

HASIL CEK_Small-scale production of biodiesel through transesterification process of waste or used cooking oil

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Small-scale production of biodiesel through transesterification process of waste or used cooking oil

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Abstract. One of environmentally friendly fuel is biodiesel, where the raw material for its manufacture comes from vegetable oils. In the process of biodiesel development, raw materials can come from waste such as waste cooking oil or commonly referred to as jelantah. The ability of biodiesel that can replace existing diesel or diesel fuel, becomes a big potential to be developed on an industrial scale. Biodiesel is made by reacting an alcohol with vegetable oil with the addition of an alkaline catalyst. The reaction of biodiesel took place inside a three-neck flask equipped with a stirring motor as well as a waterbath. Variables used in this research are a variation of stirring speed starting from 300, 400, 500, 600, and 700 rpm. Determination method of biodiesel component using GC-MS analysis, as well as analysis of fuel characteristics and heat test. The results showed that used cooking oil materials have low FFA content that is below 2% so it can be directly processed into biodiesel. At 500 rpm stirring speed produces 150 ml of biodiesel and 94.70% yield of biodiesel from 150 ml of cooking oil with biodiesel characteristics produced in accordance with the requirements of biodiesel quality in the National Standardization Agency 2012 document with the calorific value of biodiesel 8609,7956 calories/ gram.

1. Introduction ⁴

Energy is one of basic requirement for the economic development of every country. Every sector of the economy, including the transportation, industry, agriculture, domestic and commercial sectors require energy. According to a report available on the United States Energy Information Administration (EIA) website, total world energy consumption was 406 quadrillion British thermal units (Btu) in 2000 and is projected to increase to 769.8 quadrillions Btu by 2035. This is an increase of approximately 47.25%, and energy consumption will definitely increase further [1]. Biodiesel is environmentally friendly fuel. Biodiesel does not contain harmful as Pb, biodegradable, its emissions are also lower than diesel fuel emissions. Biodiesel has a high lubrication effect that can extend engine life and have a high cetane number (> 50) [2]. Biodiesel is a type of fuel alternative diesel derived from biological materials that are processed vegetable oil transesterification using methanol and catalyst NaOH. Waste or used cooking oil is one of the vegetable oil. Waste or used cooking oil is one of the raw materials that have a high chance for the manufacture of biodiesel because it still contains triglycerides in addition to free fatty acids. Biodiesel is made by giving some physical treatment, such as temperature and duration of settling time [3].

Utilization of waste or used cooking oil for biodiesel production will provide several benefits, including: can reduce household or food industry waste and the cost of biodiesel production can be



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reduced so that the price is cheaper than using pure plant oil [4]. Tan, et.al. [5] studied about catalyst-free biodiesel production from the potential of waste or used palm cooking oil. He investigated the parameters that influence the reaction are temperature, reaction time, and the molar ratio of alcohol to oil. He concluded that waste or used palm cooking oil has high potential as an economical and practical future source of biodiesel. Yakoob, et.al. [6] overviewed the production of biodiesel from waste or used cooking oil. Waste or used cooking oil has high free fatty acid (FFA) and water contents but it is considered the most promising biodiesel feedstock. The most common process in the production of biodiesel is transesterification, and using a mixture of methanol-ethanol will combine the advantages of both alcohols in production of biodiesel.

Seeing the above conditions, there is an opportunity to utilize waste or used cooking oil especially in Indonesia because of the number of food stalls or restaurants that use cooking oil in processing the food so that the amount of waste or used cooking oil that is regarded as waste will also be more and more. So with the research to be executed, it expected that existing cooking oil can be recovered or processed using esterification and/or transesterification process into biodiesel or fuel source. Conversion of waste or used cooking oil into biodiesel using KOH catalyst through transesterification process with and without esterification process using activated natural zeolite (ZAH) catalyst has been carried out. The transesterification was done using KOH catalyst 1% (w/w) from oil and methanol weight and oil/methanol molar ratio 1:6 at 60 °C without esterification process. The esterification reaction was also done using ZAH catalyst then continued by transesterification using KOH catalyst in methanol media. The results showed that the transesterification using KOH catalyst without esterification produced biodiesel conversion of 53.29%. The optimum condition of biodiesel synthesis via esterification process was reached at 60 °C and concentration of ZAH catalyst of 2% (w/w), that could give biodiesel conversion = 100.00%. The physical properties were confirmed with biodiesel ASTM 2003b and Directorate General of Oil and Gas 2006 specification [7]. ZAH also used as a catalyst in triacetin production from gliserol and acetic acid and also used as an adsorbent in water purification.

Calcined snail shell used as a heterogeneous base catalyst to produce biodiesel from waste frying oil. Transesterification reactions were carried out and the yield and conversion of the product were optimized by varying the methanol to oil molar ratio, catalyst amount, reaction temperature, and time. The conversion of biodiesel of 99.58% was obtained with a yield of 87.28%. The fuel properties of the biodiesel were measured according to ASTM D 6751 and found to be within the specifications. Snail shell is one of novel source that can be successfully utilized for the production of heterogeneous base catalyst and for the synthesis of biodiesel of high purity [8]. Chen, et.al. [9] studied about improving biodiesel yields from waste or used cooking oil by using a microwave heating system and sodium methoxide as catalyst. microwave heating system can be used to improve the yields of waste or used cooking oil biodiesel, experimental results indicate that it outperforms conventional heating, with the best performances found with 0.75 wt% (NaOH) and 0.75 wt% sodium methoxide (CH_3ONa) catalysts, respectively. The biodiesel yields produced with CH_3ONa catalyst are higher than those produced with NaOH catalyst. The biodiesel yields increase with increasing reaction power. The optimal reaction conditions are 0.75 wt% CH_3ONa catalyst, a methanol-to-oil molar ratio of 6, a reaction time of 3 min, and a microwave power of 750 W. Same as snail shell, shrimp shell or known as chitosan can be used as catalyst. Chitosan also can be used as raw material to produce biodegradable plastic.

Noshadi, et. al. [10] did research about, continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid. Reactive distillation is a reactor which can be distillation tower to purify product resulted from the reaction. $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ catalyzed the reaction and overcomes the neutralization problem that occurs in the conventional transesterification of a waste cooking oil with high free fatty acid (FFA) and water content. Response surface methodology (RSM) based on central composite design (CCD) was used to design the experiment and analyzed four operating parameters: total feed flow, feed temperature, reboiler duty and methanol/oil ratio. The optimum conditions were determined to be 116.23 (mol/h) total feed flow,

29.9 °C feed temperature, 1.3 kW reboiler duty, and 67.9 methanol/oil ratio. The optimum and actual free fatty acid methyl ester (FAME) yield was 93.98% and 93.94%. Reactive distillation also used as reactor to produce triacetin as bioadditive from glycerol and acetic acid [11][12]. Glycerol is a side product of biodiesel production, which is colorless, odorless, viscous liquid. Conversion of glycerol become triacetin in reactive distillation unit is depend on the recycle stream [13]. Triacetin as bioadditive also produce from the batch reactor to find out the chemical kinetics [14][15] and triacetin can be produced using solid catalyst Zr-Natural Zeolite [16].

Farooq and Ramli [17] also found out that chicken bones can be catalyzed waste or used cooking oil to produce biodiesel. When the heterogeneous catalyst calcined at 900 °C, the experimental results showed that good catalytic activity in the transesterification of waste or used cooking oil, providing maximum biodiesel yield of 89.33% at 5.0 g of catalyst loading, 15:1 methanol to oil molar ratio at a temperature of 65 °C in reaction time of 4 h. The better catalytic activity of the aforementioned catalyst in the biodiesel reaction could be attributed to the presence of an optimal number of catalytically active basic site density on its surface. Moreover, the catalyst was successfully recycled for 4 times for biodiesel production. Unfortunately the chicken bones needed to do a lot of treatment before it can be used as catalyst. Some kind of treatment are cleaning, washing, drying etc. Green biodiesel production from waste cooking oil using an environmentally benign acid catalyst also found out by Tran, et. al. [18]. The sequential hydrothermal carbonization and sulfonation of xylose was used to prepare the catalyst. The catalytic activity was tested for biodiesel production from waste or used cooking oil via a two-step reaction to overcome reaction equilibrium. The highest biodiesel yield (89.6%) was obtained at a reaction temperature of 110 °C, the duration time of 4 h, and catalyst loading of 10 wt% under elevated pressure 2.3 bar and 1.4 bar for first and second step, respectively. The reusability of the catalyst was investigated and showed that the biodiesel yield decreased by 9% with each cycle; however, this catalyst is still of interest because it is an example of green chemistry, is nontoxic, and makes use of xylose waste.

Influence of diesel fuel blended with biodiesel produced from waste or used cooking oil on diesel engine performance. The main results of the current work showed that the location and value of the in-cylinder peak pressure depend mainly on the engine load and the biodiesel blending ratio. The best value of Brake Specific Energy Consumption (BSEC) is attained at blended fuel containing 20% WCOME (B20) where the maximum brake thermal efficiency is also observed. While there was a range of blending ratio from B20 to B50 throughout the best engine environmental behavior is attained. Results indicated that, the use of neat biodiesel fuel (B100) at different engine loads leads to an increase of BSEC by about 8%, an increase of engine smoke opacity by about 15%, a decrease of NOx emissions by about 10% with slight decrease of CO emissions and a decrease of the unburned hydrocarbons by about 15%. At this recommended blending ratios, the engine performance provides the following results in comparison with the corresponding values for neat fuel around 10% higher BSFC, insignificant change in η_{bth} , around 3% higher BSEC, and 2% lower TE_{exh}, while the corresponding engine emissions include 25% lower CO, 20% lower UHC, 6% lower NOx, and 20% higher smoke opacity [19]. From those researches, biodiesel from waste or used cooking oil is most promising liquid fuel which easy to produce and has low production cost because the raw material is a waste. In this research biodiesel produced from waste or used cooking oil using methanol and KOH as catalyst.

2. Research Methods

2.1. Materials

In this research, we used waste or used cooking oil as raw material that collected from food stall or roadside food seller. Methanol was added as reactant and KOH or potassium hydroxide as a catalyst. Unit production of biodiesel in this research used three neck flask as a reactor that completed by the mixer, refrigerant, and thermometer. Variation of the speed of mixing used to know the optimum

speed for biodiesel production. The variation of the speed of mixing is 300, 400, 500, 600, and 700 rpm. Unit production of biodiesel shows in figure 1.

2.2. Methods

Waste cooking oil and methanol were prepared as a main reactant (oil: methanol ratio = 2:1) and KOH 0.1 N as a catalyst. Waste cooking oil, methanol and KOH 0.1 N 1.5%wt of oil reacted in a three-neck flask which equipped with a refrigerator, stirring speed at 300 rpm and thermometer with 60 °C of temperature, in waterbath for 90 minutes. After 90 minutes, the mixture cooled and poured into separating funnel and then stand for 24 hours to form two layers, the bottom layer is glycerol and the top layer are biodiesel. Glycerol also can be synthesized as bioadditive [20]. Washing the biodiesel with aquades to retrieve the remains of a KOH catalyst. Separated using a separation funnel and then stand for 24 hours. Measuring the volume of biodiesel obtained using a measuring cup. Repeating work step with variable speed of stirring 400, 500, 600, 700 rpm. Analysis of biodiesel characteristic was in Petroleum, Gas, and Coal Technology laboratory and analysis of biodiesel composition was in MIPA Laboratory of Gadjah Mada University.



Figure 1. Unit production of biodiesel.

3. Result and Discussion

Waste cooking oil has different Free Fatty Acid levels depending on its use when frying. Waste cooking oil which has FFA content below 2% can be directly processed by transesterification to be biodiesel without going through the esterification process. The transesterification process begins by reacting the cooking oil with methanol which KOH has added as a catalyst. The reaction takes place at 60 °C for 90 minutes on a three-neck flask. the results of transesterification with a variation of stirring speed was obtained data as in table 1.

Table 1. The result of transesterification on the variation of stirring.

No.	Stirring speed (rpm)	Volume of biodiesel (mL)	Conversion (%)
1.	300	148	98.667
2.	400	149	99.333
3.	500	150	100.00
4.	600	148	98.667
5.	700	145	96.667

From the variation of the stirring speed seen in Table 1, that the higher the stirring rate the higher the biodiesel conversion is due to the reaction process, the speed of contact between reactants greatly influences the conversion of the result. The greater the contact rate between reactants will increase the reaction or increase the conversion. However, each reaction has an optimum condition, wherein the

process of transesterification of this cooking oil, 500 rpm stirring speed gives an optimum result with the volume conversion reaches 100%.

Mass of waste cooking oil and biodiesel can be known by multiply the volume by its density. From the mass of waste cooking oil and biodiesel, the yield of biodiesel can be calculated. the yield of biodiesel from different stirring speed is obtained as in table 2. as follow:

Table 2. The yield of biodiesel.

No.	Stirring speed (rpm)	Mass of waste cooking oil (gram)	Mass of biodiesel (gram)	Yield (%)
1.	300	138	128.94	93.44
2.	400	138	129.81	94.07
3.	500	138	130.68	94.70
4.	600	138	128.94	93.44
5.	700	138	126.32	91.54

From the variation of the stirring speed seen in Table 2, that the higher the stirring rate the higher the biodiesel yield is due to the reaction process, the speed of contact between reactants greatly influences the yield of the biodiesel. The greater the contact rate between reactants will increase the reaction or increase the yield. However, each reaction has an optimum condition, wherein the process of transesterification of this cooking oil, 500 rpm stirring speed gives an optimum result with the yield of biodiesel reaches 94.70%.

Biodiesel results obtained from the transesterification are analyzed for its characteristics at Petroleum Gas and Coal laboratory, UGM. The result of the characteristic test of biodiesel is shown in table 3. as follow:

Table 3. Characteristics of biodiesel from waste cooking oil.

No.	Parameter	Unit	Result	Standard	Method
1.	Density	gr/ml	0.8712	0.850-0.890	ASTM D 1298
2.	Viscosity kinematic	mm ² /s	4.802	2.3-6.0	ASTM D 445
3.	Flash point	°C	185	100 (min)	ASTM D 93
4.	Cloud point	°C	12	18 (maks)	ASTM D 97

From biodiesel characteristics, for density, viscosity, flash point, and cloud point are in accordance with the quality requirements of biodiesel. Biodiesel transesterification results are also tested to determine the calorific value, from three times the heat test with the same biodiesel obtained biodiesel calorific value of 8609,7956 calories/ gram.

4. Conclusion

Waste cooking oil can be processed into biodiesel fuel by reacting with methanol 50% of waste cooking oil volume with the addition of a catalyst of 1.5% by weight of waste cooking oil. 500 rpm stirrer speed gives optimum results close to 100% with biodiesel characteristics according to biodiesel quality standards. the calorific value of biodiesel is 8609,7956 calories/ gram.

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