Influence of diesel acidification on dibenzothiophene removal: A new desulfurization practice

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Abstract

Commercial diesel is often loaded with organosulphur compounds including hard-to-remove dibenzothiophene DBT and other derivatives. Following uncommon and simple procedure, dibenzothiophene was selectively removed upon diesel acidification by acetic acid prior to activated carbon adsorption. Initially, competitive adsorption tests from synthetic fuel proved that dibenzothiophene is preferentially removed over di/tri and tetra-aromatic hydrocarbons upon fuel acidification by 5% (by vol.) acetic acid. The efficacy of the proposed method was further validated by removing dibenzothiophene from commercial diesel containing 2578 (±15) mg kg−1. The removal of DBT from complex diesel has increased from 27% to 55% upon acidification by 5% acetic acid. Acidity value of the treated diesel is within the regulated limit giving more chance for the new procedure for practical applications.

1. Introduction

The existence of organosulphur compounds OSC in diesel and gasoline fuels can cause toxic emissions and inefficient performance of exhaust catalysts [1,2]. Accordingly, efficient removal of OSC from diesel is an interesting research area and attracted attention many researchers from different specialities [1–3]. OSC are present in most fractions of crude oil distillation, the higher boiling fractions (>270 °C) like diesel contain more sulphur compounds of higher molecular weight [1]. Thiophene T, benzothiophene BT, dibenzothiophene DBT and their alkyl derivatives are the most abundant forms of OSC in diesel [2,3]. Particularly, BT and DBT are making more than 50% of OSC in diesel [3]. Commercially, hydrodesulfurization is the most adopted S-cleaning method from diesel [4]. Recently, oxidative desulfurization and adsorptive desulfurization were applied for removing OSC from diesel and other fuels [5]. The earlier reported methods are either of high cost or even not efficient for removing hardly adsorbable BT and DBT from diesel, hence, this initiated many researches to find alternative solutions for removing OSC [2,6]. Selective removal of OSC including BT and DBT from diesel using metal-loaded zeolite [7], natural aluminosilicates [8,9], and treated activated carbon [10,11] was reported.

The challenge of using commercial activated carbon in desulfurization is the difficulty of removing OSC among other diaromatic/triaromatic compounds which often present in large amounts in diesel [12,13]. Accordingly, selective adsorbents for OSC from diesel are required [2]. For effective OSC removal from diesel, special carbons of acidic nature and high micro and mesopore volumes are recommended [2,13].

In this work, uncommon desulfurization procedure for selective removal of DBT from diesel is proposed. Using model fuel, competitive adsorption of dibenzothiophene from commercial diesel containing 2578 (±15) mg kg−1. The removal of DBT from complex diesel has increased from 27% to 55% upon acidification by 5% acetic acid. Acidity value of the treated diesel is within the regulated limit giving more chance for the new procedure for practical applications.

2. Experimental

2.1. Activated carbon and commercial diesel

A coal-based activated carbon was supplied by Gainland Chemical Company (GCC, UK). Physicochemical tests in our laboratory revealed that the adsorbent has a large specific surface area 985 m²/g, pore volume 0.52 cm³/g, average pore diameter 2.1 nm, surface acidity 0.57 mmol/g, surface basicity 0.83 mmol/g, and pHₚzc (pH at zero point of charge) 9.3. A 200 g sample was sieved and the particle size 300–500 μm was collected, washed with distilled water and dried at 105 °C. A 100-litre diesel sample (0.840 g...
cm$^2$ at 25 $^\circ$C) was collected form a local fuel station. The sample was carefully filtered and kept in a closed polyethylene barrel before use. The total concentration of organosulphur compounds OSC expressed as mgS kg$^{-1}$ was accurately made using X-ray fluorescence analyser (SLFA-2100/2800 X-ray Fluorescence Sulphur-in-Oil Analysers, Horiba, USA). Dibenzothiophene DBT (a major organosulphur compound) was targeted in diesel using gas chromatography as outlined in our earlier work [14].

2.2. Adsorption isotherms and selectivity studies using model fuel

Competitive adsorption behaviour of DBT in the presence of (naphthalene NAP, anthracene ANT and chrysenene CHR) was carefully studied using synthetic diesel following the common concentration–variation procedure. Eight mixtures of the solutes (DBT, NAP, ANT, and CHR) at different levels were prepared using synthetic fuel (98.0 g of equal masses of $n$-hexane/$n$-heptane) with a final volume of 140.0 mL. For each solute in the mixtures, the concentration range was taken from 100 to 4000 mg/kg which corresponds to 0.54–21.71, 0.56–22.47, 0.44–17.52, and 0.78–31.20 mmol/kg for DBT, ANT, CHR, and NAP, respectively. For each mixture, 1.00 (±0.01) g of activated carbon was added and the mixtures were closed and agitated using a thermostated shaker (GFL, Germany) at 25 $^\circ$C for 300 min which is necessary to reach equilibrium. At the end of shaking time, the particles of activated carbon were removed by filtration, and the equilibrium concentrations of DBT, NAP, ANT, and CHR were quantified using gas chromatography as outlined in the literature [14]. The surface concentration of a certain solute $q_e$ (mmol/g-carbon) was estimated as:

$$q_e = \frac{(C_0 - C_e) \times m_1}{m_2}$$

where $C_0$, $C_e$, $m_1$, and $m_2$ are the initial concentration (mmol/kg-fuel), equilibrium concentration (mmol/kg-fuel), mass of fuel (kg), and carbon mass (g), respectively. Washing of the adsorbent and preparation of acid solutions were carried out using distilled water and ethanol, respectively.

2.3. Effect of acidification by organic acids on DBT removal from model fuel

Acidification of model fuel or commercial diesel by organic acids was carried out as following: 1.0 M of acetic, formic, oxalic and citric acids were prepared in ethanol. Different fuel/acid mixtures were prepared by adding appropriate volumes of the acid to fuel to end up with the desired level (1–5% by vol.). The fuel-acid mixtures were carefully agitated before use in adsorption tests. All chemicals were obtained from Sigma. The influence of fuel acidification on aromatics removal was studied following the experimental procedures that outlined in Section 2.2.

2.4. Effect of acidification of commercial diesel on dibenzothiophene: a practical study

The proposed desulfurization practice was evaluated by monitoring DBT removal from commercial diesel containing 2578 mgDBT/kg. Typically, 140 mL of acidified diesel was agitated with 1.0 g activated carbon (300–500 μm) for 300 min at 25 $^\circ$C. Control experiments were carried out side-by-side but without adding any acid to the fuel. The final DBT content and other aromatics were quantified as mentioned in Section 2.1.

3. Results and discussion

3.1. Level of organosulphur compounds and dibenzothiophene in commercial diesel

X-ray fluorescence analysis showed that the total concentration of OSC was 7100 (±10) mgS/kg. This level is extremely high when compared to the regulated limits [14]. Based on the chromatographic analysis, the content of DBT was 2578 (±15) mg/kg and this amount contributes to 36% of total sulphur in the fuel. Indeed, a large fraction of OSC in diesel is originated from DBT and the selective removal of this problematic compound is necessary.

3.2. Influence of fuel acidification on DBT adsorption: selectivity studies

Aromatic compounds are making a good fraction of diesel and they are negatively compete with dibenzothiophenes adsorption [2,12]. In this work, a new practice for selective removal of DBT was proposed by diesel acidification using organic acids. To have a better insight, competitive adsorption of DBT, NAP, ANT, and CHR by carbon in the absence and presence of 5% (by vol.) acetic acid was studied using model fuel and the results are shown in Fig. 1. Selectivity factors and the parameters of Langmuir model are also summarised in Table 1.

As indicated in Fig. 1, the isotherms have typical L2 shapes according to the Giles and Smith classification [16]. In Fig. 1,
the surface concentration (y-axis) is sharply increased at lower solute concentration and then a gradual removal is observed at higher concentrations. In the current system, adsorption of all aromatics by activated carbon (with and without acidification) proceeded until a monolayer is accomplished and multilayer formation was not achieved. In L2 isotherm, a high adsorption is often observed at lower solute concentration. Similar adsorption isotherms were reported for DBT uptake by porous activated carbon [12,13]. The favourable interaction of aromatics and DBT (via π–π and S interactions) with poor competition of solvent molecules would also explain the formation of L2-isotherm. As shown in Fig. 1, fuel acidification by 5% (by vol.) acetic acid has improved DBT adsorption among aromatics. Langmuir equation was tested for the current 4-solute-system due to its high ability for handling competitive systems [15]. As indicated in Table 1, all aromatics were removed from fuel with different amounts. However, in the absence of acetic acid, the maximum adsorption values were 307.3 and 238.1 mg/g for CHR and ANT, respectively. The adsorption trend of organics was increasing in the following order: NAP < DBT < ANT < CHR. Moreover, selectivity factor also confirmed the preferential uptake of CHR with a value of 1.84. The interesting point in Table 1 is the selective removal of DBT among other organics after fuel acidification. Upon acidification, the adsorption trend of solutes was increasing in the following order: NAP < ANT < CHR < DBT. Dibenzothiophene was removed over other organics as indicated from the selectivity values: 1.0, 1.39, 1.79, and 2.02 for NAP, ANT, CHR, and DBT, respectively. The favourable uptake of DBT upon acidification is attributed to the protonation of S atom, and hence enhancing the electrostatic attraction with the surface of activated carbon. The protonation of DBT prior to surface removal was preceded as following:

\[
\begin{align*}
\text{Dibenzothiophene} & \quad + \text{H}^+ \quad \rightarrow \quad \text{Dibenzothiophene}^+ \\
& (2)
\end{align*}
\]

Protonation of other aromatics is not possible and the improved DBT uptake has reduced removal other aromatics. The large reduction was observed for ANT, the adsorption capacity was reduced by 26.3% after acidification. Again, Langmuir model was effective for presenting competitive adsorption data for all cases as indicated form the high \( r^2 \) values 0.9776–0.9944. The high performance of Langmuir model is a support to assumption that aromatics adsorption was accomplished with a minimum competition for active sites. In conclusion, DBT is favourably removed among other di-, tri and tetra-aromatics after fuel acidification by 5% (by vol.) acetic acid.

### 3.3. Effect of organic acid type and content on DBT uptake

The influence of acid type on DBT removal was evaluated using 2000 mg/kg level prepared in synthetic fuel and the results are shown in Fig. 2A. As indicated in Fig. 2A, a large improvement in DBT uptake was achieved for all cases. The best performance was observed for acetic and oxalic acids (3% by vol.) with %Removal values of 63% and 68%, respectively. The efficiency of formic acid was modest compared to the other acids as the removal capacity has been increased by 11% only. The high performance for oxalic acid was attributed to its high acidity (\( pK_a = 1.25 \)) which offers more protonation for DBT molecules. Due to its lower price and availability, acetic acid was the best candidate for diesel acidification. Fig. 2B indicated that the content of acetic acid has a strong influence on DBT removal and stable removal efficiency (62%) was observed over the content 3–5% by vol.

### 3.4. Selective removal of dibenzothiophene from commercial diesel

The real application of the new method is further validated by removing DBT from commercial diesel which is loaded with this problematic compound with a level of 2578 mg/kg. The results are depicted in Fig. 2C and clearly showed that adding acetic acid to commercial diesel has improved the removal of DBT. The best desulfurization result was observed at 5% level, the removal efficiency was improved from 27% to 55% upon acid addition. In fact, removing 55% of DBT from diesel is a good sign and reflects the high performance of the proposed desulfurization method.

Organic acids are often present in diesel and can cause corrosive wear of the fuel system. Significant wearing was observed for high sulphur diesel [17]. Accordingly, acidity value of diesel fuel is an important index to be monitored after desulfurization taking into account the role of organic acids in the current method. A standard analytical procedure [18] was adopted to test the level of acidity in all treated samples. In 95% of the samples, the acidity value was less than 0.1 mg/g which is lower than the recommended limit for automotive fuels (0.5 mg/g) [18].

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**Table 1**

<table>
<thead>
<tr>
<th>Solute²³</th>
<th>( Q_{\text{max}} ) (mg/g)</th>
<th>( Q_{\text{max}} ) (mmol/g)</th>
<th>( K_1 ) (g/mmol)</th>
<th>( r^2 )</th>
<th>Selectivity factor (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No acidification</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAP</td>
<td>166.7</td>
<td>1.30</td>
<td>622</td>
<td>0.9776</td>
<td>1.00</td>
</tr>
<tr>
<td>ANT</td>
<td>238.1</td>
<td>1.33</td>
<td>858</td>
<td>0.9912</td>
<td>1.43</td>
</tr>
<tr>
<td>DBT</td>
<td>203.4</td>
<td>1.10</td>
<td>720</td>
<td>0.9944</td>
<td>1.22</td>
</tr>
<tr>
<td>CHR</td>
<td>307.3</td>
<td>1.35</td>
<td>952</td>
<td>0.9821</td>
<td>1.84</td>
</tr>
<tr>
<td><strong>Fuel Acidification (5% by vol. acetic acid)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAP</td>
<td>126.6</td>
<td>0.99</td>
<td>845</td>
<td>0.9854</td>
<td>1.00</td>
</tr>
<tr>
<td>ANT</td>
<td>175.4</td>
<td>0.98</td>
<td>817</td>
<td>0.9893</td>
<td>1.39</td>
</tr>
<tr>
<td>DBT</td>
<td>255.3</td>
<td>1.39</td>
<td>1140</td>
<td>0.9789</td>
<td>2.02</td>
</tr>
<tr>
<td>CHR</td>
<td>227.3</td>
<td>0.99</td>
<td>908</td>
<td>0.9877</td>
<td>1.79</td>
</tr>
</tbody>
</table>

NAP was selected as the reference solute due to its poor adsorption.

\(^{a}\) Langmuir model is presented as [15,16]: \( q_e = \frac{Q_{\text{max}} C_e}{K_1 + C_e} \) where \( q_e \) (mmol/g-carbon), \( C_e \) (mmol/kg-fuel), \( Q_{\text{max}} \) and \( K_1 \) (g mmol \(^{-1}\)) are the equilibrium surface concentration, the saturation value, and a constant related to the heat of adsorption [16], \( r^2 \) is the correlation coefficient.

\(^{b}\) Dibenzothiophene DBT \( C_{12}H_8S \) (184.3 g/mol), Naphthalene NAP \( C_{10}H_8 \) (128.2 g/mol), Anthracene ANT \( C_{14}H_{10} \) (178.2 g/mol), and Chrysene CHR \( C_{18}H_{12} \) (228.3 g/mol).

\(^{c}\) See Section 2.2 and Fig. 1 for experimental details.

\(^{d}\) Selectivity factor was estimated as [15]: Selectivity factor \( = \frac{Q_{\text{max}} \text{NAP}}{Q_{\text{max}} \text{DBT}} \).
4. Conclusions

A novel desulfurization procedure was proposed by adding acetic acid to diesel prior to activated carbon adsorption. Oxalic and acetic acids showed the best desulfurization results. Competitive adsorption tests indicated that adding acetic acid has improved DBT removal among other aromatics. The proposed method was found effective for removing 55% of DBT from commercial diesel initially containing 2578 mg/kg.

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