of model gasoline equation is shown in Eq. (2), in which λ is the yield rate, and m_0 and m_t stand for the initial and final weight of model gasoline, respectively.

$$\lambda = \left[\left(m_0 - m_t \right) / m_0 \right] \times 100\% \tag{2}$$

2.4. Experimental design

The DBT removal and gasoline yield rate were optimized by response surface methodology using Box–Behnken design (BBD). The statistical software Design Expert 8.0.5 was used for the analysis. Three independent parameters, extraction time, X_1 (2–20 min), extraction temperature, X_2 (30–60^{o}C) and solvent/model gasoline volume ratio, X_3 (0.5–2.5) were confirmed to optimize the DBT removal and yield rate. The coded and uncoded levels of these variables were presented in Table 1. With statistical analysis of the gained experimental data, a quadratic equation (Eq. (3)) was attained as an empirical model for the optimization process.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j \tag{3}$$

where Y is the response, β_0, β_i, β_{ii}, and β_{ij} are coefficients of the intercept, linear, square and interaction effects, respectively. The optimum response (Y_{opt}) and the corresponding process parameters were also determined. The statistical significance of the model and the coefficient were analyzed by F-test and P-value, respectively.

3. Results and discussion

3.1. Effects of different extractants on DBT removal

Effects of five different kinds of tranditional organic polar solvents applying to extractive desulfurization on DBT removal were evaluated at the following conditions: extraction temperature of 30°C, extraction and holding time were 10 and 15 min, respectively. The stirring speed of 100 rpm, volume of the model gasoline was 10 mL and volume ratio of extractant and gasoline was 1.0. In addition, the extraction process of sulfur content was conducted with one stage. As shown in Fig. 1, DMAC exhibited higher extractive activity than the other four. However, for EDS, TMS as solvent made the yield rate of the model gasoline exceeding 90.0% and the desulfurization efficiency exceeded 80%. Hereinafter, DMAC, DMF, TMS were chosen as the representative solvents for next investigation.

Next, three kinds of solvents and their mixture (volume proportion of DMAC/DMF/TMS = 3:1:1) had been used to desulfurization, respectively. As can be seen in Fig. 2a, a favourable effect of the mixed extractant was obtained with the highest sulfur extraction efficiency of 92.5 ± 3.0% in 10 min. Accordingly, the efficiencies were 88.8 ± 2.8%, 87.8 ± 2.9%, 82.2 ± 2.0% for DMAC, DMF and TMS, respectively. Probably, once they were present as a mixture, synergic effects could be operative, to facilitate the extraction. That is, these results were possibly due to the occurrence of solvent synergism [19, 20]. Therefore, the mixed solvent was selected for the successive experiments.

To evaluate the effect of the volume ratio of DMAC, DMF and TMS on extraction process, the EDS experiments were conducted under different ratios and the results were shown in Fig. 2b. The results indicated that the proportion of DMAC played a most important role on extraction. When the volume ratio of DMAC to total volume was varied from 0.2:1 to 0.6:1, the extraction efficiency was increased and reached up to 93.0 ± 0.8% at 10 min. Meanwhile, the extraction efficiency was increased and reached up to 90.8 ± 0.8% and 86.8 ± 0.4% at 10 min for DMF and TMS, respectively. Hence, the volume ratio of DMAC, DMF and TMS was set at 3:1:1 in the consequent experiments.

3.2. Effects of extraction conditions on DBT removal

3.2.1. Effect of extraction temperature

Reaction temperature is a key parameter during the extractive desulfurization process [21]. Because the melting point of TMS is 27.4-27.8°C, the lowest temperature was set at 30°C. Fig.3a showed the results of the extraction temperature (30°C, 35°C, 40°C, 45°C, 50°C, 55°C, 60°C) on the removal of sulfur. From Fig.3a, the desulfurization efficiency was stable from 30 to 45°C, and a slight decrease was presented when temperature was further increased to 60°C. It can thus be concluded that, the desulfurization efficiency of DMAC/DMF/TMS system was not sensitive to extraction temperature. This result would be very valuable for future industrial applications.

The yield rate of the model gasoline decreased slightly when the reaction temperature increased from 30 to 45°C (Fig. 3a). However, it decreased sharply from 89.7 ± 3.8% to 83.0 ± 1.4% when the temperature was further increased to 60°C. In the meanwhile, it can be seen from Fig. 3b that the yield rate of model gasoline with no sulfur decreased from nearly 100 % to 94.5 ± 0.7% when the temperature was increased from 30 to 60°C. Consequently, evaporative losses of model gasoline were obvious at higher temperatures. Taken together, the temperature of 30°C was suitable for this extraction system of DMAC/DMF/TMS, because this extraction system showed excellent desulfurization efficiency at this point and it was close to room temperature. The similar results had been reported by other published works [22-24]. However, there were different results using some ILs, in which, the extraction efficiencies increased and then decreased with the increase of the temperature [25]. The temperature dependency of extraction with ILs may be attributed to their high viscosity [25].

3.2.2. Effect of extraction time

In order to evaluate the role of the time in extraction efficiency, the DMAC/DMF/TMS extraction system was also performed. From Fig. 4, the sulfur removal efficiency increased fast at first and then gradually increased to the maximum (92.5 ± 3.0%) at 10 min. Meanwhile, the yield rate of the model gasoline shown in Fig. 4 had not a significant change before the first 10 min. As extraction time was slowly increased to 20 min, no notable difference of sulfur removal efficiency was observed, but the yield rate decreased from 90.2 ± 2.3% to 87.5 ± 1.9%. It was attributed to the fact that the extraction equilibrium had been achieved at a shorter extraction time of 10 min. Thus, 10 min was chosen as the optimal extraction time in order to be sure about equilibrium. Kianpour et al. [9] reported that the extraction equilibrium using polyethylene glycol as solvent could be approached within 5 min, but the extraction efficiency was only about 76%.

3.2.3. Effect of stirring speed

In the procedure of extraction desulfurization, the emulsion formation was a sign of the sulfur removal percentage [6]. Given this, the experiments were carried out at different stirring speeds (0 to 250 rpm). As shown in Fig. 5, when the stirring speed was increased from 0 to 100 rpm, the extraction efficiency of DBT rose considerably from 53.4 ± 2.3% to 92.5 ± 3.5%, and the corresponding yield rate decreased from 94.7 ± 1.3% to 90.2 ± 2.3%. At the stirring speed of 0 rpm, DBT-containing n-octane and extractant not mixed thoroughly during the extraction process. As stirring speed was further increased to 250 rpm, the desulfurization of model gasoline did not increase any more, and the yield rate decreased to 75.8 ± 3.3%. A reason of these results was the occurrence of mass transfer resistance and the increasing of solubility. Therefore, the optimum stirring speed was about 100 rpm. Li et al. [26] reported that required stirring speed was set at 500 rpm when ionic liquids were used as solvents for DBT removal.

3.2.4. Effect of solvent/model gasoline volume ratio

In industrial application, it is preferable that a lesser amount of DMAC/DMF/TMS be used but with high extraction efficiency [13]. Otherwise, higher energy costs for distillation and recirculation process were demanded. So the effect of the solvent to model gasoline volume ratio was carried out and the results were presented in Fig. 6. It can be seen that the extraction efficiency of DBT was increased gradually from 86.8 ± 2.9% to 92.5 ± 3.8% with the increase of solvent to model gasoline volume ratio from 0.5:1 to 1:1. Further increase of the solvent /model gasoline volume ratio to 2.5:1 led to 96.6 ± 3.2% of DBT removed. Nevertheless, the yield rate of model gasoline decreased dramatically from 90.2 ± 2.3% to 36.2 ± 2.5% with the increase of solvent /model gasoline volume ratio from 1:1 to 2.5:1. These were possibly due to the occurrence of compatibility of the model gasoline and extractant. Furthermore, excess volume of solvent deserved a higher cost of the extraction and recovery process as well [6]. Thus, 1:1 was chosen as the operation volume ratio throughout the investigation. Kianpour et al. [9] reported that volume ratio of polyethylene glycol to model fuel of 1:1 was selected for the EDS, and Mokhtar et al. [6] found that the DMF/model diesel ratio of 1:1 was the best ratio.

3.2.5. Effect of multiple extractions

As is well-known, extraction stage dominates an important position in extraction, and contributes much more to obtaining the deep higher extraction efficiency. Thus, to attain the deep desulfurization, the DBT extraction in model gasoline with multiple stages was also investigated in this study. In particular, no matter how many times the process was tautologically applied, the total volume of extraction solvent was kept in 10 mL, unchangeably. This multistage extraction strategy was conducted as follows: after single extraction of DBT over 10 min and holding for 15 min, the extractant phase was separated and fresh DMAC/DMF/TMS as the calculated volumes were added in the reactor and this procedure was repeated again and again to make sure the number of necessary extraction times for reduction of sulfur concentration to about 10 ppm. As expected, the activity of the system increased with increasing the extraction stage; noteworthy, a quantitative extraction of sulfur was obtained within five extraction stages, with value of the desulfurization efficiency reaching nearly 99.1% and the corresponding sulfur content was decreased from 1000 to 9.5 ppm (Fig. 7). For each stage, the volumes were 1.2, 0.4 and 0.4 mL of DMAC, DMF and TMS, respectively. What's more, the yield rate did not change appreciably at the various extraction stages. Thus the deep desulfurization of gasoline could be realized successfully. Li et al. [26] concluded that after five cycles of extraction using ionic liquids [DMAPN]-[CO_2Et] and [DMEE][CO_2Et] as extractants, the sulfur content of model oil decreased to 19 ppm, and as previously reported [9], polyethylene glycol exhibited the good extraction efficiency of reducing sulfur content from about 500 to 10 ppm within three extraction stages.

3.2.6. Effect of the initial sulfur concentration

Initial sulfur concentration (C_0) was an important parameter when assessing a certain extraction system, and it could be applied for determining the specific sulfur concentration of fuels [12]. In this segment, the extractive desulfurization of DBT by the mixture of DMAC, DMF and TMS from model gasoline containing different initial concentrations (400–2000 ppm) of sulfur was carried out. From Fig. 8, it showed that no relevant differences in terms of extraction efficiency were observed in the case of different initial sulfur content. It was an interesting finding that differed from the previous extraction desulfurization with polyethylene glycol, in which, the extraction efficiency just partially decreased by increasing the initial sulfur content of model fuel [9], and contrary to the results obtained in EDS with protic ionic liquids [26]. This finding might provide a reference for the industrial application, because wide range of DBT concentrations contained in liquid fuel could be effectively removed in a stable removal efficiency by the system that consisted of DMAC, DMF, TMS with volume ratio of 3:1:1.

3.2.7. Effects of extraction time on removal of thiophene compounds

In the comparative experiment, the sulfur concentrations were kept at 500 ppm by dissolving certain amount of sulfur-containing compound in n-octane for TH, BT, DBT and 4,6-DMDBT, respectively. The results were presented in Fig. 9. It showed that the extraction rate increased as 4,6-DMDBT < TH < BT < DBT. It could be deduced that the extraction of the refractory S-containing molecules depended markedly on the nature of the organo-sulfur molecule, specially on their molecular sizes, electron density and steric hindrance on sulfur atoms [27, 28]. The electron density on the sulfur atom of these sulfur compounds decreases as 4,6-DMDBT> DBT > BT >TH [28]. Consequently, higher electron density on the sulfur atom led to a higher extraction of DBT than that of BT and BT than that of TH. The electron density for 4,6-DMDBT is the highest, but its extraction reactivity is the lowest, which is due to the strict effect from the alkyl groups at the 4 and 6 positions [28, 29]. This reactivity trend reflected the intrinsic properties of the sulfur containing compounds.

3.3. Optimization by Box–Behnken design

The Box–Behnken design was applied in the study and 17-experimental runs were conducted at orders randomly for the optimization of DBT removal and gasoline yield rate in the extractive desulfurization procedure. Table 2 presented the data resulting from the experiments including the coded values of the parameters (-1, 0 and +1), their actual values, and the corresponding responses (predicted values). Three variables of extraction time (X_1), extraction temperature (X_2) and solvent/model gasoline volume ratio (X_3) and the experimental results were analyzed by means of RSM to get an empirical model for the best response. In this procedure, stirring speed and extraction stage remained unchanged at 100 rpm and 1, respectively. The final second-order polynomial was attained to explain the mathematical relation between the independent parameters and the dependent responses (Y). They were presented below:

$$\text{S-extraction efficiency } (Y_1) = 94.92 + 11.44\,X_1 - 1.37\,X_2 + 4.86\,X_3 + 0.25\,X_1X_2 - 0.075\,X_1X_3 + 0.00\,X_2X_3 - 10.52\,X_1^2 - 1.17\,X_2^2 - 3.35\,X_3^2$$

$$\text{Yield rate } (Y_2) = 62.59 - 2.90\,X_1 - 3.70\,X_2 - 30.78\,X_3 + 0.00\,X_1X_2 - 0.40\,X_1X_3 + 0.00\,X_2X_3 - 0.17\,X_1^2 - 3.62\,X_2^2 + 4.26\,X_3^2$$

Additionally, the results related with variance (ANOVA) analysis, shown in Table 3 and Table 4 illustrated the successful fitting of the experiment data to the quadratic model. The model F-values of 3534.98 for S-extraction efficiency and 15209.75 for yield rate implied the model was significant. There was only a 0.01% chance that a "Model F-Value" this large could occur due to noise. This indicated that the assumed second order polynomial (Eq.(3)) was highly significant. Value of P less than 0.0500 indicated model terms were significant. In this case X_1, X_2, X_3, X_1^2, X_2^2 and X_3^2 in Table 3 and X_1, X_2, X_3, X_1X_3, X_2^2 and X_3^2 in Table 4 were significant model terms. From Table 3, extraction time was the most influential parameter for S-extraction efficiency, which achieved18522.68 of F-value. However, solvent/model gasoline volume ratio had a maximum impact on yield rate with F-value of 131600 (Table 4).

The quite high R^2 (R-Sq) values of 0.9998 for S-extraction efficiency and 0.9999 for yield rate indicated that the predicted polynomial model was reasonably well fitted with the data. The predicted R^2 (Pred R-Sq) values of 0.9969 for S-extraction efficiency and 0.9993 for yield rate were in reasonable agreement with the adjusted R^2 (Adj R-Sq) values of 0.9995 for S-extraction efficiency and 0.9999 for yield rate. The comparisons between experimental and predicted values of S-extraction efficiency and yield rate (%) were exhibited graphically with 45°C-lines respectively in Fig. 10.

Very little deviations were discovered between points that represented experimental values and the regression line that represented predicted values.

The significance of each of three independent factors (extraction time, temperature and solvent/model gasoline volume ratio) on S-extraction efficiency and yield rate was determined by illustrating the response surfaces as three dimensional (3D) plots (Fig. 11 and Fig. 12).The solvent/model gasoline volume ratio was kept a constant at 1.5 (Fig. 11a and Fig. 12a), while the extraction temperature and time were kept constants at 45^{o}C (Fig. 11b and Fig. 12b) and 11 min (Fig. 11c and Fig. 12c), respectively. As shown in Fig. 11a, S-extraction efficiency increased with the increasing of extraction time at lower extraction temperature. The highest sulfur removal (>90%) occurred when extraction time and temperature were stayed at about 14-16 min and 36–40^{o}C, respectively. Meanwhile, in Fig. 11b, the variations of extraction time dramaticlly affected the DBT removal, while the variations of solvent/model gasoline volume ratio were less important. Fig. 11c illustrated the effect of extraction temperature and solvent/model gasoline volume ratio on sulfur removal. Obviously, the variation of solvent/model gasoline volume ratio was more important than extraction temperature. Above all, the degree of importance of the three parameters on DBT removal was: extraction time > solvent/model gasoline volume ratio > extraction temperature.

As can be seen from Fig. 12a, the extraction temperature and extraction time had a slight effect on the yield rate. In Fig. 12b, the effect of the solvent/model gasoline volume ratio on yield rate was more significant compared with the extraction time. Fig. 12c demonstrated the influence of extraction temperature and solvent/model gasoline volume ratio on yield rate at the extraction time of 11 min. It was obvious that the variation of solvent/model gasoline volume ratio was more important than extraction temperature. Overall, the degree of importance of the three parameters on yield rate was: solvent/model gasoline volume ratio > extraction temperature > extraction time.

Response optimization technique helped to identify a production of a combination of input variables that collectively optimized a single response or a set of responses. The particular desirability of both the variance and the seal strength was 1.0, which indicated that the combined desirability of these two variables was also 1.0 [30]. In order to obtain the desirability, the factor levels were set at the values given to maximize the S-extraction efficiency and yield rate by adjusting at the starting point of optimization. The values of the process variables for the maximum rate were presented in Table 5. The optimum values of the independent variables were attained by considering the starting values of extraction time, temperature and solvent/model gasoline volume ratio of 10min, 30^{o}C and 1.0, respectively. The maximum S-extraction efficiency and yield rate of 90.2% and 97.3% respectively could be estimated by choosing the optimum extraction time of 15 min, extraction temperature of 37^{o}C with solvent/model gasoline volume ratio of 0.5. Therefore, the RSM could be successfully applied to maximize the DBT removal and yield rate of gasoline. In order to confirm the agreement of the model and experimental results, an additional experiment was carried out under the optimum conditions. The experimental values (91.0% for S-extraction efficiency and 95.1% for yield rate) were in great agreement with the predicted result and thus validated the findings of response surface optimization.

3.4. Reuse of DMAC/DMF/TMS and regeneration of spent DMAC/DMF/TMS

In order to obtain the information on the stability of DMAC/DMF/TMS system, reuse of the spent solvent for extraction desulfurization was investigated. As shown in Fig. 13, extraction capability of DMAC/DMF/TMS system decreased as the increase of repeated use. After three cycles, the desulfurization rates were less than 70% for DBT-octane solution. This indicated that the higher extraction capability of the DMAC/DMF/TMS extraction system was lost and it must be regenerated. However, after three cycles, the extraction efficiency of DBT was about 10 percentage higher than the research which used polyethylene glycol as extractant for desulfurization [9].

The effect of regenerated extractant was important for industrial applications. In general, the extracted polar organic solvent could be recovered by using any conventional separation method, for instance, distillation, adsorption and back-extraction processes [31]. Note that distillation was the main recycling method for ILs, but the cost of this technique was higher [26]. In this context, the spent extractant was regenerated by adsorption method, which was similar to the study of DBT removal by polyethylene glycol [9]. From Fig.9, the extraction ability of the extractant regenerated by powder 4A molecular sieve (volume mass ratio of spent extractant/adsorbent 50:1) increased from 65.0 ± 1.4% to 85.3 ± 1.5% for DBT removal. The results indicated that the regenerated extractant had a very good recycling performance in the desulfurization.

4. Conclusions

The DMAC/DMF/TMS system was highly effective for extraction of dibenzothiophene from gasoline. This system reached high extraction efficiency of 92.5% for DBT at the optimal extractive condition of a volume ratio of DMAC/DMF/TMS of 3:1:1, a volume ratio of the extractant to model gasoline of 1:1 at a stirring speed of 100 rpm over 10 min for extraction at 30°C (ambient temperature) with one extraction stage. The sulfur content reduced from 1000 to 9.5 ppm (99.1%) within five extraction stages, 1:5 of extractant to gasoline by volume for each stage. Moreover, Sulfur extraction efficiency of DMAC/DMF/TMS was nearly independent of initial sulfur content at the above optimal conditions.

The results were verified by Box–Behnken experimental design. Among the three relevant variables (extraction time, extraction temperature and solvent/model gasoline volume ratio), extraction time and solvent/model gasoline volume ratio were the most influential parameters for S-extraction efficiency and yield rate, respectively. The model equation attained using BBD presented the high coefficient of determination ($R_1^2 = 0.9998$ and $R_2^2 = 0.9999$) indicating that the predicted data fitted well with the experimental data. On the basis of the statistical design method, the optimal operation conditions were determined at extraction time = 15 min, extraction temperature =

37°C and solvent/model gasoline volume ratio = 0.5. The experiment for verification was conducted under the optimum conditions and the actual values (91.0% for S-extraction efficiency and 95.1% for yield rate) nearly agreed with predicted values (90.2% for S-extraction efficiency and 97.3% for yield rate).

Then DMAC/DMF/TMS was reused three cycles and spent DMAC/DMF/TMS was regenerated by adsorption method. Regenerated extractant could effectively extract DBT from fresh model gasoline with extraction efficiency of 85.3%.

The DMAC/DMF/TMS extraction system shows the potential to overcome the disadvantages of existing technologies, and could be a cost-effective process for ultra-deep desulfurization.

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Table lists

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Table1 The amount and levels (coded and uncoded) of the independent variables in experimental design.

Independent variables	Range and levels		
	-1	0	1
Extraction time, X_1 (min)	2	11	20
Extraction temperature, X_2 (^{o}C)	30	45	60
Solvent/Model gasoline volume ratio, X_3	0.5	1.5	2.5

Table 2 Box–Behnken design matrix.

Run	Coded values			Actual values			S-extraction efficiency			Yield rate		
	X_1	X_2	X_3	X_1	X_2	X_3	Y_{exp}	Y_{pred}	Residual	Y_{exp}	Y_{pred}	Residual
1	-1	0	1	2	45	2.5	74.35	74.55	-0.20	38.95	39.20	-0.25
2	0	-1	-1	11	30	0.5	86.75	86.91	-0.16	97.65	97.70	-0.050
3	-1	1	0	2	60	1.5	70.20	70.16	0.038	58.2	58.00	0.20
4	0	-1	1	11	30	2.5	96.55	96.64	-0.087	36.2	36.15	0.050
5	1	0	1	20	45	2.5	97.40	97.28	0.13	32.75	32.60	0.15
6	0	1	-1	11	60	0.5	84.25	84.16	0.087	90.25	90.30	-0.050
7	1	-1	0	20	30	1.5	95.75	95.79	-0.037	59.4	59.60	-0.20
8	0	0	0	11	45	1.5	94.90	94.92	-0.020	62.45	62.59	-0.14
9	0	0	0	11	45	1.5	94.80	94.92	-0.12	62.55	62.59	-0.036
10	0	1	1	11	60	2.5	94.05	93.89	0.16	28.8	28.75	0.050
11	1	1	0	20	60	1.5	93.25	93.54	-0.29	52	52.20	-0.20
12	-1	-1	0	2	30	1.5	73.70	73.41	0.29	65.6	65.40	0.20
13	1	0	-1	20	45	0.5	87.90	87.70	0.20	95.2	94.95	0.25
14	-1	0	-1	2	45	0.5	64.55	64.67	-0.12	99.8	99.95	-0.15
15	0	0	0	11	45	1.5	95.10	94.92	0.18	62.5	62.59	-0.086
16	0	0	0	11	45	1.5	94.90	94.92	-0.020	62.68	62.59	0.094
17	0	0	0	11	45	1.5	94.90	94.92	-0.020	62.75	62.59	0.16

Table 3 Analysis of variance (ANOVA) for S-extraction efficiency.

Source	SS[b]	DF[b]	MS[b]	F[b]	P[b]	CE[b]
Model[a]	1797.54	9	199.73	3534.98	< 0.0001	
Time, X_1	1046.53	1	1046.53	18522.68	< 0.0001	11.44
Temperature, X_2	15.13	1	15.13	267.70	< 0.0001	-1.37
Volume ratio, X_3	189.15	1	189.15	3347.81	< 0.0001	4.86
$X_1 X_2$	0.25	1	0.25	4.42	0.0735	0.25
$X_1 X_3$	0.023	1	0.023	0.40	0.5480	-0.075
$X_2 X_3$	0.000	1	0.000	0.000	1.0000	0.000
X_1^2	466.20	1	466.20	8251.37	< 0.0001	-10.52
X_2^2	5.79	1	5.79	102.45	< 0.0001	-1.17
X_3^2	47.18	1	47.18	835.08	< 0.0001	-3.35
Residual	0.40	7	0.056			
Lack of fit	0.35	3	0.12	9.65	0.0265	
Pure error	0.048	4	0.012			
Cor total	1797.93	16				

[a] *R*-Sq = 99.98%; R-Sq (adj) = 99.95%; R-Sq (pred) = 99.69%.

[b] SS: sum of square; DF: degree of freedom of different source; MS: mean of square; F: degree of freedom; P: probability; CE: coefficient estimate.

Table 4 Analysis of variance (ANOVA) for yield rate.

Source	SS[b]	DF[b]	MS[b]	F[b]	P[b]	CE[b]
Model[a]	7879.26	9	875.47	15209.75	< 0.0001	
Time, X_1	67.28	1	67.28	1168.87	< 0.0001	-2.90
Temperature, X_2	109.52	1	109.52	1902.71	< 0.0001	-3.70
Volume ratio, X_3	7576.81	1	7576.81	1.316E+005	< 0.0001	-30.78
$X_1 X_2$	0.000	1	0.000	0.000	1.0000	0.000
$X_1 X_3$	0.64	1	0.64	11.12	0.0125	-0.40
$X_2 X_3$	0.000	1	0.000	0.000	1.0000	0.000
X_1^2	0.12	1	0.12	2.06	0.1939	-0.17
X_2^2	55.12	1	55.12	957.53	< 0.0001	-3.62
X_3^2	76.30	1	76.30	1325.63	< 0.0001	4.26
Residual	0.40	7	0.058			
Lack of fit	0.34	3	0.11	7.20	0.0433	
Pure error	0.063	4	0.016			
Cor total	7879.66	16				

[a] *R*-Sq = 99.99%; *R*-Sq (adj) = 99.99%; *R*-Sq (pred) = 99.93%.

[b] SS: sum of square; DF: degree of freedom of different source; MS: mean of square; F: degree of freedom; P: probability; CE: coefficient estimate.

Table 5 Values of the process parameter for maximum S-extraction efficiency and yield rate.

Parameter	Values
S-extraction efficiency, %	90.2
Yield rate, %	97.3
X_1 (extraction time, min)	15
X_2 (extraction temperature, ^{o}C)	37
X_3 (Solvent/Model gasoline volume ratio)	0.5

Composite desirability = 1.000000.

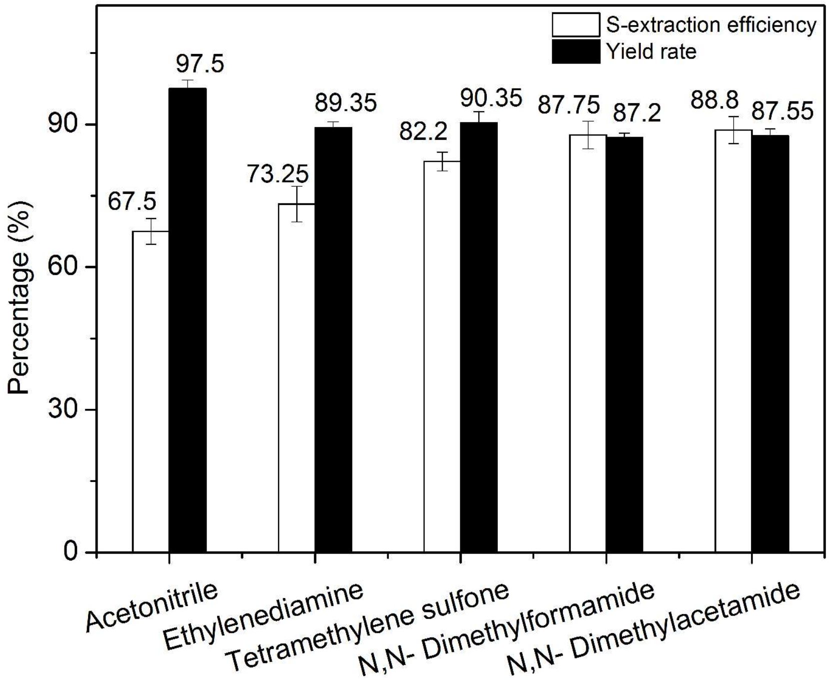
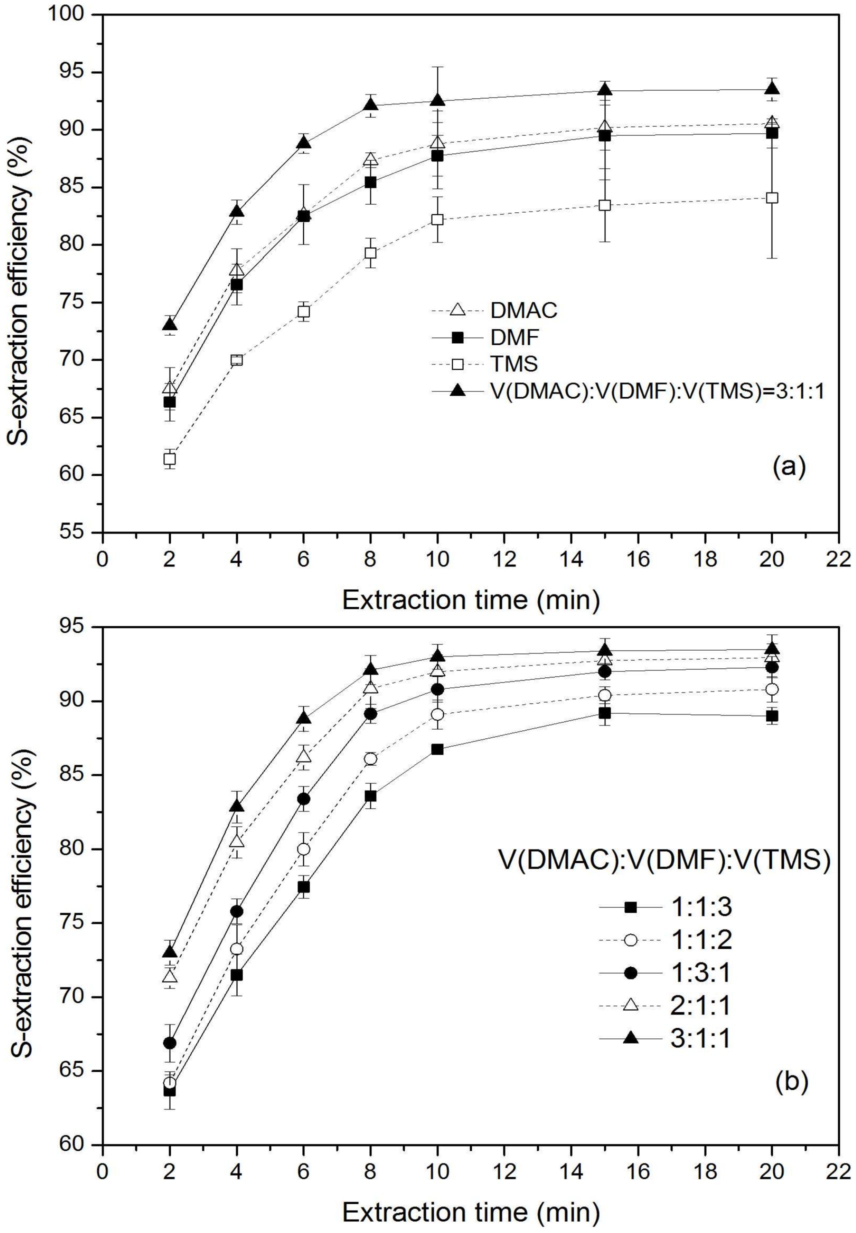


Fig. 1. Influence of extractant types on the extractive desulfurization.



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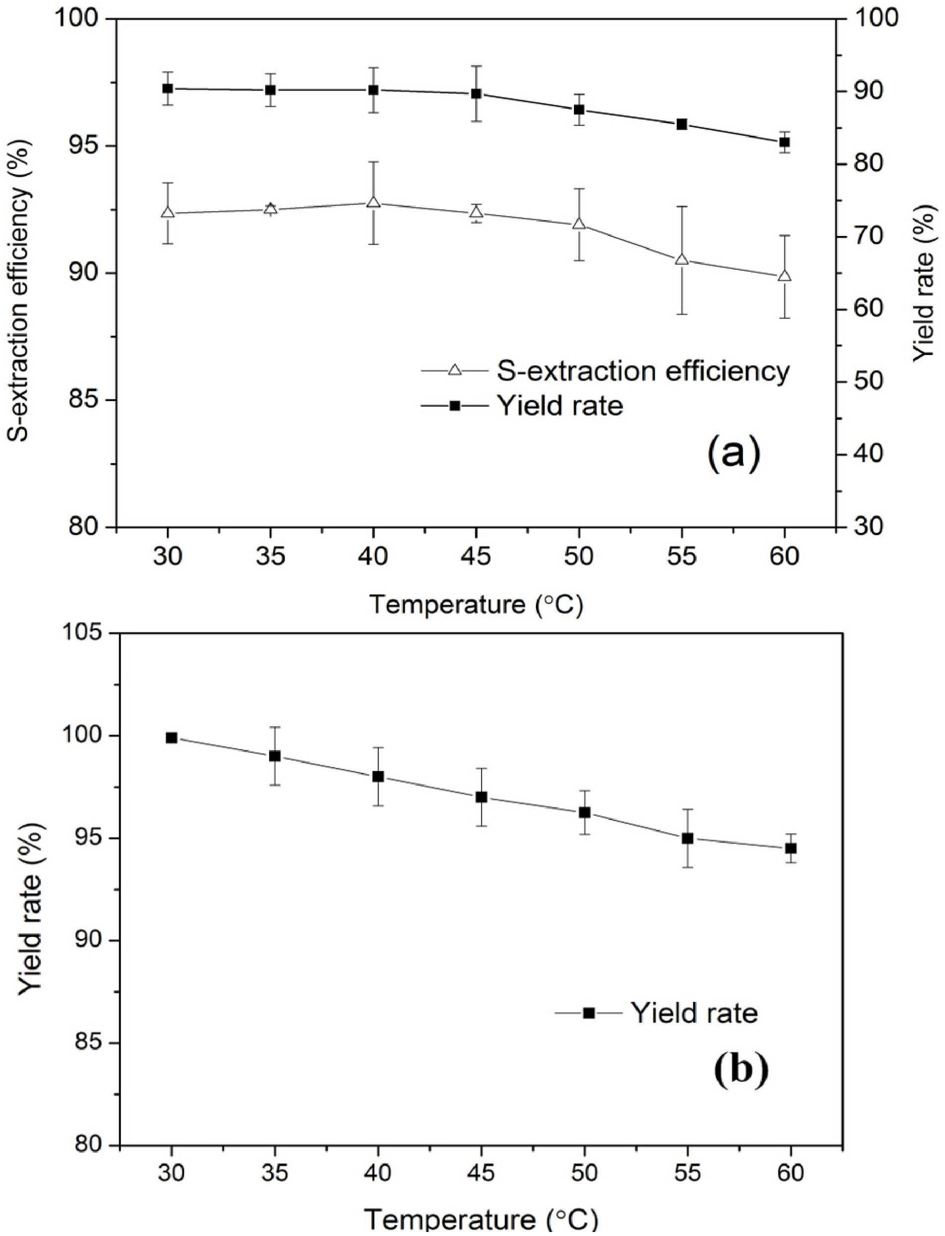


Fig. 3. (a) Effect of extraction temperature on DBT removal. Conditions: solvent/gasoline volume ratio = 1.0, $t_{extraction}$ = 10 min, stirring speed = 100 rpm, number of extraction stage = 1. (b) Effect of temperature on model gasoline (without sulfur) yield rate. Conditions: t= 10 min, stirring speed = 100 rpm.

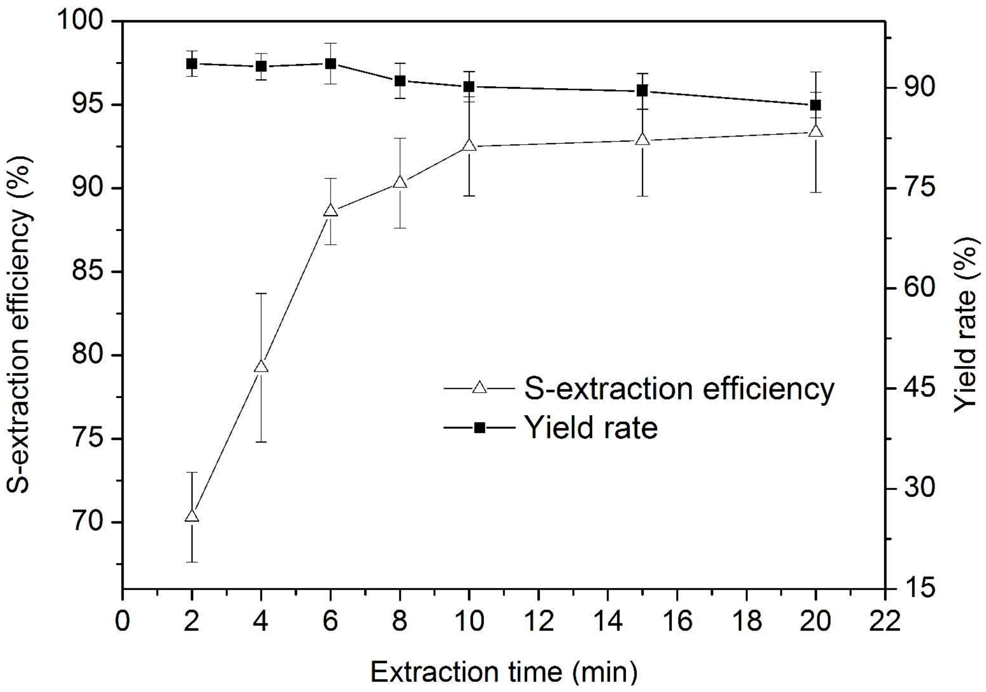


Fig. 4. Effect of extraction time on DBT removal. Conditions: solvent/gasoline volume ratio = 1.0, T = 30°C, stirring speed = 100 rpm, number of extraction stage = 1.

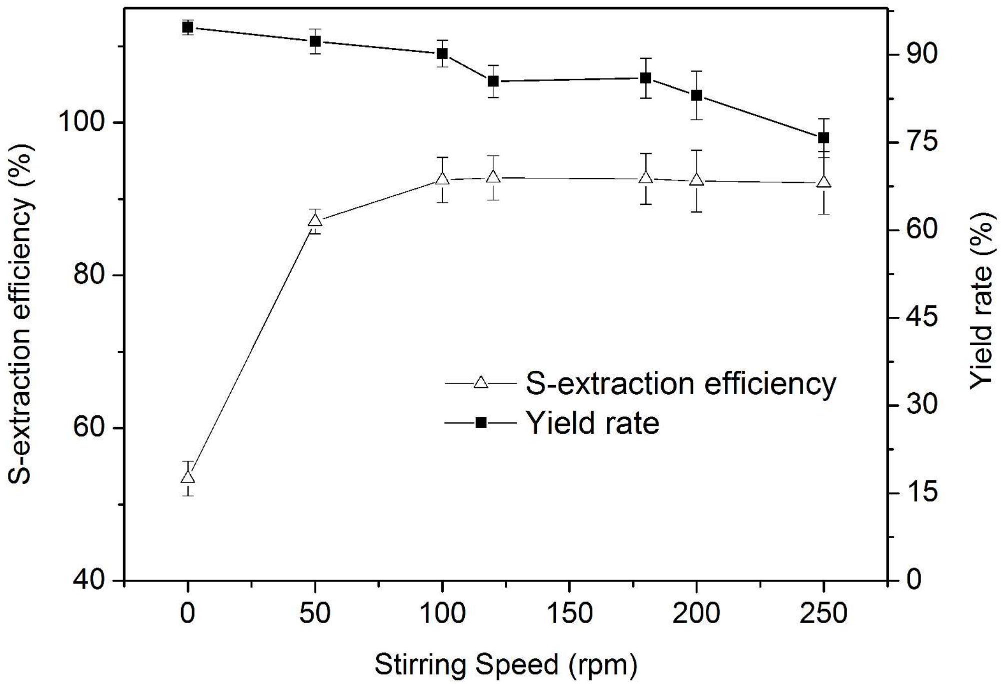


Fig. 5. Effect of stirring speed on DBT removal. Conditions: solvent/gasoline volume ratio = 1.0, T = 30°C, $t_{extraction}$ = 10 min, number of extraction stage = 1.

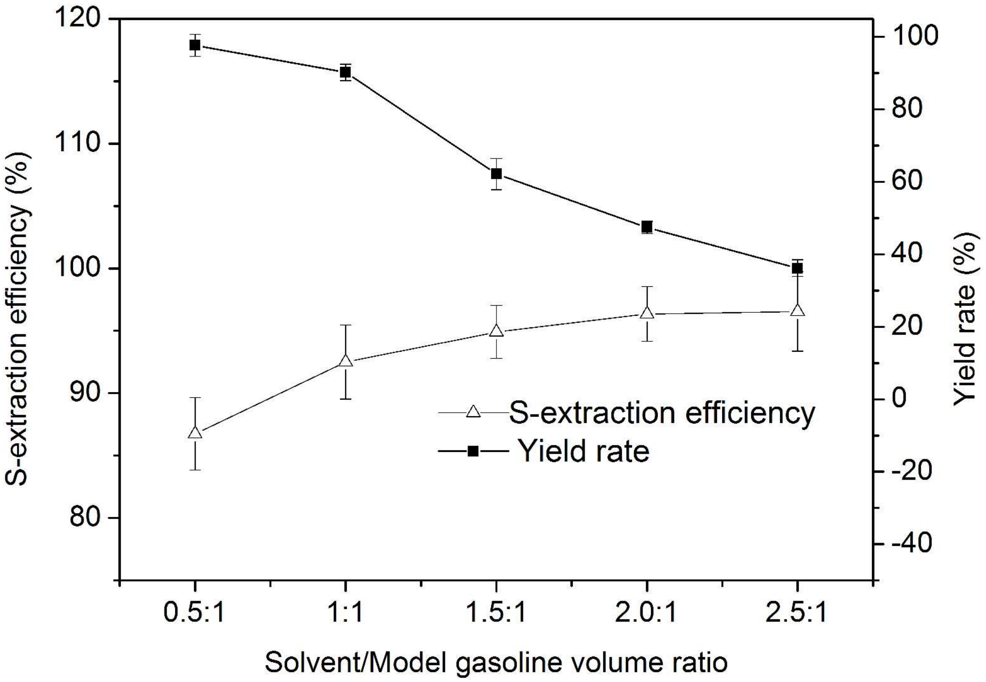


Fig. 6. Effect of solvent/model gasoline volume ratio on DBT removal. Conditions: T = 30°C, $t_{extraction}$ = 10 min, stirring speed = 100 rpm, number of extraction stage = 1.

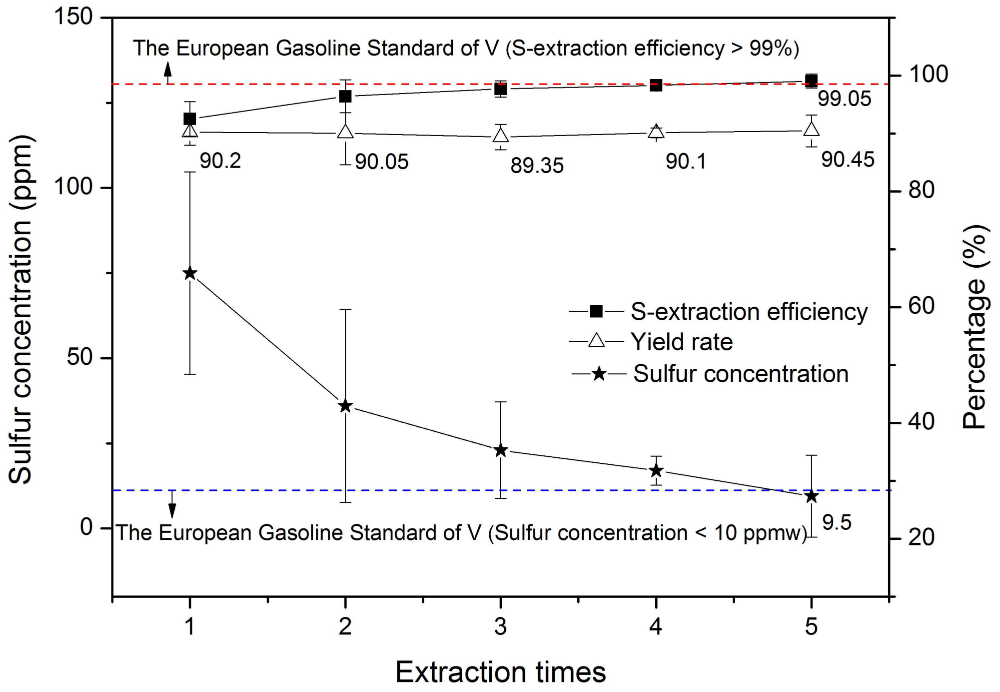
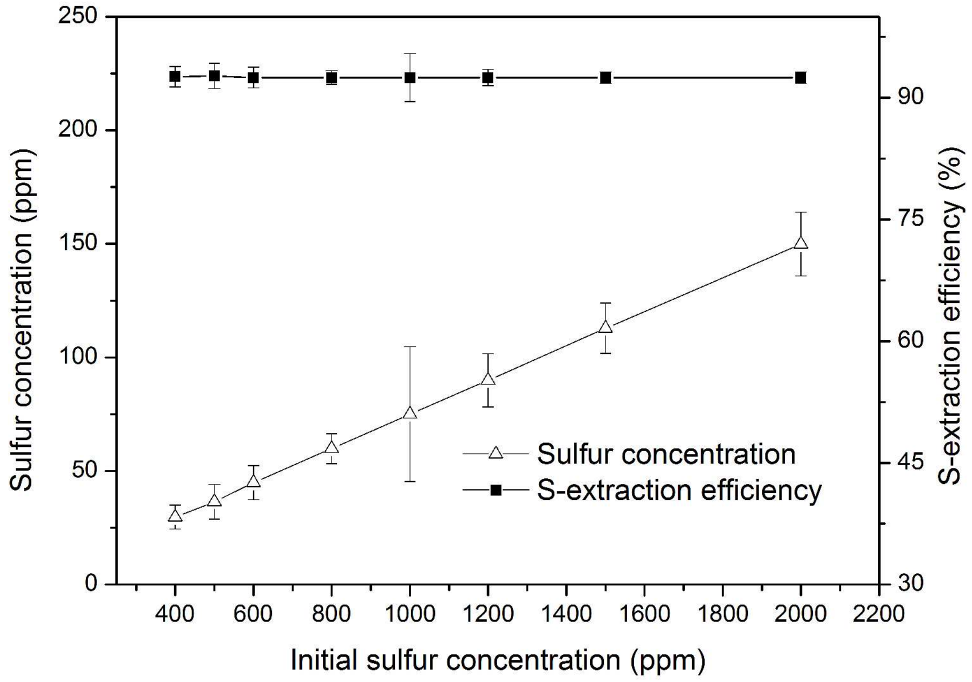


Fig. 7. Influence of multiple extraction stages on desulfurization. Conditions: total volume of solvent/gasoline volume ratio = 1.0, T = 30^{o}C, stirring speed = 100 rpm.



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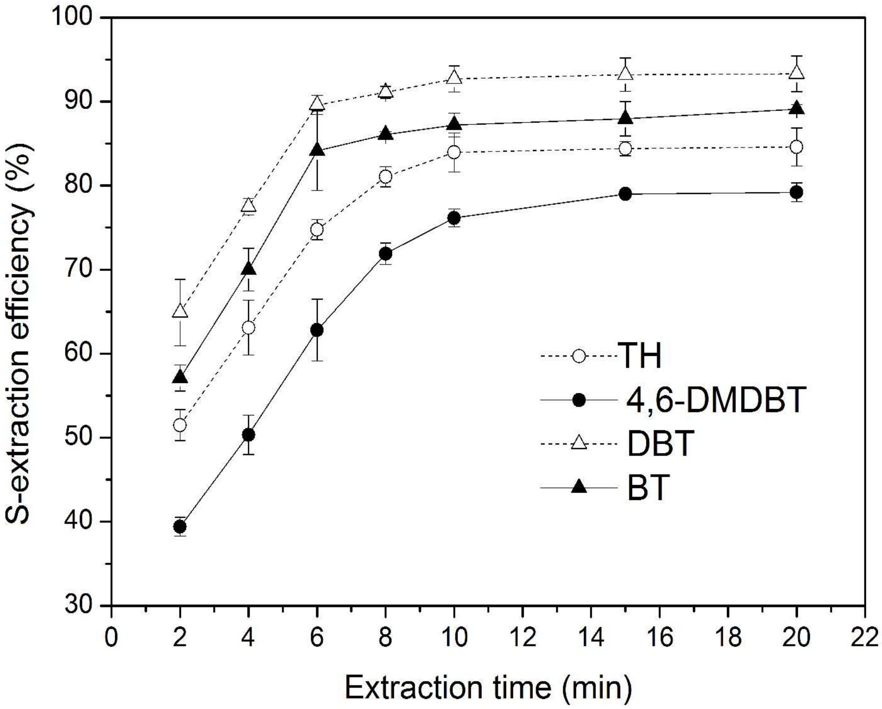

Fig. 9. Effects of extraction time on the removal of thiophene compounds. Conditions: solvent/gasoline volume ratio = 1.0, T = 30°C, stirring speed = 100 rpm, and number of extraction stage = 1.

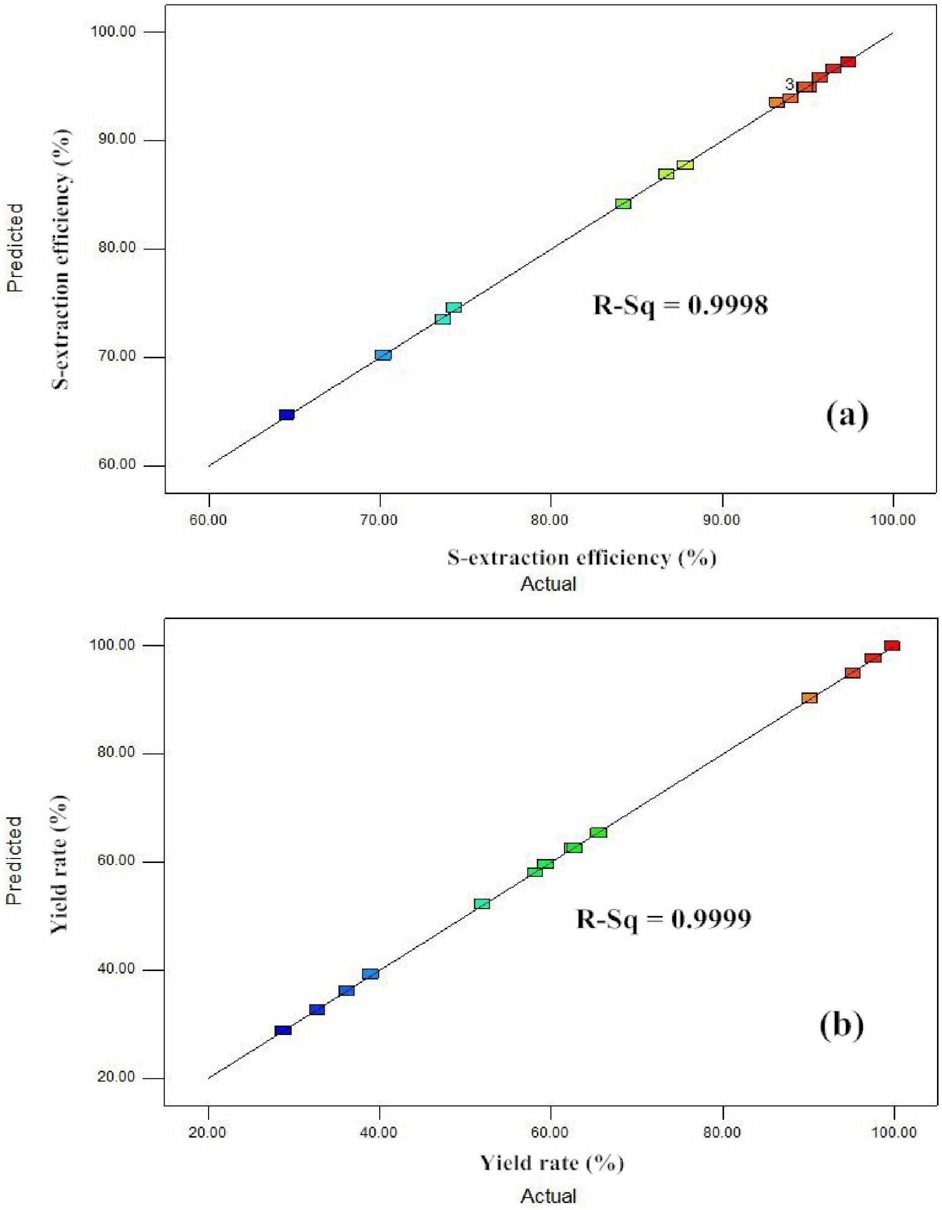

Fig. 10. Comparison of the experimental results of S-extraction efficiency (a) and gasoline yield rate (b) with those calculated via Box–Behnken design (BBD) resulted equation.

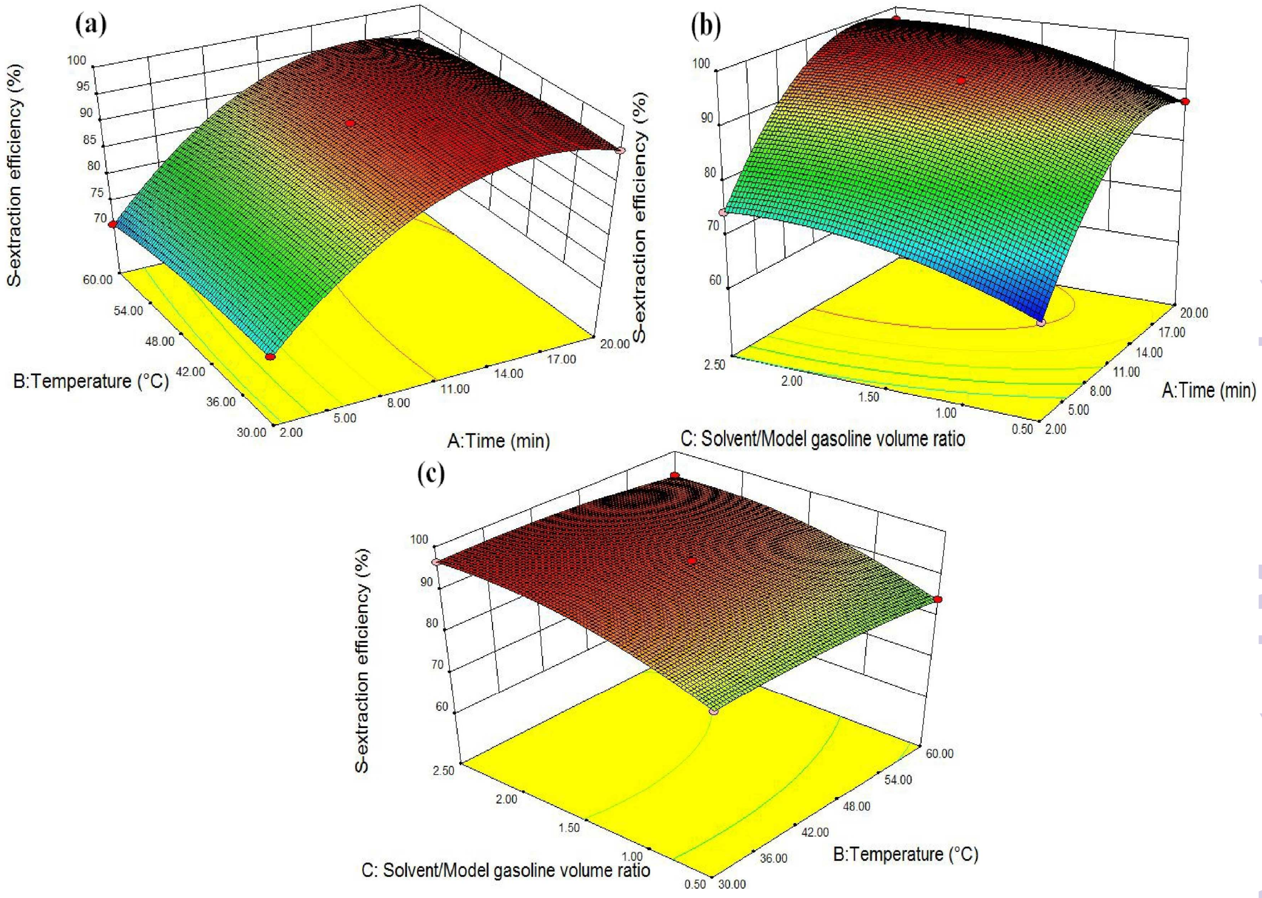

Fig.11. 3D surface plots of DBT removal as a function of (a) extraction time and extraction temperature, (b) extraction time and solvent/gasoline volume ratio and (c) extraction temperature and solvent/gasoline volume ratio.

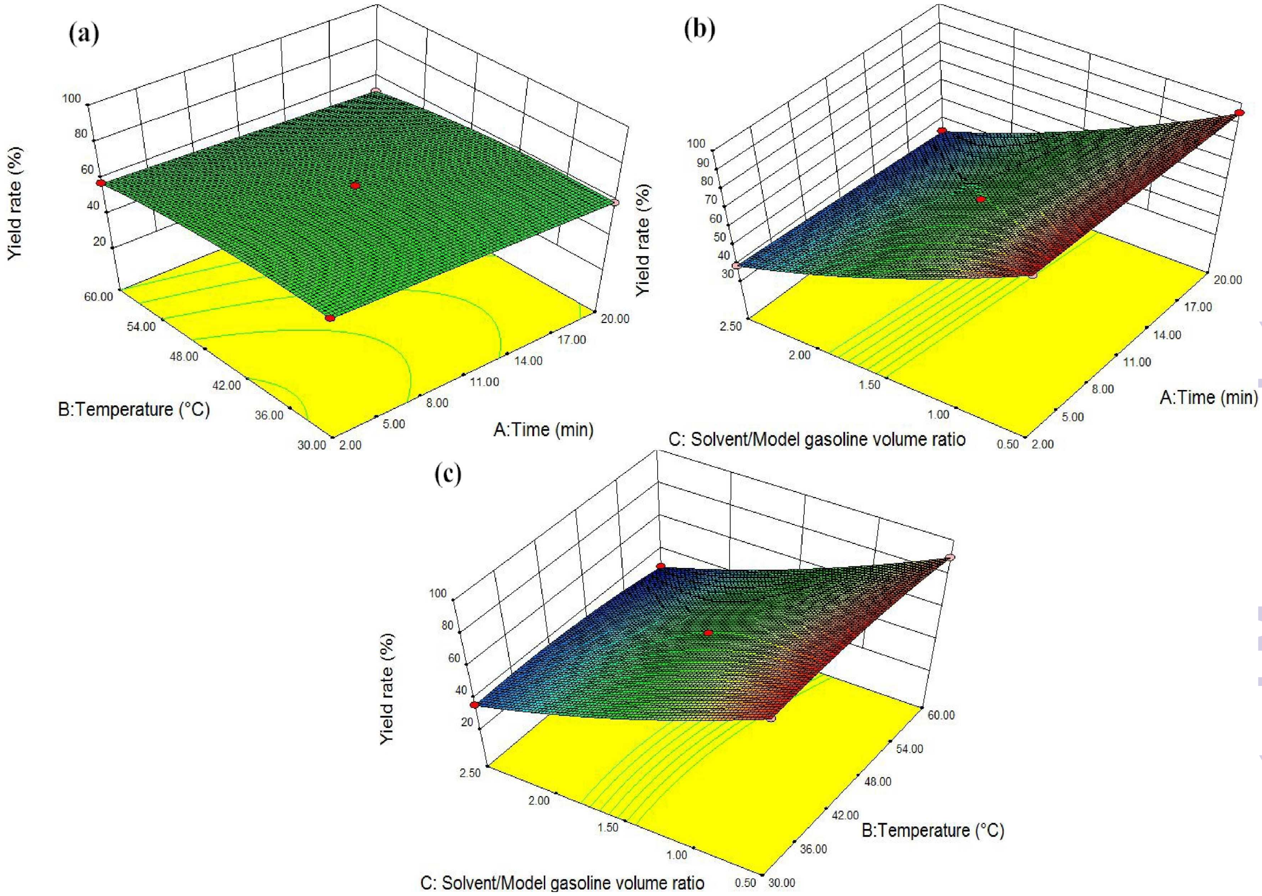

Fig.12. 3D surface plots of yield rate as a function of (a) extraction time and extraction temperature, (b) extraction time and solvent/gasoline volume ratio and (c) extraction temperature and solvent/gasoline volume ratio.

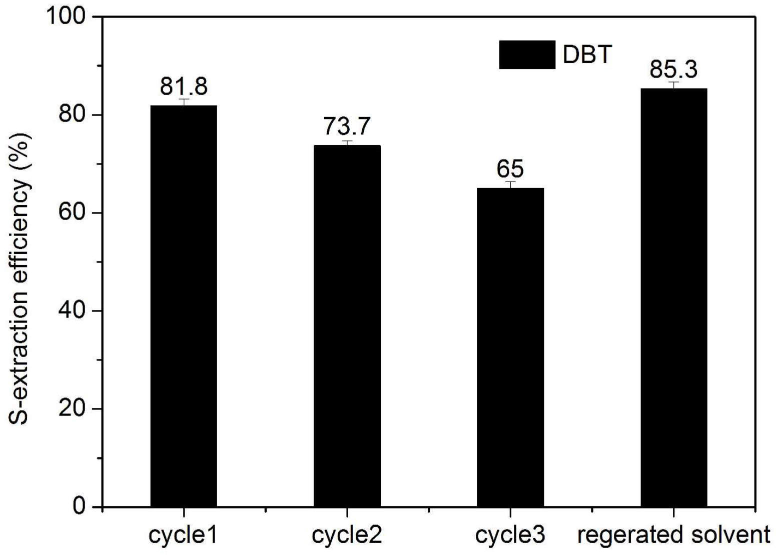

Fig. 13. Extraction efficiencies of DBT by used extractant at different cycles and regenerated spent extractant by 4A molecular sieve. Conditions: volume ratio of used extractant /gasoline = 1:1, T = 30°C, $t_{extraction}$ = 10 min, stirring speed = 100 rpm, number of extraction stage = 1.