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Leucaena–Derived Biochar for Biodiesel Production

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ABSTRACT. Giant leucaena wood was utilized to prepare heterogeneous catalysts through a fast pyrolysis method and chemical activation for transesterification. The obtained catalysts were investigated using SEM, CHNS/O analyzer, XRF and XRD. The influence of the concentration of KOH (3-9 M), catalyst amount (0.25-2.0 g), methanol to oil ratio (4:1-10:1), and reaction time (30-75 min) on FAME yield was also studied on transesterification reaction carried out at 60°C under a 750 rpm stirring speed. The experiment results demonstrate that chemical activation was required to improve the porosity of the catalyst. The result showed that a well-developed porous structure was observed, as the concentration of KOH increased activated biochar become more porous. 7M-KOH for chemical activation was the best condition to obtain a porous catalyst. It was found that the main factors affecting the FAME yield were dependent on various parameters including methanol: oil ratio, catalyst loading, reaction time and stirring speed via transesterification process. The highest yield of 94.06% was achieved on 0.5g of the catalyst activated by 7M-KOH, a methanol:oil ratio of 6:1 and a 1-hour reaction. The obtained biodiesel mainly composed of different fatty acid in follow order C18:1 > C16:0 > C18:2 > C18:0. Properties reached the ASTM D6751-12 and EN 14214:2012 standard, indicating that leucaena-derived biochar is potentially utilized in biodiesel production.

Keywords: Biochar, Catalyst, Transesterification, Biodiesel, Giant leucaena wood

INTRODUCTION

Electric vehicles are going to be a part of road transportation. However, the transformation of fossil fuel consumption into zero CO_2 emissions still requires advanced biofuels such as biodiesel, biomethane, ethanol, or synthetic fuel (Panoutsou et al., 2021). Of these biofuels, biodiesel plays a key role in decarbonization of the road transportation and the aviation sector (Panoutsou et al., 2021; Ogunkunle & Ahmed, 2019). Biodiesel is typically prepared by transesterification reaction in which triglycerides react with methanol or ethanol in the presence of a catalyst. Homogenous alkali catalysts including KOH and NaOH are commonly used at industrial scale because of their high catalytic activities under mild conditions (Mayvan, Ghobadian, Omidkhah, & Najafi, 2012). However, the homogeneous alkaline catalysts are corrosive and sensitive to water and free fatty acids, leading to a decrease in the catalytic performance (Younes, Amadine, Len, & Larzek, 2017). Considerable amount of hot distilled water is needed for neutralizing the products to remove the basic catalyst, emulsion and soups (Hernandez-Altamirano & Violeta, 2019). In addition, when non-edible oils are employed as a feedstock, large amount of free fatty acids (FFA) in the oils react with the basic catalyst, resulting in saponification, thus inhibiting transesterification reaction (Balat & Balat, 2010; Ramadhas, Jayaraj, & Muraleedharan, 2005).

Subsequently, heterogeneous solid catalysts have been of interest to many researchers because they are environmentally friendly, readily separated and reusable (Semwal, Arora, Badoni, & Tuli, 2011). The use of heterogeneous catalysts instead of homogeneous ones could potentially reduce the overhead costs of catalysts. Solid catalysts used in biodiesel production include sodium modified hydroxyapatite (NaHAP) (Younes, Amadine, Len, & Larzek, 2017), CaO (Maneerung, Dai, Kawi, & Wang, 2016), $MgO/MgAl_2O_4$ (Rahmanivahid, & Haghighi, 2016), K_2CO_3/palygorskite (Shan et al., 2016), $K_2CO_3/\gamma\text{-}Al_2O_3$ and $KF/\gamma\text{-}Al_2O_3$ (Liu, He, Wang, Zhu, & Piao, 2008). Owing to its availability, economical reasons and environmental perspectives, CaO is more commonly utilized when compared to the other catalysts (Marinkovic et al., 2016). CaO catalysts have been proven highly effective in synthesizing biodiesel (Marinkovic et al., 2016). A biodiesel yield (above 95%) could be obtained when CaO was used (Calero et al., 2014). However, the use of CaO could raise a common concern involving chemical stability and reusability because H_2O and CO_2 can be readily absorbed on the surface of pure CaO catalyst upon exposure to air (Boonphayak, Khansumled, & Yatongchai, 2021), resulting in a decrease of the catalytic performance (Kouzu, Yamanaka, Kasuno, Hidaka, & Tajika, 2008). Besides, it was reported that CaO catalyst was partially dissolved during transesterification process, leading to a reduction of reusability (Teo, Rashid, & Taufiq-Yap, 2014).

Biochar is a viable alternative to CaO catalysts. It shares the same properties with CaO-based catalysts such as operating conditions, reaction rate and biodiesel yield (Balajii & Niju, 2019; Marinkovic et al., 2016). However, biochar used as the catalyst for transesterification has a definite advantage over CaO. Biochar catalysts are typically prepared at a lower temperature (Balajii & Niju, 2019), which is defined as an economical choice for biodiesel production. Moreover, biochar-based catalysts suffer a slight loss of catalytic performance after ten consecutive runs (Tao et al., 2015). Through simple pyrolysis of biomass, biochar can be synthesized as the main component or as a by-product depending on the heating rate. Slow pyrolysis results in a high yield of biochar which is usually 30-50 wt% (Zheng et al., 2018). Comparatively, a higher heating rate favors the preparation of bio-oil, generating biochar as a by-product (15-25 wt%) (Yu, Dehkhoda, & Ellis, 2011). In recent years, biomass feedstock such as wood, rice husk, oat hull and palm kernel shell, was used to synthesize a biochar catalyst (Ahmad, Rashid, Patuzzi, Baratieri, & Taufiq-Yap, 2018; Gonzalez et al., 2017; Kostic, Bazargan, Stamenkovic, Veljkovic & Mckay, 2016; Tao et al., 2015; Li, Chen, & Zhu, 2013). The synthesized biochar could be highly effective in biodiesel production, generating a higher biodiesel yield than 90%. Pameo peel was also employed. The pameo biochar could yield 82% biodiesel. Pyrolysis of giant leucaena wood does not result in only bio-oil but also biochar which is porous carbon-rich solid. Its size is favorable for biodiesel synthesis without pulverization. However, chemical or physical activation is required to achieve high porosity.

In the current work, giant leucaena wood was utilized as the feedstock to prepare the biochar catalyst for biodiesel production. Fast pyrolysis of the leucaena wood was carried out in a fluidized bed reactor to obtain the biochar with low contamination and fine particles. The synthesized catalysts were characterized in terms of chemical composition, phase formation, specific surface area, and morphology. The catalytic properties were also investigated. Different reaction parameters such as activation, catalyst loading, methanol to oil ratio and reaction time were optimized.

EXPERIMENTAL SECTION

Materials

Methanol (≥99% assay, ≤0.2% water content, and 64-65 °C boiling point) and all other used solvents were purchased from Sigma-Aldrich Merck Limited. For the transesterification reaction, commercial cooking palm oil, used in the biodiesel production consisting of esters of saturated and unsaturated monocarboxylic acid (triglycerides), 48% saturated fatty acids with 42 palmitic acid (C16:0) and the unsaturated fatty acids of 38% with oleic acid (C18:1), 12.0% of linoleic acid (18:3) with 2.1% of free fatty acid was employed. The amount of free fatty acid content was below 2.5% that was acceptable in an alkali-catalyst system. The process is not necessary pretreatment step before transesterification process. The biochar used in this study was obtained from fast pyrolysis of giant leucaena wood as the biomass feedstock carried out via fast pyrolysis process in a bubbling fluidized-bed reactor at 600 °C for 3 hrs. The biochar obtained from pyrolysis process was applied for biodiesel production. The biochar was then activated with a strong base solution to prepare the heterogeneous active catalyst. To prepare a KOH base solution (analytical grade) with the concentration of 3, 5, 7 and 9M was used as solvent to activate biochar catalyst. In the activation process, KOH solution was added into the biochar under vigorous stirring at a constant rate of 500 rpm for 30 minutes. After that, the suspension was then filtered and dried in an oven at 105°C for 2 hrs in the dry oven to obtain a dry mass. The catalyst obtained was powder form and used to carry the transesterification reaction with oil and alcohol to produce biodiesel.

Materials Characterization

The heterogeneous active catalyst (activated biochar) was characterized for its physical and chemical properties. The Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) content in the biochar was analyzed by a Flash 2000 CHNS-O analyzer (Thermo Scientific, Italy) using dynamic flash combustion. Surface morphology and the microstructures of the leucaena-derived biochar were examined using an Apero 2 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscope. Element chemical compositions were determined using a Panalytical Zetium XRF Spectrometer under energy dispersive mode. IKA Calorimeter System C 5000 control was employed to find calorific value. Crystal structures were investigated by X-ray diffraction technique (XRD) employing an X'pert-MPD Diffractometer (Panalytical, the Netherlands) using CuKα radiation over a 2theta range from 10° to 80°. Porosity was also determined using an ASAP2460 surface area and porosimetry analyser (Micromeritics, USA) by static volumetric N_2 gas adsorption method.

Transesterification Process

The obtained catalyst was applied to produce biodiesel product via transesterification process. Firstly, methanol was mixed with the catalyst and then the cooking palm oil was reacted in a 500 mL glass reactor. The transesterification reaction was performed under vigorous stirring at 750 rpm in a batch vessel reactor for continuous biodiesel production in which the reaction temperature was maintained at 65°C at atmospheric pressure. The effect of operating conditions on the biodiesel yield in terms of different dosages of the catalyst (0.25, 0.5, 1.0, 1.5 and 2.0 g) and different molar ratios of methanol to oil (4:1, 6:1, 8:1 and 10:1) prior to the mixing were investigated. Typical reactions were performed with 100 ml of the cooking palm oil. The reaction time was varied from 30 to 60 minutes. The design of equipment used in this study is shown in **Figure 1**. After the reaction completion, the catalyst and glycerol phase were removed from biodiesel. Biodiesel product was taken out from reactor for analysis. The biodiesel yield was calculated and the composition of a fatty acid methyl ester was then determined by a gas chromatography-mass spectrometry (GC-MS). Biodiesel was determined the properties. Kinematic viscosity, specific gravity, acid value, flash point, fire point and cloud point were analyzed according to ASTM methods. All experiments were repeated three times.

RESULTS AND DISCUSSION

Characterization of The Biochar-Derived Catalyst

The elemental composition of the leucaena-derived catalyst is displayed in **Table 1**. Major elements found in the catalyst were carbon (C), hydrogen (H), nitrogen (N) and sulphur (S), which is a characteristic of fuelwood (Friedl, Padouvas, Rotter, & Varmuza, 2005). The carbon content reported in this work is much higher than the work by Anupam et al. (Anupam, Swaroop, Deepika, Lal, & Bist, 2015), who prepared leucaena biochar for soil amendment. Chemical composition of pyrolyzed biochars depends on various parameters such as type of feedstock, heating temperature, residence time of volatiles and heating rate (Chen et al., 2016; Pereira, 2011). Compound analysis indicated the synthesized biochar was comprised of Na_2O MgO Al_2O_3 SiO_2 P_2O_5 SO_3 Cl K_2O CaO MnO Fe_2O_3 CuO ZnO Rb_2O and SrO.

The X-ray powder diffraction pattern of the obtained biochar powder is illustrated in **Figure 2**. The XRD pattern revealed hybrid amorphous/crystalline structure, a characteristic of biochar derived from biomass (Balajii & Niju (2019). The biochar showed higher number of crystalline phases. The broad diffraction peaks were attributed to the presence of amorphous carbon (Lokman, Rashid, & Taufiq-Yap, 2015). The major diffraction peaks were observed at 2θ = 29.37°, 36.2°, 39.4°, 43.3°, 47.5°, 48.6°, 57.4°, 60.8° and 64.6°, identified as calcite. The appearance of calcite crystal was consistent with the alkalinity of biochar. After 7M-KOH activation, the XRD pattern of the activated biochar was similar to that of the un-activated one. However, the peak at 2θ = 12.06 was observed, identifying the occurrence of potassium hydrogen carbonate following KOH activation.

Pore structure is the primary requirement in the presence of solid catalyst for transesterification reaction. Pore size of the un-activated biochar ranged from 0.6 to 2.1 nm. Moreover, it increased with KOH concentration as seen in **Table 2**. It increased up to larger than 2.5 nm, which is in favors of triglyceride and glycerin the molecules of which is about 2.5 nm.

Similar trend was observed in pore volume determination. Pore volume of biochar was 0.27 cm^3/g before activation. However, it increased to 0.35, 0.39, and 0.42 after activation with 3, 5, and 7M KOH, respectively.

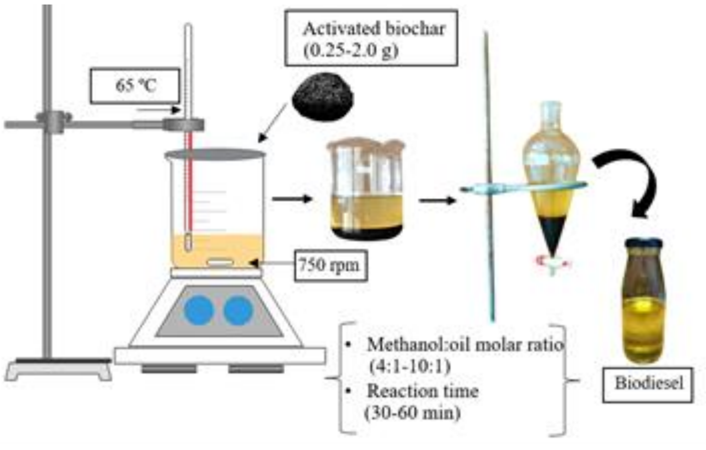

Figure 1. The experimental setup for transesterification process.

Table 1. Elemental characteristic of the biochar-derived catalyst compared with the previous work

Component (%)	This work	Anupam et al.	Zhang 2018
C	74.076 ± 0.065	62.9	41.2 ± 0.1
H	2.979 ± 0.121	3.12	1.4 ± 0.1
O	16.062 ± 0.174	20.74	20.7 ± 0.1
N	0.722 ± 0.024	2.65	2.7 ± 0.1
S	0.019 ± 0.010	0.05	-
O/C	0.16	0.25	0.38
H/C	0.48	0.60	0.40

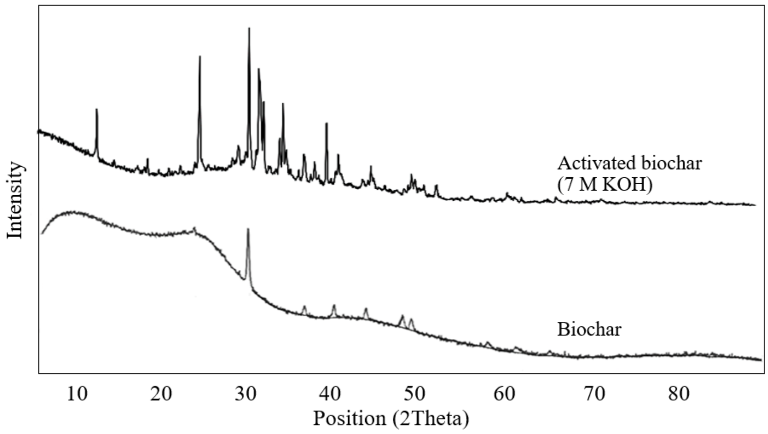

Figure 2. XRD pattern of the raw biochar and activated biochar catalyst.

Table 2. The physical properties of biochar-derived catalyst.

Physical property	Without activation	3M	5M	7M	9M
A narrow pore size distribution (nm)	0.6-2.1	0.6-2.4	0.9-3.2	2.2-3.5	2.4-4.4
Pore volume (cm^3/g)	0.27	0.35	0.39	0.42	0.37

SEM was used for the surface observation and characterizing biochar. All the activated biochar were analyzed for surface morphology. As illustrated in **Figure 3**, according to the SEM image, the unactivated catalyst exhibited a smooth surface with an irregular pore structure resulting from the removal of volatile matters (Zhang et al., 2018) and more compact with little pore. The image in **Figure 3(a)** showed elongated fibrous and wrinkled structures probably arising from the cellulosic fibers, as the activated biochar condition, the activated catalyst surface become a rough and corroded surface. Well-developed porous structure was observed in **Figure 3(b)-(c)**, as the concentration of KOH increased further (7M) activated biochar become more porous and showed a regular channel structure with uniform-sized porous structure morphology that was clearly shown in **Figure 3(d)**. Elliptical pores with a pore size of 0-100μm of aligned honeycomb-like groups of pores were clearly visible in the catalysts treated with 7M KOH solution. The pore structures were cross-linked on the surface and became more corroded with 9M solution, implying an adverse effect of the treatment shown in **Figure 3(e)**. The results clearly showed that the strong base concentration for activation was an effect on the structure of the activated biochar catalyst. Overall the SEM micrographs showed that 7M was the best condition to obtain a porous catalyst.

Performance of the Activated Biochar as a Catalyst

Biodiesel yield is dependent on various parameters including methanol to oil ratio, catalyst loading, and type of catalyst. The activated biochar was produced at different concentrations 3M, 5M, 7M and 9M of KOH to convert the cooking palm oil feedstock to fatty acid methyl ester (FAME) was investigated. **Figure 4** shows the effect of KOH activation on FAME conversion, whereby the temperature, catalyst dosage, methanol to oil ratio, and reaction time was fixed at 65°C, 1g, 6:1 and 1 hour, respectively. It was found that the FAME yield increased with KOH concentration. It reached 90.52% and 91.07% when the concentration was increased to 5M and 7M, respectively. The increase in FAME yield could be attributable to an increase in active site accompanied by an increase in specific surface area because of KOH activation. However, the FAME was found to drop markedly to 87.6% when the 9M-KOH solution was used. The decrease of FAME yield is attributable to a reduction in active site caused by the physical distortion of the catalyst surface when treated with a solution with high basicity (as previously seen in **Figure 4**).

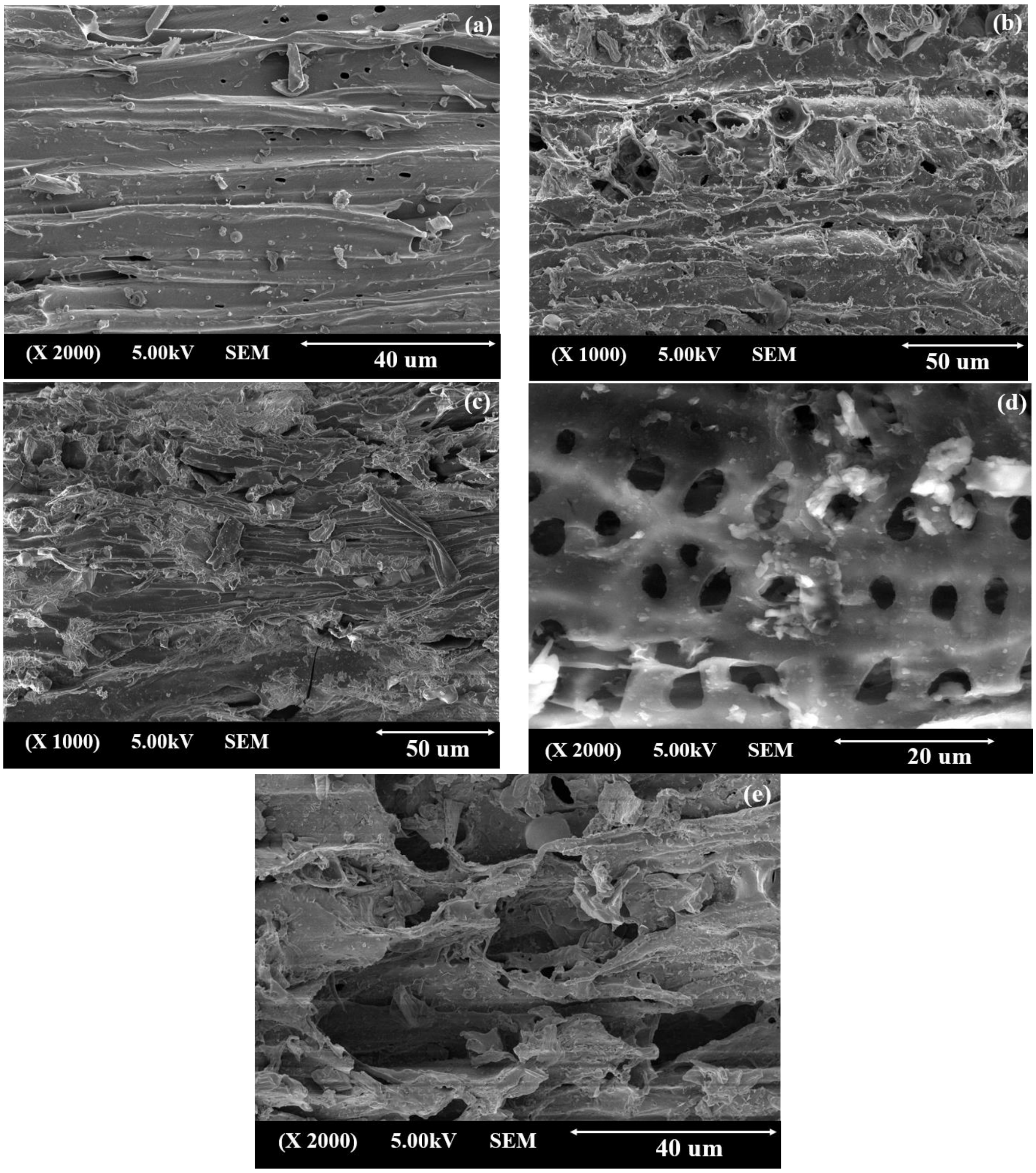

Figure 3 SEM micrographs of samples. (**a**) raw biochar and activated biochar catalyst by (**b**) 3M KOH (**c**) 5M KOH (**d**) 7M KOH, and (**e**) 9M KOH.

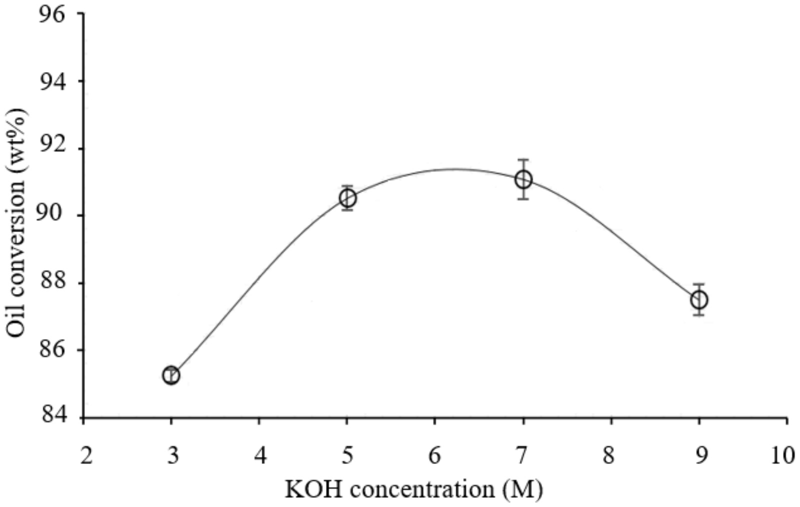

Figure 4 Influence of KOH concentration on oil conversion.

Effect of catalyst loading on oil conversion was investigated using activated catalyst at 7M-KOH condition in a range of 0.25-2.0 g. Regarding methanol to oil = 6:1, as seen in **Figure 5**, Catalyst loading was affected the biodiesel production yield the FAME increased with the increase of catalyst concentration (0.25 to 0.5 g of catalyst). The maximum FAME (94%) was recorded at 0.50 g of catalyst loading that was due to the increase in catalytic site. This is higher than that observed in the work by Yin et al. (2016) and Narowska, Kulazynski, Lukaszewicz, & Burchacka (2019) in which eggshell-derived catalyst and activated carbons were used. The oil conversion then steadily decreased with increasing the catalyst amount. The FAME yield drops to 90.31, 82.93 and 62.12% when 1.0, 1.5 and 2g of the catalyst were used. Higher loading of catalyst beyond 0.5 g finding could be attributed to an overdose of the catalyst leading to formation of viscous slurry (suspension of catalyst and reactants) and created catalyst accumulation on the wall of the vessel reactor.

Effect of methanol to oil ratio is the main component required for FAME conversion. As demonstrated in **Figure 5**, the molar ratio of alcohol was the main factor affecting the yield of biodiesel. The effect of methanol to oil ratio showed a similar trend for all catalyst doses. The FAME yield followed an increasing trend for methanol to oil ratio below 6:1, while the yield decreased when methanol to oil ratio was changed from 6:1 to 8:1 and 10:1. This is in line with the trends reported in previous studies (Naveenkumar, & Baskar, 2021; Keihani, Esmaeili, & Roohi, 2018; Musa, 2016). An increase in the amount of alcohol to oil increases the breakage of the glycerin-fatty acid linkages, which in turn gives rise to greater alkyl ester conversion (Miao & Wu, 2006). However, the excessive methanol causes an increase in solubility of glycerol, making it remain in the biodiesel phase, leading to a decrease in biodiesel yield (Lee & Saka, 2010). The stepwise reaction is reversible and requires optimal molar ratios of methanol to oil to shift the reaction equilibrium toward the FAME formation. The highest FAME yield was achieved at a molar ratio of 6:1. Tao et al. and Ahmad et al. reported the highest biodiesel conversion at a molar ratio of 10:1 and 9:1 using wood-based biochar, while Kostic, Bazargan, Stamenkovic, Veljkovic, & Mckay (2016) noted that methanol to oil ratio of 9:1 could provide the maximum yield using palm kernel shell biochar. Thus, the maximized molar ratio is dependent on the type of catalyst and quality of oil feedstock. In this study, the highest FAME was 94.06% which is higher than that observed in previous works in which rice husk, oat hull and palm kernel shell were used as a raw material for synthesis of biochar catalyst (Gonzalez et al., 2017; Nuradila, Ghani, & Alias, 2017; Li, Chen, & Zhu, 2013). An excess of methanol was not increased the biodiesel yield but was increased the cost for alcohol. These were undesirable reaction results in a negative effect on FAME yield.

The effect of reaction time on biodiesel conversion was studied using the optimal parameters obtained in the previous section (reaction temperature, 65°C; catalyst amount, 0.5 g; methanol to oil ratio, 6:1). As shown in **Figure 6**, it was found that the conversion rate of the yield increased with reaction time. The rate of chemical reaction was slow at the beginning and then the reaction proceeded more rapidly and finally reached equilibrium in about 60 min. The results showed that the FAME content increased significantly when the reaction time was changed, the oil conversion rapidly increased from 75% to 92% with reaction time at the beginning of the reaction (30-45 minutes). However, it showed a slight increase from 92% to 94% when the time was increased from 45 to 60 minutes. As the reaction proceeded 60 minutes, a noticeable change was not observed. An excess of reaction time was used in the reaction process resulting in a reduction in the biodiesel yield due to the backward reaction of transesterification. The reduction of FAME could be attributable to the formation of mono and diglycerides (Supraja, Mahera, & Paramasivan, 2019).

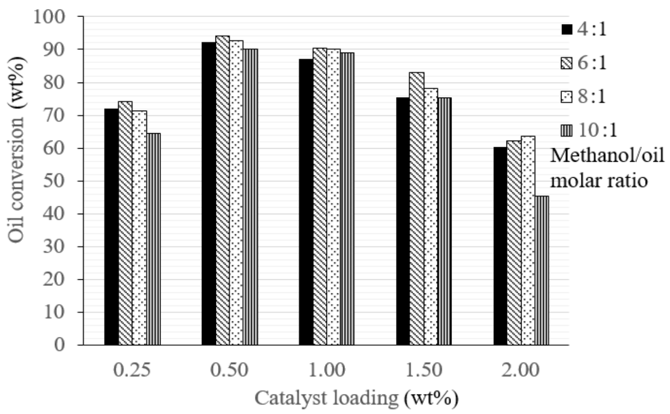

Figure 5. Influence of catalyst loading and methanol to oil molar ratio on oil conversion.

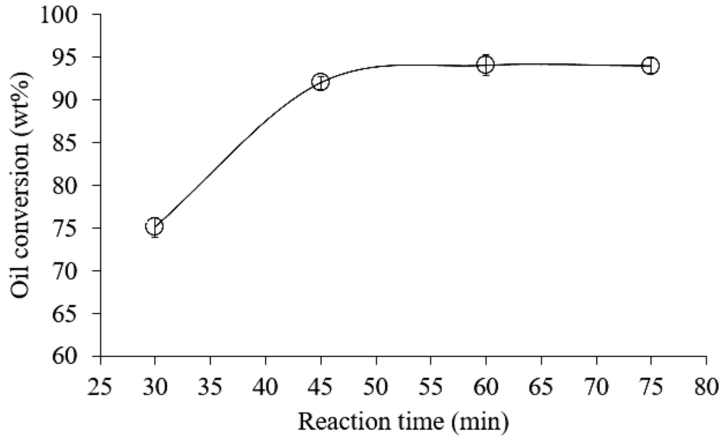

Figure 6. Effect of reaction time on oil conversion.

Table 3. Physical and fuel properties of biodiesel produced in this work.

Property	This work	ASTM D6751-12/ EN 14214:2012
Kinematic viscosity at 40 °C (mm^2/s)	4.28	1.9-6.0
Specific gravity (Kg/m^3)	887	860-900
High heating value (MJ/kg)	39.1	-
Acid value (mgKOH/g)	0.56	0.8 max
Flash point (°C)	145	≥ 130
Fire point (°C)	152	-
Cloud point (°C)	-6	-

Physical and Fuel Properties of Yield Under Optimum Condition

The obtained biodiesel was analyzed for its FAME compositions. The mainly fatty acid was observed following order C18:1 (oleic acid) > C16:0 (palmitic acid) > C18:2 (linoleic acid) > C18:0 (steric acid). Characteristics of biodiesel processed under the optimum condition were detailed in Table 3. Kinematic viscosity and density were 4.28 mm^2/s and 887 Kg/m^3, respectively. HHV (39.1 MJ/kg) were also examined to ensure the suitability of biodiesel for biodiesel fuel. It was clearly seen that Kinematic viscosity, Specific gravity, Acid value and Flash point of the obtained biodiesel lay in the standard range suggested by ASTM D6751-12 and EN 14214:2012. This indicates that the biodiesel obtained in this work has the potential for automotive fuel application.

CONCLUSIONS

Herein, the study showed leucaena-derived biochar was successfully synthesized through a fast pyrolysis method as catalyst for this process. A well-developed porous structure was achieved by KOH activation. The key factors influencing the yield of biodiesel were the catalyst dosage, methanol to oil ratio and reaction time. Activated by a concentrated-KOH solution, the leucaena biochar effectively catalyzes the transesterification process, corresponding to a 94% FAME yield which was achieved on 0.5g of the catalyst with 7M-KOH activation, 6:1 methanol to oil molar ratio and in 1 hour of reaction time with atmospheric pressure in vessel reactor. In addition, the biodiesel obtained in this work met the requirements for automotive fuels recommended in the ASTM D6751-12 and EN 14214:2012 standard. The experiment results showed that catalyst had excellent activity during transesterification and decreased the cost step of purification. As a heterogeneous catalyst, the leucaena-derived biochar proposes an economical method for biodiesel production at an industrial scale.

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