Evaluation of Methyl Ester Production Using Cement as a Heterogeneous Catalyst

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(Received 22 December 2017, Accepted 4 March 2018)

This experiment is an investigation of used cooking oil as a sustainable and renewable resource for methyl ester production. With more than 95.5% production yield, thermally activated hydrated cement has been carefully discussed as a catalyst in the transesterification of used cooking oil into methyl ester to use waste cement as a heterogeneous catalyst for methyl ester production through electrolysis method. Acetone as a co-solvent was added to the reaction system for mass transfer-intensification. Theoretically, electrolysis can convert any biodegradable waste into biodiesel, as well as other by-products such as glycerol. In transesterification through electrolysis, OH^- ions are produced in the cathode and turn into nucleophile (CH_3O^-) which lead to the production of biodiesel through attacking carbon UCO. The maximum free fatty methyl ester yield was obtained under the optimized conditions of 7:1 methanol/oil molar ratio, 10 wt% amount of co-solvent, in the range of 300 rpm, calcination temperature 750 °C, 30 V, amount of catalyst 12 wt% within 2 h. Methyl ester production was done at room temperature in the absence of saponification. The physical and fuel properties contents of the synthetized biodiesel were characterized applying EN standard method.

Keywords: Cement, Heterogeneous catalyst, Electrolysis method, Methyl ester, Used cooking oil

INTRODUCTION

Biotechnological transformation of oils and fats such as renewable fuels have been greatly considered as a result of decline of fossil fuels and the harmful environmental effects of green-house gases [1-3]. Drastic climate changes in recent decades have aroused a notable attention in safer and less polluting renewable energy sources to replace a part of fossil energy [4,5]. Nowadays, the use of low carbon energy sources and the introduction of environmentally-friendly green technology appear to be a viable option [6]. One of the commonly-used types of these alternative energy sources is methyl ester, which typically has significant advantages over the conventional fossil fuels [7]. As many scholars have mentioned, biodiesel is typically renewable, non-toxic, low-emitting, biodegradable, and environmentally-benign, *etc.* [8].

Biodiesel can be obtained through several methods including ultrasound, reflux, microwave and electrochemistry [9-11]. Among these methods, electrochemical methods have proven practical and convenient in environmental and process applications [12, 13]. In the electrolysis technique decomposition of chemical species is carried out by means of electrical power. In this process, to obtain alkyl esters of fatty acids and glycerol, the prepared biodiesel is reacted with methanol in presence of base catalyst (KOH, NaOH *etc.*). Guan and Kusakabe (2009) reported the first use of a simple electrolysis method to produce biodiesel from corn oil and used cooking oil at room temperature [14]. In electrolysis method, the water molecules are continuously electrolyzed by electricity current (Eqs. (1), (2)) [11].

Cathodic reaction:

$$2H_2O + 4e^- \rightarrow H_2 + 2OH^- \tag{1}$$

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Anodic reaction:

$$2H_2O \rightarrow O_2 + 4H + 4e^- \tag{2}$$

Proton transfer reaction:

$$CH_3OH + OH^- \rightarrow CH_3O^- + H_2O \tag{3}$$

Methoxide ion can be produced when methanol reacts with hydroxyl ion (OH$^-$) in Eq. (3) [14]. The metoxide ion is strongly nucleophile and attacks the carbonyl moiety in glyceride molecules to produce methyl ester and glycerol [12]. As a result, electrolysis method can produce biodiesel fuel. Electrolysis method is of great advantages including lower energy consumption due to the reaction at room temperature, saving the reaction time using the co-solvent, removing the purification stage of the waste oil and dewatering, and decreasing water consumption in water-washing of biodiesel and production of less wastewater [13, 14]. Economic advantages of biodiesel production are very important since feedstock cost contributes directly to the biodiesel production cost [15]. Thus, using nonedible and waste biomass feedstock for producing biodiesel can be beneficial to reduce the high production cost [16]. Used cooking oil or frying oils are currently being used as inexpensive feedstock for biodiesel production [17]. Phan *et al*. [18] reported that biodiesel yield of 88-90% can be obtained from used cooking oil using potassium hydroxide as catalyst through the transesterification reaction. The utilization of heterogeneous catalysts is another important benefit of the commercial production of biodiesel [19]. The use of heterogeneous insoluble solid catalyst has greatly obviated the problems of homogeneous catalysis including soap formation, catalyst separation [20], recycling and regeneration [21]. Thus, extensive product purification steps have been eliminated to offer a more economical method for biodiesel production [22]. When a solid catalysis is used in transesterification, controlling steps include adsorption of reactants, desorption of products or mass transfer [23]. The recycling of different industrial solid wastes can be considered the recent general trend to decrease environmental pollution. Waste cement with high yearly production rate and active metal oxides can be a source of

solid catalysts for methyl ester production. Al-Sakkari *et al.* studied the kinetics of soybean methanolysis using cement kiln dust as a heterogeneous catalyst [24]. Cement has been used as a construction material, adsorbent and fertilizer in many studies [25,26].

The purpose of this study is to investigate used cooking oil methanolysis to generate methyl ester through electrolysis system in the presence of cement as a catalyzer in the transesterification process to optimize concentration of catalyst, methanol/oil molar ratio, co-solvent amount, voltage, reaction time and agitation rate and reaction temperature. In all experiments the oil type and alcohol type were fixed as common parameters to consider economic issues for minimizing the process cost by decreasing the use of methanol and increasing the utilization of waste catalyst. In this research, the optimized values of the parameters and the production yield for each experiment were used to obtain higher efficiency in methyl ester production from used cooking oil.

EXPERIMENTAL

Materials and Apparatuses

Acetone and methanol (99%), sodium sulfate (99%) and potassium hydroxide (99%) were the products of Merck Company (Germany). The waste cooking oil used in this work was collected from a restaurant in Tehran city. Waste cement was obtained from debris collapsed building in Tehran. The equipment in this study are BATE PC21 furnace (Iran), heater magnetic stirrers Heidolph (Germany), DC Power Supply model 2500SV (China), XRD model STADI P, EDX Bruker & Flash 6110 and SEM Cam Scan, EDX Bruker & Flash 6110 (Germany).

Properties of the Used Oil

The acid numbers of the initial used cooking oil and acid numbers after using in the free fatty acids esterification were determined following the ASTM D 664 international standard method. In this method a test sample is dissolved in a mixture of diethyl ether and ethanol and a further titration with a KOH solution. A pH-meter equipped with glass and calomel electrodes was used to determine the end-point. Equation (4) was used to determine the acid value A:

$$A = \frac{56.1 \times V \times c}{m} \tag{4}$$

where:

V is volume of standard potassium hydroxide solution, c stands for concentration, in moles per liter, of the standard volumetric potassium hydroxide solution used, and m is mass, in grams of the test portion 56.1 = molecular mass of potassium hydroxide. The conversion of FFAs was defined as the fraction of FFAs that reacted during the esterification reaction with alcohol. Equation (5) was used to determine the conversion of FFAs% from the acid number ratio using:

$$Conversion\ of\ FFA\% = \frac{A_i - A_f}{A_i} \times 100\% \tag{5}$$

A_i stands for the initial acid number of the used cooking oil and A_f is the final acid number of used cooking oil after the FFAs esterification reaction [27].

Soap index was calculated as follows:

$$S = \frac{N \times 56.1 \times (A - B)}{W} \tag{6}$$

In this equation, S is soap index, A stands for HCl 0.5 N for the control titration, B is the amount of HCl 0.5 N in milliliters for the sample titration, W is the weight of the oil in grams and N is normality. Finally, molecular weight of the oil is calculated using [11,12]:

$$Molecular\ weight\ of\ used\ cooking\ oil = \frac{3 \times 56100}{5} \tag{7}$$

Used cooking oil with an initial saponification number of 196.2 mg_{KOH} g^{-1}, acid value of 76 mg_{KOH} g^{-1}, free fatty acid level of 38% was obtained from local restaurant in Tehran with the following composition in fatty acids (w/v): 32.2% palmitic acid, 40.6% oleic acid, 17.6% linoleic acid, and 5.2% stearic acid. The molecular weight of the oil calculated from its saponification value was 856.3 g mol^{-1}. Water content in the oil measured by Karl Fischer titration method was determined to be 0.01% (w/w).

Catalyst Preparation

Cement used to catalyze the reaction of used cooking oil with methanol to produce methyl ester was calcined with K_2CO_3 (1:4 ratio) for 4 h at 740 °C to ensure that no humidity remained in the catalyst and to convert potassium carbonate into potassium oxide which play an important role in transesterification [11,24,25]. The catalysts were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and X-ray diffraction (XRD).

Transesterification Reaction

The conversion of used cooking oil to biodiesel was carried out in a 100 ml electrolysis cell equipped with a DC power, 2 electrodes (2 cm × 2 cm × 0.1 cm) and a magnetic stirrer (Fig. 1). Stirring at 300 rpm, the transesterification reaction of used cooking oil and methanol was performed in liquid phase under atmospheric pressure at room temperature for 2 h. As soon as the mixture of methanol and the catalyst was added into the reactor, the timing of the reaction was initiated. The effects of molar ratio of oil/methanol (3:1-9:1), voltage (20-50), catalyst/oil weight ratio (11-14 wt%) and different amount of co-solvent (5, 7.5, 10, 12.5 and 15 wt%) in presence of 2 wt% water on the conversion of triglycerides to methyl ester were investigated. The mixture was filtered in order to remove any suspended solids and then carefully transferred to a separating funnel which lasted overnight. The lower layer including glycerol and methanol and the upper layer containing methyl esters and some methanol were separated in two separate beakers and methanol evaporated at 80 °C. Due to density differences of ester and glycerol layers, overnight gravity separation was essential to separate them which is facilitated by solubility of glycerol in ester methanol layer. The purity and the content of the composition of methyl ester were characterized using GC-MS. The column employed was hp5 column type of 30 meter length and 0.5 mm internal diameter. The production yield was calculated through the Eq. (8) [28].

$$Production\ yield\ (\%) = \frac{Weight\ of\ biodiesel}{Weight\ of\ UCO} \times 100\% \tag{8}$$

Fig. 1. A schematic of the process to produce biodiesel through electrolysis method.
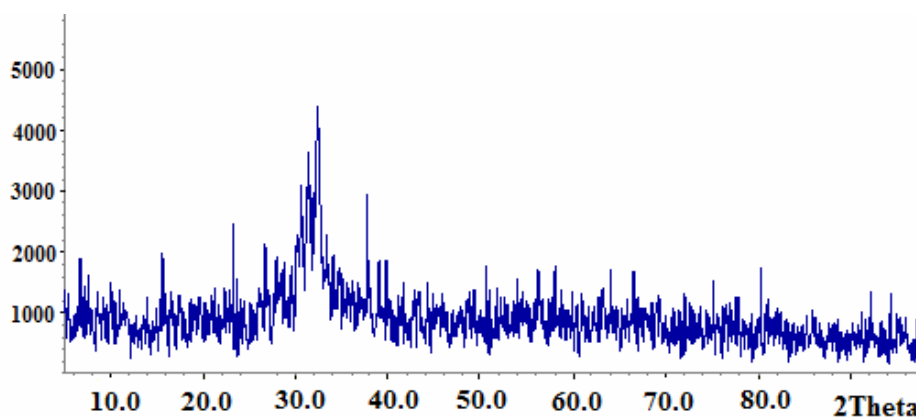

Fig. 2. XRD of catalyst.

RESULTS AND DISCUSSION

Catalyst Characterization

The cement as a rather less-porous material is generally composed of O, Ca, Si, Mg, Fe and Al elements. The main structures of cement are limestone ($CaCO_3$), silica sand (SiO_2), iron oxides (Fe_2O_3) and clay (aluminum silicate and magnesium silicate) [29,30]. Figure 2 indicates the XRD patterns of the hydrated cements being calcined for 4 h at 740 °C. The peaks in XRD pattern corresponding to $3CaO.SiO_2$, $2CaO.SiO_2$, $Ca(OH)_2$, CaO and $CaCO_3$ are the main components of cement. Though cement is a complex material and the main peaks of XRD pattern usually overlay one another, the major phase change of $Ca(OH)_2$ in the cement is obvious when the calcination is performed. The catalyst calcined at 740 °C indicates peaks at 18.0°, 34.1°, 47.3° and 50.8° due to the presence of $Ca(OH)_2$. Diffraction peaks which are related to CaO are seen at 32.2°, 37.4° and 53.9° during calcinations at 740 °C. The new phase of K_2O is emerged at Bragg angle (2θ) = 31°; 39°; 51°; 55°; and 62°. CaO and K_2O enjoy an important catalytic role in transesterification reaction (Fig. 2. XRD of catalyst).

Scanning electron microscopy (SEM) image of the waste cement and catalyst are shown in Fig. 3 containing dense particles with different morphologies but different heterogeneous distribution of particle sizes. It is known that
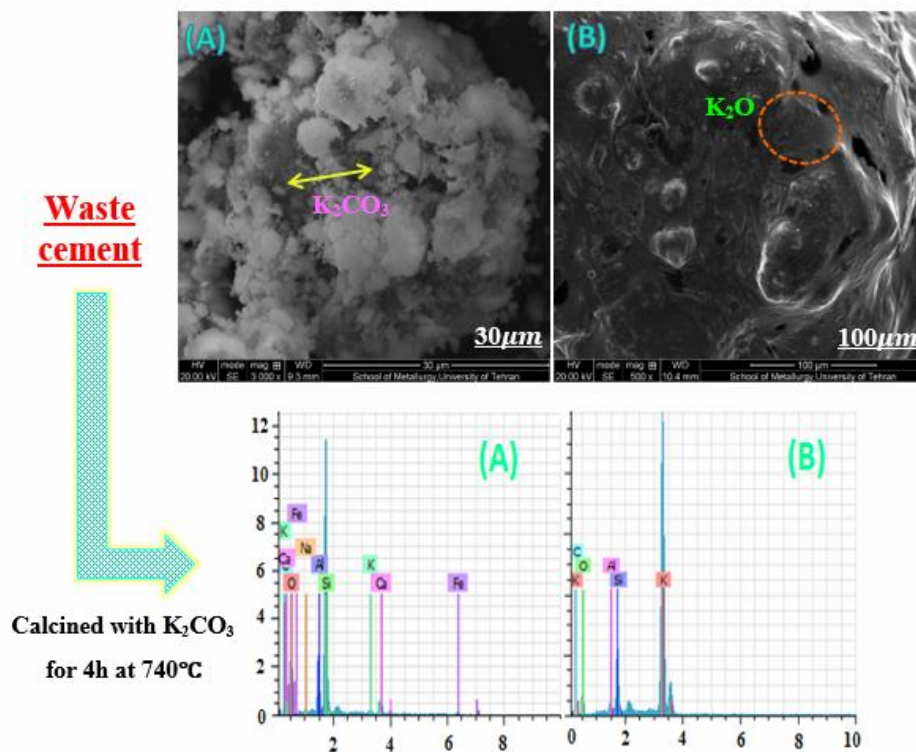
Fig. 3. SEM-EDX of A: Waste cement was calcined with K_2CO_3 for 4 h at 740 °C and B: Catalyst.
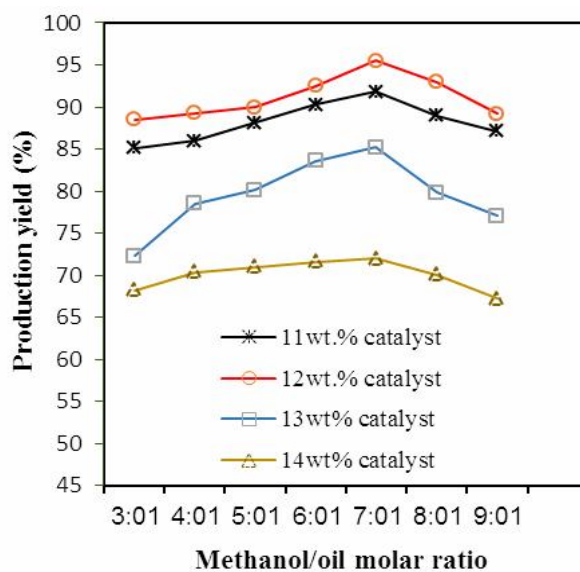

Fig. 4. Effect of methanol/oil molar ratio and concentration of catalyst. Reaction conditions: Voltage 30 v, co-solvent:10 wt% oil, reaction time 2 h and reaction temperature 25 °C.

the bonding strength of catalyst can be weakened by dehydration of heating [31]. It can be observed that dispersion of K_2O on the surface of base catalyst can be caused by the increment of the dispersed particles. This might be caused by heating in the preparation step resulting in the formation of K_2O species by thermal decomposition [20]. Cement and the fine aggregate were used as a catalyst together because it is difficult to separate from each other.

Figure 3 shows the results of EDX spectrometry. Potassium cation in cement was 30.97 wt% showing that potassium molecules were attached or incorporated into catalyst structure during the impregnation process. The basic sites on the surface of the catalyst decompose methanol methoxide ions which generate reactive radical species for trans-esterification reaction. When combined with heating, the cations K^+ are calcined to K_2O which has high catalytic activity [32] for trans-esterification of oil into methyl ester.

Parameters Affecting the Transesterification Reaction

Effect of methanol/oil molar ratio. Electrolysis voltage was investigated to understand its effect on the transesterification of used cooking oil. Excessive methanol increases the conversion of oil into methyl ester since transesterification is an equilibrium reaction. Moreover, excessive methanol can enhance the consumption of energy which is needed for the recovery of methanol [33]. Therefore, this parameter was changed in the range of 3:1-9:1 to study the effect of the amount of methanol/oil ratio. The analysis revealed that the highest yield of 95.5% was achieved with 7:1 methanol/oil molar ratio. Therefore, increasing the methanol/oil molar ratio to 7:1 resulted in the highest methyl ester yield. Largely due to its wide availability and low cost, methanol is the most commonly-used alcohol for the synthesis of methyl ester [34]. Equation (3) depicts that water in the reaction system converts the hydroxide/alkoxide equilibrium toward the formation of hydroxide [28]. Since methanolysis is catalyzed by methoxide ions as a true catalyst, the equilibrium between the hydroxide and methoxide species (CH_3O^-) is of a great importance [33,35] (Fig. 4. Effect of methanol/oil molar ratio and concentration of catalyst. Reaction conditions: Voltage 30 v, co-solvent: 10 wt% oil, reaction time 2 h and

reaction temperature 25 °C).

Concentration effect of catalyst. As shown, the absence of cement as a heterogeneous catalyst hampered the formation of methyl ester indicating that the electrolysis by itself did not promote transesterification process. In order to enhance production yield of the transesterification reaction, the appropriate concentration of catalyst is a necessary element. However, the excess of catalyst (>12 wt%) could lead to increased saponification and reduced production yield [36,37]. Moreover, excessive catalyst (>12wt%) lowers the final methyl ester yield in the separation process as a result of a gelatinous substance that is formed when the soap and glycerol are adsorbed on the cement. In this study, the highest biodiesel yield was 95.5%, obtained with 12 wt% catalyst (Fig. 4). Higher concentration of catalyst also produced higher amounts of K_2O highly increasing methyl ester yield. The heating process caused cement to convert into K_2O during catalyst preparation [38,39]. The formation of K_2O as active sites for transesterification reaction enhanced. The catalytic property shows that waste cement as a catalyst was successfully used in the transesterification reaction.

Effect of co-solvent amount. The reaction rate is considerably affected by the mass transfer between oil and alcohol phases since these 2 phases are immiscible in transesterification process [40]. One of the main benefits of using co-solvent is the intensification of the mass transfer which confines mass transfer-controlled regime [41]. In this study the optimum co-solvent to methanol volume ratio was 10 wt% which resulted in 95.5% methyl ester yield. Further increase in the ratio (>10 wt%) decreased the methyl ester content which could possibly be caused by the dilution of the reactants (Fig. 5. Effect of co-solvent amount on methyl ester yield. Reaction conditions: Voltage 40 v, methanol/oil molar ratio: 7:1, catalyst amount 12 wt% oil, reaction time 2 h and reaction temperature 25 °C).

Effect of voltage. Electric current enhances with the increase of electrolysis voltage to form hydroxyl ions at the cathode [14]. Hydroxide ions are unceasingly formed at the cathode and react with methanol in electrolysis process. Trans-esterification of oil occurs in methanol phase. Also, methyl ester yield increases with the enhancement of electrolysis voltage. However, the region near the cathode, where water molecules were electrolyzed constantly was the
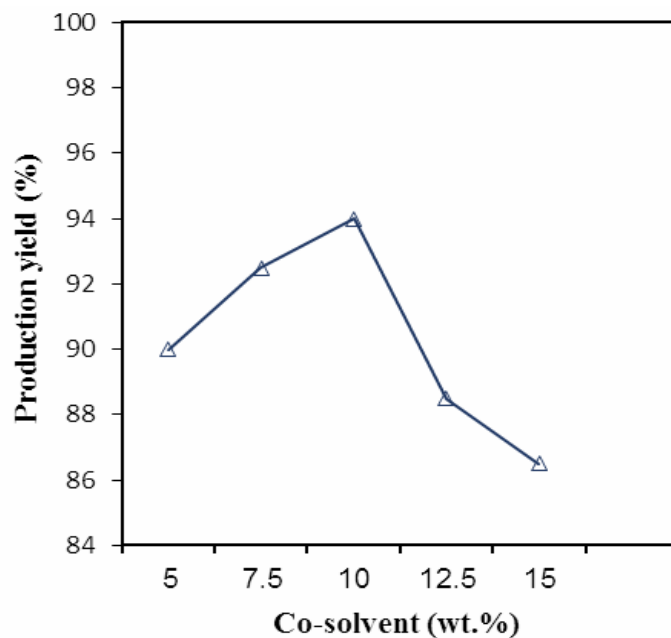
Fig. 5. Effect of co-solvent amount on methyl ester yield. Reaction conditions: Voltage 40 V, methanol/oil molar ratio: 7:1, catalyst amount 12 wt% oil, reaction time 2 h and reaction temperature 25 °C.
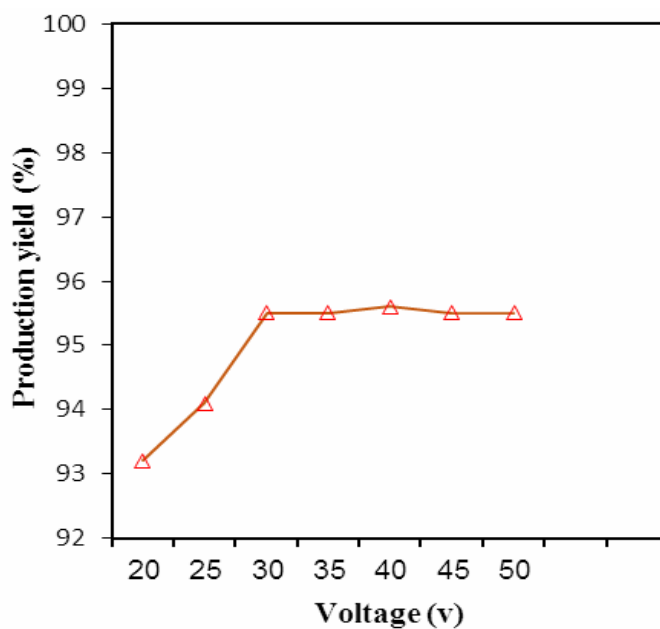

Fig. 6. Effect of voltage on methyl ester yield. Reaction conditions: Methanol/oil molar ratio: 7:1, co-solvent amount 10 wt% oil, catalyst amount 12 wt% oil, reaction time 2 h and reaction temperature 25 °C.

Table 1. Physical Properties of Methyl Ester

Property	EN standard	Methyl ester
Density (15 °C, kg m^{-3})	860–900	880
Pour point (°C)	-15 to 16	-15
Cloud point (°C)	-3.0 to 12	0
Oxygen content (wt%)	140-180	100
Flash point (°C)	10-12	10
Cetane number	46-65	51
Kinematic viscosity/40 °C (mm^2 s^{-1})	3.5-6.2	4.3

most active region for transesterification. Water usually plays an important role for the electric charge transfer between the electrodes. Moreover, a small amount of water was electrolyzed and consumed gradually with the electrolysis time. So, it can be said that the transesterification of oil takes place with the hydroxide ion concentration around the cathode. In this study, the increase of electrolysis voltage appears to considerably enhances biodiesel production. Among the voltages of 20-50 volts, 30 V was selected for the next stage of the research (Fig. 6. Effect of voltage on methyl ester yield. Reaction conditions: Methanol/oil molar ratio: 7:1, co-solvent amount 10wt% oil, catalyst amount 12wt% oil, reaction time 2 h and reaction temperature 25 °C).

Biodiesel Characterization

Several properties including viscosity, density, cetane number, flash point and cloud point are employed to characterize biodiesel. Having favorable properties and environmental benefits, biodiesel is practically an ideal substitute fuel for direct-ignition compression ignition in diesel engines. Table 1 indicates the physical and chemical properties of methyl ester. Density is the main characteristics of any fuel. Engine characteristics such as heating value and cetane number are related to density which directly impact the performance of the engine. The range of density limit established by EN standard is 860-900

kg m^{-3} [42]. Viscosity of methyl ester is influenced by several factors including position, number and nature of double bonds, chain length and nature of oxygenated moieties. The high value of viscosity causes harms to engine such as incomplete combustion, carbon deposition on the injectors and poor fuel atomization [43]. Density increases with decreasing chain length and enhancing degree of unsaturation. Biodiesel's flash point temperature is higher than conventional diesel fuel which increases the safety of fuel storage and transportation [44]. These properties of the product were compared against EN standard proving to be based on international standard range (Table 1. Physical properties of methyl ester).

CONCLUSIONS

Electrolysis method has been used as a convenient tool for methyl ester production. Waste cement catalyst was also successfully tested in the transesterification process of used cooking oil into methyl ester. Under the optimal conditions of calcination temperature 740 °C for 4 h, reaction temperature 25 °C, catalyst amount 12 wt%, acetone as co-solvent 10 wt%, agitation rate 300 rpm, voltage 30 V and oil/methanol molar ratio 7:1, the methyl ester conversion reached 95.5% after 2 h reaction at room temperature. Moreover, it was shown that using a co-solvent in the electrolysis reaction increased the production yield in lower

time.

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