

# Deep Oxidative Desulfurization Utilizing Hybrid Keggin Catalyst with 1-methyl-3-octyl imidazolium hexafluorophosphate

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## Abstract

Deep oxidative desulfurization is a crucial topic for environmental catalysis research for producing a low-sulfur diesel. One of the effective catalysts that have been used recently for oxidative desulfurization of the refractory sulfur compound from model diesel is Keggin-type polyoxometalate. In this work, a Keggin-type catalyst TBAPW<sub>11</sub>O<sub>39</sub>, model diesel, Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and 1- methyl 1-3-octyl imidazolium hexafluorophosphate (OMIM(PF<sub>6</sub>)) were tested under different reaction conditions. The sulfur compound dibenzothiophene (DBT) in model diesel was captured in ionic liquid (IL) and then oxidized to produce related sulfones with H<sub>2</sub>O<sub>2</sub> as an oxidant using TBAPW<sub>11</sub>O<sub>39</sub>, in a batch reactor. The impacts of reaction temperature (T)(303,323 and 343)K and time (30-180) min, catalyst dosage 0.5-6 g/l, H<sub>2</sub>O<sub>2</sub>/DBT(O/S) molar ratio from 1:1 to 5:1(mole/mole) and IL/oil volume ratio 1/10 – 5/10 (ml/ml) were investigated. The catalyst exhibited high effectiveness for removing DBT using H<sub>2</sub>O<sub>2</sub>, with the highest sulfur removal of 96% under the optimum conditions (10 ml of model diesel, T= 343 K, catalyst dosage= 3 g/l, H<sub>2</sub>O<sub>2</sub>/DBT = 5:1 (mole: mole) and IL/diesel = 2:10 (ml/ml) for 120 min). These results indicate that the extraction with catalytic oxidation desulfurization using Keggin hybrid catalysts for model diesel fuels is an efficient method and offers promise for achieving ultra-deep desulfurization.

**Keywords:** Dibenzothiophene, Ionic Liquids, Model Diesel, Oxidative Desulfurization, Polyoxometalate.

## Introduction

Petroleum fuels and their fraction containing organic sulfur compounds (OSCs) are the fundamental cause of pollution. Due to severe environmental issues concerning sulfur emission reduction agents, the deep desulfurization of fuel oil has gained great concern recently<sup>1</sup>. Sulfur-containing compounds in gasoline and diesel fuels release SO<sub>x</sub> gases and sulfur particles, contributing to acid rain and other pollutants, emphasizing desulfurization<sup>2</sup>.

Deep desulfurization methods are desirable to supplement the conventional technology for

producing low-sulfur content fuel. The traditional technology, hydrodesulfurization (HDS), is a chemical process utilized in petroleum refining operations for obtaining low-sulfur content fuel. HDS reduces reactivity towards eliminating refractory sulfur-containing compounds, especially dibenzothiophene and its derivatives, such as 4-methyl dibenzothiophene (4-MDBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) because of a steric hindrance<sup>3,4</sup>. The HDS method can eliminate either aliphatic or acyclic sulfur compounds on a commercial large scale under severe

conditions. The rise of sulfur content of oils results in elevated operational requirements and costs required to achieve low sulfur fuel in HDS<sup>5,6</sup>.

One of the most interesting desulfurization methods is oxidative desulfurization (ODS) using non-hydrogen techniques (extraction, adsorption, bio-desulfurization). Consequently, different complementary desulfurization methods, such as extraction, adsorption, oxidation, and biological methods, are desirable worldwide<sup>7,8</sup>. Combining these processes, such as extraction and oxidation methods called extractive and catalytic oxidative desulfurization (ECODS) method, can be displayed to effectively eliminate resistant sulfur compounds with high selectivity by favorable operating conditions<sup>9,10</sup>.

Several efficient ECODS systems use catalysts with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidant, such as zeolites, metallic, ionic liquids, layered double hydroxides, polyoxometalates (POMs), and Activated carbon-based solid catalysts<sup>11</sup>. Amongst these catalysts: POM-based systems have been demonstrated to eliminate effectively sulfur compounds either in the model or in the real diesel.

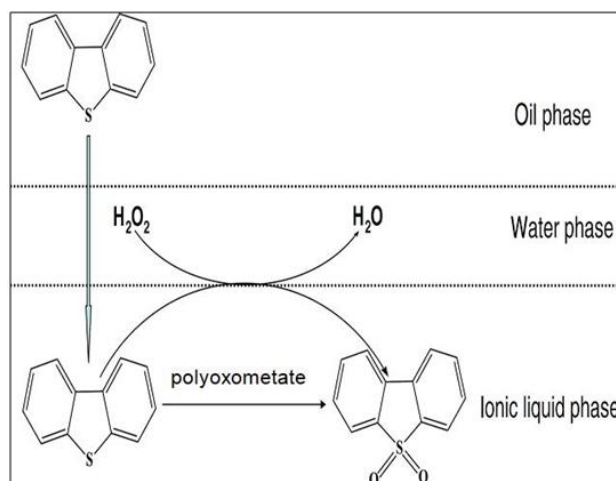
Among various polyoxometalates, the Keggin-type structure is widely utilized in catalytic applications due to its special strength of the acid, oxidation potential and hydrolytic stability. In the last few decades, polytungstophosphate-based catalysts have been widely employed to oxidize sulfur-containing fuel oil<sup>5,9</sup>. The oxidation reaction produces related monomeric or polymeric peroxy species resulting from the reaction between POM and H<sub>2</sub>O<sub>2</sub>. The modification of polyoxometalates using organic groups as an effective approach to producing a hybrid catalyst that exhibits superior catalyst performance, recovery and reusability potential, a common POM hybrid is quaternary ammonium POM salts have become important as phase transfer agents in emulsion catalysis for oxidative desulfurization<sup>12</sup>.

## Materials and Methods

Dibenzothiophene 98% and Tetra-butylammonium bromide were purchased from Sigma- Aldrich/USA, n-Heptane 99% was purchased from J.T.Baker, Toluene 99.7% was purchased from Scharlau/ Spain,

Organosulfur compounds can be effectively oxidized in the ODS process to produce the corresponding slightly more polar: sulfoxides(1,1-dioxides) and sulfones (1-oxides) than hydrocarbon molecules. These oxidation products can also be extracted using organic solvents or ionic liquids (ILs)<sup>13,14</sup>. Ionic liquids (ILs) possess many benefits versus organic solvents. These advantages include a low melting point, little volatility, superior thermal stability, perfect solubility, and various structures that can be used as extraction solvents. Also, ionic liquids perform a dual role as an extraction and trapping medium for sulfur compounds and as a way to provide oxidation conditions for the conversion of sulfur into sulfones. Fig. 1 illustrates the polyoxometalate catalyst at the intermediate interface between the aqueous and ionic liquid phases; consequently, the peroxy species promoted the oxidation of the sulfur compound to sulfones in the ionic liquid phase<sup>15</sup>.

In this work, an efficient deep oxidative desulfurization for DBT in model diesel fuel is developed. The Keggin-type polyoxometalate catalyst TBAPW<sub>11</sub>O<sub>39</sub> within OMIM(PF<sub>6</sub>) catalytic efficiency to oxidize DBT with H<sub>2</sub>O<sub>2</sub> under moderate conditions will be assessed.



**Figure 1. The probable mechanism of oxidative desulfurization in the presence of polyoxometalate using ionic liquids<sup>15</sup>.**

1-methyl-3-octyl imidazolium hexafluorophosphate OMIM(PF<sub>6</sub>) 95% was purchased from Macklin/china, H<sub>2</sub>O<sub>2</sub> (30 wt.%) was purchased from Honeywell Fluka/Germany. Sodium Tungstate

dihydrate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) from Fluka/Switzerland, sodium hydrogen phosphate dihydrate ( $\text{Na}_2\text{HPO}_4$ ) and Hydrochloric acid 37% were purchased from Himedia/India. All the chemicals used as supplied without further treatment.

The equipment used in the experimental works: the hot plate magnetic stirrer was made in the United Kingdom, Stuart and model Cat No. CD-162, digital pH meter manufactured by Vivosun/China. And the Centrifuge manufactured by Cgoldenwall 80-1 Desktop Electric Centrifuge Laboratory 4000 rpm.

The sulfur content in the model diesel and the products was measured at the Refining and Gas Research Department of Petroleum Research and Development Center in the Ministry of Oil in Iraq. The sulfur content was measured by the sulfur analyzer, XOS, Sindie OTG / USA, through monochromatic wavelength-dispersive X-ray fluorescence following ASTM D7039.

### Preparation of catalyst

Our research team has recently successfully synthesized and characterized the  $\text{TBAPW}_{11}\text{O}_{39}$  catalyst, as reported in our previous study<sup>16</sup>, and was utilized in this present research. The synthesis of polyoxometalate catalyst ( $\text{TBAPW}_{11}\text{O}_{39}$ ) involved the dissolution of certain amounts of  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in purified water, followed by the reduction of pH = 4.8 with HCl 4M. Subsequently,

## Results and Discussion

### Effect of $\text{TBAPW}_{11}\text{O}_{39}$ on desulfurization efficiency of model diesel

Fig. 2 displays the desulfurization efficiency (DE) of extraction with oxidation and extraction combined with catalytic oxidation desulfurization. The combination of extraction and oxidation only exhibited a low performance on desulfurization efficiency for DBT removal, which reached 38.5%. In comparison, desulfurization employing the extraction with the oxidation in the presence of polyoxometalate was more effective, and the desulfurization efficiency sharply improved to 90.3% using  $\text{TBAPW}_{11}\text{O}_{39}$  with  $\text{H}_2\text{O}_2$  and  $\text{OMIM}(\text{PF}_6)$ .

The immiscibility between model diesel and ionic liquid  $\text{OMIM}(\text{PF}_6)$  was observed. The ability to disperse polyoxometalate in the ionic liquid is significantly higher than in the model diesel. The hydrogen peroxide could not disperse in

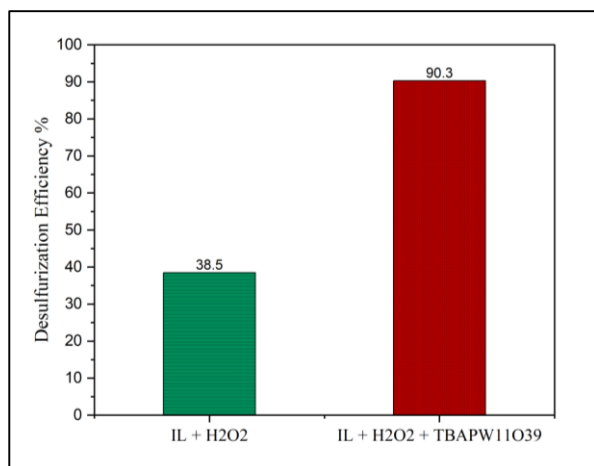
the solution in a magnetic stirrer with the temperature was raised to 353-358 K and continued to agitate for an hour; after that, the solution of TBA bromide was gradually added. The resultant was a white residue separated through filtration. The product was dried for one night within a desiccator containing silica gel.

### Oxidative desulfurization of model diesel

The ECODS batch experiment was performed at atmospheric pressure utilizing a 25 ml two-necked round-bottom flask supplied with a magnetic stirrer and submerged in a pot of water to ensure a constant temperature distribution. The flask is connected to a condenser in one of the two side necks and the thermometer on the other side. The model diesel was produced according to the needed quantity of dibenzothiophene in a solution of 80% (v/v) n-Heptane and 20% (v/v) Toluene with a sulfur content of 300 ppm to achieve the deep desulfurization. The mixture of model diesel 10 ml and a variable volume of 1,2,3,4,5 ml of ionic liquid was added to the flask and heated to the 303- 343 k temperature range needed for the reaction. After 10 minutes, adding the amount range 1:1 to 5:1 of  $\text{H}_2\text{O}_2$ /Sulfur (O/S) and catalyst ( $\text{TBAPW}_{11}\text{O}_{39}$ ) to commence the catalytic step and agitated at a speed of 500 rpm; after passing each run time 30-180 min, the solution was separated using centrifugation with 2000 rpm for 10 min before testing the sulfur content of the upper phase.

$\text{OMIM}(\text{PF}_6)$ . The desulfurization system of extraction combined with catalyst oxidation is three-layer (model diesel/  $\text{H}_2\text{O}_2$ /IL), the model diesel was in the top layer,  $\text{H}_2\text{O}_2$  was in the intermediate layer, and IL together with  $\text{TBAPW}_{11}\text{O}_{39}$  was in the lower layer. In the presence of the catalyst, the suggested mechanism initially involves the extraction of dibenzothiophene from the model diesel layer to the ionic liquid layer. Then oxidation reaction initiates with the generation of active peroxy species through active oxygen provided by  $\text{H}_2\text{O}_2$  to the  $\text{TBAPW}_{11}\text{O}_{39}$ . The peroxy species are an interim oxidant capable of oxidizing the sulfur compound to the sulfoxide, then reinitiating the catalytic cycle; the sulfoxides are oxidized to sulfone in the ionic liquid layer. In the absence of  $\text{TBAPW}_{11}\text{O}_{39}$ , the sulfur compound oxidation is performed using active oxygen only. As a result, the polyoxometalate catalyst served a crucial role as a cocatalyst in the desulfurization process. The proposed mechanism

corresponds with previously published for ECODS catalyzed by POMs with  $H_2O_2$ <sup>17</sup>.



**Figure 2. Effect of TBAPW<sub>11</sub>O<sub>39</sub> on desulfurization**

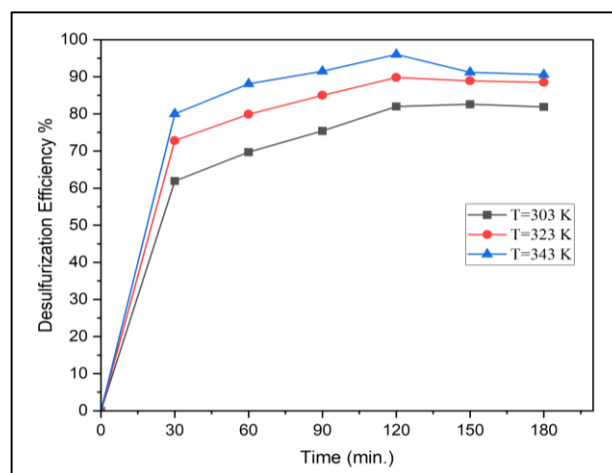
**[Condition: T= 343 K, IL/diesel ratio= 4/10, O/S ratio=5:1, Catalyst dosage of TBAPW<sub>11</sub>O<sub>39</sub>=3 g/l and Time = 120 min]**

#### **Effect of Temperature and oxidation reaction time on desulfurization efficiency of model diesel**

The impact of varying temperatures and batch time on ODS was examined at 303K, 323K, and 343K and various oxidation times from 30 to 180 min. Fig. 3 indicates that increasing the oxidation time led to superior oxidation of DBT at different temperatures. The optimum desulfurization efficiency was found to be 88.1% after 60 min, whereas the maximum sulfur removal of 96% as the reaction time increased to 120 min at a temperature of 343K. These results may be assigned to extended residence time among the oxidant and sulfur compounds, causing more conversion of sulfur to sulfone through the electrophilic added oxygen to sulfur. However, after that time, the sulfur removal declined significantly by approximately 90%. The reason may be slowing the oxidation process due to exhausting the amount of  $H_2O_2$ , which provides the active oxygen to oxidize sulfur compounds<sup>18</sup>.

As seen in Fig. 3, the desulfurization efficiency improves when the reaction temperature rises over time. In contrast, the increase in temperature can enhance the oxidation of dibenzothiophene owing to further peroxy complex formation and accelerating the thermal decomposition of  $H_2O_2$ . Moreover, It seems that the sulfur diffusion and movement from model diesel to ionic liquid improved at elevated temperatures due to a decrease in the viscosity of

ionic liquids with a temperature rise, increasing desulfurization efficiency. The desulfurization efficiency reached 82.0%, 89.8%, and 96% in 120 min, when the temperature was 303 K, 323 K, and 343 K, respectively. The highest desulfurization efficiency was obtained at a temperature of 343K; therefore, the temperature was set at 343 K in the present study as the optimum temperature. The results agree with the findings reported in the previous research<sup>19,20</sup>.

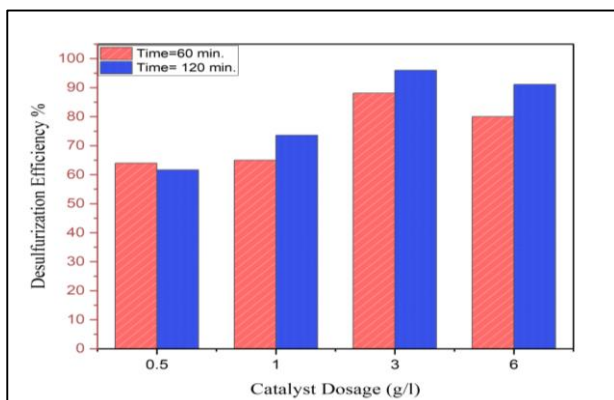


**Figure 3. Effect of Time & Temperature on desulfurization efficiency**

**[Condition: Catalyst dosage of TBAPW<sub>11</sub>O<sub>39</sub> = 3 g/l, O/S ratio=5:1, IL/diesel ratio=2/10]**

#### **Effect of catalyst dosage on desulfurization efficiency of model diesel**

The impact of the dosage of the catalyst on ODS is seen in Fig. 4; it was concluded that the dosage strongly influenced the desulfurization efficiency. The desulfurization efficiency grew as the TBAPW<sub>11</sub>O<sub>39</sub> dosage increased up to 3 g/l. Increasing the catalyst dosage may increase peroxy active intermediates compound generation, affecting ODS efficiency. The results revealed that the dosage of TBAPW<sub>11</sub>O<sub>39</sub> ranged between 0.5 to 3 g/l, and the DBT removal increased significantly from 61.7% to 96% for model diesel. As a result, 3 g/l of TBAPW<sub>11</sub>O<sub>39</sub> was chosen for the following ODS tests. Nevertheless, the DE was less when the catalyst dose increased to 6 g/l may be caused by particles of catalyst building up on the model diesel phase, which inhibits DBT from extraction and oxidation. The findings presented are comparable with the studied results<sup>21,22</sup>.

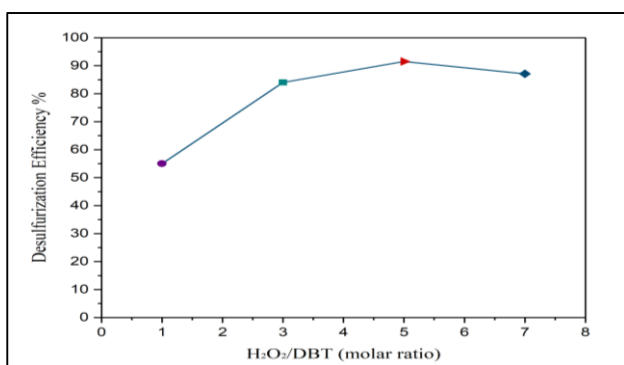


**Figure 4. Effect of Catalyst Dosage on desulfurization efficiency**

[Condition: T= 343 K, O/S ratio=5:1, IL/diesel ratio=2/10 and Time=60 & 120 min.]

#### Effect of H<sub>2</sub>O<sub>2</sub>/DBT molar ratio on desulfurization efficiency of model diesel

Several tests were carried out at 343 K to examine the influence of oxidant dosage on the oxidative desulfurization system using various H<sub>2</sub>O<sub>2</sub>/DBT(O/S) molar ratios to oxidize dibenzothiophene. As seen in Fig. 5, sulfur removal from the model diesel increased as the O/S increased from 1:1 up to 5:1, then slightly decreased. The stoichiometric reaction requires 2 moles of oxidant for every 1 mole of the sulfur compound to oxidize the dibenzothiophene to their corresponding sulfones. However, a higher O/S ratio than the stoichiometric ratio was required and the value of O/S = 5 was selected in the present study; when O/S molar ratio was higher than this value, the desulfurization efficiency decreased because the catalyst could decompose the large amount of H<sub>2</sub>O<sub>2</sub> into the water which is a negative impact for the sulfur removal. Additionally, with a molar ratio of O/S less than 5, the oxidation of DBT is relatively low. These results agreed with previous research<sup>23,24</sup>.

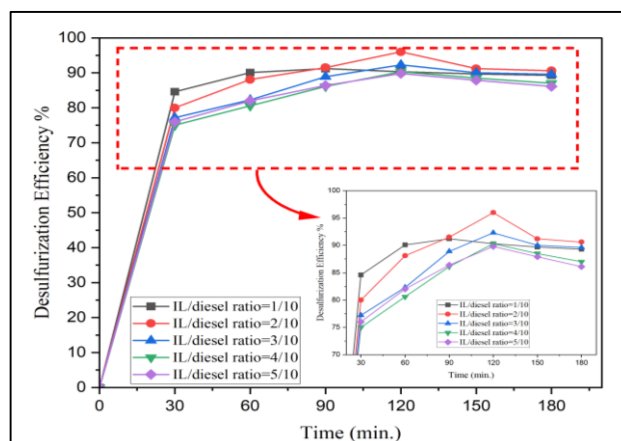


**Figure 5. Effect of O/S molar ratios on desulfurization efficiency**

[Condition: T=343 K, Catalyst dosage of TBAPW<sub>11</sub>O<sub>39</sub>=3 g/l, IL/diesel ratio=2/10 & Time=90min.]

#### Effect of IL/diesel volume ratio on desulfurization efficiency of model diesel

As seen in Fig. 6, the same set of oxidative catalytic reactions was studied for model diesel at 343 K over time with various volume ratios of [OMIM]PF<sub>6</sub>. The desulfurization efficiency of the model diesel decreases slightly with the rising volume ratio of the IL/diesel. The desulfurization efficiency reached 89.8%, 90.35, 92.3%, and 96% in 120 min, at a volume ratio decreasing from 5/10 to 2/10. While with the volume ratio of IL/diesel of 1/10, the DE was 90.1% in 60 min and almost unchanged with time, and a reasonable reason might be that when the IL/diesel ratio rises, the O/S ratio decreases (more DBT may be extracted into the ionic liquid phase) the quantity of H<sub>2</sub>O<sub>2</sub> is maintained constant in these experiments which is consistent to previous work<sup>25</sup>.



**Figure 6. Effect of IL/diesel volume ratios on desulfurization efficiency**

[Condition: T= 343 K, Catalyst dosage of TBAPW<sub>11</sub>O<sub>39</sub> = 3 g/l, O/S ratio=5:1]

## Conclusion

In conclusion, this study described the deep oxidative desulfurization of a model diesel under mild conditions using extraction with OMIM(PF<sub>6</sub>) and catalytic oxidation with Keggin-type polyoxometalate catalyst TBAPW<sub>11</sub>O<sub>39</sub> at moderate conditions. It was found that the extraction combined with catalytic oxidation desulfurization can be classified as an efficient method due to the high removal of sulfur, which reached 96% under the

following operating conditions (temperature = 343 K, catalyst dosage= 3 g/l, H<sub>2</sub>O<sub>2</sub>/DBT (molar ratio)= 5:1 and IL/diesel (volume ratio)= 2/10 for 120 min in 10 ml of model diesel). These results indicate that using Keggin hybrid catalysts in the oxidative desulfurization of model diesel fuels offers promise as an appropriate method for achieving ultra-deep desulfurization in industrial applications.

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## Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.

## Authors' Contribution Statement

Y. M., H. Q.H. and B. A.A. contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

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## ازالة الكبريت بالاكسدة العميقة باستخدام العامل المساعد المركب كيجن مع 1-ميثيل-3-أوكثيل إيميدازوليوم سداسي فلوروفوسفات

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### الخلاصة

تعتبر إزالة الكبريت بالأكسدة العميقة موضوعاً مهماً لأبحاث التحفيز البيئي لإنتاج الديزل منخفض الكبريت. أحد العوامل المساعدة التي تم استخدامها مؤخراً لإزالة مركبات الكبريت المقاوم من نموذج الديزل بالأكسدة هو بولي أوكسوميثالات من نوع كيجن. في هذا العمل، تم اختبار العامل المساعد من نوع كيجن  $TBAPW_{11}O_{39}$ ، نموذج الديزل، بيروكسيد الهيدروجين ( $H_2O_2$ ) وسائل ايوني من نوع (OMIM)(PF6) تحت ظروف تفاعل مختلفة. تم التقاط مركب الكبريت ثنائي بنزوثيوفين (DBT) من نموذج الديزل في السائل الايوني (IL) ثم يتأكسد الى سلفون مع بيروكسيد الهيدروجين كمؤكسد باستخدام  $TBAPW_{11}O_{39}$  في مفاعل نوع (batch). تم دراسة تأثير من (30-180 دقيقة) و درجة حرارة (T) التفاعل (343,3232,303 كلفن) و وزن العامل المساعد (0.5-6) غم / لتر و النسبة المولية  $H_2O_2/DBT$  (O/S) من 1:1 الى 1:5 (مول/مول) والنسبة الحجمية IL/diesel (1/10 – 5/10) (مل/مل). أظهر العامل المساعد فعالية عالية لإزالة DBT باستخدام بيروكسيد الهيدروجين ، وبلغت اعلى ازالة للكبريت بنسبة 96% في الظروف المثلى (10 مل من نموذج الديزل ،  $T = 343 K$  ، وزن العامل المساعد = 3 غم / لتر، النسبة المولية المؤكسد/مركب الكبريت  $(H_2O_2/DBT) = 1:5$  والنسبة الحجمية السائل الايوني/الديزل = 10/2 لمدة 120 دقيقة). تشير هذه النتائج إلى أن ازالة الكبريت بالأكسدة التحفيزية مع الاستخلاص باستخدام العامل المساعد كيجن الهجينة لنموذج وقود الديزل هي طريقة فعالة وتوفر وعداً لتحقيق ازالة الكبريت بعمق كبير.

**الكلمات المفتاحية:** ثنائي بنزوثيوفين، السائل الايوني، نموذج الديزل، ازالة الكبريت بالأكسدة، بولي أوكسوميثالات.