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Optimization of oxidative desulfurization of Malaysian Euro II diesel fuel utilizing *tert*-butyl hydroperoxide–dimethylformamide system

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HIGHLIGHTS

- TBHP–DMF system shows highly efficient oxidative performance.
- TBHP/sulfur ratio is the most important parameter in Box–Behnken design.
- 320 ppm of sulfur in real diesel was successfully removed.
- A mechanistic study on ODS is proposed.

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ABSTRACT

Deep oxidative desulfurization of model diesel consisting of thiophene, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) was investigated with various oxidants followed by extraction step using dimethylformamide (DMF). Response surface methodology based on Box–Behnken design was used to evaluate the effects of the main operating parameters, including the oxidant to sulfur molar ratio (2.0–4.0), oxidation temperature (40–60 °C) and oxidation time (10–60 min), on the 4,6-dimethyldibenzothiophene conversion. Among the oxidants used; *tert*-butyl hydroperoxide (TBHP) was led to the highest oxidation of model sulfur compounds. Meanwhile, the statistical results revealed that TBHP/sulfur ratio was the most important parameter followed by oxidation time and oxidation temperature. The optimum oxidative desulfurization conditions for 4,6-DMDBT conversion had been attained at TBHP/sulfur ratio of 3.0, temperature of 48 °C and period time of 31 min, respectively with the highest conversion of 4,6-DMDBT of 84.5%. The experimental optimum yield fitted-well with the predicted value with less than 5% error. The mechanistic study showed that the reaction between TBHP and 4,6-DMDBT was efficient to produce corresponding sulfoxide, instead of sulfone compound.

1. Introduction

Numerous usage of the daily used of diesel fuel contributes a significant source of air pollution and which lead to become a major producer of toxic emissions. During combustion, organosulfur compounds (OSCs) are converted to sulfur dioxide (SO_2), one of the contaminants that received parliamentary regulations over the past decade [1,2]. The improvement of diesel fuels quality with regard to ecological standards is directed continuously toward lower sulfur content, which can be achieved by different desulfurization methods [3–5].

Presently, industries use hydrodesulfurization (HDS) technology for desulfurization of diesel fuel, but it is able to lower the sulfur content to few hundreds ppm only [6]. The major shortcoming of HDS is the requirement of high operating cost and conditions, particularly in removing of refractory sulfur compounds that will limit the capabilities to produce ultra low sulfur diesel [7,8]. Therefore, to meet the economic and environmental technologies for ultra low sulfur diesel, numerous methods are appeared such as adsorption, biodesulfurization, extraction etc. Recently, extractive desulfurization (EDS) has been reported as alternative system to reduce the sulfur content [9–11]. Our previous study on EDS [12] showed that dimethylformamide (DMF) was the best solvent, with maximum of 78.7% sulfur removal from real diesel. However, EDS is limited by the incapability of removing the bulkier and heavier alkyl dibenzothiophene (DBT) compounds to meet ultra low sulfur diesel [13].

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Alternatively, oxidative desulfurization (ODS) has received great attention from researchers because of its advantage; mild operating conditions and no hydrogen required. In general, the principle of ODS process consists of two consecutive steps; oxidation of organosulfur compounds to their corresponding sulfone by oxidizing agents followed by separation of these compounds by extraction into a polar solvent [14–17]. Common ODS methods utilized hydrogen peroxide (H_2O_2) and/or mixture of strong or organic acid with H_2O_2 to enhance the performance of sulfur removal [18,19]. However, there are few studies which concerning *tert*-butyl hydroperoxide (TBHP) as an oxidant [20,21] and also no detailed work to define the appropriate oxidation conditions.

On the other hand, Response Surface Methodology (RSM) has been widely used for the optimization of extractive desulfurization [22] and catalytic oxidative desulfurization [23,24]. However, as far as we know, the optimization of the oxidative desulfurization by RSM has not been reported yet in the literature. In fact, a proper experimental design should be used to study effects of oxidation parameters and their interactions with a minimum number of experiences. Among RSM designs, Box–Behnken design (BBD) shows a good design to fit the quadratic model and operating at a high efficiency [25]. Additionally, almost previous works postulated or suggested the mechanism study in the presence of catalysts [8,18]. No work has been found which deals between the oxidizing agent and sulfur pollutants solely.

Therefore, the main purpose of this paper is to explore the effectiveness of TBHP–DMF oxidation system utilizing the response surface methodology (RSM) method as a novel approach for examination of the interactive effects of ODS process variables including TBHP/sulfur ratio, oxidation temperature and oxidation time on the yield of 4,6-DMDBT oxidation. Furthermore, this paper presents the optimal operational conditions for maximum efficiency of DBT oxidation for deep oxidative desulfurization of commercial diesel. The selectivity of DBT oxidation as well as the mechanistic study was discussed based on the obtained results.

2. Experimental

2.1. Materials

All chemicals used in the present study were used without further treatment. Aqueous *tert*-butyl hydroperoxide (70 wt.% TBHP), aqueous hydrogen peroxide (30 wt.% H_2O_2), peracetic acid [PAA, the combination of H_2O_2 and glacial acetic acid (GAA, 99%)] and the mixture of TBHP-GAA (TG) were utilized as oxidizing agents while dimethylformamide (DMF, 99%) was used as extraction solvent, respectively. *N*-octane (99%) was exploited as solvent for model sulfur compounds: thiophene (Th, 99%), dibenzothiophene (DBT, 97%), and 4,6-dimethyldibenzothiophene (4,6-DMDBT, 95%). Model diesel for the ODS reaction was prepared with 500 ppmw; including thiophene (50 ppmw), DBT (150 ppmw), and 4,6-DMDBT (300 ppmw)—representing the actual diesel fuel.

2.2. Oxidative desulfurization reaction

The oxidative desulfurization experiment was initially performed in a three-necked 50 mL round-bottomed flask including 10 mL of model diesel and various oxidants (H_2O_2, TBHP, PAA and TG) with ratio of 2.0. The reaction was conducted by stirring mixture at a constant speed at 50 °C for 30 min. Further experiments were varied with different TBHP to sulfur molar ratios (2.0–4.0), oxidation temperatures from 40 °C to 60 °C and oxidation times between 10 min and 60 min. The oxidized diesel was then extracted with DMF under the optimum extraction conditions; DMF/diesel ratio of 1.0, for 30 min at an ambient temperature (29 °C) as reported before [12]. After the solvent and treated diesel was completely separated, the treated diesel was analyzed using gas chromatography coupled with a flame photometric detector (GC-FPD). A 50 m × 0.25 mm inner diameter × 0.25 μm film thickness HP-1 capillary column was used for separation. High purity helium and hydrogen were used as carrier and fuel for FPD, respectively. Sample volume of 1.0 mL was injected without any solvent dilution. The percentage conversion of sulfur was calculated using the following relationships [26]. The data gathered from the experiments were used to calculate the removal percentage of model sulfur compounds as follows:

$$\text{Sulfur removal } (\%) = \frac{(A_0 - A_t)}{A_0} \times 100$$

where A_0 is the initial sulfur concentration of sulfur in the *n*-octane solution and A_t is the sulfur concentration of the treated diesel phase after reaction time (t).

In case of the mechanistic study, the formation of oxidized DBT products; either sulfoxide or sulfone were confirmed using GC-FPD equipped with HP-5 column (30 m × 0.25 mm × 0.25 μm). The sample was taken from dimethylformamide phase for sulfoxide and/or sulfone analysis. The extracted DMF was analyzed after 5 to 45 min.

2.3. Design of experiments

Response surface methodology was used for statistical analysis of the experimental data using Design Expert software version 7.0. The Box–Behnken design (BBD) was selected to evaluate the optimum reaction conditions for maximizing the 4,6-DMDBT. The effects of the main operating parameters including TBHP/sulfur ratio (A), oxidation temperature (B) and oxidation time (C) were studied. The choice of 4,6-DMDBT conversion as a response was due to these compounds are the most abundance in the real diesel. Moreover, among thiophene, DBT and 4,6-DMDBT model sulfur compounds; 4,6-DMDBT showed the distinct percentage of desulfurization as compared to the other two. The variable parameters were coded as −1, 0 and 1, which denoted the low level, center point and high level, respectively as indicated in Table 1. Seventeen experiments were performed in a randomized order and the results are summarized in Table 2. The quadratic equation or optimization is given in the following equation:

$$\eta = \beta_0 + \Sigma\beta_i\chi_i + \Sigma\beta_{ii}\chi_i^2 + \Sigma\Sigma\beta_{ii}\chi_i\chi_j + \varepsilon$$

where η is the response, β_0 is constant coefficient, β_i, β_{ii} and β_{ij} are linear, quadratic and second order interaction coefficient, respectively. X_i and X_j are independent variables where ε is the error. The response was then completely analyzed using analysis of variance (ANOVA) while the quality of fit of the polynomial model equation was expressed by the coefficient of determination (R^2). Furthermore, the interaction of the independent variables was investigated by constructing the response surface and contour plot [23,24].

Table 1
Range and levels of the operating parameters.

Independent variables	Range and levels		
	−1	0	+1
Oxidant/sulfur ratio, A	2	3	4
Oxidation temperature, B (°C)	40	50	60
Oxidation time, C (min)	10	35	60