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OPTIMIZING REACTION CONDITIONS OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING GREEN SOLID CATALYST

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ABSTRACT

Biodiesel production from waste cooking oil in two steps reaction of esterification and transesterification is low efficient, due to twice methanol consumption and need more reaction time. Optimizing reaction conditions of CaO as a matrix of solid catalyst prepared from crab shell (green CaO) and modified by K2O/TiO2 for converting waste cooking oil to biodiesel have been carried out. Catalytic process of waste cooking oil to biodiesel took place in one step reaction of esterification and transesterification. The research result showed that optimum conditions in its one step reaction such as methanol to oil molar ratio was 9:1, amount of CaO/K2O-TiO2 catalyst to oil was 5% and reaction time of 60 minutes with biodiesel yield was 88.24%. Physical and chemical properties of biodiesel which produced from one step reaction of esterification and transesterification of waste cooking oil were suitable with Indonesian National Standard (SNI-04-7182-2006) namely density at 40oC of 850 kg/m3, kinematic viscosity at 40oC of 3.32 cSt, water content of 0.046%, iodine number of 59.25 g I2/100g and acid value of 0.29 mg KOH/g. Gas chromatography-mass spectrometry (GC-MS) analysis of biodiesel formed fatty acid methyl esters from conversion of waste cooking oil.

1. INTRODUCTION

Biodiesel is a mixture of mono alkyl esters produced from long chain fatty acids from biological feedstocks such as vegetable oils, animal fats and waste cooking oil in esterification and transesterification reactions with short chain of alcohol (methanol or ethanol) and using catalyst (Sivasamy et al., 2009; Math et al., 2010; Panudare and Rathod, 2015; Musa, 2016). The catalyst increased the rate of reaction to produce biodiesel (Abed et al., 2019). Waste cooking oil is a source feedstock to biodiesel production, because of economically prize and abundant sources. Besides, using waste cooking oil can solve disposal of its waste. Waste cooking oil has free fatty acids (FFAs) higher relatively, where FFAs <15% for yellow grease and >15% for brown grease due to content of FFAs (>1%) causes saponification, it makes separation of biodiesel from mixture hardly, then obtaining less biodiesel yield (Mangesh and Ajay, 2006: Panudare and Rathod, 2015).

Generally, production of biodiesel is held in two steps reaction such as esterification by acid catalyst for reducing of FFAs content and transesterification by base catalyst for converting triglycerides (Zhang et al., 2010; Abed et al., 2019). In other hand, those process have weakness, namely need great amount of methanol and longer reaction time (Setiawan and Fatmir, 2012). Moreover, waste of base catalyst increased unburnt ash, whereas waste of acid catalyst makes corrosive in engine (Enweremadu and Mbarawa, 2009).

Bifunctional solid catalyst enables to catalytic process in esterification and transesterification reactions by one step, so that biodiesel production from waste cooking oil in high FFAs can performed to simple step (Borges and Diaz, 2012). Besides, the solid catalyst application does not produce soaps through triglycerides saponification or FFAs neutralization (Guo and Fang, 2011). Salinas et al. (2010) studied activity of potassium catalyst with titanium supported (K/TiO_2) for biodiesel production from canola oil. Converting canola oil to biodiesel of 100% with methanol to oil molar ratio of 36:1, 5 hours reaction time, temperature of 70°C and amount of 6% catalyst (w/w oil). Loading potassium performed base active sites of titanium which has acid active sites. This catalyst described good activity, without initial preparation of feedstock. Istiadi et al. (2015) had explored and studied activity of K_2O/CaO-ZnO catalyst for transesterification reaction soybean oil to biodiesel. The best catalyst performance showed by producing biodiesel yield of 81.8% with methanol to oil molar ratio of 15:1 and amount of 6% catalyst in temperature at 60°C (Istadi et al., 2015). Additional of 2% K_2O in CaO-ZnO increased catalytic activity to cause new raising surface area and basicity. Calcium oxide (CaO) is solid catalyst usually used for triglycerides transesterification reaction to biodiesel production (Niju et al., 2016; Degfie et al., 2019). Activity of CaO catalyst can be advanced by adding promotor for increasing its surface basicity and acidity, increasing stability as well as surface area.

Base on that, the study held by optimizing one step reaction conditions of esterification and transesterification for biodiesel production from waste cooking oil using green solid catalyst of CaO/K_2O-TiO_2. Its reaction conditions optimization such as optimizing amount of catalyst to oil, optimizing methanol to oil molar ratio and optimizing reaction time.

2. METHODS

2.1. SYNTHESIS OF CAO/K_2O-TIO_2 GREEN SOLID CATALYST

CaO powder from crab shell was prepared and dried in oven at 110°C for 2 hours, then calcinated at 800°C for 5 hours. Dried green CaO was sieved to obtain a particle size of 100 mesh (Astuti et al., 2019). CaO as matrix was mixed with 10% K_2CO_3 (w/w) in porcelain crush by solid state reaction. Homogeneous mixture of CaO and K_2CO_3 was cacined at 550°C for 3 hours (Degirmenbasi et al., 2015; Astuti et al., 2019) to form CaO/K_2O. Furthermore, the CaO/K_2O was mixed with TiO_2 at mass ratio of 3:1 homogeneously in the porcelain crush, then calcinated at 500°C for 5 hours (labelled by CaO/K_2O-TiO_2).

2.2. OPTIMIZING CATALYTIC ACTIVITY TEST OF BIODIESEL PRODUCTION

In initial step, waste cooking oil was filtered for reducing contaminant, continued heating to evaporate water in oil. Heating process at 110°C for 30 minutes. After process, oil was cooled till temperature range of 50-55°C (Bobade and Kyade, 2012). The production of biodiesel in one step reaction of esterification and transesterification of waste cooking oil was conducted by using green solid catalyst of CaO/K_2O-TiO_2. Its reaction conditions optimizing amounts of catalyst to oil at 3, 5 and 7%; methanol to oil molar ratios at 6:1, 9:1, 12:1 and 15:1 as well as reaction time at 30, 60, 120 and 180 minutes. All process were studied in reaction temperature at 65°C. Produced biodiesel yield was calculated as percent yield $= \frac{amount\ of\ produced\ biodiesel}{amount\ of\ oil}\ x\ 100$ (Abbah at al., 2016).

3. RESULTS AND DISCUSSION

3.1. OPTIMIZING AMOUNT OF CATALYST

Base on Figure 1, showed that the biodiesel yield increased in accordance with increasing amount of catalyst to oil, when additional from 3 to 5% but declining in 7%. The amount of optimum catalyst influence to reactant mass transfer with catalyst. Additional amount of catalyst in mixture can increasing bulk hindrance, so that decline mass transfer on catalyst surfaces (Enciner et al., 2010). The result showed that optimum amount of catalyst was 5%.

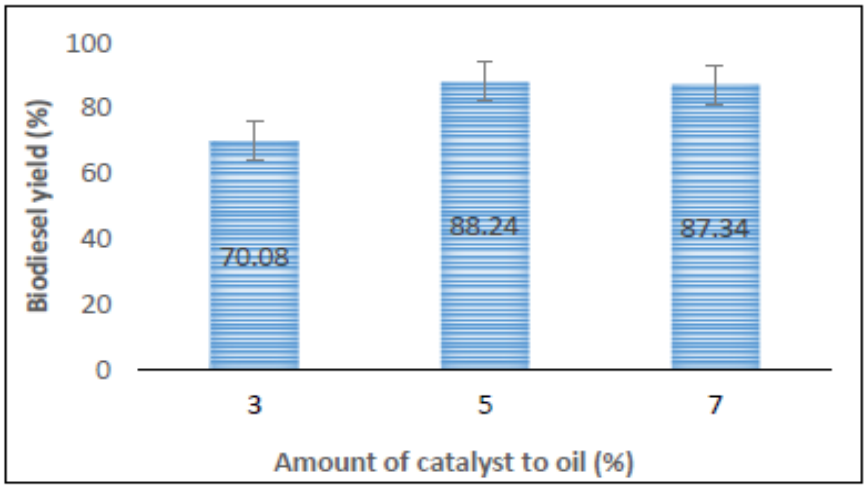

Figure 1: Effect of various amount of catalyst to oil for biodiesel yield

3.2. OPTIMIZING TIME REACTION

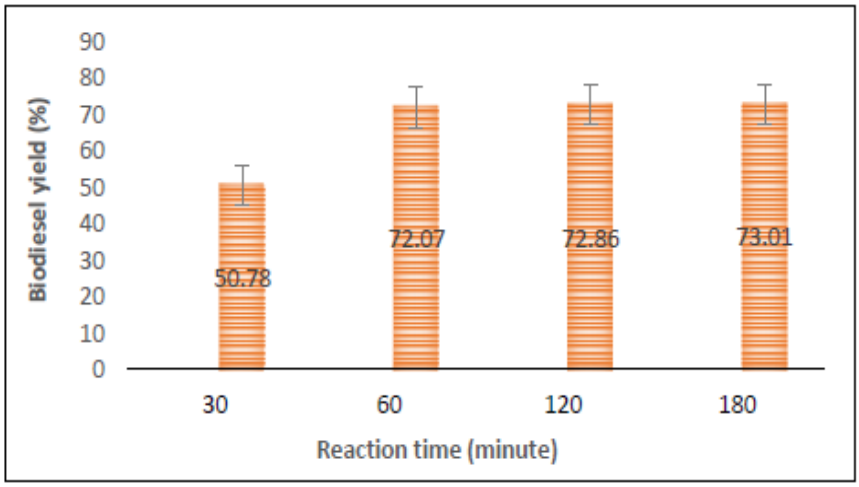

Figure 2: Effect of various reaction time for biodiesel yield

In Figure 2 described that at reaction time of 30 minutes was obtained the lowest biodiesel yield (50.78%). It means that reaction time had not reached equilibrium. In reaction time of 30 to 60 minutes were obtained more biodiesel yield significantly (72.07%). In reaction time of 120 to 180 minutes were obtained yield of 73.01%. Fatty acid methyl esters production was faster in reaction time of 60 minutes, then declined till equilibrium was reached. It is explained that transesterification reaction is equilibrium. When equilibrium was reached additional of reaction time not affect to fatty acid methyl esters yield. Therefore, the optimum reaction time was 60 minutes.

3.3. OPTIMIZING METHANOL TO OIL MOLAR RATIO

Base on Figure 3, the highest biodiesel yield was obtained in methanol to oil ratio molar of 9:1 and 12:1 were 88.24% and 89.10%, respectively. The methanol to oil molar ratio of 6:1 showed that reaction time was not in optimum, whereas it is higher 12:1 causes soluble glycerol in methanol, so that equilibrium position was replaced to reactant. Therefore, this process decreased the biodiesel yield (Mahreni, 2010). According to Encinar et al. (2010), transesterification reaction using solid catalyst on higher methanol to oil molar ratio caused three phase formed, because the methanol was not soluble in oil. Its three phase formed restricted contact inter-reactant in the initial step reaction, so that reaction time needed is more long duration to get equilibrium. Therefore, optimum methanol to oil molar ratio was 9:1.

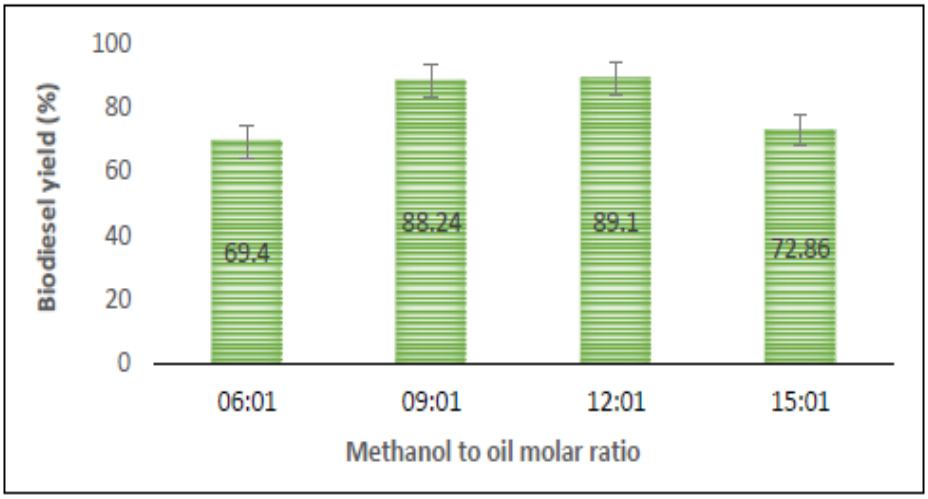

Figure 3: Effect of various methanol to oil molar ratio for biodiesel yield

3.4. ANALYSIS OF BIODIESEL COMPOSITION

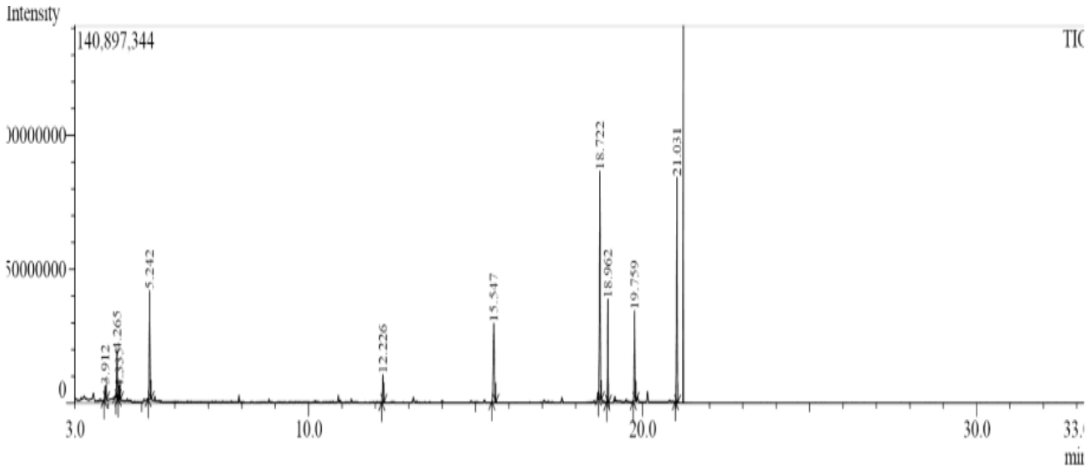

Figure 4: GC-MS analysis for biodiesel produced from waste cooking oil

Result of GC-MS analysis (Figure 4) described six main peaks and fragmentation pattern information. The highest peak was at retention time of 18.72 minutes. The fragmentation pattern information was identified as fatty acid methyl esters composition. It means that waste cooking oil was converted to fatty acid methyl esters (biodiesel) composition.

3.5. ANALYSIS OF PHYSICAL AND CHEMICAL PROPERTIES OF BIODIESEL

Physical and chemical properties of biodiesel on optimum reaction conditions of conversion result base on the SNI-04-7182-2006 (SNI, 2006) and the biodiesel standards of EN 14214 are presented in Table 1. The physical and chemical analysis result of produced biodiesel were suitable with the SNI-04-7182-2006 and the biodiesel standards of EN 14214. In analysis result of biodiesel density at 40^{o}C (850 kg/m^{3}) was agreement with the SNI-04-7182-2006 and lower than the standards of EN 14214 at 15^{o}C (Essamlali et al., 2017). Density of biodiesel produced presented that contaminants in product such as catalyst waste, methanol, glycerol, soap, water and un-conversion of fatty acids to methyl esters (Setiawati and Fatmir, 2012). The more pure of biodiesel the lower its density, thus it was agreement with heating value and energy produced by diesel engine. The low density has high heating (Azis, 2011).

Table 1: Physical and chemical properties of biodiesel from esterification and transesterification reactions of waste cooking oil base on the SNI-04-7182-2006

Property	Produced biodiesel	Biodiesel Standards (SNI-04-7182-2006)	Biodiesel standards of EN 14214
Density at 40°C (kg/m^3)	850	850-890	860-900 (at 15°C)
Viscosity at 40°C (cSt)	3.32	2.3-6.0	3.50-5.00
Iodine number (mg I_2/100g)	59.25	Max 115	Max 120
Acid value (mg KOH/g)	0.29	Max 0.5	<0.5
Water content (%)	0.046	Max 0.05	<0.05

Viscosity is an important parameter for biodiesel application in diesel engine. Viscosity connected with flow rate of fuel through injector that affecting as an indicator of atomization degree in injection burning room (Lestari et al., 2017; Abed et al., 2019). The range is made sure that injecting biodiesel to easier burning room. The highest viscosity will cause be3d atomization of fuel and oxygen so that burning process unideal. Kinematic viscosity of produced biodiesel (3.32 cSt) which is suitable with its SNI and the standards of EN 14214.

Iodine number determine amount of double bond of fatty acid in biodiesel is connecting with stable oxidative state. Higher iodine number as an indicator of lower oxidation stability, so that oxidation and precipitation in engine is easier (Abed et al., 2019). Iodine number of produced biodiesel (59.25 mg I_2/100g) that is suitable with its SNI and the standards of EN 14214.

Acid value related with corrosion rate of engine. When acid value increasing, the corrosion risk of engine is increasing too. Acid value of produced biodiesel from converting waste cooking oil still in range quality standard of the SNI and the standards of EN 14214. It indicated that converting process was effective.

Water content is a parameter to indicate the biodiesel quality. High water content in biodiesel cause to reduce heat burning, hydrolysis and corrosion trigger (Setiawati and Fatmir, 2012; Abed et al., 2019). Water content of produced biodiesel was in range standard of the SNI and the standards of EN 14214.

4. CONCLUSIONS

Optimum one step reaction condition of esterification and transesterification of waste cooking oil to biodiesel using green catalyst of CaO/K_2O-TiO_2, such as methanol to oil molar ratio was 9:1, amount of CaO/K_2O-TiO_2 catalyst to oil was 5% and reaction time of 60 minutes with biodiesel yield was 88.24%. The physical and chemical properties of biodiesel were suitable with the SNI-04-7182-2006. The GC-MS analysis of biodiesel showed that fragmentation pattern information identified as fatty acid methyl esters composition.

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CONFLICT OF INTEREST

None.

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