

Preparation and Characterization of Molybdenum Oxide Biochar Catalyst for Efficient Desulfurization Process

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Abstract

Producing low-sulfur commercial fuel became one of the concerns nowadays in order to curb the environmental pollution. Extensive studies were developed in refining crude oil industries such as oxidation-extraction method and adsorption techniques, which utilizes small amount of catalyst with low pressure and temperature yet effective and cost saving. In this study, activated carbon (AC) from empty fruit bunch EFB was successfully prepared and impregnated with molybdenum oxide MoO₃ for removal of sulfur from sulfur-added oil. The prepared activated carbon-molybdenum oxide AC/MoO₃ was characterized by using Brunauer-Emmett-Teller (BET), field emission-scanning electron microscopy (FESEM), X-ray fluorescence (XRF), X-ray diffraction (XRD) and energy dispersive X-ray (EDX). Meanwhile, two-step sulfur removal was carried out by catalytic oxidative-extractive desulfurization (Cat-OEDS) method. The characterization of the chemically treated AC shows high surface area, pore size and pore volume which is 1575.5 m² g⁻¹, 0.835 cm³ g⁻¹ and 2.120 nm respectively. From the results obtained, the 15% metal oxide molybdenum displays the highest sulfur removal by adsorption of 66.7% (500 ppm) and 51.12% (800 ppm) while 97.96% (500 ppm) and 96.54% (800 ppm) sulfur reduction in the presence of oxidant TBHP and DMF as an extractant which the oxidation performed at 30°C while

extraction conducted on ambient temperature for 30 minutes of both processes. As conclusion, the prepared AC/MoO₃ derived from EFB promises as an excellent metal oxide catalyst for absorptive-oxidative-extractive sulfur removal from any sulfur contained fuels.

Keywords: Activated Caron; Empty fruit bunch; Molybdenum Oxide; Heterogeneous Catalyst; Desulfurization; Oxidative-extractive Desulfurization; Adsorption

Introduction

Nowadays, the usage of petroleum is directly increased due to the vast economic growth and the escalated number of vehicles. Basically, crude oil contained high number of hydrocarbon and other organic compound such as sulfur [1]. Upon fuel combustion, the release of sulfur oxide (SO_x) and other poisonous gas such as carbon monoxide (CO) which hardly to degrade, thus in long-term it will contribute hazards towards the environment [2-4]. The combination of sulfur oxide with the atmosphere produces acidic rain and causes mass corrosion, killing the aquatic animals and plants.

As been reported in previous work removing of sulfur or known as desulfurization can be done either by adsorptive desulfurization [5,6], extractive desulfurization [7], bio-desulfurization [8], photocatalytic desulfurization [9], hydrodesulfurization [10] and oxidation desulfurization [11] techniques. However, the only common method like hydrodesulfurization (HDS) and oxidation desulfurization (ODS) are commonly applied. Basically, sulfur removal by HDS process requires high temperature and pressure, large amount of hydrogen and catalyst: making it a non-economic method. HDS effectively remove aliphatic sulfur compound like mercaptane, sulphide and disulphide. However, thiophenic sulfur compound cannot be removed by HDS [12]. Meanwhile, the ODS is an alternative of thiophenic sulfur compound removal, which operates under mild condition and low-cost method [13,14] Another alternative recommended method is adsorptive desulfurization (ADS). Operates at mild condition, which has high affinity towards the thiophenic sulfur compound and indeed the correct adsorbent is important to determine the efficiency of the process [15].

Activated carbon (AC) are commonly used as a support or adsorbent in ODS process, in fact it commercially available and can be synthesis. The unique characteristic such as large surface area, excellent

electron conductivity, high porosity, and inert makes AC an excellent support catalyst which can be synthesis from many sources of residual such as sawdust [16], waste tire [17] and empty fruit bunch (EFB). This not only producing value-added material but also manufacturing greener catalyst support. Basically, EFB is the main biomass waste for Malaysia and Indonesia who are producing and exporting large amount of palm oil annually. It easily modifiable at specific condition to produce a stable AC which has high surface area and theoretically has great surface characteristics as absorbance and catalyst's support. In the field of catalysis development, introduction of support catalyst could improve catalytic activity, stability and selectivity [18]. From the previous study, metals could have excellent boost for desulfurization process and the common transition metals used as active site such as Co [6], Mo [10], Mn [15], Zn [19], Ni [20], Cr [21], Pd [22], Ti [23], Fe [24], Cu [25], W [26] and V [27].

In this work, the main focus was to analyze the potential of impregnated MoO₃ on AC derived from EFB as a catalytic absorbance in desulfurization process. The absorption followed by catalytic oxidative-extractive desulfurization (OEDS) processes were carried out to remove dibenzothiophene (DBT) as model sulfur compound from the sulfur added-model oil under different catalyst and active sites loading. It was believed that this research has high potential for development of low sulfur fuel.

Experimental

Materials

Ammonium molybdate tetrahydrate, (NH₄)₆Mo₇O₂₄·4H₂O, 99%, analytical grade reagent was purchased from QReC. Meanwhile, the potassium hydroxide, KOH and N,N-Dimethylformamide, DMF were obtained from R&M Chemical and Chemiz, respectively. The solvent such as hydrochloric acid, HCl, ethanol absolute, CH₃CH₂OH and isooctane were purchased from

Emsure chemical company. The tert-Butyl hydroperoxide (TBHP) (70% solution in water) and dibenzothiophene (DBT) were supplied from Merck. All the chemicals were directly used without any purification process.

Preparation of AC-derived EFB

Readily carbonized empty fruit bunch (EFB) was grounded with KOH pellets of weight ratio 1:1, in order to increase the porosity of the carbon based EFB. Subsequently, the paste of EFB-KOH mixed was calcined at 800°C for 2 hr. The resulted of black powdered of carbon was rinse thoroughly with 1M hot HCl and hot distilled water until the pH 6~7 and dried at 110°C to produce AC-derived EFB.

Preparation of AC/MoO₃ Catalyst

In this work, thermal co-precipitation method was used to synthesis the catalyst which was adopted from Saleh, et al. [6] and Abdullah, et al. [28] with slight modification. About 1g of AC-EFB was dispersed in 25 mL of water-ethanol mixture (3:2 v:v) for 5 hours. To prepare 5% of MoO₃ onto the structure of AC, about 0.85g of (NH₄)₆Mo₇O₂₄.4H₂O was diluted with distilled water to form 0.1M metal solution, which subsequently added dropwise into the AC suspension followed by pH adjustment with KOH solution to basic pH 8-9. The mixture was stirred for 2 hours and aging for 12 hours followed by refluxed at 80°C for 6 hours. The catalyst formed was washed with ethanol and distilled water then further dried at 110°C. The black powder was calcined at 900°C for 3 hours with temperature ramp 5°C min⁻¹ to produce AC/MoO₃ (5%) catalyst. This method was used to prepare the 10%, 15% and 20% of MoO₃ on the structure of AC-EFB and annotated as AC/MoO_{3(x)}, where 'x' is the percentage of metal oxide loading.

Characterization of AC/MoO₃ Catalyst

The surface characteristics of the prepared catalyst was analysed by Brunauer-Emmett-Teller (BET) technique using nitrogen adsorption/desorption on BEL Japan Inc, Belsorp II. The structure pattern and phase crystallography of sample was characterized using X-Ray Diffraction (XRD) recorded at 2θ between 10° and 80° using the Malvern Panalytical diffractometer, X'Pert Pro, UK with the Cu Kα radiation operates at 40 kV and 40 mA with λ = 1.5418 Å. To study the morphology of particle, catalyst was examined using US Thermo Fisher Scientific, scanning electron microscope (SEM), Phenom XL. Thermo gravimetric Analyzer (TGA) using model SETARAM SETSYS Evolution 1750, US instrument was performed to

understand the decomposition pattern of the functional group of the catalyst particles. Meanwhile, the X-ray fluorescence (XRF) conducted by using UK Malvern Panalytical, Epsilon 3XL Benchtop XRF Spectrometer for determination of MoO₃ presence on the AC particles.

Sulfur Removal by Adsorption and Oxidative-extractive Desulfurization

The desulfurization activity of the catalyst was tested by mixing with 500 ppm and 800 ppm DBT in isoctane as model oil in the presence of oxidizing agent TBHP and extractant N,N-Dimethylformamide (DMF). The operating parameters such as oxidant-to-sulfur molar ratio, reaction time, reaction temperature, catalyst loading, catalyst dose-to-model oil and DMF-to-model oil ratio were at constant.

For adsorption process, 10 ml model oil containing 500 ppm sulfur was added and stirred with 0.1g catalyst for 30 minutes at room temperature. The treated model oil was filtered afterwards and an aliquot of the filtered desulfurized oil was analyzed for sulfur content by gas chromatography with flame ionization detector (GC-FID).

In the other hand, for oxidation-extraction process, 10 ml of 500 ppm sulfur in model oil, 0.1 g catalyst and tert-butyl hydroperoxide (TBHP) oxidant with oxidant to sulfur ratio of 3 mol (O/S = 3) placed in a flask and stirred for 30 minutes at 50°C. The oxidized model oil then further subjected for sulfur extraction by liquid-liquid extraction technique. In this process, catalyst was removed by filtration and the oxidized model oil was mixed with DMF with ratio 1:1 (v:v) and stirred vigorously for 30 minutes at ambient temperature and atmospheric pressure. The resultant extraction produces two separate layers of treated model oil and extractant where an aliquot of the treated oil was examined for sulfur content by gas chromatography with flame ionization detector (GC-FID).

Sulfur Determination by GC-FID

Analysis of DBT content was conducted by using Agilent 7890 gas chromatography flame ionization detector (GC-FID) equipped with HP-5MS capillary column (30m × 0.250mm, 0.25 μm film thickness). The inlet and detector temperatures were set at 230°C and 250°C respectively. The column temperature retained for 0 min at 100°C followed by temperature risen to 180°C for 5 min with heating rate at 10°C min⁻¹. The heating was continued risen to 230°C and held for 5 min with heating

rate $10^{\circ}\text{C min}^{-1}$. Flow rate of air, nitrogen and hydrogen were 350, 30 and 30 mL min^{-1} respectively with injection volume of $1.0 \mu\text{L}$. Determination of sulfur compound was calculated by using the [Equation 1];

$$\frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

Where:

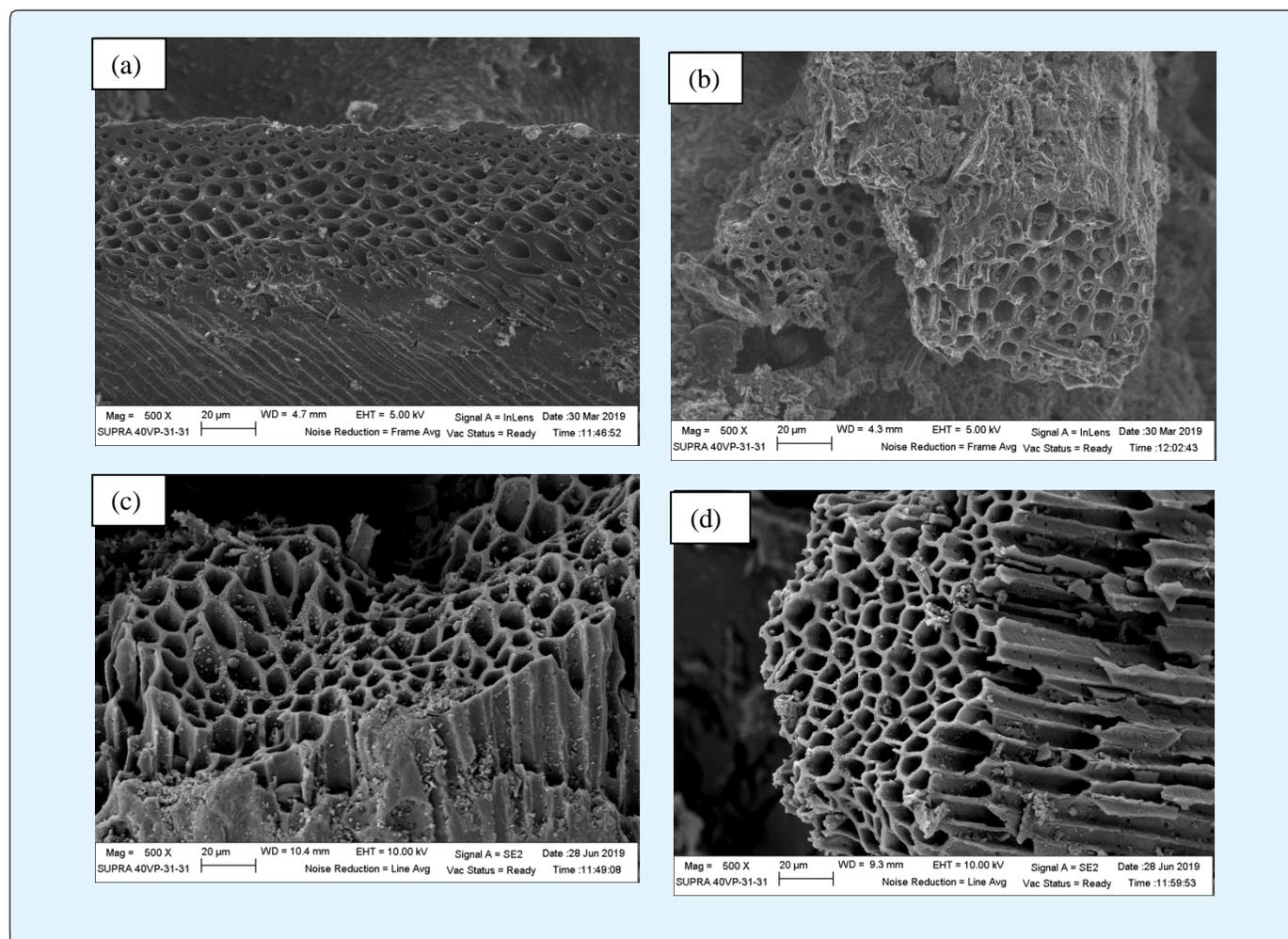
C_i represents the initial concentration of sulfur
 C_f represents the amount of sulfur of treated model oil

Results and Discussion

Characterization of The Catalyst

The morphology of the prepared catalyst was characterized by FESEM. The images displayed in Figure

1(a - f) shows the non treated AC-EFB, KOH treated AC-EFB, AC/MoO₃ (5%), AC/MoO₃ (10%), AC/MoO₃ (15%) and AC/MoO₃ (20%), respectively. From the images, it was observed that there was pore enlargement after carbonized EFB was treated with KOH using 1:1 weight ratio. Averagely, the pore diameters before KOH treatment was about $9 \pm 2 \text{ nm}$, after treated showing the increasing of pore diameter ranging from $9.5 \pm 2 \text{ nm}$ to $11 \pm 2 \text{ nm}$. This is due to the chemical treatment by the KOH which commonly known as activation agent [29]. The chemically treated AC showing fine distribution of porous, this could improve the surface area, pore volume and pore size. Hence, theoretically can boost the absorption capability and also it can provide larger sites for the catalytic reaction.



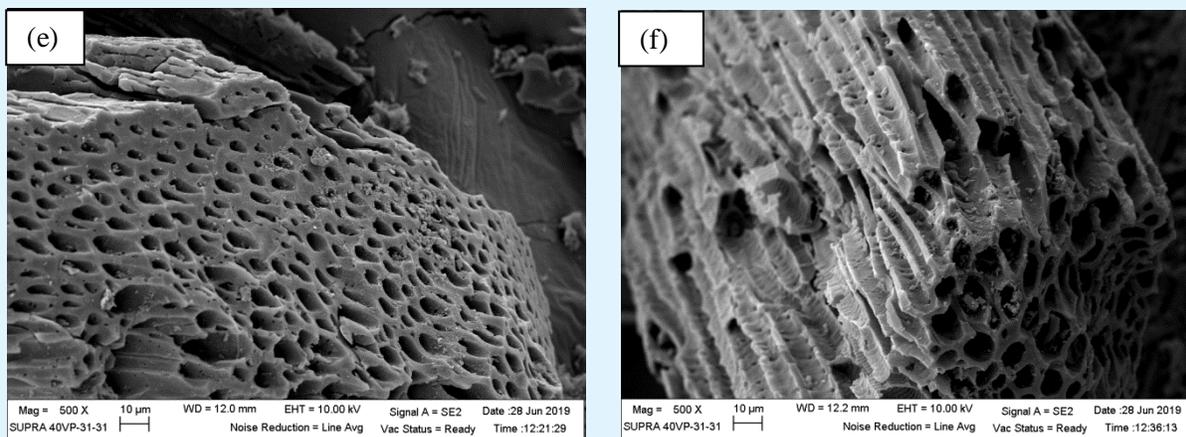


Figure 1: FESEM images of (a) non treated AC-EFB, KOH treated (b) AC-EFB (1:1 w/w), (c) AC/MoO₃ (5%), (d) AC/MoO₃ (10%), (e) AC/MoO₃ (15%) and (f) AC/MoO₃ (20%) with 500 × magnification.

To determine the success of Mo impregnation, the prepared catalyst was qualitatively characterized using XRD. Through the XRD pattern recorded, there was obvious appearance of several peaks at 2θ of 25° (2 0 0), 32° (0 0 2), 37° (0 2 1), 45° (3 1 1) and 51° (4 0 0) when MoO₃ was incorporated onto the AC-EFB support. These peaks corresponds to MoO₃ according to JCPDS (file

number: 00-047-1081). Moreover, there was an ascending in intensity of MoO₃ peaks as the weight percent of the impregnated metal increased. Another study conducted [27] where MoO₃ was incorporated onto MCM-41 shares similar planes of Mo with the current study conducted.

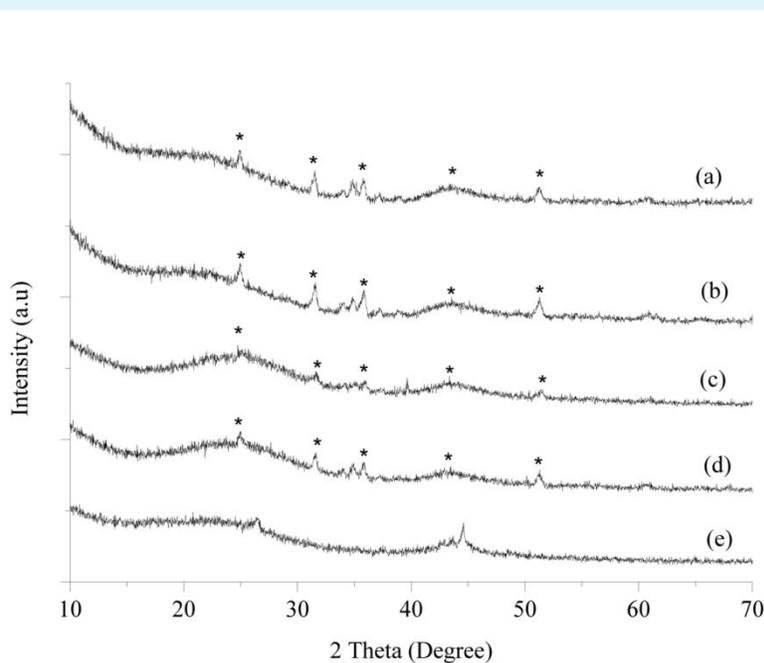


Figure 2: XRD diffractogram of AC/MoO₃ with different MoO₃ loading (a) 20% MoO₃, (b) 15% MoO₃, (c) 10% MoO₃, (d) 5% MoO₃ and (e) AC-EFB.

Further characterization using XRF was performed to quantify the actual amount of the Mo impregnated on the AC-EFB support as shown in Table 1. Based on analysis result, the highest concentration of Mo detected was 590.6 ppm equivalent to 0.59 mg Mo/g AC and lowest was

480.7 ppm equivalent to 0.48 mg Mo/g AC for the AC/MoO₃ (20%) and AC/MoO₃ (5%), respectively. Obvious increasing trend of metal loaded resulting higher concentration of the actual impregnated MoO₃.

Type of catalyst	Concentration of Mo (ppm)	Percentage of Mo (%)	Mass of Mo (mg Mo/g AC)
AC/MoO ₃ 5%	480.7	0.48	0.48
AC/MoO ₃ 10%	513.3	0.51	0.51
AC/MoO ₃ 15%	563.1	0.56	0.56
AC/MoO ₃ 20%	590.6	0.59	0.59

Table 1: Concentration of Mo on the AC/MoO₃ catalysts.

Furthermore, Table 2 summarizes the surface area, pore volume and pore size of the prepared AC with comparison to another synthesized AC from previous reported study. The carbonized EFB has the largest pore size of 8.04 nm yet have the least surface area 7.90 m² g⁻¹ and pore volume 0.0158 cm³ g⁻¹ compared to the non-treated AC-EFB of 614.59 m² g⁻¹ and 2.0686 cm³ g⁻¹ respectively. It was observed that, the dry chemical treatment applied in this work was successfully carried out, as a result the surface area from raw to calcined without chemical treatment and chemically treated was

improved significantly from 7.90 m² g⁻¹ to 614.59 m² g⁻¹ and further increased to 1575.50 m² g⁻¹, respectively. As compare to the other study on AC derived EFB stated in Table 2, the current study shows higher BET aspects. This proves the proposed technique has increased the porosity of the AC derived EFB. However, the catalyst prepared shows a decrease in the surface area and pore volume for the impregnated AC with MoO₃, where, more impregnation of metal oxides reducing the surface area and thus indicated the successful dispersion of MoO₃ on the AC-EFB support.

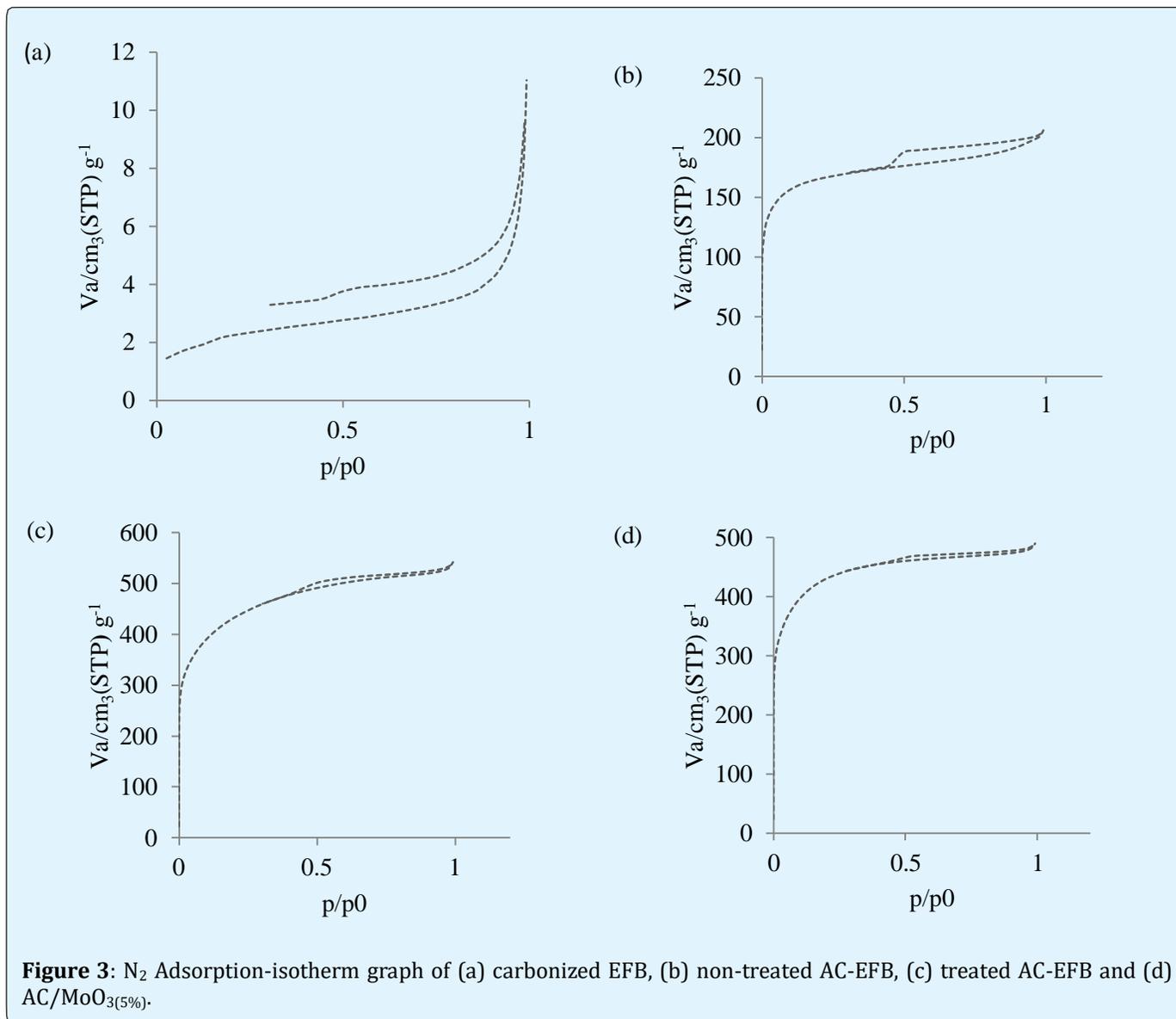
Catalyst	Surface area, S _{BET} , (m ² g ⁻¹)	Pore Volume, (cm ³ g ⁻¹)	Pore Size, (nm)	Reference
Raw EFB	7.8959	0.015871	8.0403	In this work
Non treated AC-EFB	614.59	0.3178	2.0686	In this work
Treated AC-EFB*	1575.5	0.8347	2.1192	In this work
AC/MoO ₃ 5%	1350.20	0.7558	2.2392	In this work
AC/MoO ₃ 10%	1322.00	0.7164	2.1675	In this work
AC/MoO ₃ 15%	1314.30	0.7315	2.2262	In this work
AC/MoO ₃ 20%	1277.90	0.7411	2.3196	In this work
AC-EFB	720.00	0.341	-	[30]
AC-EFB	36.64	-	5.76	[31]
AC-EFB clinker	2.48	0.0038	-	[32]

*treated with KOH (1:1 w/w)

Table 2: Surface characteristics of prepared AC of non-treated and chemically treated with KOH, AC/MoO₃ with different metal loadings and other studies.

Figure 3 illustrates the N₂ adsorption-desorption isotherm graph of the carbonized EFB, non-treated and treated AC-EFB and AC/MoO₃ (5%). In accordance of the IUPAC classification, (a) was a nonporous which confirms the morphological data where the pores observed was small compared to the treated AC-EFB. In the other hand, Figure 3(b), (c) and (d) exhibit type-II isotherm, which

was macro-porous, at the beginning of the almost linear middle section of the isotherm indicated that the stage at which monolayer coverage was complete and multilayer adsorption about to begin. The trends were aligned with the FESEM images which pore enlargement and thinning of the AC wall were observed.



Desulfurization Processes

The performance of the EFB derived activated carbon containing MoO₃ was evaluated through the removal of sulfur compound from model oil, which has been divided into two techniques known as absorption and oxidative-extractive desulfurization processes.

Absorption Activity of Activated Carbon on Sulfur Removal

In order to study the absorption performance of the AC-EFB, the prepared catalysts without any

implementation of oxidant or extractant were employed into the desulfurization process for 30 minutes of vigorous stirring in 500 ppm and 800 ppm of DBT (sulfur compound) in model oil, and the data was presented in Figure 4. For 500 ppm sulfur, the highest removal was 60.7% using AC/MoO₃ (20%), followed by AC with 60.9% and 57.2% by AC/MoO₃ (5%).

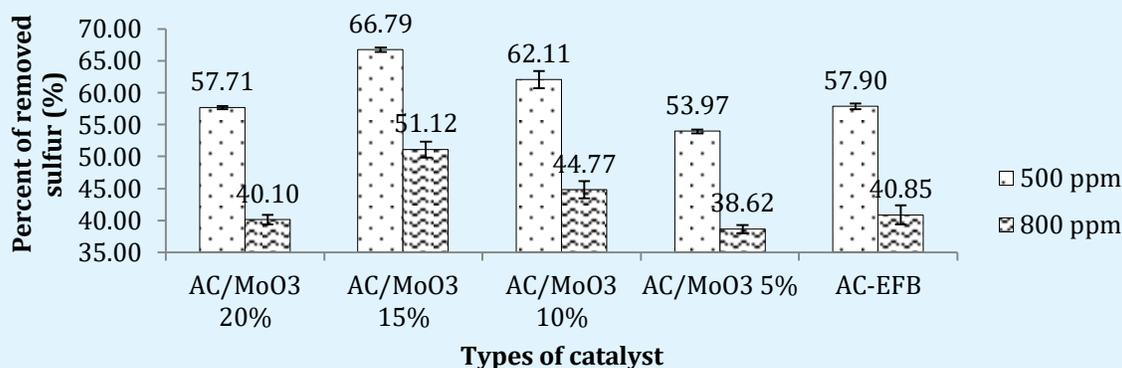


Figure 4: Adsorption of 500 ppm and 800 ppm of DBT using Ac/MoO₃ 20%, Ac/MoO₃ (15%), Ac/MoO₃ (10%), Ac/MoO₃ (5%) and treated AC. (Parameter condition: stirring speed 500 rpm, absorption time of 30 min and 1% catalyst (0.1 g/10 mL)).

For 800 ppm of sulfur, the AC successfully removes highest amount of sulfur about 42.1%, followed by AC/MoO₃ (20%) and AC/MoO₃ (5%) with 41.4% and 40% respectively. Furthermore, the data collected shows that there was no significant difference of sulfur removal among the AC and Mo impregnated AC. Even though MoO₃ has a tendency as the absorption affinity, yet, the surface area of the AC was higher as compared to other impregnated AC with metal oxide, thus increasing the absorption of the sulfur compound.

Effect of Molybdenum Oxide on Sulfur Removal

In order to maximize the desulfurization efficiency, oxidative-extraction desulfurization was applied onto 500

ppm and 800 ppm DBT in model oil with the addition of oxidant and extractant under vigorous stirring speed at 500 rpm, at 60 °C for oxidation process and 30 minutes of contact time followed by extraction process at room temperature. Figure 5 shows the percentage of sulfur removal using AC/MoO₃ (20%), AC/MoO₃ (15%), AC/MoO₃ (10%), AC/MoO₃ (5%) and AC. As a result, both 500 ppm and 800 ppm successfully exceeded 95% sulfur removal of highest 98.1% and 96.7% respectively. There was a quite huge difference in sulfur removal comparing to the process without applying oxidant and extractant.

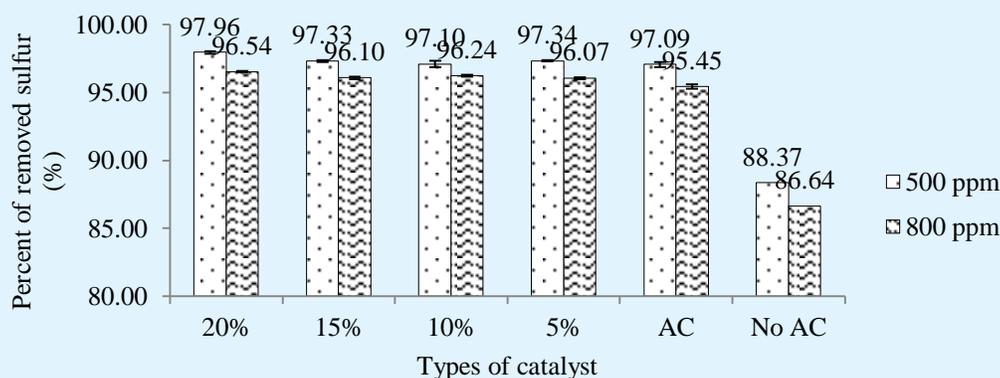


Figure 5: Oxidation extraction of DBT of 500 ppm and 800 ppm using Ac/MoO₃ 20%, Ac/MoO₃ 15%, Ac/MoO₃ 10%, Ac/MoO₃ 5% and treated AC (parameter condition: Oxidant : sulfur 3:1 molar ratio, oxidation at 50°C, catalyst 0.1g, extraction at room temperature, extractant to oil 1:1 volume ratio).

However, only slight increment was observed when the MoO₃ impregnated AC is used to improve the efficiency of the desulfurization process. Theoretically, the metal oxide will initiate the oxidation process of DBT to sulfone. However, may be due to the small amount of metal oxides presence on the structure (Table 1) could not maximize the rate of desulfurization process. However, the simultaneous absorption-oxidation-extraction process assisted by AC/MoO₃ showed remarkable removal of sulfur compound up to 97.9%. This might be due to the interaction of oxidant TBHP and catalyst MoO₃ which initially form peroxidic complex and oxidizes the DBT to form DBT sulfoxide (intermediate) and further oxidized by another peroxidic complex to form DBT sulfone [33].

Conclusion

The evaluation on the capability of the value-added EFB as a catalyst support was successfully carried out. Treatment of carbonized EFB with KOH successfully improves the surface characteristics by increasing the surface area and pore sizes, which experimentally increased the absorption affinity toward sulfur compound. The results showed that the presence of impregnated MoO₃ on AC derived EFB, oxidant TBHP and extractant DMF had successfully increased the desulfurization up to 97.9%, as compared to the normal absorption process only 66.8%. This can be concluded that the MoO₃ impregnated AC derived EFB has catalyzed the absorption-oxidation-extraction process effectively and has high potential for the sulfur removal from sulfur-contained fuels.

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