Influence of Molybdenum Disulfide (MoS_2) Catalyst on Carbon from Sugarcane Bagasse Via Hydrothermal Carbonization for Jatropha Oil Residue Upgrading

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Abstract

Molybdenum disulfide (MoS_2) catalyst has been successfully synthesized for carbon support from lignocellulosic in sugarcane bagasse using hydrothermal carbonization and calcination techniques. The hydrothermal carbonization of lignocellulosic material into carbon support was studied between 160 to 200 °C for 24 h. The MoS_2 precursor is prepared by mixing thiourea and ammonium molybdate tetrahydrate then impregnate on carbon support. Surface area and carbon content from lignocellulosic structure as hemicellulose and cellulose were improved at high temperature via hydrothermal carbonization and calcination. The hydrodeoxygenation reaction in molybdenum disulfide catalytic upgrading was studied oxygenated compounds in jatropha oil residue using pyrolyzer gas chromatography mass spectroscopy (Py-GC/MS). It showed that the molybdenum disulfide on carbon support from sugarcane bagasse prepared at 200 ºC for 24 h can reduce oxygenated compounds in jatropha oil residue.

KEYWORDS: Molybdenum disulfide; Hydrothermal carbonization; Sugarcane bagasse; Pyrolysis

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Introduction

At present, renewable energy sources such as biofuels are more important from the shortage of energy sources such as fossil fuel and environmental pollution awareness. Bio-oil can be extracted from lignocellulosic structure in biomass by fast pyrolysis process at high temperature rapidly and give bio-oil yield approximately 75% [1]. The bio-oil characteristics are dark brown, high viscosity and contained many complex elements from biomass materials. Jatropha oil is a kind of biofuel that can be extracted from jatropha seed residue [2]. There is a tendency to utilize bio-oil in place of biodiesel because the heating value is similarly. However, utilization of bio-oil in engine directly is not suitable due to its high acidity and oxygen content [3 – 4]. Hydrodeoxygenation (HDO) is the process of removal oxygen atoms in a form of water molecules using metal catalyst, hydrogen in pressure range of 2 – 10 MPa and temperature between 300 – 450 ºC which improves chemical stability of bio-oil [5 – 6]. The molybdenum disulfide (MoS_2) is a metal catalyst used in industrial applications for improvement of bio-oil via hydrodeoxygenation reaction because of its high activity and low cost. The molybdenum disulfide (MoS_2) catalyst is most often supported on γ-Al_2O_3. This support has high surface area and strong bonding from Al-O but the disadvantage is high acidity and coking reaction which result in reduced efficiency in hydrodeoxygenation [6 – 7]. The carbon support from biomass are good candidates as catalyst support due to its diverse porous characteristic, high resistance to acid, abundant sources and no coking reaction in hydrodeoxygenation. Sugarcane bagasse is a by-product agricultural waste from sugarcane extraction. It contains mostly lignocellulosic compound including cellulose, hemicellulose, lignin and extractives that contain polyphenol. Sugarcane bagasse can be used in paper production, wood furniture and support for metal catalyst. For example, sugarcane bagasse was used to synthesis magnetic carbon composites for absorption of tetracycline by hydrothermal carbonization [8]. Hydrothermal carbonization (HTC) is a thermochemical conversion process using temperature between 160 – 250 ºC, and pressure at 4 – 22 MPa in closed-system. This process converts lignocellulosic structure with hydrolysis and dehydration reactions to produce carbon support [9 – 10]. The lignocellulosic as cellulose and hemicellulose were changed to monomer-chains and gave porous structure on carbon support. In this research, sugarcane bagasse was synthesized into carbon support by hydrothermal carbonization using temperature between 160 – 200 ºC. Molybdenum disulfide catalyst was used for jatropha oil residue upgrading. The catalyst was prepared by loading MoS_2 on carbon support via impregnation and pyrolysis at 300 – 500 ºC under N_2 atmosphere.

Materials and Methods

Sugarcane bagasse was milled and dried at 90 ºC for 24 h. 30 g of sugarcane bagasse was mixed with 120 ml of deionized water (water to biomass ratios of 4:1) and loaded into reactor for HTC. The temperature for sugarcane bagasse treatment was applied at 160 – 200 ºC for 4 – 24 h. After HTC, the reactor was quenched in water to stop the reaction immediately then the products were dried at 90 ºC for 24 h. Molybdenum disulfide catalyst was prepared by mixing 40 mmol of thiourea (CH_4N_2S) and 1 mmol of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in deionized water. The precursor catalyst was loaded on carbon support materials by impregnation process at 80 ºC and dried at 90 ºC for 24 h. MoS_2 was formed with pyrolysis at 300 – 500 ºC for 2 h under N_2 atmosphere heating rate 10 ºC min^{-1}. The morphology of carbon support by hydrothermal carbonization (HTC) and pyrolysis were characterized by scanning electron microscope ; SEM (EVO®MA10) and the functional group in lignocellulosic under HTC treatment were investigated by fourier transform infrared spectroscopy ;FT-IR (PerkinElmer UATR Two). Finally, jatropha oil residue upgrading products were analyzed for oxygenated, fatty acid and hydrocarbon compounds by pyrolyzer gas chromatography mass spectroscopy;Py-GC/MS (Shinmadzu GCMS-QP2010 Plus) and pyrolyzer (Py-2020).

Results and Discussion

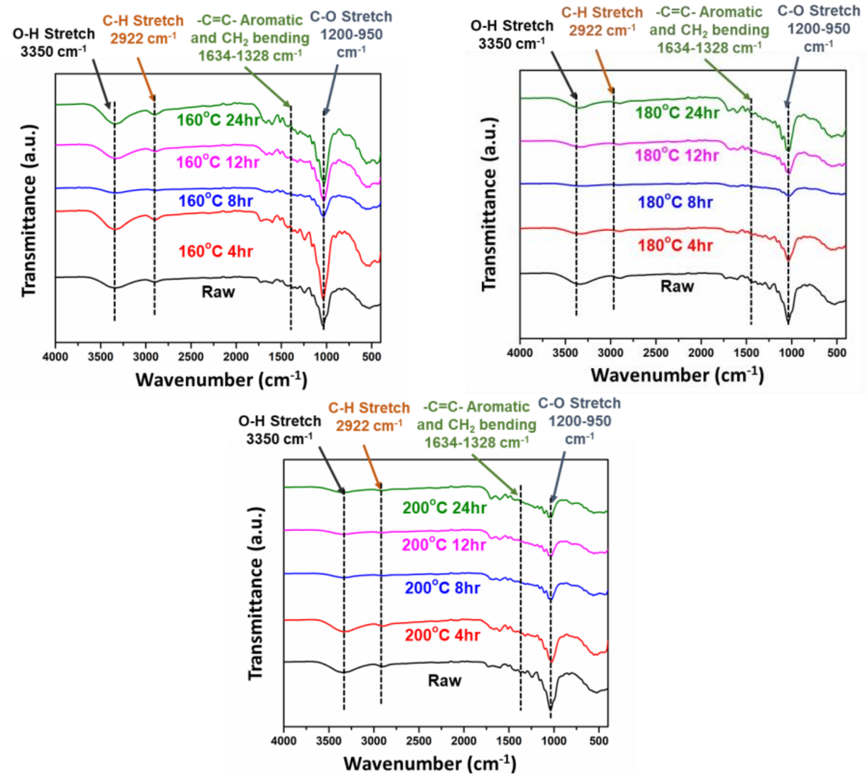

Fig. 1 FTIR Analysis of sugarcane bagasse after hydrothermal carbonization at 160, 180 and 200 ºC for 4, 8, 12 and 24 h

Fig. 1 shows the functional group from FT-IR analysis of sugarcane bagasse under hydrothermal carbonization. At 3350 cm^{-1} indicates OH stretch peak in cellulose, hemicellulose and lignin. At 2922 cm^{-1} indicates CH stretch peak in cellulose. At 1634 – 1328 cm^{-1} indicates C=C aromatic and CH_2 bending peak of lignin. At 1200 – 950 cm^{-1} indicates C-O stretch peak in hemicellulose. At 900 – 700 cm^{-1} indicates CH bending peak. The OH and C-O stretch at 160 ºC has been slightly changed because HTC temperature is too low for decomposition. At 180 ºC, The C-O and OH peak has been decreased and reduced dramatically at 200 ºC. Decreasing of OH and C-O peak show that hemicellulose in lignocellulosic has been decomposed with hydrolysis and dehydration reaction in HTC reaction. At C=C aromatic and CH_2 bending peaks has been slightly changed because both peaks are lignin structures and high stability.

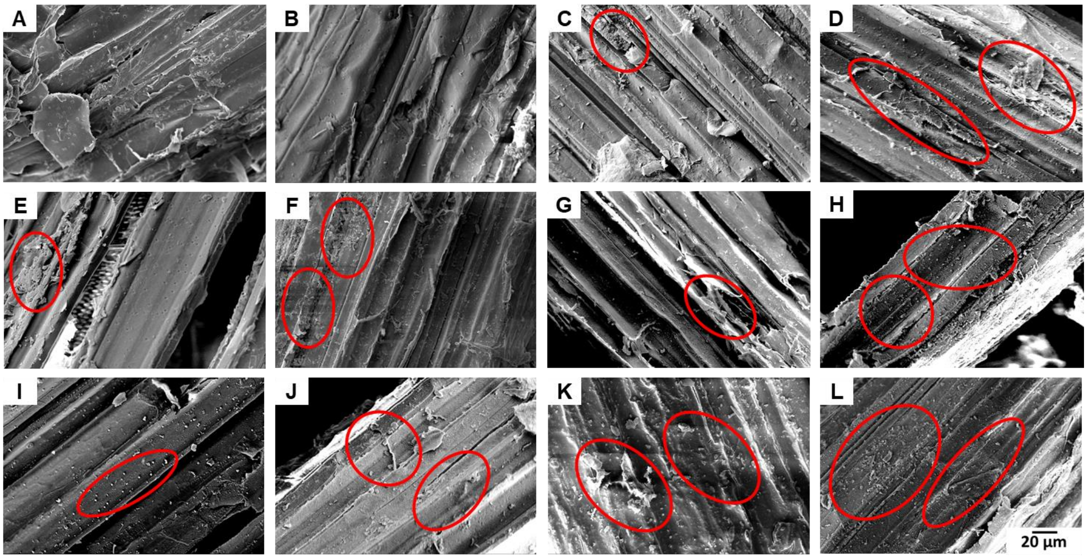

Fig. 2 SEM image (500X) of catalyst on sugarcane bagasse from hydrothermal carbonization

(A) 160 ºC for 4 h, (B) 160 ºC for 8 h, (C) 160 ºC for 12 h, (D) 160 ºC for 24 h

(E) 180 ºC for 4 h, (F) 180 ºC for 8 h, (G) 180 ºC for 12 h, (H) 180 ºC for 24 h

(I) 200 ºC for 4 h, (J) 200 ºC for 8 h, (K) 200 ºC for 12 h, (L) 200 ºC for 24 h

Fig. 2 indicates the morphology of sugarcane bagasse after hydrothermal carbonization. Lignocellulosic as cellulose and hemicellulose were decomposed due to increasing of HTC temperature and duration time. Decomposition of lignocellulosic in sugarcane bagasse indicate that the particle on biochar surface. It is caused by hydrolysis and dehydration reaction in HTC with lignocellulosic. β-1,4 glycosidic bond in hemicellulose and cellulose will change into a monomer structure such as mannose, galactose, glucose and xylose [4].

Fig. 3 shows the percentage yield of biochars from sugarcane bagasse after hydrothermal carbonization. Increasing of HTC temperature and reaction time resulted in biochars yield decreases and yields approximately 57% at 200 ºC for 24 h. The mass yield was changed from solid to liquid and gas phase. Liquid phase consists of glucose, mannose, sucrose etc. was produced by hydrolysis process of cellulose and hemicellulose of sugarcane bagasse in hydrothermal carbonization process [4]. The amount of liquid and gas phase that will change depends on the temperature and duration time in hydrothermal carbonization.

Fig. 4 indicates the functional group from FT-IR analysis of sugarcane bagasse under pyrolysis process. At 3350 cm^{-1} shows OH stretch peak in cellulose, hemicellulose and lignin. At 2922 cm^{-1} shows CH stretch peak in cellulose. At 1634 – 1328 cm^{-1} shows C=C aromatic and CH_2 bending peak of lignin. At 1,200 – 950 cm^{-1} shows C-O stretch in hemicellulose. At 900 – 700 cm^{-1}

shows CH bending peak. At 470 cm^{-1} shows Mo-S peak of MoS_2. The C-O, C=C aromatic and CH_2 bending has been decreased dramatically. While, CH stretch and OH stretch peak has been disappeared in pyrolysis under N_2 atmosphere by using high temperature. Decreasing of all peaks show that increasing of carbon content and porosity on sugarcane bagasse from decompose of lignocellulosic structure in pyrolysis process.

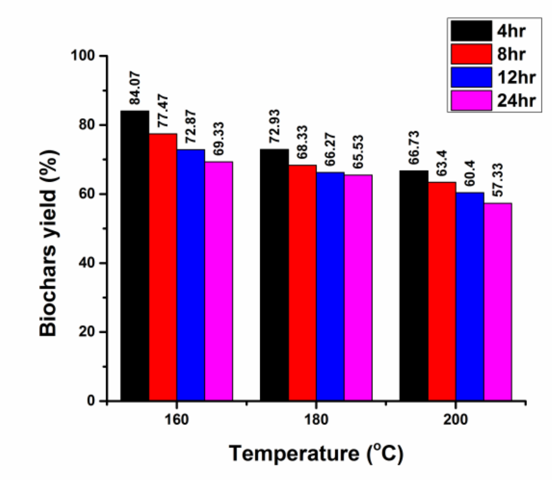

Fig. 3 The percentage yield of biochars from sugarcane bagasse with hydrothermal carbonization

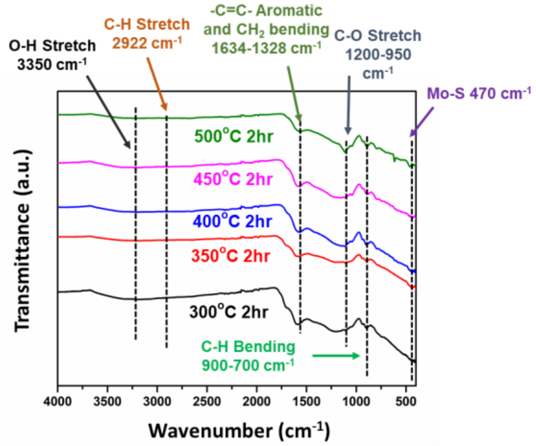

Fig. 4 FTIR Analysis of sugarcane bagasse after hydrothermal carbonization at 200 °C for 24 h and pyrolysis at different temperature for 2 h

Fig.5 shows the morphology of catalyst and carbon support from hydrothermal carbonization and calcination. The lignocellulosic in carbon support has been decomposed dramatically at high temperature and molybdenum salt on surface changed to molybdenum disulfide particle. The MoS_2 particle has been appeared on the surface of carbon support materials and particle size decrease at high temperature. SEM micrograph reveals that the average particle size measure by ImageJ software are 2.70, 2.79, 2.68, 2.24 and 1.25 μm in A, B, C, D and E image, respectively. The MoS_2 particle size depend on increasing of temperature and heating rate in calcination. At calcination temperature, cellulose and hemicellulose has been eliminated while the highly stable structure of lignin begins to decompose range of 350 °C.

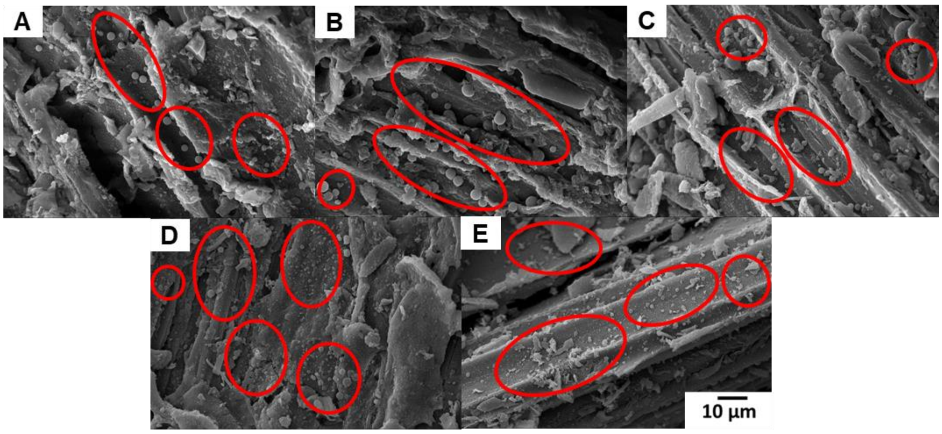

Fig. 5 SEM image (1000X) of catalyst on sugarcane bagasse from hydrothermal carbonization at 200 °C for 24 h and pyrolysis under N_2 atmosphere for 2 h (A) 300 °C (B) 350 °C (C) 400 °C (D) 450 °C and (E) 500 °C

Table 1 shows the increasing percentage of molybdenum and sulfur in MoS_2 as temperature is increased in pyrolysis process. Increasing of pyrolysis temperature results in higher dispersion of the MoS_2 particles because the carbon support is high in porosity from decomposition of lignocellulosic in pyrolysis process. Increasing dispersion of the particle indicates that carbon support from sugarcane bagasse has high surface area.

Table 1 Shows percentage of Molybdenum (Mo) and Sulfur (S) in MoS_2 on sugarcane carbon support

Pyrolysis	Mo (%wt)	S (%wt)
300 °C	3.10	2.39
350 °C	5.65	1.73
400 °C	7.44	2.69
450 °C	7.58	2.80
500 °C	8.15	3.78

Fig. 6 shows the organic compounds in jatropha oil residue after catalytic pyrolysis using MoS_2 (loaded on carbon support from using sugarcane bagasse) by pyrolyzer gas chromatography mass spectroscopy (Py-GC/MS). The total oxygenated compounds including fatty acid, ketone, alcohol, aldehyde, and nitrogen oxygenated compounds were reduced by using MoS_2 loaded on carbon support. While the total hydrocarbon compounds including aliphatic, olefins and aromatics ring were increased. Catalyst on carbon support pyrolyzed at 400 °C reduces fatty acid compounds about 14% compared with jatropha seed (raw). Decreasing of the total oxygenated compounds (fatty acid and oxygenated) indicates the hydrodeoxygenation reaction by MoS_2 catalyst on carbon support. Molybdenum disulfide removes oxygen molecules in oxygenated compounds via hydrogenation and hydrogenolysis in hydrodeoxygenation reaction. As a result, hydrocarbon compounds (aliphatic, olefins and aromatic) increased and the quality of jatropha bio-oil is improved. MoS_2 catalyst structure including the Mo-S like a sandwich planar can assist reaction between the hydrogen molecule and oxygenated compound via sulfur vacancies. After that, hydrogen molecule on MoS_2 will react with the oxygenated compound through hydrogenation process and remove H_2O by hydrogenolysis reaction, respectively [6 – 7]. As a result, hydrocarbon compounds (aliphatic, olefins and aromatic) are increased and the quality of jatropha oil is improved.

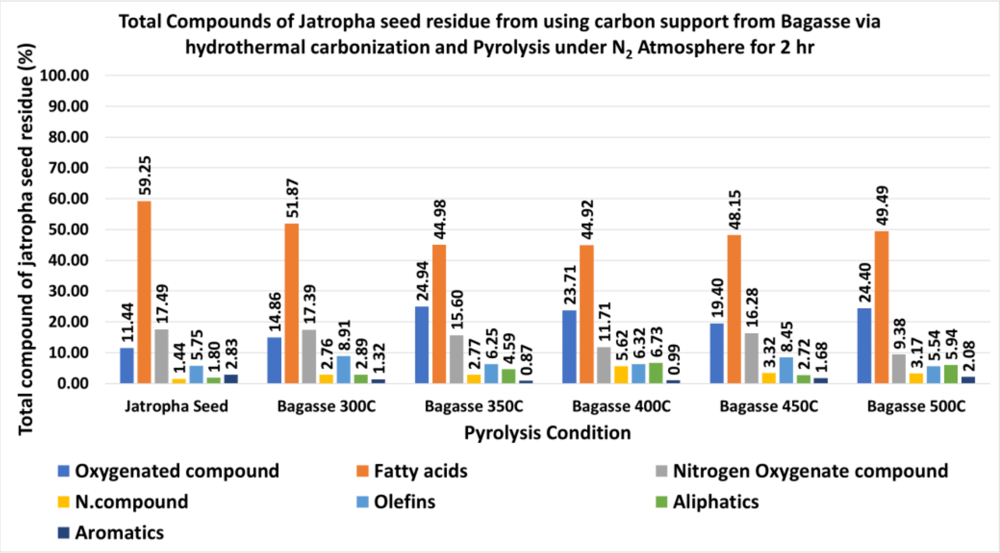

Fig. 6 The total compound of jatropha oil residue by using MoS_2 catalyst (loaded on carbon support) from pyrolysis under N_2 atmosphere for 2 h

Conclusion

The MoS_2 catalysts have been successfully synthesized and loaded on carbon support from sugarcane bagasse via hydrothermal carbonization and pyrolysis process. Fatty acid compounds in jatropha oil residue were changed to hydrocarbon compounds using MoS_2 catalyst supported on carbon support at 400 °C via hydrodeoxygenation reaction. Approximately 14% of fatty acid compounds were reduced after catalytic pyrolysis process compared to the original jatropha oil residue.

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References

[1] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass. Bioenerg. 38 (2012) 68 – 94.

[2] M. Min Aung, Z. Yaakob, S. Kamarudin L. Chuah Abdullah, Synthesis and characterization of Jatropha (Jatropha curcas L.) oil-based polyurethane wood adhesive, Ind. Crop. Prod. 60 (2014) 177 – 185.

[3] Z. Si, X. Zhang, C. Wang, L. Ma, R. Dong, An overview on catalytic hydrodeoxygenation of pyrolysis oil and its model compounds, Catalysts. 7 (2017) 169.

[4] S. Nizamuddin, H. Ahmed Baloch, G.J. Griffin, N.M. Mubarak, A. Waheed Bhutto, R. Abrod, S. Ali Mazari, B. Si Alie, An overview of effect of process parameters on hydrothermal carbonization of biomass, Renew. Sust. Energ. Rev. 73 (2017) 1289 – 1299.

[5] Y. Elkasabi, C.A. Mullen, A.L.M.T. Pighinelli, A.A. Boateng, Hydrodeoxygenation of fast pyrolysis bio-oils from various feedstocks using carbon-supported catalysts, Fuel Process. Technol. 123 (2014) 11 – 18.

[6] Z. He, X. Wang, Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading, Catalysis Sust. Energ. (2013) 28 – 52.

[7] V. Itthibenchapong, C. Ratanatawanate, M. Oura, K. Faungnawakij, A facile and low-cost synthesis of MoS_2 for hydrodeoxygenation of phenol, Catalysis Commun. 68 (2015) 31 – 35.

[8] N. Rattanachueskul, A. Saning, S. Kaowphong, N. Chumha, L. Chuenchom, Magnetic carbon composites with a hierarchical structure for adsorption of tetracycline, prepared from sugarcane bagasse via hydrothermal carbonization coupled with simple heat treatment process, Bioresource Technol. 226 (2017) 164 – 172.

[9] Z. Liu, A. Quek, S. Kent Hoekman, R. Balasubramanian, Production of solid biochar fuel from waste biomass by hydrothermal carbonization, Fuel.103 (2013) 943 – 949.

[10] M. Knez Hrncic, G. Kravanja and Z. Knez, Hydrothermal treatment of biomass for energy and chemicals, Energy. 116 (2016) 1312 – 1322.