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Biofuel Production from Jatropha Bio-Oil Derived Fast Pyrolysis: *Effect and Mechanism of CoMoS Supported on Al₂O₃*

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Abstract. The aims of this research was to understand the CoMo/Al₂O₃ sulfide catalyst effect to remove oxygen-containing and nitrogen-containing molecules from Jatropha bio-oil derived fast pyrolysis converted to biofuels via hydrotreating process. The activity and selectivity of CoMo/ γ -Al₂O₃ sulfided catalysts in hydrodeoxygenation (HDO) of Jatropha bio-oil derived fast pyrolysis was evaluated in a Parr batch reactor under 50 bar of H₂ atmosphere for 2 h at 300 320 and 340 °C. It appeared that the CoMo/Al₂O₃ sulfide catalyst have high performance in activity for promoting the fatty acid, fatty ester, fatty amide and fatty nitrile compounds were converted to paraffin/olefin (Diesel range), this could be the CUS site on supported Al₂O₃ catalyst. The difference in selectivity products allowed us to propose a reaction scheme.

1. Introduction

The condensed pyrolysis liquid of bio-oil derived fast pyrolysis is a promising sign of renewable energy source, which can be substituted for petroleum fuels owing to its composition that looks like petroleum fuels, having an advantage of its short span and the zero net carbon emissions because it can be used to produce completely a biomass. This could solve the reduction of a greenhouse gas. However, these liquids is a complex mixture that mainly includes acid, ketone, phenols and ester etc, their high oxygen content cause to the poor thermal, high viscosity and corrosion [1]. Moreover, the bio-oil derived fast pyrolysis from Jatropha residues can present the nitrogen-containing compounds such as pyridine and amide groups in bio-oil, leads to concern with NO_x when the combustion of engine and catalyst deactivation occurred. Consequently, the conversion of condensed pyrolysis liquids to biofuels is needed to reduce the oxygen and nitrogen content via hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) reaction.

The hydrodeoxygenation (HDO) is one of the methods for bio-oil upgrading, of which commonly hydrodeoxygenation catalysts is widely studied such as supported noble reduced metal sulfided CoMo and sulfided NiMo supported on γ -Al₂O₃ catalysts [2]. However, one of the defects of supported noble catalysts is very costly and more percentage of metal leading to be active. Then the found refineries oil using the sulfide CoMo and NiMo supported on γ -Al₂O₃ catalysts are widely utilized for hydrotreatment process [3]. It was reported that the ZrO₂ and TiO₂ supports can promote the HDS activity due to the good redox properties, however, both are as poor as mechanical properties and low surface area. In addition, hydrodenitrogenation (HDN) reactions are more difficult to remove and poisons the catalysts [4]. Then we needs to the acidity sites in the catalysts for the improvement of promoting the mild hydrocracking [5].



2. Experimental

2.1. Catalyst preparation and characterization

The supported catalyst Mo/ γ -Al₂O₃ was prepared by the sol-gel method, after that the all catalysts were dried at 50 °C for 48 h and calcined at 550 °C for 4 h. The calcined catalysts were prepared by using incipient wetness impregnation of 3% solution of cobalt nitrate, drying and calcination as same the supported catalysts condition and denoted as 310CMA. Before each test, the catalysts were sulfided ex-situ at 400 °C for 4 h under H₂S/H₂ 5% (v/v). The specific surface area, pore volume and average pore diameter of synthesized catalysts was determined in oxide-form by nitrogen adsorption using a BELSORP: MINI II instrument and the acidity was determined by temperature programmed desorption of ammonia (NH₃-TPD) using a BELCAT-B instrument. The Powder X-ray diffraction (XRD) patterns of the catalyst was performed on Rigaku TTRAX III an instrument for confirmed the phase identification of catalyst. Finally, the morphology of Mo sulfide catalysts was evaluated by transmission electron microscopy (TEM) on a JEOL JEM-2100 transmission electron microscope operated at 200 kV.

2.2. The jatropha bio-oil derived fast pyrolysis

The Jatropha bio-oil derived fast pyrolysis-ESP fraction (JBP) samples used in the current study were provided by Thailand Institute of Scientific and Technological Research (TISTR), Thailand. The water content of JBP was determined for using a Karl Fischer titration method on an automatic titrator and the total acid number was measured by using an automatic potentiometric titrator (Metrohm 888 Titrand equipped). The elemental analysis of oxygen nitrogen carbon and sulfur content in bio-oil are measured in percent of weight by CHN628 Series Determinators. The chemical composition of JBP was diluted in tetraline and analyzed before hydrotreatment reaction with GC-MS and GC-FID.

2.3. Catalytic activity test

The high temperature and pressure batch reactor (Parr 4848) was used for hydrotreatment reaction of JBP. These samples extracted with 1:5 ratio of bio-oil: tetralin solvent were weighed 20 g with 0.4 g of catalysts, persulfide carried out at 300-340 °C under hydrogen pressure initial 50 bar for 2 h. The liquid products were analyzed by Agilent 7890 gas chromatograph (GC) equipped with the flame ionization (FID) detector interfaced with an Agilent model 5975 mass spectrometer (MS).

3. Results and discussion

3.1. Catalyst characterization

The results in table 1, found that the specific surface area of 310CMA was 231.2 m²/g, and pore diameter was 3.97 nm, including the total amount acid sites was 1.05 mmol/g.cat, due to the γ -Al₂O₃ support its high acid sites, stability and surface area [6].

Table 1. The synthesized catalysts properties.

Catalysts	Total surface area (m ² /g cat)	Pore diameter (nm)	Pore volume (cm ³ /g)	Acidic (mmol NH ₃ /g.cat)	NO absorbed (μ mol/g)
Commercial	246.7	6.90	0.43	0.86	-
10CMA	248.8	3.75	0.23	1.12	49.12
310CMA	231.2	3.97	0.25	1.05	58.05

Figure 1a displays the XRD patterns of the calcined catalysts, then this research was focused on the diffraction patterns of catalyst support 310CMA exhibiting the characteristic peaks at the 2 θ angle of 37.5°, 46° and 66.7° that indicated the γ -Al₂O₃ crystalline, while TEM images (figure 1b) display the MoS₂ slabs and MoS₂ stack oriented on support as a dark line, that was presented short slab length (2-3 nm) and low stacking of 2-3 stacks, as a result, its high dispersion, and low stacking of MoS₂ increased the number of rim site as the HYD active site for olefins [6, 7].

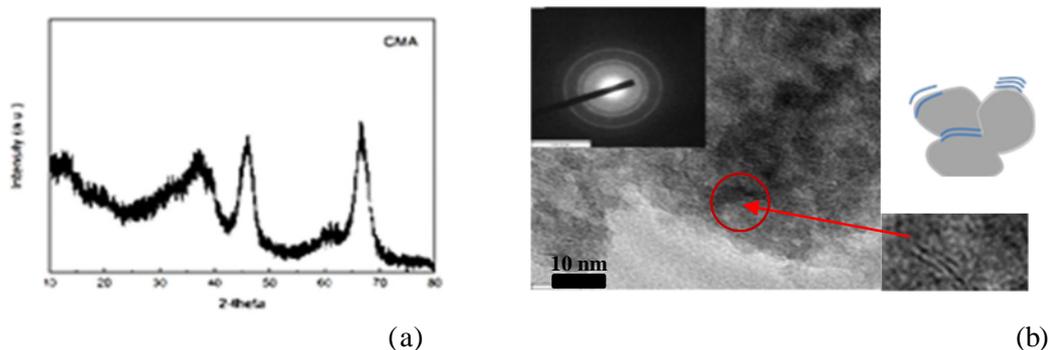


Figure 1. (a) The XRD pattern and (b) TEM image of 310CMA.

3.2. Physical properties of Jatropha bio-oil derived fast pyrolysis

The feed derived fast pyrolysis Jatropha bio-oil has total acid number of 84.37 mg KOH/g due to their contain large amount of fatty acid compounds and, the water contents of these samples were presented as 3.19 %. The elemental compositions were present as C H O and N elements were 69.27 9.86 14.60 and 6.27% respective, they're decomposed from lignocellulose hemicellulose and N element decomposed from protein are displayed in table 2. As the result, the oxygenate and nitrogen content in this bio-oil more than diesel fuel, their high oxygen content cause to the poor thermal, high viscosity and corrosion [7]. It needs to upgrading by removed the oxygen via HDO reaction.

Table 2. Properties of Jatropha bio-oil derived fast pyrolysis.

Properties	This bio-oil	Diesel [8]
HHV (MJ/kg)	33.92	< 0.02
Water content (%)	3.19	-
Total acid number (mg KOH/g)	84.37	-
Elemental composition (received basis, wt.%)		
% C	69.27	86.0
% H	9.86	13.6
% O	14.60	0
% N	6.27	< 0.05

3.3. Chemical Properties of Jatropha bio-oil derived fast pyrolysis

The products in JBP presented a complex mixture, mainly including organic acid ketone phenolic aromatic naphthene N-heteroatom alcohol ester fatty-acid fatty-amide paraffin or olefin and fatty-nitrile as shown in figure 2, then we are classified as two groups are gasoline and diesel range products, followed by a number of carbon atom in the products [9].

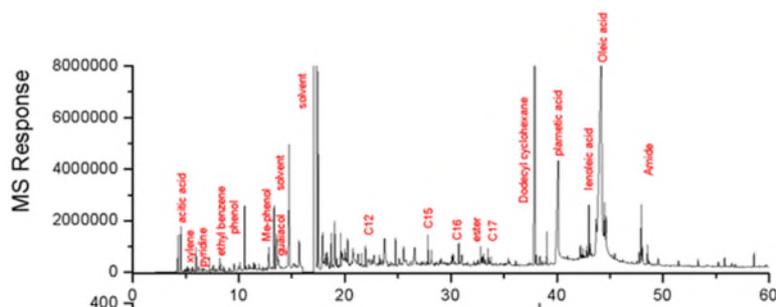
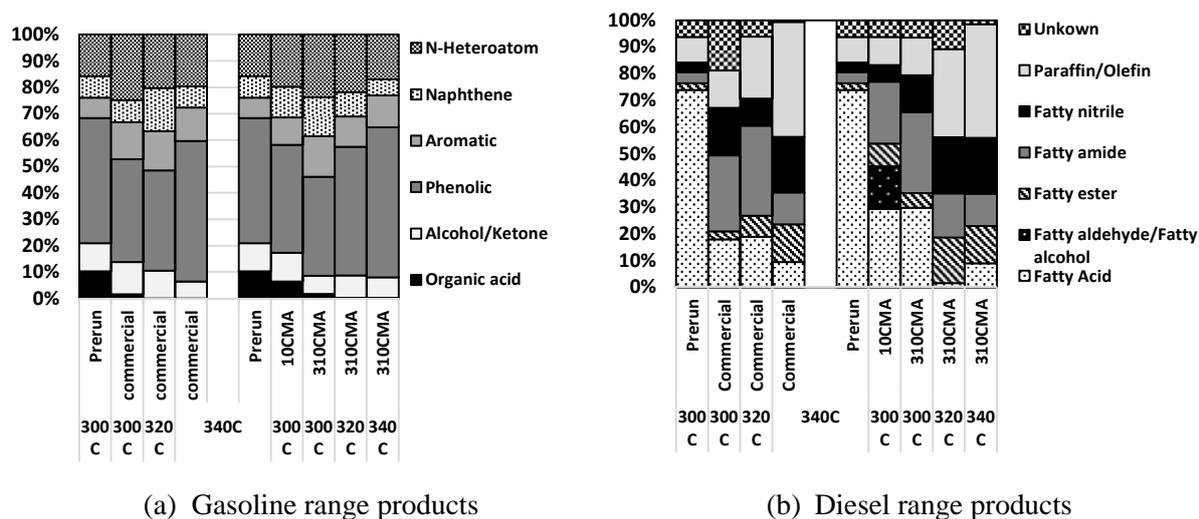


Figure 2. GC-MS chromatogram of Jatropha bio-oil derived fast pyrolysis.

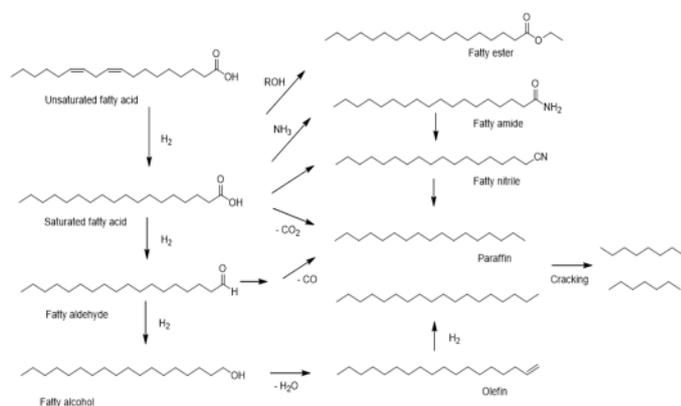
3.4. Catalytic activity test on Jatropha bio-oil derived fast pyrolysis

Figure 3a shows the selectivity of catalytic reaction of bio-oil as gasoline range that includes organic acid alcohol/ketone phenolic aromatic naphthene and N-heteroatom compounds, then the increase of the reaction temperature from 300 to 340 °C found that its has a slight difference products in all

catalysts because the large molecules of fatty acid hindered catalytic hydrotreating on active sites [13]. While the yield products of diesel range (fatty acid, fatty ester, fatty amide, fatty nitrile and paraffin/olefin), it has a large products exchange as seen in figure 3b. The reaction pathway involves esterification ammonolysis decarboxylation decarbonylation and dehydration, then each pathway through the hydrogenation (HYD) of unsaturated fatty acid to saturated fatty acid, which the reaction can be written as in scheme 1.



(a) Gasoline range products (b) Diesel range products
Figure 3. Product selectivity obtained with the CoMoS/Al₂O₃ of Jatropha bio-oil derived fast pyrolysis at 300 320 and 340 °C.



Scheme 1. Reaction network of deoxygenation of JBP over sulfide catalysts.

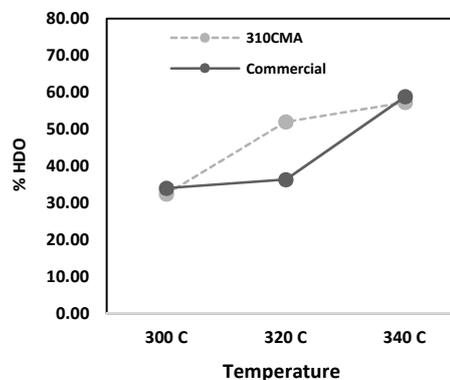


Figure 4. HDO conversion of commercial and 310CMA catalysts.

As in figure 3b, the 10CMA show fatty aldehyde/fatty alcohol are intermediately and give low the remove oxygen-containing at 300 °C compared with commercial catalysts, whereas the fast pyrolysis with 310CMA catalyst products such as fatty acid compounds are decreasing compared with crude Jatropha bio-oil derived fast pyrolysis, whereas fatty amide fatty ester can be covered to via hydrogenation, and its can reacted with nitrogen compounds are formation to fatty amide, while some reaction of fatty acid can be produced the paraffin /olefin via deoxygenation pathways and not found them immediately of fatty aldehyde/fatty alcohol, then increasing temperature at 320 °C appears the higher activity for converted fatty acid to paraffin/olefin and the increasing temperature is 340 °C, it's dramatically decreased of fatty amide compounds., there are summarized in figure 3b. This results the 310CMA promoted deoxygenation of fatty acid, fatty ester and fatty amide to paraffin/olefin, due to the important site for HDO reaction is the HYD active site, which the Al₂O₃ has a large amount of rim

site shown in of sulfide MoS₂ catalysts [10, 11]. In addition, the HDO percentage of the 310CMA catalyst compared with the commercial catalysts, it's found that the 310CMA was presented the high HDO activity than the commercial catalysts at 320-340°C as shown in figure 4.

The HDN of this research was found that there was nothing removed, because of the amide compounds transformed to nitrile through hydrogenation, However, all catalysts cannot apparently remove nitrogen due to nitrogen tolerance limitation of the catalysts [6].

4. Conclusion

From all results, we could assume that the main pathways for the removed oxygen content in JBP of the CoMoS base on Al₂O₃ catalysts reacted undergo acid site and HYD active sites leading to the cracking reaction isomerization hydrogenation direct-oxygenation decarboxylation and decarbonylation reaction as fatty acid → ester → paraffin or olefin.

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