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Full Length Research Paper

A kinetic study of biodiesel in waste cooking oil

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Methyl esters are produced by transesterification of waste cooking palm oil with methanol in the presence of a catalyst, potassium hydroxide (KOH). These reactions were carried out in 4:1 (molar ratio of methanol and oil) with 0.45 weight % of the catalyst used. The rate of reaction was enhanced with increasing temperature of 50, 55 and 60 up to 65°C, and for every temperature, three samples were taken with 10 min intervals. The concentrations of methyl esters in the collected samples were determined by gas chromatography method. The kinetic mechanism of second order system was plotted in graph between 1/[G] versus t and log K versus 1/T. This graph shows activation energy for both forward, reverse reactions and correlation constant for each point. The optimum values of the rate constants are 0.018 to 0.168 weight % per min for transesterification of biodiesel from various temperatures and the activation energies included 2.53, 1.93 and 1.29 Kcal/mol for final concentration of triglycerides (TG), final concentration of diglycerides (DG) and final concentration of monoglycerides (MG) hydrolysis reactions, respectively. These activation energy values are more effective to precede the reaction.

Key words: Biodiesel, kinetics, methyl esters, waste cooking oil, transesterification, gas chromatography.

INTRODUCTION

The search for environmental friendly materials that have potential to substitute mineral oil in various industrial applications is currently being considered a top priority research topic in the fuel and energy sector (Jha et al., 2007). Biodiesel is a clean burning fuel derived from a renewable feedstock such as vegetable oil or animal fat. It is biodegradable, non-inflammable and non-toxic and produces lesser carbon IV oxide ($CO_{2)}$, sulphur dioxide and unburned hydrocarbons than petroleum based fuel. The use of waste material as a source of alternative fuel is a practice of increasing popularity among the researchers worldwide. Such a high value of waste cooking oil (WCO) or abused fryer was made from fat and this oil is available in restaurants, and hotels. Transesterification of vegetable oils with simple alcohols has long been a preferred method for preparing fatty esters. These esters have good potential as alternative fuels (Freedom et al., 1986).

The high cost of biodiesel is mainly due to the cost of virgin vegetable oil. It is not surprising that the biodiesel produced from vegetable oil for example, pure soybean oil costs much more than petroleum based diesel.

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Abbreviations: FAME, Fatty acid methyl ester; **ME,** methyl ester; **TG,** triglycerides; **DG,** diglycerides; **MG,** monoglycerides; **GC,** gas chromatography; **E_a,** energy of activation; **R,** gas constant; **C,** a constant; **T,** absolute temperature; **k,** overall pseudo rate constant; **t,** reaction time; **TGo,** the initial highest triglyceride concentration; **DGo,** the initial highest diglycerides concentration; **MGo,** the initial highest monoglycerieds concentration; **k_{TG}, k_{DG}, k_{MG},** rate constant for tri, di, and monoglycerides.

Therefore, it is necessary to explore ways to reduce the production costs of biodiesel. In this sense, methods that permit to minimize the costs of the raw material are of special interest. The use of waste frying oil, instead of fresh oil, to produce biodiesel is an effective way to reduce the raw material cost because waste frying oil is estimated to be about half of the price of fresh oil. In addition, the utilization of waste frying oils diminishes the problems of contamination, because the reusing of this waste oil can reduce the burden of the government in disposing waste, maintaining public sewers and treating the oil wastewater. The fact is, so far, that only a very small percentage of these oils has been collected and used for soap production. The high temperatures of typical cooking processes and the water from the foods accelerate the hydrolysis of triglycerides which increase the free fatty acid content in the oil. Also, problems with the stability of the mixtures and increases in the peroxide value have been observed. Likewise, the viscosity, iodine value, saponification value and density are different when the fresh oil is used.

Many questions about the optimization of methanolysis or ethanolysis of used frying oil have not been reported. The resolution of these questions is very important for biodiesel manufacture (Encinar et al., 2007). Transesterification of vegetable oils can be carried out using homogeneous or heterogeneous catalysts that are base, acid or enzymes. Homogeneous alkaline catalysts are widely used because the reaction is completed in a short time under mild temperature and pressure conditions (Pilar et al., 2004). Coteron et al. (1997) tested several vegetable oils with a free fatty acids (FFA) content of up to 2.8% and concluded that transesterification with methanol proceeds very rapidly using strong basic homogeneous catalysts. Hanna et al. (1999) was given a detailed review about biodiesel production. Methanol is the most common alcohol used in esterification although ethanol, isopropanol and butanol have also been reported (Pilar et al., 2004; Ma and Hanna, 1999). The factors that affect transesterification are alcohol to oil ratio, catalyst quantity, reaction temperature, pressure, time and FFA content in oils.

Conversion of oil into biodiesel by transesterification is complicated if it contains higher amounts of FFA (> 4 mg KOH/g). Freedman et al. (1984) studied the kinetics of the acid- and base –catalyzed transesterification of soybean oil with 1-butanol and methanol at 30:1 and 6:1 molar ratio of alcohol to oil. Aheikpor et al. (2010) studied about kinetics of palm kernel oil and ethanol transesterification. Anusan et al. (2011) studied a detailed of reaction kinetics of transesterification between palm oil and methanol under subcritical conditions. Noureddini et al. (1997) studied the kinetics of base – catalyzed transesterification of soybean oil with methanol 6:1 molar ratio of alcohol to oil. Darnoko and Munir et al. (2000) studied the kinetics of base –catalyzed transesterification of palm oil with methanol at 6:1 molar ratio of alcohol to oil. Thiruvengadaravi et al. (2009) discussed about the kinetic study of the esterification of FFA in non-edible pongamia pinnata oil using acid catalyst. Karmee et al. (2004) discussed about the kinetic study of the base-catalyzed transesterification of monoglycerides from pongamia oil. Narvaez et al. (2007) studied about kinetics of palm oil methanolysis. Berrios et al. (2007) studied a kinetic of the esterification of FFA in sunflower oil. They reported that the best kinetics mechanism appeared to be a pseudo second order. Although there are a number of kinetics studies in literature on transesterification of esters with alcohol, but only a few researchers are concerned with transesterification of vegetable oil like palm oil (Ahiekpor et al., 2010; Anusan et al., 2011; Narvaez et al., 2007; Theerayut et al., 2004).

The kinetic model of transesterified biodiesel can be derived using three step process. In the first step, final concentration of tri glycerides (TG) is converted to final concentration of di glycerides (DG) and methyl esters, which in turn are converted to final concentration of mono glycerides (MG) and methyl esters in the second step. In the third which is the final step, MG is converted to glycerol and methyl ester. In each step, one molecule of methyl ester is formed for every molecule of glyceride reacted. In addition to these three steps, a shunt reaction involving the direct reaction of TG and methanol to yield methyl ester and glycerol also has been considered (Noureddin and Zhu, 1997; Darnoko and Munir, 2000). In recent times, kinetic studies of transesterification focused on soybean oil (Noureddin and Zhu, 1997; Darnoko and Munir, 2000) and palm oil (Ahiekpor et al., 2010; Anusan et al., 2011; Narvaez et al., 2007; Theerayut et al., 2004)

The overall reactions are:

$$\mathrm{TG} + 3\,\mathrm{ROH} \rightarrow 3\,\mathrm{R'COOR} + \mathrm{GL} \quad (1)$$

The stepwise reactions are:

$$\mathrm{TG} + \mathrm{ROH} \underset{k_2}{\overset{k_1}{\leftrightarrow}} \mathrm{DG} + \mathrm{R'COOR} \quad (2)$$

$$\mathrm{DG} + \mathrm{ROH} \underset{k_4}{\overset{k_3}{\leftrightarrow}} \mathrm{MG} + \mathrm{R'COOR} \quad (3)$$

$$\mathrm{MG} + \mathrm{ROH} \underset{k_6}{\overset{k_5}{\leftrightarrow}} \mathrm{GL} + \mathrm{R'COOR} \quad (4)$$

Where, k_1, k_2, k_3, k_4, k_5 and k_6 are the rate constant values of both forward and back reactions. The rate of transesterification of any oil will depend on its initial composition. Sanji et al. (2004) which undertook the first kinetics study of transesterification of pongamia oil, reported that the oil comprised of a mixture of TG, DG and MG in the ratio 42:26:11, respectively.

The objective of the paper was to characterize the kinetics of transesterification reaction leading us to undertake kinetic studies. Also, evaluation of a second order kinetic mechanism of palm oil transesterification with methanol with KOH used as a catalyst solubility of KOH in methanol is better than that of sodium hydroxide (NaOH). These reaction conditions were focused on the optimum values of transesterification of palm oil at atmospheric pressure: 4:1 molar ratio of alcohol to oil, temperature used from 50 to 65°C with 0.45 wt. % of the catalyst used based on the oil ratio. The obtained results can predict the rate constant and activation energy of the reaction.

MATERIALS AND METHODS

Characteristics of materials

Waste cooking palm oil was collected from restaurants which contained food waste and dust materials and were removed by 10 micron filter cloth. The tested FFA value of the waste cooking oil was 2.64 mg KOH/g and this oil can be used directly to biodiesel process because it had only less than 4 mg KOH /g. The materials sources were: methyl alcohol of 99.9% purity and KOH pellets of 98.2% purity which were purchased from SD fine chemicals. The gas chromatographic values for methyl esters were obtained from Sargam Laboratory, Chennai. Briefly, 0.45 weight % stock solution of KOH in methanol was prepared and used in the entire reaction. The methanol and oil mixture was taken in 4:1 mole ratios.

Reaction condition

Experiments were designed to determine the reaction rate constants and activation energies for the temperature of 50, 55, 60 and 65°C. This temperature dependence was carried out using 4:1 molar ratio of alcohol to oil and also to identify the hypothesis of the process. A certain amount of catalyst was dissolved in methanol to prepare methoxide and then, it was added into waste cooking oil reactor and the samples were collected for kinetic study. Based on the temperature ranges for every temperature collected from the three samples with respect to 20 min intervals, a total of 12 samples were collected with respect to time intervals. All experiments were carried out at atmospheric pressure level.

Apparatus

A 1000 ml glass cylindrical reactor equipped with a magnetic stirrer, thermometer, reflux condenser and a sample port was used. The reactor was kept in a constant heating mantle with a temperature controller, which was capable of maintaining the temperature within ± 0.3°C. Agitation was provided with a magnetic stirrer, which was set at a constant speed throughout the experiments. Initially, the reactor was filled with 500 g waste cooking oil and heated to the required temperature.

Analysis

The samples were analyzed for TG, DG, MG, total methyl esters and glycerol content by gas chromatography-mass spectrometry (GC-MS). The composition of the methyl esters was analyzed by GC using a SHIMADZU QP2010 series gas chromatograph system equipped with a split injection system, a flame ionization detector and a GC-MS solution version 2.53 software were used. The column was a 30.0 m × 0.25 mm, and 0.25 µm capillary column with helium 99.9995% purity at 1.50 ml/min as the carrier gas and split ratio of 10:1. Injector and detector temperature were 260°C. Oven temperature started at 70°C for 2 min, were increased to 300°C at a rate of 5°C/ min and held at this temperature for 5 min. Methyl heptanoate was used as the interval standard.

RESULTS AND DISCUSSION

Effect of molar ratios

This experiment was carried out with 4:1 molar ratio of methanol to oil. Generally, biodiesel process requires only 3:1 molar ratio of alcohol to oil to form 3:1 molar ratio of methyl ester and glycerol. The FFA value of this palm oil is containing only 0.65% and the process required small amount of catalyst to perform the transesterification reaction. So, we decided to use 4:1 molar ratio of alcohol to oil for biodiesel kinetic study. Further increase of molar ratio (5:1 to 9:1) leads to decrease in the methyl ester value and increase in the cost of methanol. We observed the effect of molar ratio of ester yield of both because of the variation in the molar ratio reported as necessary by various investigators and no correlation has been found for the system variation in molar ratio with ester yield. At same time, the change in concentrations of tri, di and monoglycerides were also monitored.

The results obtained from menthanolysis of waste cooking palm oil is shown in Figure 1. Anusan et al. (2011) described the experimental investigation that was carried out with pure palm oil and methanol at molar ratio of 46:1, temperatures between 150 to 200°C and pressure around 140 to 190 atm in a 400 ml batch reactor. Encinar et al. (2007) studied molar ratios of alcohol to oil as 3:1 to 12:1 and it depicts that as molar ratio increases it led to decrease in the methyl ester content. Also, transesterification reaction carried out with 4:1 molar ratio of alcohol to oil gave more than 95% of the methyl ester.

Optimization of reaction parameters

Classical optimization technique was used to optimize the reaction parameters such as catalyst quantity, methanol to oil ratio and temperature. 0.45 weight % catalysts were taken as the optimum amount as further increase in catalyst concentration shows significant improvement in

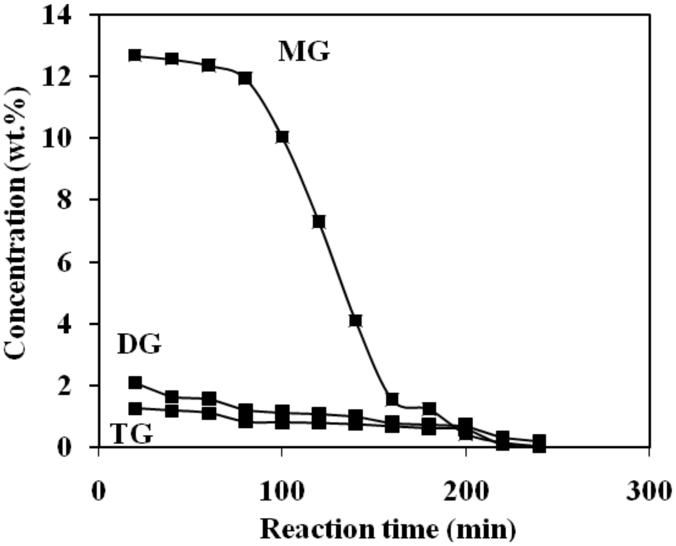

Figure 1. Rate of reaction time with glycerides concentration.

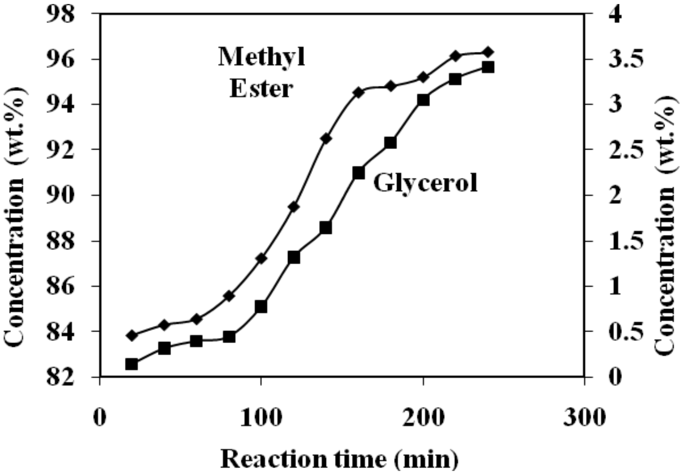

Figure 2. Biodiesel and glycerol conversion with reaction time.

the reaction. Transesterification reaction was carried out with methanol to oil ratio from 4:1 to 9:1. An increase in transesterification was observed till a ratio of 6:1, beyond which no substantial increase in transesterification rate was observed. Temperature studies were done in the range of 50 to 65°C. The optimum value was found at 60°C, because at a temperature greater than 60°C, methanol is lost from the reaction medium in spite of using a condenser. If further increase in temperature leads to formation of methyl ester, it will be less due to alcohol volatility.

Effect of concentration of glycerides

Figure 2 shows the progress of the transesterification reaction for waste cooking oil in every 20 min of reaction time, when temperature of 50, 55, 60 and 65°C were used. The conversion of methyl ester was obtained at 95% and the glycerol concentration was increased with the maximum limitation of 3.5%. In the initial stages of the reaction, triglycerides were first converted into diglycerides, diglycerides were converted into monoglycerides and finally monoglycerides were converted into methyl ester with glycerol. If increased, the effect of concentration of triglycerides leads to formation of fat or oil, whereas, diglycerides and monoglycerides lead to formation of triglycerides. For transesterification process, methaoxide was added into the heated palm oil reactor and the reaction led to the formation of tri-di, di-mono and mono-glycerol. As the rate of reaction proceeds, concentration of glycerides contents diminished and finally reached equilibrium time at the 240 min as shown in Figure 2. Concentration of tri, and diglycerides decreased slowly with reaction time and monoglycerides decreased gradually with the reaction time. After 200 min, all three glycerides coincided and after 240 min, all the three glycerides were attained at equilibrium (that is, all three glycerides were converted into glycerol and formed 100% methyl ester).

The increase in methyl ester (ME) concentration was followed by an increase in glycerol concentration as it was liberated from TG molecules. However, the relative proportion of glycerol produced is not always the same as that of the esters produced. This is due to intermediate products such as DG, MG and TG concentrations that decreased as the reaction proceeded after particular time interval and TG concentration was only 0.16% with the highest concentration of DG and MG observed in the first minute their levels of each 20 min intervals. The concentration of the decrease of the three triglycerides conversion into biodiesel is described in Figure 1. Theerayut et al. (2004) had discussed 6:1 ratio of methanol and oil used for transesterification reaction of palm using 1 weight % of the catalyst whereas, the work used only 0.45 weight % for effective transesterification reaction from vegetable waste cooking oil. In this work, the molar ratio of methanol and oil used only 4:1, but, Noureddini et al. (1997) described about 6:1 molar ratio of the mixture was used.

American Society of testing and materials (ASTM) does not have a standard limit for triglycerides, diglycerides and monoglycerides content in the final product. However, European biodiesel standard (EN14214) recommends that the triglycerides, diglyceride and monoglyceride content should not exceed 0.8 and 0.2, respectively. These experimental results were found to be within the limit of the European Standard and if

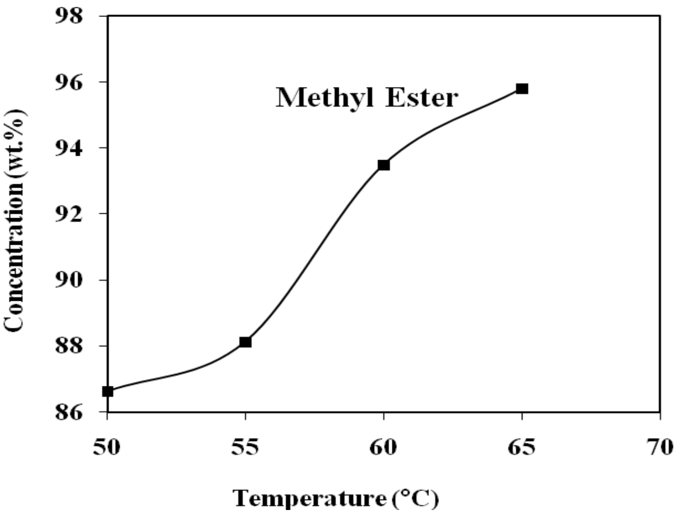

Figure 3. Methyl ester conversion with temperature.

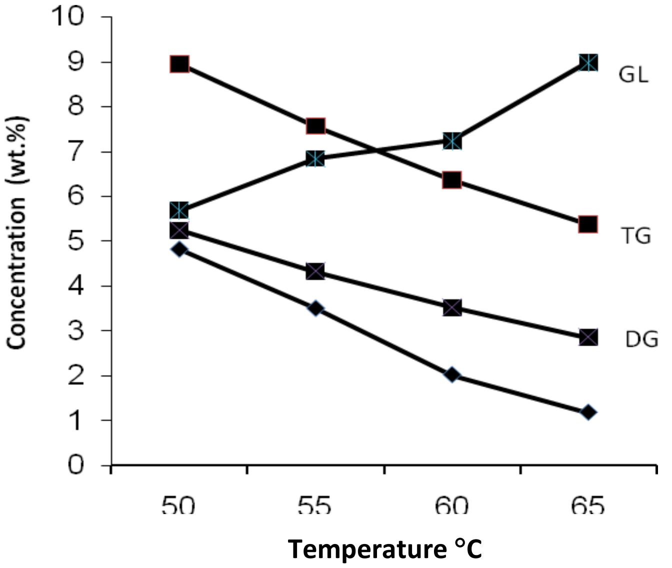

Figure 4. Glycerides concentrations with temperature.

increased the values of the glycerides leads to more alcohol content to neutralized transesterification of biodiesel.

Effect of temperature

To determine the effect of temperature on methyl esters formation, transesterification reactions of waste cooking palm oil were carried out with molar ratio of methanol to oil is 4:1, the best condition found in Figure 3, at various temperatures; 50, 55, 60 and 65°C. Generally, oil is solids at room temperature but the minimum temperature will give optimum value to the process; the minimum temperature of 50°C was used. Below 50°C, the high viscosity of the oil caused problems in pumping and stirring and storage temperature of oil were about 50 to 55°C to maintain its liquidity. The maximum temperature was studied at 65°C because the boiling point of methanol is 68°C (boiling point of methanol at atmospheric pressure is 65°C). Temperature had noticeable effect with methyl ester on the transesterification reaction as shown in Figure 3. At 50°C, conversion of TG to ME was 85% and at 60°C conversion of TG to ME was 94%, further increase in temperature that is almost 95% of the conversions of methyl ester were found at 65°C. Therefore, increase in temperature up to particular point of methyl ester conversion would be high beyond that limiting period again conversion would be negative effect of the process due to the increase in methanol and catalyst requirement with respect to methyl ester production, optimum temperature was 60°C (due to volatility).

The typical glycerides results with temperature increments as shown in Figure 4. Initially from 50 to 60°C, the glycerides concentrations slowly decrease with respect to temperature increase and after 60°C glycerol concentration only increase and other three glycerides concentration got decreased. So, optimum temperature for waste cooking palm oil is 60°C. Owing to the semisolid nature of palm oil at room temperature discussed by Darnoko and Munir et al. (2000) studied ,the effect of temperature on palm oil transesterification was studied at 50°C and a catalyst (KOH) concentration of 1% with 6:1 molar ratio of methanol/oil gives 83% the methyl ester. Freedman et al. (1984) also reported rapid formation of ME during transesterification of soybean oil and sunflower oil after 1 min, 80% of TG was converted to ME and after 1 h, ME concentration was 93 to 98% of the reaction mixture. At 60°C, this study gives 95% of methyl ester conversion for 4:1 molar ratio of methanol to oil with 0.45 wt. % of catalyst was used.

Reaction kinetics

The feasibility of a reaction is determined from the thermodynamic parameters. Arrhenius equation was used to study the influence of temperature on specific reaction rate. The best kinetic model for our data appears to be a second order model kinetics. To test this hypothesis, a model was developed based on the kinetics of TG, methanolysis (Darnoko and Munir, 2000). The second order reaction rate for TG in Equation (6) would be as follows (Smith, 1981):

$$d\,[TG]\,/dt = k\,[TG]^2 \qquad (5)$$

Table 1. Reaction rate constant k (wt%.min^{-1}) for triglycerides (TG), diglycerides (DG) and monoglycerides (MG) methanolysis at different temperatures.

Glycerides	Temperature (°C)	Reaction rate constant (Wt. %.min^{-1})	R^2
	50	0.0180	0.9157
TG → DG	55	0.0188	0.9176
	60	0.0208	0.8861
	65	0.0244	0.8608
	50	0.0360	0.8514
DG → MG	55	0.0420	0.8454
	60	0.0610	0.8348
	65	0.0801	0.8114
	50	0.1012	0.8101
MG → GL	55	0.1431	0.7981
	60	0.1528	0.7856
	65	0.1682	0.7813

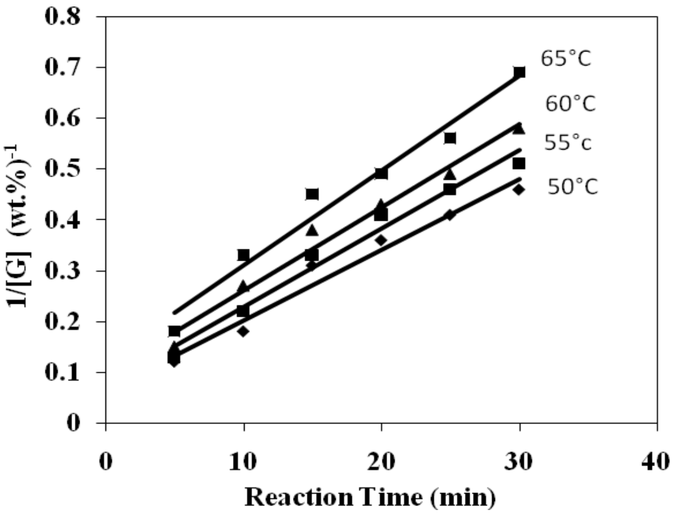

Figure 5. Rate constant plot for glycerides at different temperatures.

Integration of Equation (5) yields:

$$-k_{TG}.t = 1/ [TG] - 1/ [TG_O] \quad (6)$$

Similarly, the same procedure applied to Equations (7) and (8) would result in:

$$k_{DG}.t = 1/[DG] - 1/ [DG_O] \quad (7)$$

$$k_{MG}.t = 1/ [MG] - 1/ [MG_O] \quad (8)$$

Where k is the over all second order rate constant, t is the reaction time, TGo is the initial triglyceride concentration, DGo is the initial highest diglycerides concentration, MGo is the highest monoglycerieds concentration, TG is final concentration of triglycerides, DG is the final concentration of diglycerides, MG is the final concentration of monoglycerides and k_{TG}, k_{DG}, k_{MG} are rate constant for tri, di and monoglycerides of oil.

For methanolysis of TG a plot of reaction time versus.1/[TG] will be straight line if the model is valid. A second order rate Equation (5) was applied to found the rate constant. Figure 5 shows rate constant values calculated by plotting concentration of different glycerides at different temperatures (50, 55, 60 and 65°C) with respect to time variation. From Figure 5 select various points of concentration with respect to temperature with applying scatter model graph and found the rate constant, correlation coefficient (R^2). From the plot, the slope is called rate constant k_{TG} (wt. % min)$^{-1}$. Rate constant values for triglycerides can be calculated by using Equation (6). From Figure 5 values of rate constant, correlation coefficient (R^2) can be tabulated and obtained in Table 1. For TG-DG plot, at 50°C, the rate constant value was 0.0180 (wt. % min)$^{-1}$ and correlation coefficient (R^2) was 0.9157 and at 65°C, the k value was 0.0244 (wt. % min)$^{-1}$ and correlation coefficient was 0.8608. There is an increase in k at higher temperature and the order of magnitude also increases. Similarly, straight lines were obtained for DG and MG methanolysis by applying the Equations (7) and (8). These data were used to determine the energy of activation (E_a) from a plot of the rate constant (k) versus the reciprocal of absolute temperature (T), according to the Equation (9):

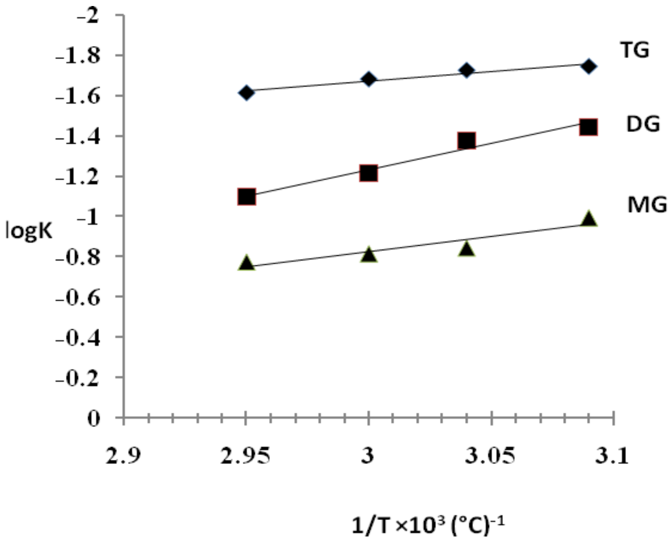

Figure 6. Arrhenius plot of reaction rate with reciprocal temperature.

Table 2. Activation energy for methanolysis of TG, DG and MG during transesterification of waste cooking oil.

Glycerides	E_a (Kcal/mol)	R^2
TG → DG	2.53	0.7772
DG → MG	1.93	0.2904
MG → GL	1.29	0.2904

$$\log_{10} k = (-Ea / 2.303R) / T + C \tag{9}$$

Where E_a is the energy of activation, R is the Gas constant, k is rate constant and C is a constant.

The Figure 6 shows activation energy values calculated, similar from rate constant procedure and plotted values can be obtained in Table 2. Based on the plot of Arrhenius, values of E_a with respect to TG – DG was 2.53 (Kcal/mol), DG – MG was 1.93 (Kcal/mol) and MG - GL was 1.29 (Kcal/mol). Also, observed activation energy of this three triglycerides reaction had only less energy required exhibiting the conversion of triglycerides. The activation energy is defined as the energy that must be overcome in order for a chemical reaction to occur. Activation energy may also be defined as the minimum energy required to starting chemical reaction. The activation energy of a reaction is usually denoted by E_a and given in units of mole. Based on the definition of activation energy, Table 2 shows good results and compatibility to precede the reaction easily. Also, compared with other process from waste cooking oil kinetics highlights higher values of activation energy only and may promotes the reaction effectively.

Conclusion

The biodiesel kinetics was studied from waste cooking palm oil by GC method and Arrhenius plot. Based on the results, kinetics from waste cooking oil on 4:1 mole ratio of the methanol and oil with 0.45 wt. % of catalyst used for transesterification of biodiesel. Waste cooking oil is cheaply available sources of fuel to utilize our necessity due to insufficient of fossil fuel level. Concentration of methyl ester formation showed good results with reaction temperatures of 50 to 65°C. From the GC results, the average composition of the waste cooking oil biodiesel had methyl ester in 90.5 wt.% with remaining MG of 1 wt.%, DG of 3.10 wt.% and TG 5.4 wt.%. From the kinetic plot, optimum level of rate constant (k) of 0.018 to 0.168 (wt. % min^{-1}) and also activation energy of the three triglycerides are 2.58, 1.93 and 1.29 (Kcal/mol) is effective to produce the biodiesel. This kinetic study gives a unique idea to further work because each triglyceride had enough lesser activation energy to promote the transesterification and due to temperature response of the reaction to methyl ester formation.

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