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TRANSESTERIFICATION OF *Calophyllum inophyllum* OIL USING CaO-K_2CO_3 CATALYST FROM *Corbicula fluminea* SHELLS AND BANANA PEELS

(Transesterifikasi Minyak *Calophyllum inophyllum* Menggunakan Mangkin, CaO-K_2CO_3 daripada Cangkerang *Corbicula fluminea* dan Kulit Pisang)

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Abstract

Utilizing *Calophyllum inophyllum* oil (CIO) and waste-based calcium oxide-potassium carbonate (CaO-K_2CO_3) catalyst can bring down the biodiesel production cost and this has become the main issue. CIO is a non-edible feedstock that has the potential to be used as biodiesel feedstock. The acid value and free fatty acid (FFA) content of CIO were 124.54 mg KOH/g and 62.64%, respectively. The acid values were reduced to 11.21 mg KOH/g with 5.60% of free fatty acid (FFA) by acid-catalyzed esterification reaction using a 12:1 methanol to oil ratio. CIO had iodine value of 94.33 mg I_2/g, 1.37% moisture content, a density of 929.1 kg/m^3, and viscosity of 119.5 mm^2/s. It was extracted using a cold maceration method and was found to be predominantly made up of oleic acid. CaO-K_2CO_3 was used to avoid the problems faced by the single metallic catalysts (CaO and K_2CO_3). It was synthesized using physical mixing and used as a heterogeneous catalyst for the transesterification of CIO to produce biodiesel. The base heterogeneous catalyst was characterized and analyzed using TGA, FTIR, XRD, FESEM-EDX, BET, and Hammett indicators. These analyses have proven that calcium oxide (CaO) and potassium carbonate (K_2CO_3) were well incorporated catalyst. CaO-K_2CO_3 is a moderate catalyst with the basic strength of H $\leq$9.3. Two parameters, which are methanol to oil ratio and reaction time, were optimized to obtain a higher methyl ester yield. The maximum yield of methyl ester obtained from transesterification of CIO at 65 °C was 86.7% using 6 wt.% of 1:1 CaO- K_2CO_3 and 9:1 methanol to oil ratio within 4 h reaction time. CaO-K_2CO_3 appeared as a promising catalyst in converting CIO to biodiesel.

Keyword: banana peels, *corbicula fluminea* shells, methyl ester

Abstrak

Kegunaan minyak *Calophyllum inophyllum* (CIO) dan pemangkin kalsium oksida-potasium karbonat (CaO-K_2CO_3) berasaskan sisa boleh mengurangkan kos pengeluaran biodiesel yang telah menjadi isu utama. CIO adalah bahan mentah tidak boleh dimakan yang berpotensi untuk digunakan sebagai bahan mentah biodiesel. Kandungan nilai asid dan asid lemak bebas bagi CIO adalah 124.54 mg KOH/g dan 62.64%. Penurunan nilai asid telah berkurang kepada 11.21 mg KOH/g dengan 5.60% of asid lemak bebas melalui tindakbalas esterifikasi asid dengan menggunakan metanol pada minyak (12:1). CIO mempunyai nilai iodin value 94.33 mg I_2/g, 1.37% kandungan lembapan, ketumpatan 929.1 kg/m^3, dan kelikatan 119.5 mm^2/s. Ia diekstrak dengan kaedah pemekatan sejuk dan kebanyakannya terdiri daripada asid oleik. CaO-K_2CO_3 digunakan untuk mengelakkan masalah yang dihadapi oleh pemangkin logam tunggal (CaO dan K_2CO_3). Ia disintesis dengan pencampuran fizikal. Pemangkin heterogen telah dicirikan dan dianalisis dengan menggunakan TGA, FTIR, XRD, FESEM-EDX, BET dan Hemmett. Analisis ini telah membuktikan bahawa kalsium oksida (CaO dan K_2CO_3) telah digabungkan dengan baik. CaO-K_2CO_3 merupakan mangkin sederhana dengan kekuatan alkali H_≤9.3. Dua parameter iaitu nisbah metanol kepada minyak dan masa tindak balas telah dioptimumkan untuk mendapatkan hasil metil ester yang lebih tinggi. Hasil maksimum metil ester yang diperoleh daripada transesterifikasi minyak biji CIO pada 65 °C ialah 86.7% menggunakan 6 wt.% CaO- K_2CO_3, nisbah metanol kepada minyak 9:1 selama 4 j masa tindak balas. CaO-K_2CO_3 sebagai mangkin yang dijanjikan dalam perubahan CIO kepada biodiesel.

Kata kunci: Kulit pisang, cangkerang *corbicula fluminea*, metil ester

Introduction

Nowadays, fossil fuels are the dominant energy source worldwide. Human relies heavily on fossil fuels for daily activities because of their reliability and energy efficiency. However, fossil fuels belong to non-renewable energy derived from the remains of ancient animals and plants buried millions of years ago. The burning of fossil fuels leads to an increased rate of environmental deterioration. To overcome this problem, biofuel, such as biodiesel, appears as a promising alternative to fossil fuel for diesel engines [1]. Biodiesel is a form of alternative fuel derived from vegetable oil or animal fat. Biodiesel production leads to a cleaner emission profile and higher energy efficiency compared to fossil fuel [1] and is the most outstanding biofuel due to several excellent properties such as non-toxic and high biodegradability. [2, 3]. The primary obstacle in commercializing biodiesel is the cost since the production of biodiesel from edible oil is not economically viable. The extensive use of edible oils, especially palm oil, for biodiesel production may cause a food crisis. As a result, biodiesel is very expensive to be used as a fuel due to the tremendous demand for edible oils [4]. These issues can be addressed by utilizing low-cost feedstock such as non-edible oil for biodiesel production.

Calophyllum inophyllum (CI), commonly known as Penaga Laut in Malaysia, is a medium-sized plant that grows up to 20 to 30 m high [5;6]. It thrives in sub-tropical, tropical climates, and can grow in harsh conditions [7]. CIO is a good candidate for green energy production due to its high oil content. The seed oil content of CI ranges from 40-75% (dry weight basis), which is greater than Jatropha seed oil (40-60%) and rubber seed oil (40-50%) [8]. CI grows in mixed cultures with minimal cultivation, thus minimum cultivation cost is required [9]. Since CIO is a non-edible oil, the utilization of CIO as a biodiesel feedstock will not interfere with food provision hence reducing the food crisis problem caused by edible oils. In terms of a heterogeneous catalyst, the monometallic catalyst exhibits low stability towards carbon dioxide and moisture. Even though CaO has high catalytic performance, it will leach out Ca^{2+} due to moisture from the surrounding. The leaching of Ca^{2+} deteriorates the quality of biodiesel by reacting with the FFA of the oil resulting in saponification and deactivation of catalyst function. Besides that, it also has low catalytic activity due to the poor basic site on the surface of the catalyst.

Therefore, in this research, a CaO-K_2CO_3 bimetallic catalysts (catalyst compose of two metals) heterogeneous catalyst is used to produce biodiesel. Bimetallic catalysts exhibit a synergistic effect that makes the catalysts superior to monometallic catalysts [10]. The two metallic elements can form an effective bimetallic catalyst although they do not mix each other to form an alloy. They have superior stability towards moisture and carbon dioxide, thus effectively increasing the lifetime of the catalyst [11]. In addition, bimetallic catalysts have a larger surface area and stronger basic strength resulting in better catalytic performance. Due to these reasons, researchers have mixed CaO or magnesium oxide (MgO) with other monometallic catalysts to increase the selectivity and catalytic activity of the catalyst [12]. This study aims to investigate the possibility of using CaO-K_2CO_3 as a heterogeneous base bimetallic catalyst for biodiesel production from CIO. To the best of our knowledge, the synthesis of CaO-K_2CO_3 bimetallic catalyst in catalyzing the transesterification of CIO for biodiesel production has never been reported.

Materials and Methods

The CI fruits were collected from the UiTM landscape to obtain the seed oil as feedstock for fatty acid methyl ester production. Banana peels and *corbicula fluminea* were obtained from a local stall in Pahang. ACS grade of methanol, chloroform, Thin Layer Chromatography (TLC) plate, and isopropanol were purchased from Merck KGaA (Germany). AR grades of n-hexane, sulphuric acid and petroleum ether were obtained from Bendosen and Fisher Scientific, respectively. Iodine resublimed from R&M Chemical and potassium hydroxide (KOH) extra pure from Loba Chemie were also used in this study. HPLC grade n-heptane (99%) and C_{17} methyl heptadecanoate as the internal standard for methyl ester were purchased from Friedemann Schmidt. Phenolphthalein (H_= 9.3), 2,4-Dinitroaniline (H_= 15.0), and 4-nitroaniline (H_= 18.4) from Sigma-Aldrich were used as Hammett indicators.

CI fruits were dried under the sun for five days. The seeds were obtained from the crashed outer layers of the dried fruits and were washed with warm water to remove dirt and impurities. Then, the seeds were dried in an oven at 100℃ overnight to remove moisture content. The dried seeds were then ground into fine powder for further extraction [13, 14]. A total of 200 g of powdered seed was placed in a 500 mL beaker. The extraction solvent of n-hexane was then poured into the beaker until the powdered seed was completely covered. The beaker was sealed with aluminum foil and kept for 5 days. The seed oil was separated from the powdered seed by filtration. Subsequently, the seed oil was separated from n-hexane using a Buchi R-100 rotary evaporator at 70 °C. The extracted oil was then transferred to 30 mL vials and kept in the refrigerator.

The bimetallic catalyst was prepared in a 1:1 CaO/ K_2CO_3 molar ratio. The washed clamshells were dried under the sun for two days and crushed using a pestle and mortar. The *corbicula fluminea* shell fine powder was then calcined at 900 °C using a tube furnace. Banana peels that contained K_2CO_3 were sectioned and cut into several pieces. The peels were dried in an oven at 100 °C overnight before grounding the dried peels using a grinder. The banana peels fine powder was then calcined using a tube furnace at 550 °C. A bimetallic catalyst with a CaO/ K_2CO_3 molar ratio of 1:1 was prepared by physically mixing (ball milling) the same ratio of CaO and K_2CO_3. The catalysts were characterized and analyzed using Thermogravimetric Analysis (TGA), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), Field Emission Scanning Electron Microscopy and Electron Dispersive X-ray (FESEM-EDX), and Fourier Transform Infrared Radiation (FTIR) analyses. Furthermore, Hammett indicators were also used to determine the basicity of the catalyst. High contents of FFA in CIO were converted to triglyceride using a sulfuric acid catalyst. The conversion of FFA was performed at 60 °C for 2 hours using methanol to oil ratio of 12:1 and 1 wt.% catalyst [13]. This procedure was repeated with the same methodology to reduce the acid value of the oil to less than 5 mg KOH/g oil.

The resulting mixture was transferred to centrifuge tubes to separate excess methanol and contaminants from triglyceride [14]. Transesterification reactions were carried out in a 50 mL round bottom flask equipped with a condenser, thermometer, and magnetic stirrer immersed in a water bath. A total of 5 g of CIO was added to the calcined catalysts and methanol mixture. The mixture was refluxed under constant 500-600 rpm magnetic stirring with a 1:1 CaO/ K_2CO_3 ratio, 6 wt.% catalyst loading, 65 °C reaction at varied reaction times (2 - 5 hours), and several methanol to oil ratios (7:1, 9:1, 11:1, 13:1 and 15:1). After the transesterification reaction, the product mixture was cooled to room temperature. Then, the product mixture was centrifuged at 4000 rpm for 5 min to separate the desired product from the by-products. The FAME content in the sample was analyzed using GC-FID. GC-FID (Agilent 7890A GC-System) with a polar capillary column (MEGA-Wax, 30 m length, 0.32 mm internal diameter, and 0.50 µm film thickness). Samples were prepared by mixing

20 mg of the methyl ester with 400 µL of internal standard using a micropipette. A total of 10 mg/mL of methyl heptadecanoate (C_{17}) was used as an internal standard. For each sample analysis, a sample volume of 1µL was injected into GC. The carrier gas was helium, which had a linear velocity of 40 cm s^{-1}. The initial oven temperature was 190 °C with a 2 min equilibration interval. The temperature of the oven was raised 10 °C per minute until it reaches 230 °C and held for 8 min. The methyl ester content was observed and calculated following the EN14103 European regulation procedure.

Results and Discussion

The characterization of CIO was performed based on acid value, FFA %, iodine value, moisture content, density, and viscosity to determine seed oil quality before transesterification reaction following standard test methods (ASTM D1298; ASTM D1298). The acid value and FFA content of CIO were 124.54 mg KOH/g and 62.64%, respectively in which the values reduced to 91% (acid value: 11.21 mg KOH/g, FFA: 5.60%) after the esterification reaction. It has an iodine value of 94.33 mg I_2/g, 1.37 % moisture content, a density of 929.1 kg/m^3, and viscosity of 119.5 mm^2/s. Oleic acid (73.21%) is predominantly found in the seed oil followed by linoleic acid (13.5%) and palmitic acid (11.7%) play a major FFA in CIO. A similar observation of abundant fatty acids was seen in previous research [8; 14].

Based on Figure 1(a), a weight loss occurred in a single stage ranging between 600 °C and 780 °C. The decreasing TGA thermal curve indicates the thermal decomposition of calcium carbonate ($CaCO_3$) to CaO [15]. The CaO product was stable after 780 °C in which 55% of the sample weight remained. About 44% of TGA weight was loss from $CaCO_3$ suggesting the elimination of carbon dioxide. Meanwhile, as shown in Figure 1(b), involving four stages of the decomposition phase. Firstly, 9.57% of weight loss between 41 °C and 194 °C was attributed to the dehydration of banana peels from the loss of moisture content [16;17]. In the second stage, the volatile matter contents such as hemicellulose, cellulose, and lignin were broken down [18]. This led to a drastic weight loss (39%) of the sample resulting in the lowest value in the DTA plot curve between 200 ℃ and 400 ℃. The final stage ranging between 800 °C and 1000 °C was associated with the solid decomposition of the sample.

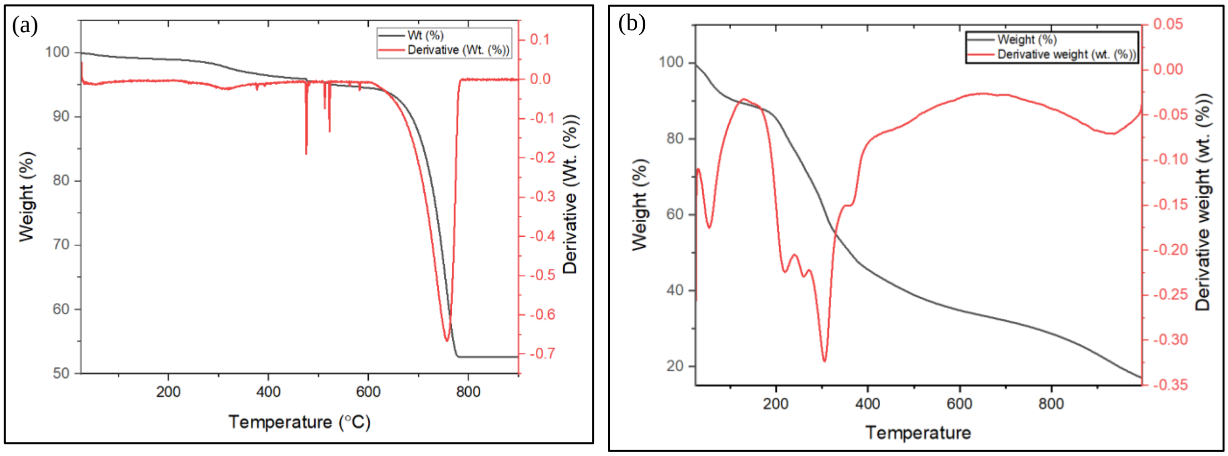

Figure 1. TGA/DTA curve of (a) uncalcined *corbicula fluminea* shells (UCFS) and (b) uncalcined banana peels (UBP)

Based on Figure 2, the peaks of calcined *corbicula fluminea* shells (CCFS) observed at 2θ = 32.484°, 37.635°, 54.109°, 64.404°, and 67.644° were attributed to lime (CaO). $CaCO_3$ was completely transformed into CaO. The appearance of sharp and narrow peaks in CCFS defined the highly crystalline structure of the catalysts [19]. The XRD pattern of calcined banana peels (CBP) presented the characteristic peaks associated with K_2CO_3. It was found that the species exhibited at 2θ value of 43° and 67.7° referred for UBP and 2θ value of 32.48°, 40.679°, 50.326°, 57.94°, 66.513°, and 73.82° referred for CBP. After thermally calcined at 600 °C, it was observed that K_2CO_3 appeared as the main component of CBP. Compared to CBP, there were small and unclear peaks found in UBP, indicating the importance of the calcination process in producing catalysts with higher crystallinity. The XRD pattern revealed that the CCFS has higher crystallinity compared to CBP. The characteristic peaks of CaO-K_2CO_3 at 2θ = 29.80°, 40.694°, 50.298°, 50.89°, 66.54°, and 73.906° were attributed to K_2CO_3 while the peaks exhibited at 2θ = 32.379°, 37.553°, 54.035°, 64.403°, and 67.611° were assigned to CaO. CaO and K_2CO_3 were considered the principal constituents in the bimetallic catalyst.

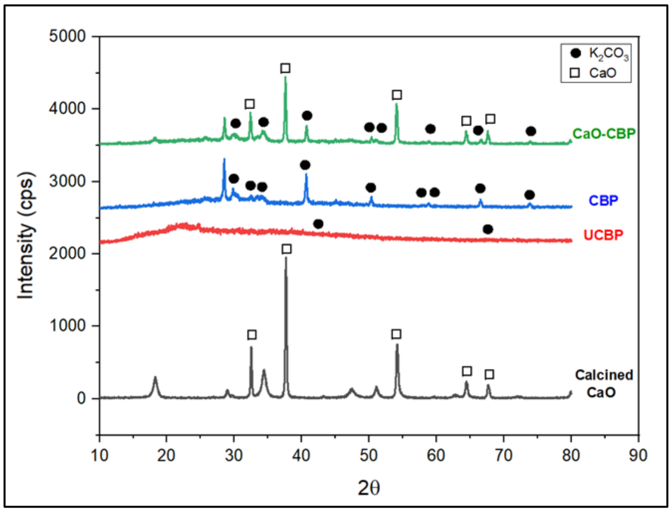

Figure 2. XRD pattern of CCFS, UBP, CBP and CaO-K_2CO_3

The FTIR spectra were used to identify the functional groups involved in CCFS, UBP, CBP, and CaO-K_2CO_3. The intense broad IR peaks at 3436.52 cm^{-1} (CCFS), 3420.60 cm^{-1} (CaO-K_2CO_3), 3436.63 cm^{-1} (CBP), and 3447.11 cm^{-1} (UBP) were assigned to the bending and stretching vibration of O-H bonds indicating the presence of water molecules on the surface of the catalysts [20]. The weak peaks observed at 874.43 cm^{-1} (CCFS), 869.48 cm^{-1} (CaO-K_2CO_3), 669.09 cm^{-1} (CBP), and 667.71 cm^{-1} (UBP) may be due to the stretching vibration of metal-O bonds. The peaks indicated the presence of carbonates in the catalysts at 1384.51 cm^{-1} (CaO-K_2CO_3), 1384.26 cm^{-1} (CBP) and 1384.58 cm^{-1} (UBP), which were assigned to C-O bending and stretching vibration. However, based on Figure 3, the peak at 1384 cm^{-1} was strong only in the calcined catalysts, CBP and CaO-K_2CO_3, representing K_2CO_3. The sharp characteristic bands at 3643.77 cm^{-1} (CCFS) and 3643.97 cm^{-1} (CaO-K_2CO_3) show the presence of the hydroxide (OH) group of calcium hydroxide ($Ca(OH)_2$). The production of this group may be via the hydration reaction between CaO and water molecules. The peak of 1419.83 cm^{-1} in CCFS was assigned to the symmetrical and unsymmetrical O-C-O stretching attached to CaO [21].

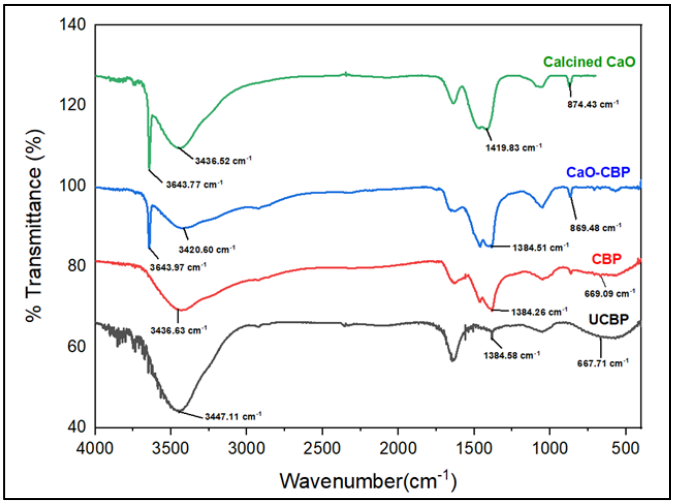

Figure 3. FTIR spectra for CCFS, UBP, CBP and CaO-K_2CO_3

The Hammett indicators used in this analysis are phenolphthalein (H_= 9.8), 2,4-dinitroaniline (H_= 15.0), and 4-nitroaniline (H_= 18.4). CaO-K_2CO_3 turned the colorless phenolphthalein into pink, but the yellow color of 2, 4-dinitroaniline and 4-nitroaniline remains unchanged indicating the basic strength within the range of 9.8 < H_ < 15.0. According to Ngaosuwan et al. [22] the La_2O_3/CaO developed from the eggshells by physical mixing indicated the basic strength within the range of 7.2 < H_ < 9.8. CaO-K_2CO_3 that was synthesized in this work showed higher basicity compared to bimetallic catalyst in the previous study.

The Brunauer-Emmett-Teller (BET) analysis was used to determine the BET surface area, pore volume, and pore size of the catalysts. It was observed that the BET surface areas of both calcined compounds, CCFS and CBP were greater than the uncalcined samples. Thus, it can be concluded that the calcining process contributes to the enhancement of the catalyst's surface area. The pore volume and pore size of the corbicula fluminea shell was discovered to be in an increasing trend from 0.0106 cm^3/g to 0.0358 cm^3/g and 155.8632 Å to 157.1291 Å, respectively after calcination process. The same trend was observed in banana peels, whereby the pore volume and pore size increased from 0.0031 cm^3/g to 0.0205 cm^3/g and 25.8222 Å to 51.3117 Å, respectively. This was expected to provide a better interaction between the oil sample and catalysts. On the other hand, CaO-K_2CO_3 was found to have a BET surface area of 22.5885 m^2/g demonstrating a greater surface area compared to CBP and CCFS. The bimetallic catalyst was expected to contain a greater catalytic property than a monometallic catalyst. However, the pore volume and pore size of CaO-K_2CO_3 were smaller compared to CCFS and CBP. It was suspected that the pore of the catalyst was blocked by CCFS on the CBP [23].

The agglomerated particles of CCFS with irregular shapes were observed in Figure 4 (a). In contrast, Figure 4(b) reveals the irregular structure of UBP with a smooth surface. Calcination plays a significant role in the morphology of banana peels. After the calcining process, the catalyst structure changes dramatically. Figure 4(c) demonstrates a porous morphology of CBP. The cross-sectional view of CBP shows the presence of multiple pores. The microstructure possesses a rough surface with aggregated particles on top of the surface. The binding of CaO on the surface of CBP is illustrated in Figure 4 (d). The agglomerated structures of CCFS fill the pores of CBP in which it binds with CBP forming a bimetallic catalyst. CaO serves as a medium to fill the available voids in CBP with the aim to enhance the surface area of the catalysts hence diminishing the pore volume. EDX analysis was performed to determine the surface elemental composition of the catalysts. Figure 5 shows the EDX spectra of CCFS, UBP, CBP, and CaO-

K_2CO_3 bimetallic catalyst. The spectra show a significant amount of carbon, oxygen, potassium, and calcium on the catalysts. CCFS has 55.36% of O, 30.87% of Ca, and 13.77% of C. UBP has 45.58% of O, 25.49% of K, and 24.67% of C whereas CBP has 51.83% of O, 29.57% of K, and 16.42% of C. CaO-K_2CO_3 consists of 47.32% O, 22.19% Ca, 20.26% C, and 10.24% K.

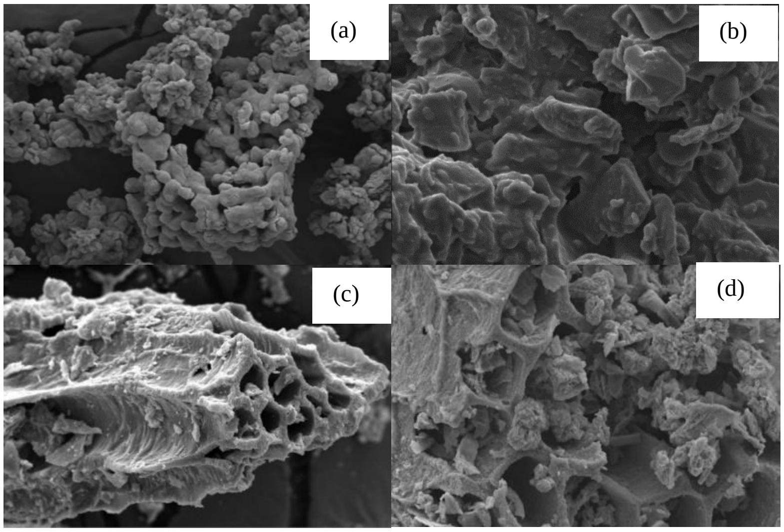

Figure 4. FESEM photographs of (a) CCFS, (b) UBP, (c) CBP and (d) CaO-K_2CO_3 under magnification of 5000

Since the stoichiometric molar ratio of methanol to oil for the transesterification process is 3:1, an excess amount of methanol is required to drive the equilibrium towards biodiesel production. Therefore, the 7:1 molar ratio was taken as the starting value for investigation [24]. As shown in Figure 6(a), the yields of the biodiesel increased as the methanol to oil ratio increased from 7:1 to 9:1. In this study, the molar ratio of 9:1 is determined as the optimum methanol to oil ratio with an 81.4% yield of methyl ester. When the methanol to oil ratio was further increased beyond the optimum ratio (9:1), the biodiesel yields gradually dropped. Glycerol, the side product of the transesterification reaction could dissolve in the excess of methanol and inhibit the reaction of methanol with triglyceride and catalyst. This reaction hampers the separation of glycerol from methyl ester and thus, reduces the methyl ester yield [24]. Therefore, methanol to oil ratio of 9:1 was used to optimize the transesterification of CIO since it produced the highest yield of methyl ester of 81.4 % at 65 ℃ using 6 wt.% 1:1 CaO-K_2CO_3 in 3 h reaction time.

The methyl ester yield increased as the reaction duration increased from 2 to 4 hours. However, after an optimal reaction duration, a further increase in the reaction time will reduce the methyl ester conversion. Since transesterification reaction is a reversible process, the backward or reverse reaction started when equilibrium has been achieved. This would lead to the loss of methyl ester and soap formation [25]. Thus, it is significant to determine the optimal reaction time to obtain a higher biodiesel yield [26]. Therefore, the optimal reaction time was 4 hours with 86.7% biodiesel yield at 65 ℃ using 6 wt.% of 1:1 CaO-K_2CO_3 and 9:1 methanol to oil ratio.

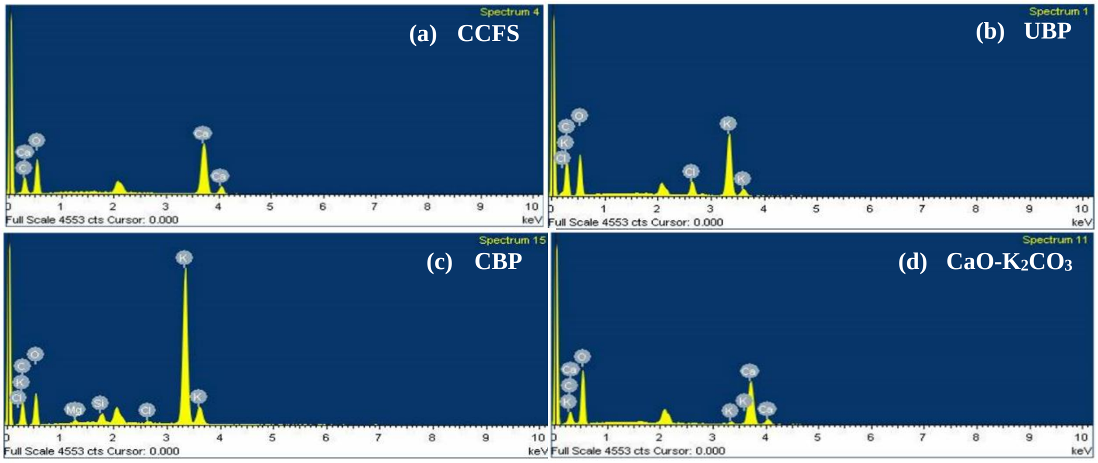

Figure 5. EDX spectra of (a) CCFS, (b) UBP, (c) CBP and (d) CaO-K_2CO_3 bimetallic catalyst

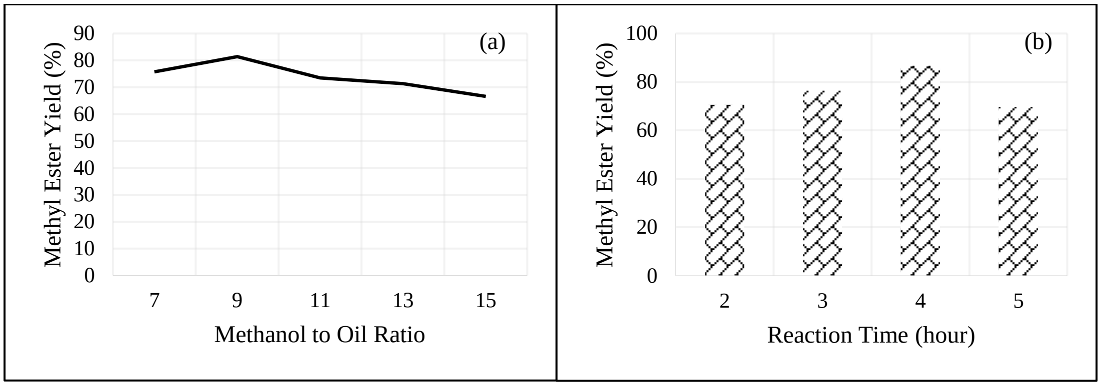

Figure 6. Effect of (a) methanol/oil molar ratio and (b) reaction duration

Conclusion

In this study, a heterogeneous CaO-K_2CO_3 bimetallic catalyst derived from *Corbicula fluminea* shell and banana peels was synthesized and successfully utilized in the transesterification of CIO for the conversion of biodiesel. Bimetallic catalyst CaO-K_2CO_3 was synthesized by physical mixing of CaO and K_2CO_3. Bimetallic catalysts CaO-K_2CO_3 characterized using TGA, XRD, FTIR, FESEM-EDX, BET, and Hammett indicators revealed the potential to be utilized as a solid catalyst in biodiesel conversion. A maximum of 86.7% of methyl ester yield could be obtained at 65 °C using a 9:1 methanol to oil ratio and 6 wt.% of 1:1 CaO-K_2CO_3 at 4 hours reaction time. Using waste materials is an eco-friendly approach that minimizes the cost of catalysts and adds value to these waste materials. Biodiesel from CIO is considered cost-effective renewable energy.

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