International Journal of Engineering & Technology, 7 (4.35) (2018) 700-704

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper



Utilization of Carbide Lime Waste as Base Catalyst for Biodiesel Production

Koguleshun Subramaniam[1], Sasidevan Munusamy[2], Fei-ling Pua[3]*, Mohd Aizat Mohd Nasir[5] , Rohaya Othman[6], Sharifah Nabihah Syed Jaafar[6]

[1]Department of Mechanical Engineering, UNITEN, 43000 Kajang, Selangor, Malaysia.
[2]Institute of Sustainable Engineering (ISE), UNITEN, 43000 Kajang, Selangor, Malaysia.
[3]Mineral Research Centre, Rock Based Technology Section, Department of Mineral and Geoscience Malaysia, Perak, 31400 Ipoh, Perak, Malaysia.
[4]Bioresources and Biorefinery Laboratory, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.
**Corresponding author E-mail: gracepua@uniten.edu.my*

Abstract

Calcium rich solid base catalyst was synthesized from local waste carbide lime and its catalytic performance was evaluated via biodiesel production. Carbide lime waste was used to produce CLW-I and CLW-II solid base catalyst using different preparation methods. Characterization including base strength analysis, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) were investigated. Catalytic strength was examined by deploying the solid base catalysts for transesterification reaction of palm oil. Fourier Transform Infra-red (FTIR) was used to analyze the presence of ester group in biodiesel. The yield of biodiesel conversion was calculated based on the mass of biodiesel and glycerol. The highest biodiesel conversion rate of 75.30% was achieved by CLW-I solid base catalyst at 9% loading. The good catalytic performance of carbide lime waste derived solid base catalysts proves that it has high potential to replace the usage of conventional catalyst in the biodiesel industry.

Keywords: *Catalyst; Carbide lime waste; Base catalyst; Transesterification; Biodiesel*

1. Introduction

Rapidly rising population growth and the increasing demand for energy has awakened the need to prepare an alternative energy resource to tackle these challenges. Alternative energy resource in the form of renewable energy is seen to be the best fit for this issue for a number of reasons. The major reason being that this particular type of energy resource is capable of meeting existing and future energy demands and also being environment-friendly at the same time. Renewable energy is replenishable, hence it can be used for a long period of time without worrying that it might run out anytime soon. Existing energy resources are mainly fossil fuel extracts such as coal, petroleum, and natural gas. Though these resources are still available for use, its impact on the environment rings a bell and calls for attention. Environmental pollutions caused by non-renewable energy are getting greater each day, hence it is a wise move to shift towards a cleaner energy option to save what is left. Renewable energy can be classified into few types that include solar, wind, tidal, geothermal, hydropower, and biomass [1].

Petroleum diesel produces greenhouse gases (GHG) and air-contaminants such as CO_2, SO_x, NO_x, and CO, increasing the atmospheric pollution rate [2]. Meanwhile, biodiesel generates much lesser GHGs and air containments through combustion, minimizing the atmospheric pollution rate. Moreover, feedstocks used for biodiesel production is of organic origin and it is readily available in large quantities due to the large scale food industry that will constantly produce feedstocks such as waste cooking oil and animal fat. Hence, continuous supply of feedstock for biodiesel production is not something to be worried about as the food industry is not at the risk of shutting down anytime soon. Besides, biodiesel can be used in existing diesel engines without any modifications [3]. This puts biodiesel as a cleaner and considerable option to replace other traditional fuels. The transportation sector, private cars, buses, trucks, and production industries are using petroleum diesel extensively. Fossil fuel generates 80 % of the world's energy demand [4]. Therefore, replacing petroleum diesel with biodiesel is an ideal way of reducing the huge dependence on non-renewable resources.

Biodiesel is seen as a substitute to conventional petroleum diesel because it is less harmful to the environment and can be made available for a long time with proper production planning and execution. Biodiesel can be defined as a mixture of fatty acid alkyl esters (FAME) produced by transesterification or methanolysis reaction. In transesterification reaction, triglyceride reacts with alcohol in the presence of a catalyst. Biodiesel will be produced as the main product and glycerol as side product. Although there are other conventional methods of producing biodiesel, transesterification is favored among others as it is easy, can be conducted at normal conditions, and provides the best biodiesel yield and quality of fuel. The reaction is usually catalyzed by an acid or base catalyst [2] [5]. The biodiesel industry is facing problems with the existing homogenous catalysts as it's not easily separable from the end-product of transesterification. The separation is tedious and results in higher biodiesel production costs. Meanwhile, heterogeneous catalysts have more advantages i.e. non-corrosive, present lesser separation problems. Heterogeneous

Copyright © 2018 Authors. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

catalysts are easier to be separated from liquid products and it can give higher catalytic activity. [6][7].

Industrial waste is constantly being produced in large amounts, without proper planning, the waste could potentially be a huge threat to the environment. Carbide lime waste is commonly generated as a solid waste and is co-produce from the acetylene gas industry and ethyne gas. It is composed mainly of 85-95 % of $Ca(OH)_2$, 1-10 % of $CaCO_3$, and 1-3 % of unreacted carbon and silicates. The waste is highly basic in nature with pH > 12 and can also be made up of metals such as magnesium, strontium, bromine, and copper [5] [8]. According to Rohaya et. al. 2015 [9], carbide lime is considered as industrial waste from the production of acetylene gas and is classified as a scheduled waste in Malaysia. No reports to the knowledge of authors were found for the utilization of carbide lime waste as base catalyst. However, carbide lime to a small extent is used to treat sewage water, stabilizer in road constructions and other applications as hydrated lime substitutes. Improper waste disposal management will cause severe consequences towards the environment. Hence, proper disposal planning should be drafted or the waste should be utilized in other industries to minimize the negative impact that these wastes could potentially cause [8].

The main aim of this study was to study the potential of Malaysian carbide lime waste as a base catalyst for biodiesel production. In this work, two different catalysts were synthesized from carbide lime waste. Catalytic performance of the new catalysts was tested by the transesterification of palm oil with methanol. Morphology and elemental properties were characterized by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). The structures of catalysts were characterized by X-ray diffraction (XRD). Biodiesel conversion rate was calculated to identify the catalytic performance. Ester group in the biodiesel was confirmed by Fourier Transform Infra-red analysis (FTIR).

2. Experimental Details

2.1. Catalyst Preparation

Raw carbide lime waste (CLW) was collected from the Department of Mineral and Geoscience Malaysia, Perak. Different preparation methods were used to synthesize two CLW derived base catalysts. Raw carbide lime waste was first mortared and sieved to achieve a homogenous particle size. CLW-I base catalyst was prepared by calcining 50g of raw carbide lime waste in a furnace at 850°C for 4 hours. CLW-II base catalyst was prepared by adding 12g of calcined carbide lime waste into 100ml of 12% wt. ammonium carbonate solution to increase the base strength. The mixture was filtered after being under constant agitation for 0.5 hours. The residue was oven dried and calcined at 900°C for 1.5 hours. After calcination, both CLW-I and CLW-II base catalysts were cooled to room temperature and stored to be used for transesterification reaction [10].

2.2. Catalyst Characterization

The base strength of catalysts was examined by a range of Hammett indicators: neutral red (H_ = 6.8), bromothymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2,4 - dinitroaniline (H_ = 15.0). The base strength analysis was carried out by shaking 25mg of catalyst with 5ml Hammett indicator solution diluted in methanol. The mixture was left idle to equilibrate for 2 hours and the colour of catalyst was recorded after color changes was stabilized [11]. Surface morphology of catalysts was studied via scanning electron microcopy (SEM) using *JSM-6010PLUS/LV*. The elemental composition on the catalyst surface was studied using energy dispersive X-ray (EDX). The structural analysis of catalysts was determined via X-ray diffraction (XRD) analysis using *Shimadzu XRD-6000* where Cu Kα radiation was emitted at a tube voltage and current of 40 Kv and 20 mA respectively with a scanning speed of 4 deg/min and scanning range of 10-90^o.

2.3. Transesterification Reaction

Transesterification was performed in a 3-neck flat bottom flask placed on a hotplate coupled with a thermocouple probe. The system was under reflux condensation at a constant overhead stirring at 350rpm. Transesterification reaction was carried out using 30g of palm oil at a methanol to oil molar ratio of 10:1, in the presence of the prepared base catalysts. The reaction temperature was maintained at a range between 60-65°C for 2 hours. After the reaction, catalyst was separated from the mixture via vacuum filtration, followed by evaporation of excess methanol at 70°C. Then, the separation of transesterified products were observed by putting the mixture into a separation funnel. The top layer, regarded as biodiesel and the bottom layer, regarded as glycerol were recovered.

3. Results and Discussion

3.1. Base Strength Analysis

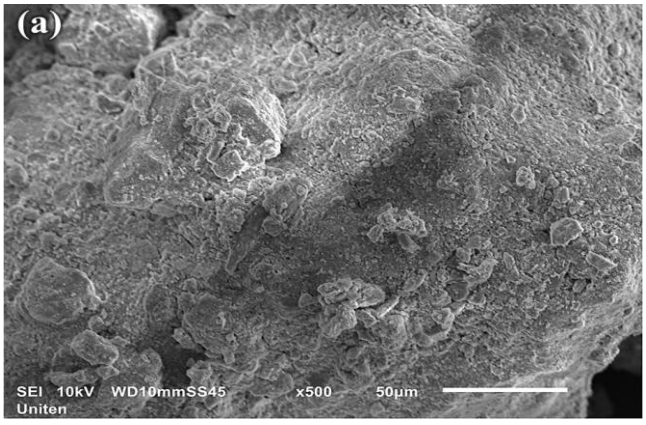
The basicity of base catalysts CLW-I and CLW-II were gauged via Hammett indicators, as tabulated on Table 1. The base strength of base catalysts are relatively the same, between the range of H_ = 9.3 and H_ = 15.0. The base strength of both catalysts was found to be similar with no significant changes. However, due to the limitations in the Hammet indicator method of catalyst basicity measurement, the exact base strength was undetermined. The result proved that both catalysts have basicity properties and are suitable to be used as alkaline catalyst in transesterification reaction.

Table 1: Base strength analysis of CLW-I and CLW-II catalyst

	Base Stregth (H_)
CLW-I	9.3 < H_ < 15.0
CLW-II	9.3 < H_ < 15.0

3.2. Morphology analysis

Scanning electron microscope (SEM) micrographs of raw carbide lime waste (500x), catalyst CLW-I (1500x) and catalyst CLW-II (1500x) are illustrated in Figure 1. The surface morphology of raw carbide lime waste appears to be uneven and irregular in shape as shown in Figure 1(a). Figure 1(b) shows the morphology of CLW-I which exhibits decrement in particle size with a uniform particle distribution after calcination at 850°C for 4 hours. The morphology of CLW-II illustrates evenly scattered particles which are of spherical shape as shown in Figure 1(c). These results suggest that the surface of raw carbide lime had been changed after calcination. Smaller particles appeared after the reaction. The surface changes might be the contributing factor for high particle crystallinity in structural analysis.



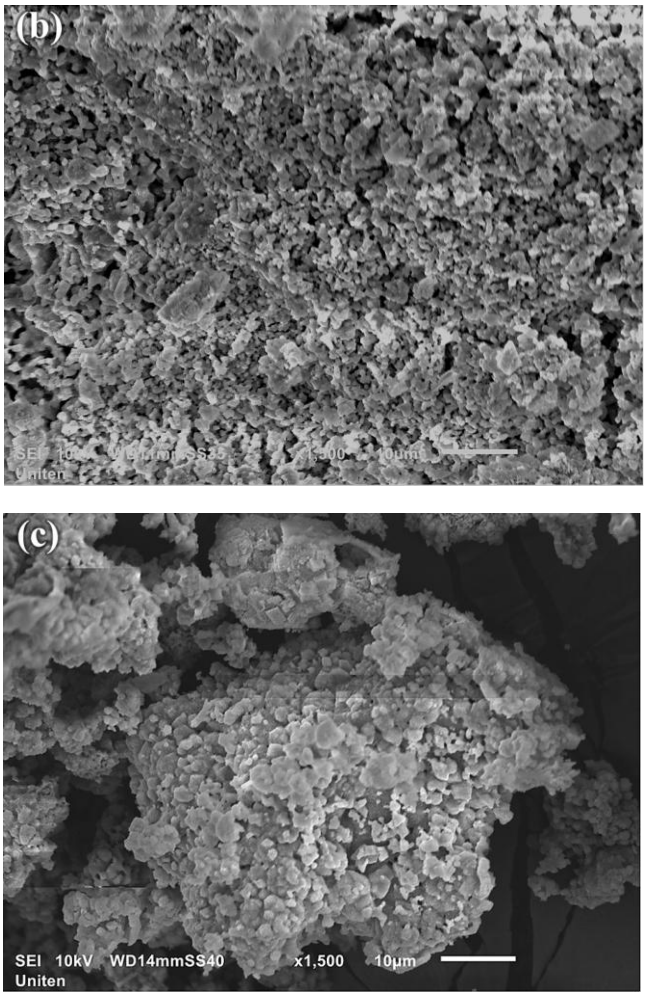
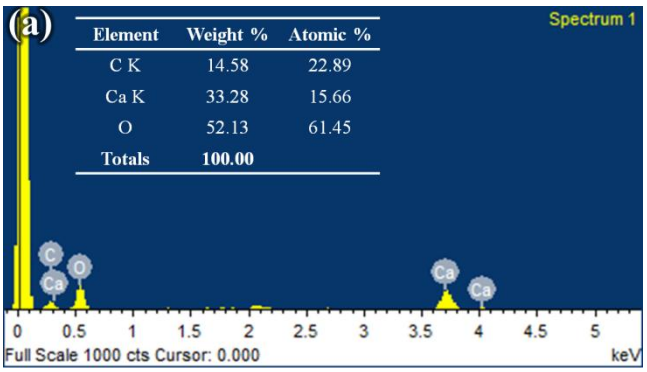


Fig. 1: SEM images of (a) Raw carbide lime waste, (b) CLW-I and (c) CLW-II.

3.3. Elemental Analysis

The energy dispersive X-ray (EDX) analysis of raw carbide lime waste, CLW-I and CLW-II is shown in Figure 2. The elemental composition of CLW-I (Figure 2(b)) has a significant increase in calcium element at 49.97 wt% in comparison with raw carbide lime waste (Figure 2(a)) at 33.28 wt%. The composition of oxygen on both raw carbide lime waste and CLW-I is about the same. However carbon element is absent on CLW-I. CLW-II has an elemental composition of carbon, oxygen and calcium of 10.24 wt%, 56.27 wt% and 33.49 wt% respectively as shown in Figure 2(c). Raw carbide lime waste has a low carbon composition at 14.58 wt%. The loss of carbon in CLW-I is perceived to be the effect of calcination, as calcination is also known to be used for carbon removing purposes [12]. Hence the presence of carbon element in CLW-II would be from ammonium carbonate that was used during catalyst preparation.



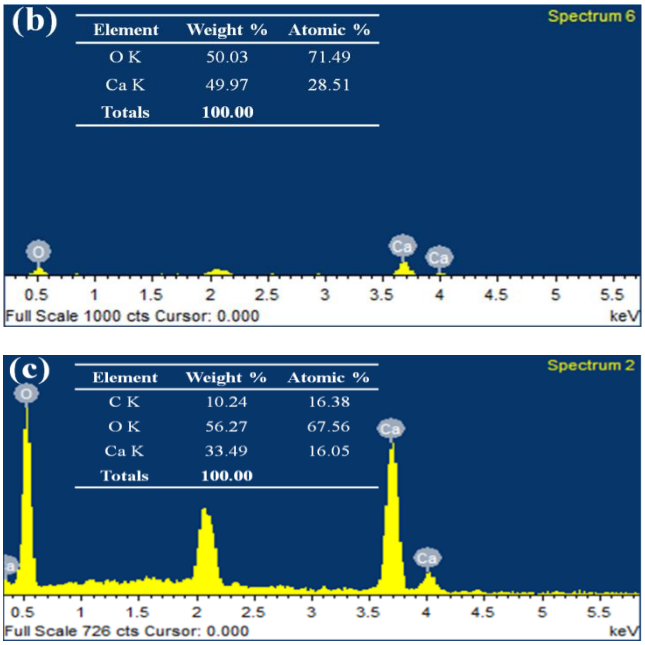


Fig. 2: EDX analysis of (a) Raw carbide lime waste, (b) CLW-I and (c) CLW-II.

3.4. Structural Analysis

The XRD analysis result of catalyst CLW-I and CLW-II in comparison with raw carbide lime waste is as shown in Figure 3. The XRD pattern of both raw carbide lime waste and CLW-I indicates that $Ca(OH)_2$ was the dominant composition. The peaks (0 0 1), (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 1 1), (2 0 1), (1 1 2), (2 0 2) and (2 1 1) to the corresponding 2θ values are in line with the library database (JCPDS 00-004-0733) for the identification of $Ca(OH)_2$ of hexagonal structure. Diffraction peaks of catalyst CLW-II at (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (3 3 1) to the corresponding 2θ values corresponded to cubic CaO (JCPDS 01-082-1691).

The crystalline size of all the samples was calculated based on *Scherrer* equation as in (1):

$$D = (K\lambda) / (\beta \cos\theta) \quad (1)$$

where D is the crystalline size, K is the dimensionless shape factor with a wavelength close to unity, λ is the x-ray wavelength, β is the line bordering at half the maximum intensity (FWHM) and θ is the bragg angle. Table 2 shows the crystalline size of raw carbide lime waste, catalyst CLW-I and CLW-II. The crystalline size of Raw carbide lime waste and CLW-I is 3.40 nm and 2.40 nm respectively. CLW-II has a crystalline size of 7.25 nm. The crystalline size increased with the calcination temperature. Sharper reflection peaks indicates the increment of crystallinity. The purpose of calcination at high calcination temperature (900°C) was to increase CLW-II catalyst stability [13]. The CLW-II was proved to be mainly composed of CaO at higher calcination temperature.

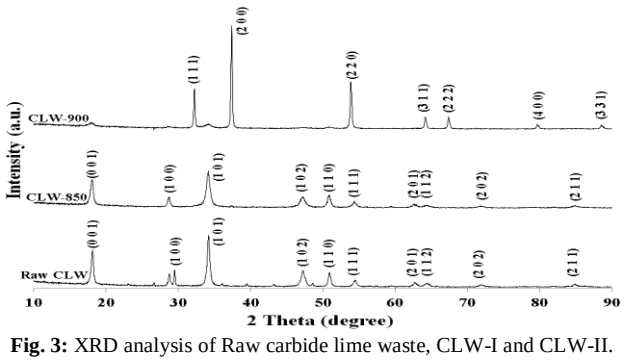


Fig. 3: XRD analysis of Raw carbide lime waste, CLW-I and CLW-II.

Table 2: Crystalline size of Raw carbide lime waste, CLW-I and CLW-II.

	Crystalline Size
Raw carbide lime waste	3.40 nm
CLW-I	2.40 nm
CLW-II	7.25 nm

3.5. Biodiesel Conversion Rate

The catalytic efficiency of CLW-I and CLW-II solid base catalyst were studied by deploying it for transesterification reaction of palm oil. Transesterification reaction was carried out using 30g of palm oil with methanol and catalyst at a methanol to oil molar ratio, reaction time and reaction temperature of 10:1, 2 hours and 60-65°C respectively. The effect of catalyst loading was studied for CLW-I and CLW-II solid base catalyst. The catalyst loadings studied were 3%, 6% and 9%, calculated by weight of oil. The biodiesel conversion rate (%) was calculated using the formula as in (2) as reported in previous studies [10]:

$$X = [1 - (M_O m_G / M_G m_{ME})] X 100 \quad (2)$$

where X is the biodiesel conversion rate (%), M_O is the molecular weight of oil, M_G is the molecular weight of glycerol, m_{ME} is the weight of methyl ester and m_G is the weight of glycerol. The molecular weight of palm oil used was 847.3 g/mol and the molecular weight of glycerol used was 92.0 g/mol.

Figure 4 shows the biodiesel conversion rate of 3%, 6% and 9% catalyst loading for CLW-I and CLW-II. The CLW-I catalyst performs best at 9% loading with a biodiesel conversion rate of 75.30%. A gradual increase in biodiesel conversion rate is observed as catalyst loading increases, with no conversion obtained at 3% loading. The result indicates that 3% CLW-I might be insufficient to catalyze the reaction compared with other loadings. The best biodiesel conversion rate for CLW-II was 68.02% at 3% catalyst loading. The biodiesel conversion rate is observed to gradually reduce with the increase in catalyst loading. This is because the increase in catalyst loading beyond the optimum amount could result in the decrease of biodiesel conversion rate. This is due to the high catalyst concentration that inhibits proper diffusion between the reactants, which are oil, methanol and solid catalyst [14].

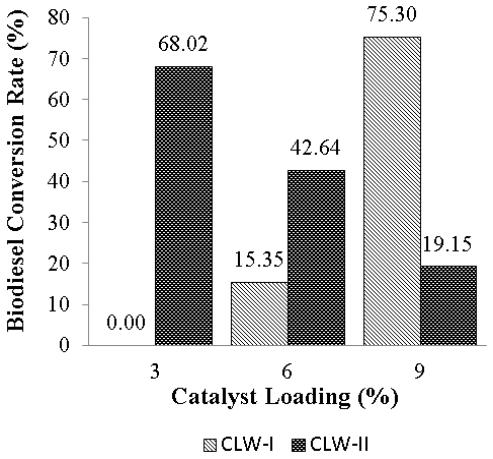


Fig. 4: Biodiesel conversion rate of CLW-I and CLW-II for 3%, 6% and 9% catalyst loading.

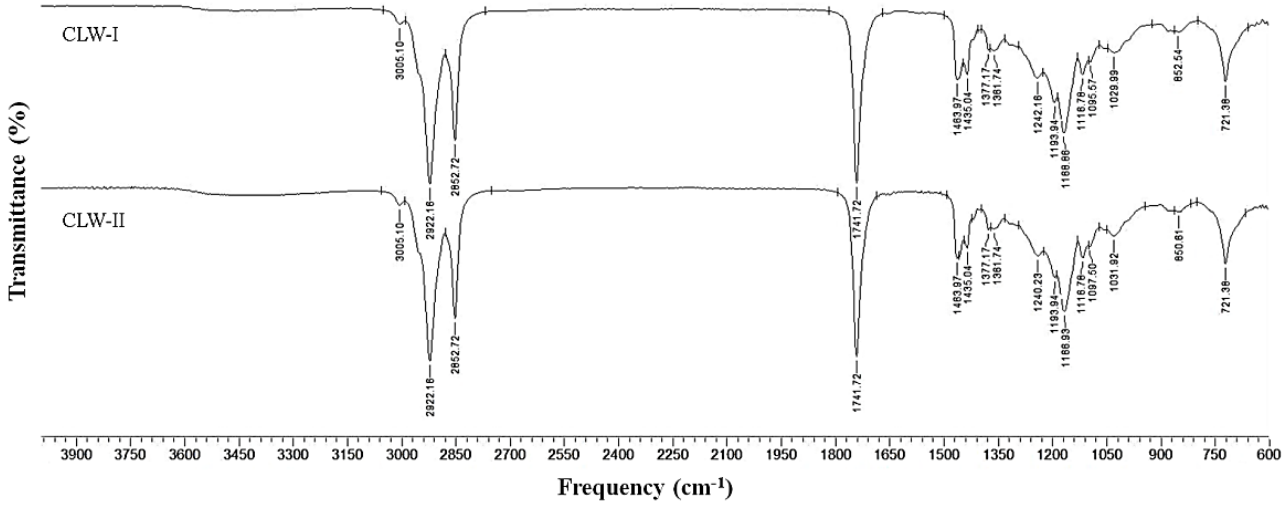


Fig. 5: FTIR spectra of biodiesel catalysed by 9% wt. CLW-I loading and 3% wt. CLW-II loading.

Table 3: FTIR peak frequencies of catalyst with corresponding bond.

	Catalyst	**Frequency (cm^{-1})**						
	CLW-I	1741.72	1242.16	1193.94	1168.86	1116.78	1095.57	1029.99
	CLW-II	1741.72	1240.23	1193.94	1166.93	1116.78	1097.50	1031.92
Ester Bond		C=O stretch	C-C(O)-C stretch			C-O stretch		

3.5.1. Determination of Ester Group

Biodiesel sample from the best catalyst loading for CLW-I and CLW-II were studied by FTIR analysis. The presence of ester group was identified. Figure 5 shows the FTIR spectra of biodiesel catalysed by 9% loading CLW-I and 3% loading CLW-II. The frequencies 1741.72 cm^{-1} are attributable to the C=O stretching ester bond, as tabulated in Table 3. Meanwhile, the frequencies 1242.16 - 1240.23, 1193.94 and 1168.86 - 1166.93 cm^{-1} are assigned to the C-C (O)-C stretching ester bond. Frequencies 1116.78, 1095.57 and 1029.99 cm^{-1} of CLW-I and 1116.78, 1097.50 and 1031.92 cm^{-1} of CLW-II indicate C-O stretch ester bond. The presence of ester group proved that palm oil has been successfully converted to methyl ester with the assistance of carbide lime waste derived solid base catalyst.

4. Conclusion

In a nutshell, new carbide lime waste derived solid base catalysts were successfully prepared using different preparation methods. The characterization and catalytic activity of CLW-I and CLW-II in biodiesel production was reported. As a result, 75.30% bio-

diesel conversion rate could be achieved with the presence of CLW-I catalyst in transesterification reaction. The structural analysis shows to be responsible for better catalytic activity. This work proves to be a new potential for Malaysia's scheduled waste – Carbide lime waste. The results show the new potential in effective utilization of waste resource. The carbide lime waste derived solid base catalysts can benefit the biodiesel industry while contributing towards a waste free world simultaneously.

Acknowledgement

The authors gratefully acknowledge the financial support given by Universiti Tenaga Nasional for the 2017 BOLD Research Grant (10289176/B/9/2017/21). Besides, the authors would like to acknowledge the support and lime sources provided by Mineral Research Centre, Rock Based Technology Section, Department of Mineral and Geoscience Malaysia. Lastly, the authors would like to acknowledge the support and facilities provided by the Institute of Sustainable Energy (ISE), UNITEN.

References

[1] Guo S, Liu Q, Sun J & Jin H (2018), A review on the utilization of hybrid renewable energy. Renewable and Sustainable Energy Reviews 91, 1121-1147.
[2] Gashaw A, Getachew T & Teshita A (2015), A review on biodiesel production as alternative fuel. Journal of Forest Products & Industries 4, 80-81.
[3] Mohd Noor C W, Noor M M & Mamat R (2018), Biodiesel as alternative fuel for marine diesel engine applications: A review. Renewable and Sustainable Energy Reviews 94, 127-142.
[4] Milano J, Ong H C, Masjuki H H, Chong W T, Lam M K, Loh P K & Vellayan V (2016), Microalgae biofuels as an alternative to fossil fuel for power ganaration. Renewable and Sustainable Energy Reviews 58, 180-197.
[5] Li FJ, Li HQ, Wang LG & Cao Y (2015), Waste carbide slag as a solid base catalyst for effective synthesis of biodiesel via transesterification of soybean oil with methanol. Fuel Processing Technology 131, 421-429.
[6] Abdullah S H Y S, Hanapi N H M, Azid A, Umar R, Juahir H, Khatoon H & Endut A (2017), A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. Renewable and Sustainable Energy Reviews 70, 1040-1051.
[7] Sharma S, Saxena V, Baranwal A, Chandra P & Pandey L M (2018), Engineered nanoporous materials mediated heterogeneous catalysts and their implications in biodiesel production. Material Science for Energy Technologies 1, 11-21.
[8] Othman A, Sulaiman A & Sulaiman S K (2017), Carbide lime in acid mine drainage treatment. Journal of Water Processing Engineering 15, 31-36.
[9] Othman R, Isa N & Othman A (2015), Precipitated calcium carbonate from industrial waste for paper making. Sains Malaysiana 44, 1561-1565.
[10] Huaping Z, Zongbin W, Yuanxiong C, Ping Z, Shijie D, Xiaohua Liu & Zongqiang M (2006), Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. Chinese Journal of Catalysis 27, 391-396.
[11] Niju S, Begum K M M S & Anantharaman N (2016), Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve calm shell. Arabian Journal of Chemistry 9, 633-639.
[12] Wu H, Geng J, Ge H, Guo Z, Wang Y, Zheng G (2016), Egg-Derived mesoporous carbon microspheres as bifunctional oxygen evolution and oxygen reduction electrocatalyst. Advanced Energy Material 6, 1600794.
[13] Zhang C, Hu X, Zhang Z, Zhang L, Dong D, Gao G, Westerhof R & Syed-Hassan SSA (2018), Steam reforming of acetic acid over Ni/Al2O3catalyst: Correlation of calcination temperature with the interaction of nickel and alumina. Fuel 227, 307-324.
[14] Mansir N, Teo S H, Rabiu I & Taufiq-Tap Y H (2018), Effective biodiesel synthesis from waste cooking oil and biomass residue solid green catalyst. Chemical Engineering Journal 347, 137-144.