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CONVERSION OF OIL RECOVERED FROM PALM OIL MILL EFFLUENT (POME) INTO BIODIESEL USING ELECTROLYSED CARBON CATALYST

Winnie Sinan Balan

Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Kota Kinabalu, Malaysia
winniesbalan@gmail.com

Jidon Janaun

Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Kota Kinabalu, Malaysia
jidon@ums.edu.my

Nancy J. Siambun

Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Kota Kinabalu, Malaysia

Abstract

Malaysia produces approximately 60 million tons of palm oil mill effluent (POME) annually. Raw POME contains 0.6-0.7% oil and it has high free fatty acids (FFAs). The residual oil in POME however, is a potential feedstock in biodiesel production. Oil in the POME was recovered and converted into biodiesel through catalysis esterification reaction. A new carbon based catalyst had been developed in this study. Carbon deposited from electrolysis process was used as carbon precursor to synthesis electrolysis carbon catalyst (CEC). The carbon was sulfonated using concentrated sulfuric acid at temperature 150 °C for 12 h followed by washing and drying

of the sulfonated carbon (CEC). CEC was characterized for its physiochemical properties using Elemental analyzer, FT-IR, SEM-EDX, TGA-DTA and back titration methods. Elemental analysis results showed that S content in CEC was ~4 times higher than the electrolysis carbon. The FT-IR detected the presence of weak sulfonic acid groups. The total acidity of CEC was 0.75 mmol g⁻¹ suggesting poor acid functionalization of the electrolysis carbon. This could be associated with the stability of the carbon and also the presence of other elements that weaken the sulfonation reaction. The structure of CEC was observed through the SEM images. CEC possessed a randomly ordered structure and discrete microporous pores. Catalytic activity of CEC was tested on esterification of oil recovered from POME with methanol. The yield was very low, which was 6.19%, this was attributable to the low active sites of the CEC. Further improvement on the electrolyze carbon need to be done in order to increase the total acidity.

Keywords

Palm Oil Mill Effluent, Carbon Electrolysis, Catalyst, Esterification, Biodiesel

1. Introduction

Malaysia produces approximately 60 million tons of palm oil mill effluent (POME) annually (Kamarudin et al., 2015; Ng, Yew, Basiron, & Sundram, 2011). Raw POME contains 95-96% of water, 0.6-0.7% oil and 4-5% total solids including 2-4% of suspended solids (Lam, Lee, & Mohamed, 2010). Besides, free fatty acids (FFAs) content in POME is relatively high. The residual oil in POME however, is a potential feedstock in biodiesel production. Biodiesel comprises mainly of fatty acid methyl esters (FAME) (J. Janaun, Sinin, Hiew, Kong, & Lahin, 2016). The most favoured reaction pathways are esterification and trans-esterification (Jidon Janaun & Ellis, 2010). The process to produce biodiesel is relatively simple by using alkaline homogeneous trans-esterification. However, it is not suitable for a high FFAs and water content feedstock like POME. This is because the reaction will undergoes saponification instead of producing biodiesel (Juan, Kartika, Wu, & Hin, 2011). Solid acid catalyst is the most ideal catalyst for a low-quality feedstock. Solid acid catalyst is able to lower the FFAs content in the feedstock and simultaneously convert it into biodiesel. It is an in-situ esterification and transesterification reaction (Jidon Janaun & Ellis, 2010; Mo, Lotero, Lu, Liu, & Goodwin, 2008).

Sulfonated carbon based catalyst is one of the most effective and “greener” acid catalysts in biodiesel production (Jidon Janaun & Ellis, 2010; Lam et al., 2010). This is due to its ability to

comprise high density of functional group such as sulfonic group (SO_3H) (Lam et al., 2010). Toda et. al., has discovered the development process of sugar catalyst which known as carbon catalyst (Mo et al., 2008). The catalyst is synthesized by sulfonating incompletely carbonized natural organic material. Sulfonation of this material was expected to generate a stable solid with a high density of active sites, enabling a high-performance catalyst.

Most of the sulfonated carbon based catalysts were derived from carbon precursors such as D-glucose and biomass (Takagaki et al., 2006). Some examples of biomass used were rice husk, kraft lignin and corn straw (J. Li et al., 2016; Liu, Li, Li, Shi, & Wang, 2013). However, carbon based catalyst derived from deposited carbon from electrolysis process has not been reported yet in any literature review. Mostly, carbons were produced from incomplete carbonization method. For this study, carbon from electrolysis process will be used to produce catalyst for producing biodiesel from oil recovered from palm oil mill effluent and the catalytic activity of the catalyst will be compared with other solid acid catalyst. This study shows that catalyst derived from electrolysed carbon has the potential to esterified oil. However, further improvement has to be done to get higher yield. Besides, the relation between total acidity and yield also had been discovered.

2. Experimental

2.1 Catalyst Preparation

Carbon precursor was obtained by electrolysis process done by a research group in UMS. The electrolysis process was conducted at temperature $510\text{ }^\circ\text{C}$. The electrolyte used was a mixture of 0.1 mol of calcium carbonate CaCO_3 with eutectic mixture of Lithium Chloride (LiCl) and Lithium Carbonate (Li_2CO_3). The electrode was then immersed in HCL to remove hard grey carbon deposit and carbonate from the powder. The carbon deposited was then collected and dried at temperature $104\text{ }^\circ\text{C}$.

The carbon precursor was then sulfonated using concentrated sulfuric acid (95 %). Two grams of electrolysed carbon was put into 500 mL three-necked round bottom flask containing 74 mL of sulfuric acid. Nitrogen gas was purged in with the flow rate of 50 ml/min and the carbon was heated at temperature $150\text{ }^\circ\text{C}$ for 12 h. After sulfonation, the functionalized carbon was washed with warm distilled water ($80\text{ }^\circ\text{C}$) and filtered until no sulfate ions detected in the

filtration water and the pH close to neutral. Precipitation of barium sulfate test was done to ensure there is no sulfate ion in the sample. Then, the catalyst was dried overnight at 104 °C.

2.2 Characterization of Electrolysis Carbon Catalyst (CEC)

Total acidity of CEC was measured by using back-titration method. 8 mM of NaOH and 20 mM of HCl were prepared. 0.1 g of the catalyst was mixed with 60 ml of 8 mM NaOH in a 250 mL conical flask and stirred for 30 min at room temperature. Then, the mixture was titrated with 20 mM of HCl. The change in the acidity was measured by pH meter (Mettler Toledo, UK). When the pH reached 7.00 it indicated the end point of the titration. The morphology of CEC was studied by using a scanning electron microscope (Quorum Q150RS SEM Spectroscopy) equipped with Energy-dispersive X-ray microanalysis. CHNS content of CEC were determined using an elemental analyzer. The thermal stability was examined by thermo-gravimetric analysis (TGA), Perkin Elmer model TGA6 under nitrogen flow. IR spectra of functional groups in CEC was observed using FTIR-Spectrometer (Spectrum 100 FT-IR Spectrometer, Perkin Elmer).

2.3 Catalytic Activity of Electrolysis Carbon Catalyst (CEC)

2.3.1 Pre-treatment of POME

POME sample was obtained from Langkon Mill, Kota Marudu, Sabah. The collected POME was preheated to remove moisture and any volatile matter. Pre-heating was performed on a hot plate at temperature 40 °C and gently stirred using a magnetic stirrer for 2 h.

2.3.2 Catalytic Esterification Method

Esterification experiments were performed in batch system using STEM Reacto at temperature 80 °C and stirring speed of 1000 rpm. The molar ratio of oil to methanol (MeOH) used was 1:10 (methanol: 250mmol; oil 25mmol). The amount of catalyst added for the reaction was 0.5 wt.% with respect to oil and the reaction was conducted for 14 h. 60 µL of product samples were withdrawn at specified time intervals and further diluted prior to gas-chromatography analysis.

2.3.2 Product Analysis

The samples were analyzed using gas chromatography equipped with flame ionization detector (GC-FID). Standard FAME sample was used to construct a calibration curve. The calibration curve was used to calculate the peak area of each component in FAME standard by integration by using external standard method. The samples were diluted in an analytical standard hexane solvent (99 %) and filtered using 0.45 µm Whatman filter before injected into GC-FID. Table below shows the GC-FID parameters used to analyze the samples.

Table 1: Gas-chromatography with flame ionization detector parameters

Inlet temperature:	250°C
Column	30 m x 320 µm x 0.25 µm
Column Flow	1mL/min
Split Flow	50 mL/min
Injection Volume	0.5µL
Oven Program Initial Temperature	210°C
Hold Time 1:	13.00 min
Ramp 1:	5°C/min
Oven Program Final Temperature	230°C
Hold Time 2:	15.00 min
Carrier Gas:	Helium
FID Temperature:	250°C
H₂ flow	45mL/min
Air flow	450mL/min

3. Results and Discussion

3.1 Characterization of the catalyst

3.1.1 Total acidity and Elemental Study of CEC

The CHNS content of carbon before and after sulfonation is presented in Table 2. From Table 2, it shows that electrolysis carbon (before sulfonation) consisted of 42.68 wt.% C, 1.63 wt.% H, 0.02 wt.% N, 0.21 wt.% S and 55.46 wt.% O. Sulfonation was done to introduce sulfonic groups (-SO₃H) onto the carbon. Table 1 shows an increase of sulfur from 0.21 wt.% to 0.78 wt.% in carbon after sulfonation. The sulfur content in CEC is 4 times higher than the sulfur content in the original carbon sample. Assuming all sulfurs in the CEC are in the form of SO₃H, (Mo et al., 2008; Peng et al., 2010) the estimated density of SO₃H is 0.25 mmol g⁻¹. Total acidity of CEC is presented in Table 3. Average acidity of CEC measured by back titration method is 0.75 mmol g⁻¹. Total acidity shows higher density since NaOH neutralized other groups as well besides -SO₃H group, which included carboxylic group (-COOH), lactonic group (-COO-) and also phenolic group (-OH).

Table 2: Elemental Composition (CHNOS) of Electrolysis Carbon and CEC

Sample	Element (wt %)					SO ₃ H (mmol g ⁻¹)
	N	C	H	S	O	
Electrolysis	0.02	42.68	1.63	0.21	55.47	0.07

Carbon						
CEC	0.04	79.52	1.16	0.78	18.50	0.25

Table 3: Total acidity of CEC using back-titration method

Replication	Total acidity (mmol g⁻¹)	Average (mmol g⁻¹)	Standard Deviation	Error Propagation (mmol g⁻¹)
1	0.83	0.75	0.076	±0.37
2	0.68			
3	0.75			

3.1.2 FT-IR analysis

FTIR spectroscopy was used to determine the functional groups on CEC. The FTIR spectrum of CEC is shown in figure 1. Weak bands of peaks at 759 cm⁻¹ to 971 cm⁻¹ are attributed to the stretching of aromatic C-H (Mo et al., 2008). Peak at wavelength 1235 cm⁻¹ represents C-O stretching (C. Li et al., 2010) meanwhile, peak at 1397 cm⁻¹ attributed to asymmetric SO₃ stretching in SO₃H (Peng et al., 2010). The peaks at 1040 cm⁻¹ and 1080 cm⁻¹ S=O symmetric stretching and S=O asymmetric stretching, respectively (Peng et al., 2010). However, very weak peaks at these particular wavelengths were observed in the IR spectra. According to Shu et. al., band at 1743 cm⁻¹ also attributed to the stretching of sulfate group (Shu et al., 2009). A peak at 1743 cm⁻¹ can be observed from the IR spectra obtained.

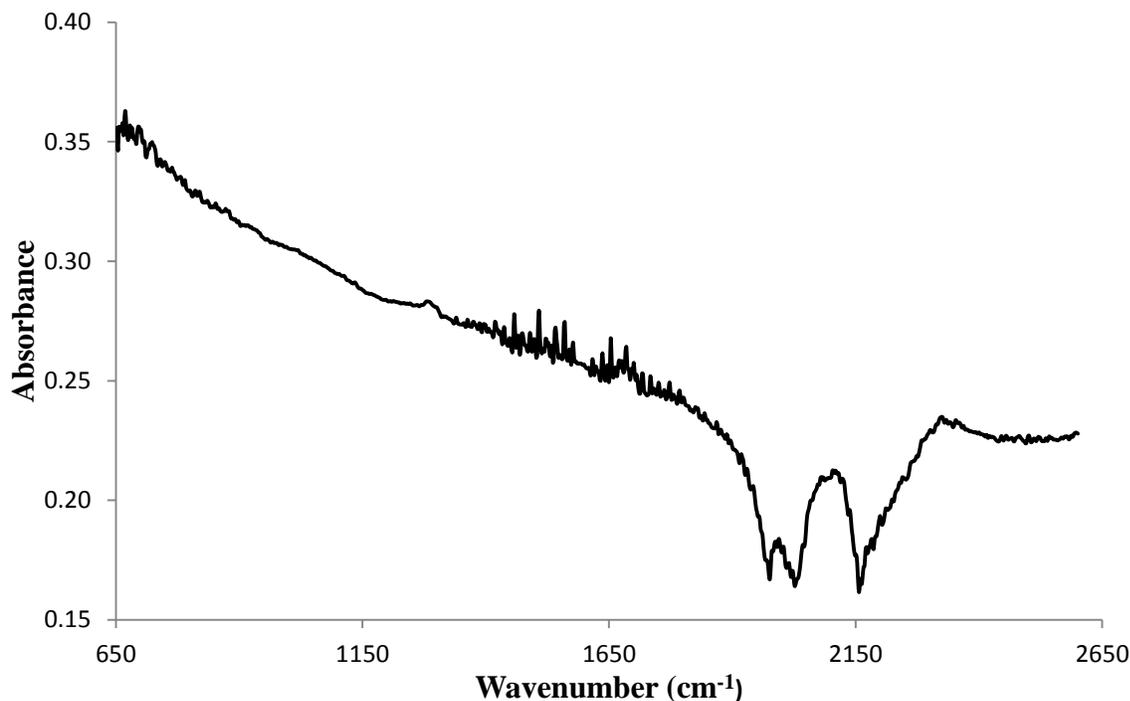


Figure 1: FT-IR Spectra of CEC

3.1.3 Morphology of CEC

From figure 2 (b) obtained from SEM image, it shows that the electrolysis carbon aggregates particle size ranging from approximately 50 μm – 60 μm . Originally, the electrolysis carbon possessed an in-ordered structure. Figure 2 (a) shows that the carbon has randomly ordered and discrete pores with diameters range $\sim 2 \mu\text{m}$ to $\sim 5 \mu\text{m}$. After subjected to sulfonation process, the structures of the carbon were remained almost similar. However, it also formed flakes-liked structure which presumably due to the harsh acid treatment (Janaun et al., 2016; Ma & Hanna, 1999). It can be observed through SEM images that CEC has a randomly ordered structure and microporous.

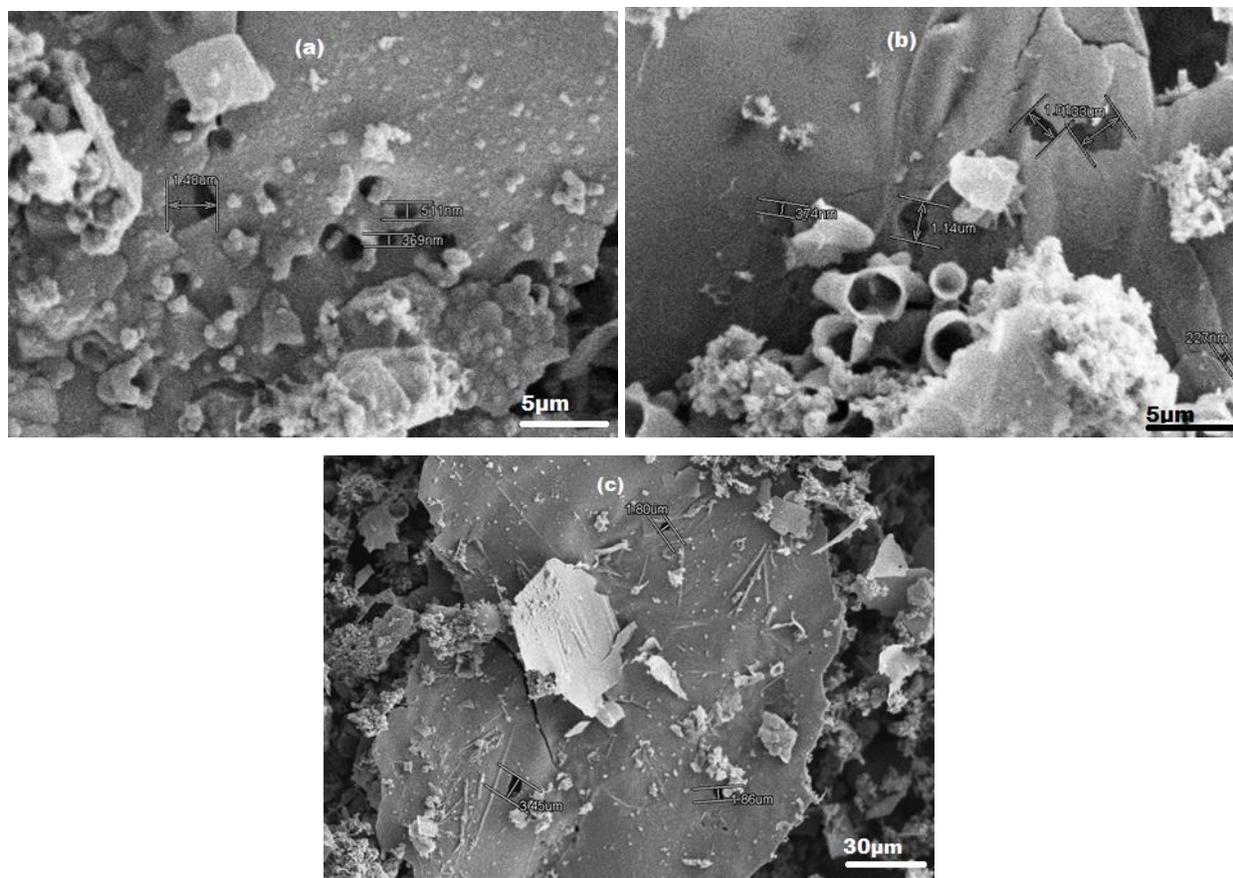


Figure 2: (a) SEM image of electrolysis carbon before sulfonation and (b)(c) SEM images of carbon after Sulfonation (CEC)

3.1.4 Thermal Stability of CEC

Stability of CEC was measured by decomposition of molecules at high temperature using TGA-DTA under nitrogen flow. Heating under nitrogen gas provides the decomposition of molecules in the sample due to thermal (Janaun, 2012). From figure 3, it shows that the catalyst started to lose its weight at 50 °C. The weight of the catalyst continues to decrease gradually until it reaches 410 °C. The weight loss before 100 °C is associated with the loss of moisture in the sample. According to Janaun, the weight loss at ~90 °C is attributed to the loss of moisture. Thus, at temperature 100 °C to 410 °C, slower rate of weight loss is observed and then the weight of the sample decreases significantly. This shows that CEC is thermally stable up to 410 °C. As compared to typical solid acid catalyst such as ion-exchange resin, CEC has a better thermal stability. Ion-exchange resin has relatively low thermal stability which only up to ~140 °C (Lotero et al., 2005).

3.2 Catalytic Activity of CEC

The reactivity of the CEC was tested by its ability to convert fatty acids into FAME. Figure 4 presents the kinetic curves of esterification reaction with methanol using various catalysts. The reaction was done using the optimum reaction condition (Janaun, 2012) reported by Janaun. From the kinetic curve of CEC, it shows that the reactivity of CEC in esterification of oil recovered from POME with methanol is relatively low. The yield is 6.19 % after 14 h of reaction time. Esterification reaction using sulfuric acid under same condition, catalyst loading and feedstock was conducted. The yield of FAME obtained using sulfuric acid after 4 h of reaction time is 44.12 %. Higher yield was obtained using sulfuric acid may due to the higher acid strength and density (Liu et al., 2013; Peng et al., 2010) in sulfuric acid as compared to CEC. To validate the relation between yield obtain and acid density, esterification of oil recovered from POME with methanol was done using sulfonated rubber tree leaves (SRTL) (Janaun et al., 2016) as catalyst. Kinetic curve of SRTL shows the yield of FAME using SRTL is 36.61% at reaction time of 14 h. The conversion of oil into FAME using SRTL is approximately 6 times of CEC. Table 4 shows that SRTL has denser acidity (mmol g^{-1}) and higher yield as compared to CEC. The acid densities were compared to a typical solid acid catalyst used widely in industry (Janaun & Ellis, 2010; C. Li et al., 2010). Tungstated Zirconia has less acid density than SRTL and CEC, resulting low yield of FAME. Thus, the low yield obtained by CEC may due to its low acid density and the weak peaks of sulfate groups in IR spectra (Figure 1) indicated the mild presence of sulfonic groups on the catalyst. However, figure 4 also shows that oil from POME can be converted into biodiesel and it is one of the potential feedstocks for biodiesel production.

To obtain higher yield of FAME, further pre-treatment of POME need to be done. From figure 4, yield of methyl oleate from esterification of oleic acid and methanol using sulfuric acid is 95.84%. This may be assigned to the purity of the feedstock. However, oil from POME contains impurities. Removal of moisture alone might not be sufficient. Watfi et. al., pre-treated POME by degumming process in order to get higher biodiesel yield (Watfi, Lau Lik Nang, & Choo, 2012). Besides, certain modification in preparation of catalyst is needed to be done such as increasing the surface area of the carbon by increasing its porosity. Higher surface area will allow more sulfonic groups to attach on the carbon structure. However, the pores have to be large enough for the long hydrocarbons to access into the bulk acid sites (Lotero et al., 2005). Incomplete carbonization of carbon assisted by microwave was proven to increase the surface

area of the carbon without causing the wall of carbon structure to collapse (J. Li et al., 2016; Touhami et al., 2017).

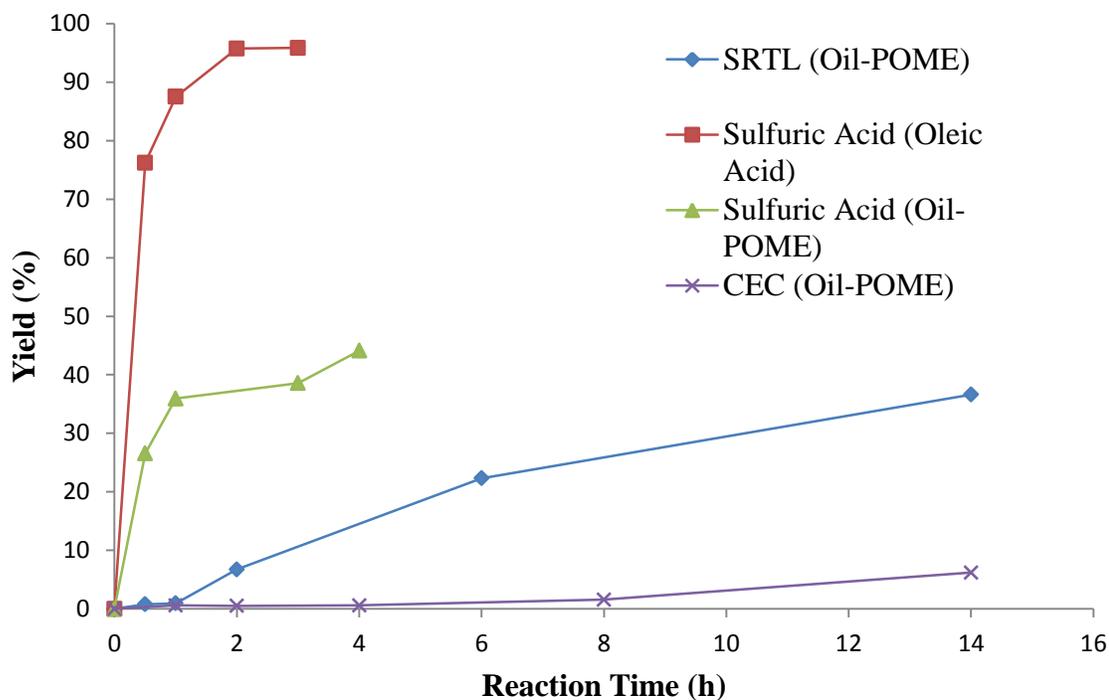


Figure 3: Comparison of catalytic activity of different catalysts

Table 4: Properties of sulfonated carbon catalyst

Sample	Acid site density (mmol g ⁻¹)	Yield (%)
Sulfuric Acid	-	44.12 ^a
SRTL	3.80 ± 0.05 *	36.61 ^a
CEC	0.75 ± 0.37	6.19 ^a
Tungstated Zirconia	0.05 (Mo et al., 2008)	4.8 ^b

^a Esterification of oil recovered from POME with methanol (MeOH) at temperature of 80 °C, molar ratio of MeOH to oil = 10 and 0.5% catalyst loading.

^b Esterification of palmitic acid with MeOH at 60 °C for 1 h with ratio of MeOH to Oil = 6 and 2 wt% of catalyst loading.

4. Conclusion

A new type of carbon precursor has been discovered through this work. The catalyst from the electrolysis carbon, also known as CEC, had the acidity of 0.75 mmol g⁻¹ and thermally stable up to 410 °C. From the FT-IR spectra, weak peaks of sulfonic groups can be observed. The yield of FAME obtained from esterification of oil recovered from POME with methanol using CEC was very low, 6.19%. This was due to the low total acidity. Nevertheless, the oil recovered from POME could be used as feedstock for biodiesel production. Further works are required to synthesize catalysts with high reactivity on the conversion of oil recovered from POME, such as optimization of carbon preparation and esterification process, and also pre-treatment of oil recovered.

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