Production of Biodiesel from Esterification of Oil Recovered from Palm Oil Mill Effluent (POME) Sludge using Tungstated-Zirconia Composite Catalyst

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Abstract

Solid acid catalyst prepared from tungsten and zirconium oxide composite had been characterized and evaluated on biodiesel production by esterification of low quality oils taken from POME sludge. Catalyst characterization was conducted using Scanning Electron Microscopy (SEM) and acidity test. Acidity test of catalyst resulted using Gravimetry method is 5.4 mole/g. Esterification to produce biodiesel using tungsten and zirconium oxide composite show increasing amount of catalyst used will also increased conversion percentage of biodiesel produced and reach optimum value at 10%. Catalyst:oil ratio used to produce optimum conversion is 8:1 which converted 74.88% oil to biodiesel.Keywords: *Euphorbia geniculata* Ortega, toxicity, lupeol acetate

Keywords: Tungsten-Zirconia composite, POME Sludge, Esterification

Abstrak (Indonesian)

Penelitian tentang preparasi dan karakterisasi katalis komposit tungsten dan zirkonium oksida serta aplikasinya untuk esterifikasi minyak hasil recovery limbah sludge industri kelapa sawit telah dilakukan. Karakterisasi katalis dilakukan dengan menggunakan SEM dan uji sifat keasaman. Sifat keasaman katalis didapat sebesar 5,4 mol/g dengan metode gravimetri. Hasil pembuatan biodiesel dengan menggunakan katalis komposit tungsten dan zirkonium oksida didapatkan bahwa semakin besar jumlah katalis yang digunakan semakin besar pula % konversi biodiesel yang dihasilkan dan optimum pada 10%. Sementara perbandingan jumlah metanol:minyak didapatkan nilai optimum pada perbandingan 8:1 dengan % konversi biodiesel sebesar 74,88%.

Kata kunci: Tungsten-Zirconia composite, POME Sludge, Esterifikasi

INTRODUCTION

Petroleum utilization as primary energy resource nowadays has triggered massive exploitation which in turn caused rapid depletion on its resources. Transportation is one of the largest user of oil approximately 95%, most of it in formed of diesel fuel used to transport people and goods [1]. Replacing diesel fuel by alternative energy therefore is very important in reducing energy dependency on petroleum. Diesel fuel derived from renewable resources known as biodiesel is mono alkyl ester produced by esterification of vegetable oils, animal fats or oilseed plants. Biodiesel has several advantages including biodegradability, non-toxic property and renewable resources in addition of low Sulphur content and aromaticity [2].

Although possess several advantages, biodiesel also has disadvantage concerning competitive usage of vegetable oils as food. Alternative resource from non-edible oils does not free from major problem. Lack of land crops available for vast production is main obstacles need to overcome. Resources from waste cooking oils start to gain more attention since it has great potential economically [3−4]. Oils recovered

from POME sludge are also take into consideration due to its abundance.

Biodiesel production via esterification of fatty acid from vegetable oils requires acid catalyst such as sulfate acid followed by transesterification of triglyceride in the oil with present of base catalyst [5]. POME sludge mainly consist of fatty acid which can be converted into alkyl esters using acid catalyst. Mineral acid i.e. sulfate acid used as catalyst has major drawback regarding corrosion on reactor vessel. Solid acid catalysts offer low risk damage on reactor vessel but almost at the same acidity used to increase reaction rate. One of solid materials with acid property suitable for acid catalyst is mixed metal oxides such as WO_3-ZrO_2 [6−7]. Site activity for catalyzing biodiesel forming transesterification had been reported to be comparable between WO_3-ZrO_2 and H_2SO_4 [8]. Application of WO_3-ZrO_2 on esterification of used vegetable oils showed good catalytic activity and gave higher conversion even compared to Amberlyst-15 and sulfated zirconia [6]. Better acidity provided by WO_3-ZrO_2 achieved without suffer from WO_3 leaching something that is not happen in case of sulfated zirconia which suffer from sulfate leaching during reaction process. Here we reported esterification of oils recovered from POME sludge in present of WO_3-ZrO_2 catalyst. The highly free fatty acid content in the wastes is an appropriate raw material for direct esterification by solid acid catalyst WO_3-ZrO_2.

EXPERIMENTAL SECTION

Oils was recovered from POME sludge provided from local Palm Oil processing. All chemicals were analytical grade and used without further purification. Catalyst was synthesized from $ZrOCl_2 \cdot 8H_2O$ (Merck) and Ammonium Meta tungstate (Merck). Merck also supplied for H_2SO_4, Methanol, Ethanol, $(NH_4)_2SO_4$ and NaOH while Ammonia, CH_3COOH and HCl were purchased from BDH.

Preparation of Tungstated Zirconia Composite

Catalyst preparation was carried out by dissolving $ZrOCl_2 \cdot 8H_2O$ into demineralized water followed by hydrolysis with addition of NaOH to formed $Zr(OH)_4$ gels at pH 10. The resulting zirconium hydroxide was washed thoroughly to remove Cl^- ions from the gels confirmed by $AgNO_3$, and then filtered and dried in oven for 24 hours. Tungstate was impregnated by introducing Ammonium meta tungstate into $Zr(OH)_4$ solid followed by dried in oven at 120°C for 24 hours. Finally, the solid was calcined in muffle furnace at 350°C to obtain tungstated-zirconia catalyst.

Catalyst characterization was conducted by Scanning Electron Microscope (SEM) to evaluate surface morphology of composite. Solid acidity was measured using ammonia adsorption combined with gravimetric method to calculate weight difference before and after the adsorption using formula as follows:

$$K_{al} = \frac{W_2 \times 1000}{M_b \times W_1} \qquad (1)$$

Where K_{al} = solid acidity (mmole/g), W_1 = solid weight (g), W_2 = weight of ammonia adsorbed (g), M_b = mass molecule of NH_3 (17.03 g/mole).

Esterification of POME Sludge using WO_3-ZrO_2 catalyst

Prior esterification process, 3 L POME sludge was heated at 120°C to remove water contained. The water-free sludge then was filtered to obtain recovered oils of CPO which was used for experiment. In typical reaction, 50 g oils were mixed with Methanol in a three-neck round-bottom flask various mole ratio in the present of Tungstated-Zirconia catalyst. The catalysts were used in several weight percentage of reaction mixtures i.e. 2%; 4%; 6%; 8% and 10%. Before catalyst was added, reactants were heated at 45°C. Tungstated-Zirconia was introduced and the temperature was increased to 70°C. The reaction mixture including catalyst was held at 70°C for 2 hours. The similar process also conducted using H_2SO_4 catalyst for comparison purpose.

Methyl ester product was separated from reaction mixture by laboratory centrifuge. The excess of Methanol was remove in a separation funnel while water formed side-product was adsorbed using sodium sulfate anhydrate. Conversion of oils was measured by using ^{1}H-NMR to detect change of methyl formed during the process. Methyl ester obtained was analyzed for viscosity and density according to ASTM methods.

RESULT AND DISCUSSION

Tungstated-zirconia prepared using impregnation method will gave different result on its surface structure compare to co-precipitation method. SEM micrograph of the samples tungsten, zirconia and tungstated-zirconia were displayed on Figure 1.

Impregnation method conducted in the catalyst preparation apparently resulted in a composite materials rather then solid solution. Tungstate (WO_3) which was dispersed onto surface of zirconia need higher temperature of calcination to formed solid solution with the host [7]. SEM micrograph displayed

on Figure 1 showed there is distinct surface structural between precursors alone and its mixture. WO_3 which was incorporated into lattice structure of zirconia could enhanced acid property of resulting material. Our result showed that calcination temperature 350°C in view of surface stucture provide the agglomeration particles were segregated from each other.
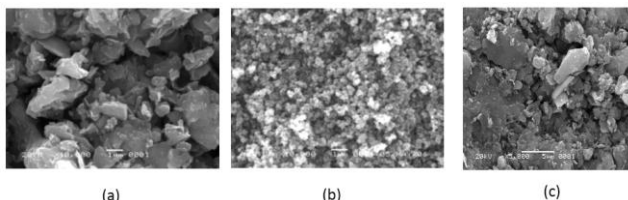

Figure 1.SEM micrograph of (a) Tungsten oxide (b) zirconia (c) Tungstated-zirconia

The composite however still provide acidity as showed on Figure 2. Acid properties of solid material was generated in form of Lewis and Brönsted acidity. The acid generation in any binary oxide composition is caused by an excess negative or positive charged present on the oxide surfaces. Negative charged resulted in protonation to produced Brönsted acidity while positive charged resulted in Lewis acidity of the materials [9]. Figure 2 showed obvious result of how mixing between two oxides will generated acidity of Tungstated-zirconia composite. Initialy zirconia has acidity 5.19 mole/g which then increased with the addition of tungstate to acidity 5.39 mole/g ammonia.
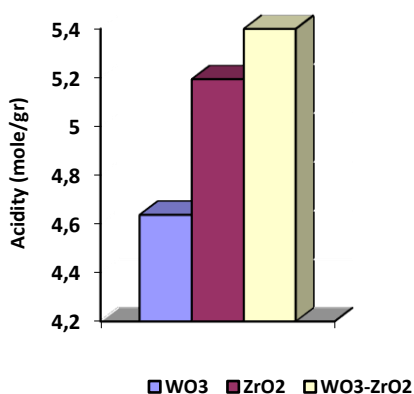

Figure 2. Acidity of the composite before and after impregnation

The Effect of catalyst weight to biodiesel produced

Catalyst plays important role in many chemical process in order to achieve reasonable rate to obtain products. It roles is to increase reaction rate in attaining equilibrium state. Figure 3 showed how amount of catalyst affected biodiesel produced on esterification.
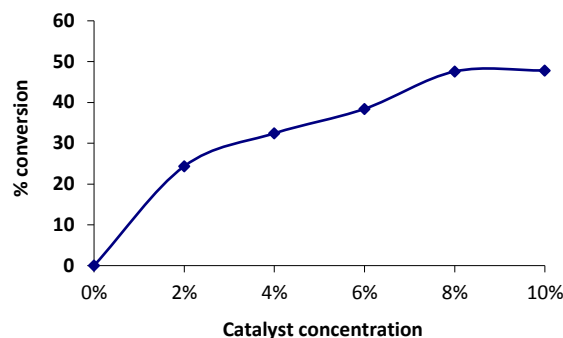

Figure 3. Effect of catalyst concentration on conversion of CPO

Catalyst concentration affected the conversion of oils into biodiesel proportionally (Figure 3). Increased of catalyst concentration result in increased of conversion until 8% catalyst. The optimum amount of catalyst according to the figure is 8% whereas at higher concentration gave no difference. Catalyst drive reaction to achieved equilibrium toward both side. Adding 8% catalyst managed to enhanced reaction rate toward product formation. At 10% catalyst, the amount of CPO converted was stagnan and no product increased observed. Other researcher had used Tungstated-zirconia (WO/Zr) as catalyst on esterification of waste cooking oil. 5% and 10% catalyst were used and produced methyl ester 27% and 48% respectively [5]. This result showed a similar amount of biodiesel acquired regarding waste oils was used as raw materials.

Table 1. Effect of catalyst amount on biodiesel properties

Properties	Method	0%	2%	4%	6%	8%	10%
Viscosity, 40ºC, $mm^2 S^{-1}$	D445	45.86	25.76	15.87	9.25	8.64	8.37
Density, $Kg\ m^{-3}$	D1298	917.2	898.5	896.3	885.2	879.5	876.8

Several studies had concluded that reaction kinetics of esterification is pseudo-first order toward esters formation and second order in reverse reaction [10−11]. This conclusion is based on condition under excess of alcohol. Under higher concentration of catalyst, reaction reached equilibrium toward product formation. Soon after, reverse reaction will proceed provided that main product, side-product and reactant co-exist in reaction mixture. Methyl ester as main product can be extended by removing it from reaction mixture, but reaction scheme is using batch mode therefore unable to remove product continuously.

Methyl ester produced in above process was characterized for kinematic viscosity and density. The result as showed in Table 1 was indicated that biodiesel nearly meet criteria required for fuel purpose.

Viscosity property is important in engine fuel. High viscosity increased the tendency of the fuel to cause formation of deposit within engine. According to the table, catalyst concentration 8% and 10% had lowest viscosity. US biodiesel specification required the methyl ester has kinematic viscosity 1.9−4.1 mm^2/s [12]. Although methyl ester produced still has high viscosity, the overall process offers promising pathway in POME sludge utilization. Improvement step could be included on POME waste sludge treatment by Palm Oil company to obtain clean oils recovery.

The effect of methanol/oils ratio to biodiesel produced

Reactant concentration is an important variable in chemical equilibrium. Increasing reactant concentration will shift equilibrium toward product formation. This step has a risk in esterification due to high methanol concentration caused neither increased in product yield nor the ester content. Hydroxyl group of methanol is polar and can act as emulfier causing emulsification. This process leads to harder and increased cost to gain pure methyl ester [13].

Figure 4 showed the proportional increased of methyl ester produced in accordance to methanol/oils ratio. Ration 8:1 and 10:1 displayed not much different in yield of methyl ester. Higher ratio will not guarantee produced more methyl ester.
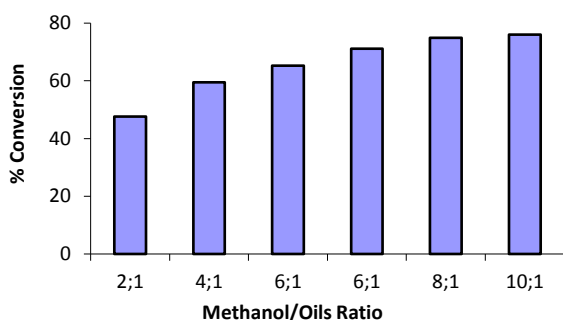

Figure 4. The effect of molar ratio methanol/oils to biodiesel produced

Analysis on biodiesel properties according to ASTM method for kinematic viscosity and density displayed on Table 2. In average, all methyl ester product has similar viscosity between 8.56 to 8.87 mm^2/s. This value still has to improve in order to achieve viscosity required by US standard of biodiesel. The value showed on table reflected a more succesfull process of reaction. It has been reported that viscosity

value related to number of carbon chain exist in the molecule and bond saturation degree. Higher number of carbon chain made substance more viscous whereas bond saturation degree prefer type of double bond confiuration (*cis* or *trans*) rather than its position [14]. Compare to viscosity value on table 1 for non catalytic esterification product, table 2 represent POME sludge was succesfully converted into lower substance compound confirmed by methyl ester yield 80% approximately.

Tabel 2. The effect of molar ratio methanol/oils to biodiesel properties

Property	Method	2:1	4:1	6:1	8:1	10:1
Viscosity, 40°C, mm^2 S^{-1}	D445	8,64	8,56	8,87	8,74	8,72
Density, Kg m^{-3}	D1298	885,2	879,5	886,3	881,2	878,5

CONCLUSION

POME sludge is a promosing raw material for biodiesel production provided that pre-treatment process conducted properly. WO$_3$-ZrO$_2$ catalyst showed good catalytic activity on esterification of lower quality oils such as POME sludge. Catalyst concentration required for optimum reaction is 10% whereas molar ratio of methanol/oils is 8:1 at 70°C within 2 hours reaction. Maximum conversion into methyl ester is 74.88% and showed remarkable decreased on viscosity compare to starting materials.

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