An Experimental Optimization Research of Methyl and Ethyl Esters Production from Safflower Oil

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Abstract – **Nowadays, biodiesel is drawing attention as a renewable and clean alternative to fossil diesel fuel because of numerous advantages such as higher flash point, cetane number and density. However, the high viscosity of biodiesel is one of the critical shortcomings and it causes poor atomization, decrease in engine performance and increase in exhaust emissions. To overcome this shortcoming, in this study, the effects of main transesterification reaction variables on the viscosities of produced safflower oil methyl and ethyl esters (biodiesel) were investigated as a full factorial experimental design, and optimum parametric values giving the lowest viscosity were determined. Density and viscosity were measured according to ISO 4787 and DIN 53015 standards. Sodium ethoxide (C_2H_5ONa) was utilized as a catalyst, and 90 and 120 minutes of reaction duration were kept constant for methanolysis and ethanolysis reactions. According to the results, the optimal reaction parameters were determined as: 0.75 % catalyst concentration, 8:1 alcohol to oil molar ratio and 56 °C reaction temperature for methanolysis; 1.00 % catalyst concentration, 12:1 alcohol to oil molar ratio and 70 °C reaction temperature for ethanolysis. Based on the reaction parameters, the methyl and ethyl esters were produced with the lowest viscosities of 3.989 mm^2/s and 4.393 mm^2/s, respectively. In the light of results obtained in this study, similar studies on production of biodiesels from different oils and alcohols can be performed.**

Keywords – **Biodiesel; ethyl ester; methyl ester; optimization; renewable energy; sodium ethoxide; transesterification; vegetable oils**

1. INTRODUCTION

In recent years, research and development of alternative fuels has attracted considerable attention because of limitation of conventional fossil resources, increasing of their prices and rising concern over greenhouse gas emissions [1]. Biodiesel, defined by ASTM as "a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats" [2], offers many important benefits over fossil diesel fuel such as:
- Higher flash point temperature making it safer to handle and store;
- Higher cetane number resulting in a shorter ignition delay period and thus smoother operation with lower noise emissions;
- Excellent lubricity property following longer engine component life;
- Reduced toxicity and exhaust emissions (especially CO, CO_2, SO_x, HC and smoke);
- Higher biodegradability;
- Renewability characteristic [3]–[8].

However, there are also important disadvantages of biodiesel such as:
- Higher copper strip corrosion;
- Lower heating value requiring more fuel to produce the same power and thus increasing

    fuel consumption;
- − High manufacturing cost;
- − Lower oxidative stability because of un-saturation degree in chemical structure;
- − Generally, slightly higher NO_x emissions;
- − Relatively poor performance in cold temperatures due to lower volatility;
- − Higher viscosity resulting in poor fuel atomization and air-fuel mixing quality, incomplete combustion, and thus lower engine performance and increasing exhaust emissions [3]–[8].

Chemically speaking, there are mainly three chemical methods in biodiesel production such as micro-emulsion, thermal cracking (pyrolysis) and transesterification [9]. Among these methods, the most widespread one is transesterification (alcoholysis) in which a monohydric alcohol (generally methanol or ethanol) reacts with fatty acids of triglycerides (vegetable oil) to form glycerol (by-product) and the corresponding fatty acid alkyl esters [6]. The reaction can be catalyzed using homogeneous (acid or base) or heterogeneous (acid, base or enzyme) catalyst. Generally, the base-catalyst (i.e. basic transesterification) ensures a better reaction rate in a relatively short time for the triglycerides including the lower amount of free fatty acids while acid-catalyst (i.e. esterification) is suggested before transesterification for the triglycerides containing higher free fatty acids [6]. Although the reaction rate in conversion of triglyceride to biodiesel is relatively slow for the enzyme-catalyzed reaction [6], the main advantages of enzymatic catalysis over base or acid catalysis are: (i) transesterification reaction at ever lower temperatures can be performed, (ii) the ester yield is relatively higher and (iii) it is not necessary to purify the produced biodiesel [10]. Moreover, methanol and ethanol as monohydric alcohol are mostly used in the transesterification. Methanol is generally preferred because of having the shortest chain and lower cost [10]. Ethanol is also used because of the many advantages such as: (i) it can be produced from renewable resources, thus decreasing dependence from petroleum-based alcohols such as methanol, (ii) it is less toxic, (iii) biodiesels produced using ethanol have higher energy content, cetane number and oxidation stability [11]. Several optimization studies on methyl or ethyl ester production from different feedstocks using basic or acidic catalyst were performed in existing literature such as: Berchmans and Hirata [12] produced methyl ester from Jatropha curcas seed oil including 15 % free fatty acid. In biodiesel production, firstly, the esterification reaction was carried out at the reaction temperature of 50 °C and by using methanol to oil molar ratio of 0.60 w/w and H_2SO_4 amount of 1 % w/w for one hour. After the reaction, the free fatty acid value of oil reduced to less than 1 %. Then, transesterification of the pre-treated oil was carried out at 65 °C and by using methanol to oil amount of 0.24 w/w and sodium hydroxide to oil amount of 1.4 % w/w for 2 hours to produce biodiesel with 90 % ester yield. In the study performed by Tiwari et al. [13], some reaction parameters (methanol amount, acid concentration and reaction time) were optimized using Response surface methodology (RSM) to reduce the free fatty acid value of Jatropha oil (14 ± 0.5 %) to about 1 %. The researchers used quadratic polynomial equations in RSM to predict acid value. The optimum reaction variables were determined as: H_2SO_4 concentration of 1.43 % v/v, methanol to oil molar ratio of 0.28 v/v, reaction duration of 88 minutes and reaction temperature of 60 °C for esterification reaction while methanol/pre-treated oil molar ratio of 0.16 v/v, reaction duration of 24 minutes and reaction temperature of 60 °C for transesterification reaction providing the average biodiesel yield more than 99 %. Sirisomboonchai et al. [14] investigated the effects of temperature, reaction duration, methanol amount and catalyst loading amount on conversion of waste cooking oil to biodiesel produced using calcined scallop shell as a catalyst. According to the results, the optimum reaction variables providing over 86 % ester yield were defined as: catalyst amount of 5 %, alcohol to oil

molar ratio of 6:1, reaction temperature of 65 °C, reaction duration of 120 min., and calcination temperature of 1000 °C for scallop shell. The catalyst was used for four cycles while the ester yield decreased to about 20 %, however, it was specified that calcined scallop shell is thought to be an alternative as a low-cost catalyst for the biodiesel industry. Eevera et al. [15] optimized transesterification reaction variables (catalyser amount (0.5, 1.0, 1.5, 2.0 and 2.5 wt. %), methanol amount (120, 150, 180, 210 and 240 mL), reaction duration (30, 60, 90, 120 and 150 min.) and reaction temperature (40, 45, 50, 55 and 60 °C)) to produce the highest ester yield biodiesel from some edible and non-edible oils. Some important fuel properties (specific gravity, moisture content, etc.) of optimized biodiesels were also measured. According to the results, the optimum reaction variables of edible oils were determined as: reaction duration of 90 min., 180 mL of methanol for 1000 mL of oil, sodium hydroxide amount of 1.5 wt. % and reaction temperature of 50 °C. These variables were determined to be similar to the non-edible oils' parameters except the methanol amount (210 mL/1000 mL of oil). Moreover, all biodiesels are determined to be generally suitable to the related international standards. There are also numerous studies on optimization of transesterification reaction variables to produce biodiesel having the highest methyl or ethyl ester yield, however, parametric research on production of the lowest viscosity methyl or ethyl ester are rarely carried out in the existing literature. Therefore, the importance of this study is to synthesize the lowest viscosity safflower oil methyl and ethyl ester for solving the high viscosity problem of biodiesel in a way mentioned above, and thus increasing the use of biodiesel in the world. For this, the effects of main reaction variables (sodium ethoxide amount of 0.75 %, 1.00 % and 1.25 %; reaction temperature of 50 °C, 55 °C and 60 °C for methanolysis, 60 °C, 65 °C and 70 °C for ethanolysis; and alcohol to oil molar ratio of 3:1, 6:1 and 9:1 for methanolysis, 9:1, 12:1 and 15:1 for ethanolysis) on viscosities of produced biodiesels were systemically investigated as a full factorial experimental design, and the reaction variables giving the lowest viscosity were determined. Reaction durations of 90 and 120 minutes were kept constant for methanolysis and ethanolysis reactions, respectively. Safflower oil was chosen as feedstock because of its high potential and low-cost in Turkey.

2. EXPERIMENTAL STUDY

2.1. Materials, Reaction Parameters and Biodiesel Production

Refined safflower oil, sodium ethoxide (C_2H_5ONa), pure ethanol (C_2H_5OH), pure methanol (CH_3OH) and anhydrous sodium sulphate were utilized in biodiesel production. The following reaction variables were investigated such as:
- C_2H_5ONa concentration, %: 0.75, 1.00 and 1.25;
- Reaction temperature for methanolysis, °C: 50, 55 and 60;
- Reaction temperature for ethanolysis, °C: 60, 65 and 70;
- Methyl alcohol/oil molar ratio: 3:1, 6:1 and 9:1;
- Ethyl alcohol/oil molar ratio: 9:1, 12:1 and 15:1.

The parametric values were selected through detail investigation of existing literature [16]–[21]. It is noted that the reaction durations of 90 and 120 minutes were kept constant throughout all experiments since the values are determined to be optimum in the authors' previous studies [22], [23]. To investigate the effects of reaction parameters given above on viscosity as a full factorial experimental design, in this study, an experimental optimization of transesterification reaction was performed by producing 27 (3·3·3) methyl and ethyl ester samples (totally 54

samples). In biodiesel production, a certain amount of C_2H_5ONa depending on catalyst to oil concentration was dissolved into a certain amount of CH_3OH (or C_2H_5OH) according to alcohol to oil molar ratio to prepare methoxide (or ethoxide) solution. The solution was blended with pre-heated safflower oil in a flask, and the reactants were mixed at a certain reaction temperature during 90 (or 120) minutes by means of a magnetic stirrer heater connected to a spiral reflux condenser and thermometer. The reaction temperature was controlled within a range of ± 1 °C. After the reaction, in the refinement step of transesterification, the reaction mixture was first discharged to a separating funnel in order to cool to room temperature, after which two layers (ester and glycerol) were separated by gravity in 24 hours. The upper layer consists of methyl (or ethyl) ester while the lower layer contains glycerol, excess alcohol, remaining catalyst, soaps, some entrained esters and partial glycerides [24]. The upper layer (biodiesel) was cleaned up by hot water, dried using anhydrous sodium sulphate and filtered.

2.2. Density and Viscosity Measurements

Densities of pure esters at 15 °C and 40 °C were measured according to ISO 4787 standard by means of a pycnometer and top loading balance (accuracy of ± 0.01 g). Their dynamic viscosities were also measured at 40 °C in accordance with DIN 53015 standard using a universal Haake Falling Ball Viscometer, Haake Water Bath, a stopwatch (accuracy of ± 0.01 s) and a thermometer (± 0.5 °C). All measurements were repeated three times, and then their average was taken to minimize the measurement errors. As is well known, the kinematic viscosity was determined by dividing dynamic viscosity to the density at the same temperature. More details on the measurements can be also found in the authors' previous studies [3], [9], [11].

2.3. Uncertainty Analysis

Measured physical quantities are used to get targeted results in experimental studies. Uncertainties of measuring devices naturally cause uncertainties in the computed quantities, too. Uncertainty analysis allows to determine uncertainties in the targeted results to be aware of the reliability of them [3], [9], [11]. Therefore, in this study, uncertainty analysis of measured and calculated physical quantities such as dynamic and kinematic viscosities and densities were performed using the method proposed by Kline and McClintock [25]. According to this method, the highest uncertainty among all data was computed as 0.0249 %, showing the results are highly reliable and accurate. An example on the calculation of uncertainty analysis can also be found in [26].

3. RESULTS AND DISCUSSION

3D Fig. 1–3(a) and Fig. 4–6(a) show the changes in viscosities of methyl and ethyl esters with respect to reaction temperature and alcohol to oil molar ratio simultaneously for different catalyst concentrations (0.75 %, 1.00 % and 1.25 % respectively). In these figures, the points and lines indicate measured viscosity data (as listed in Appendix Table 1 and Table 2), and estimated viscosity values computed from cubic spline interpolation using Matlab software, respectively. The estimated values were determined based on the measured data.
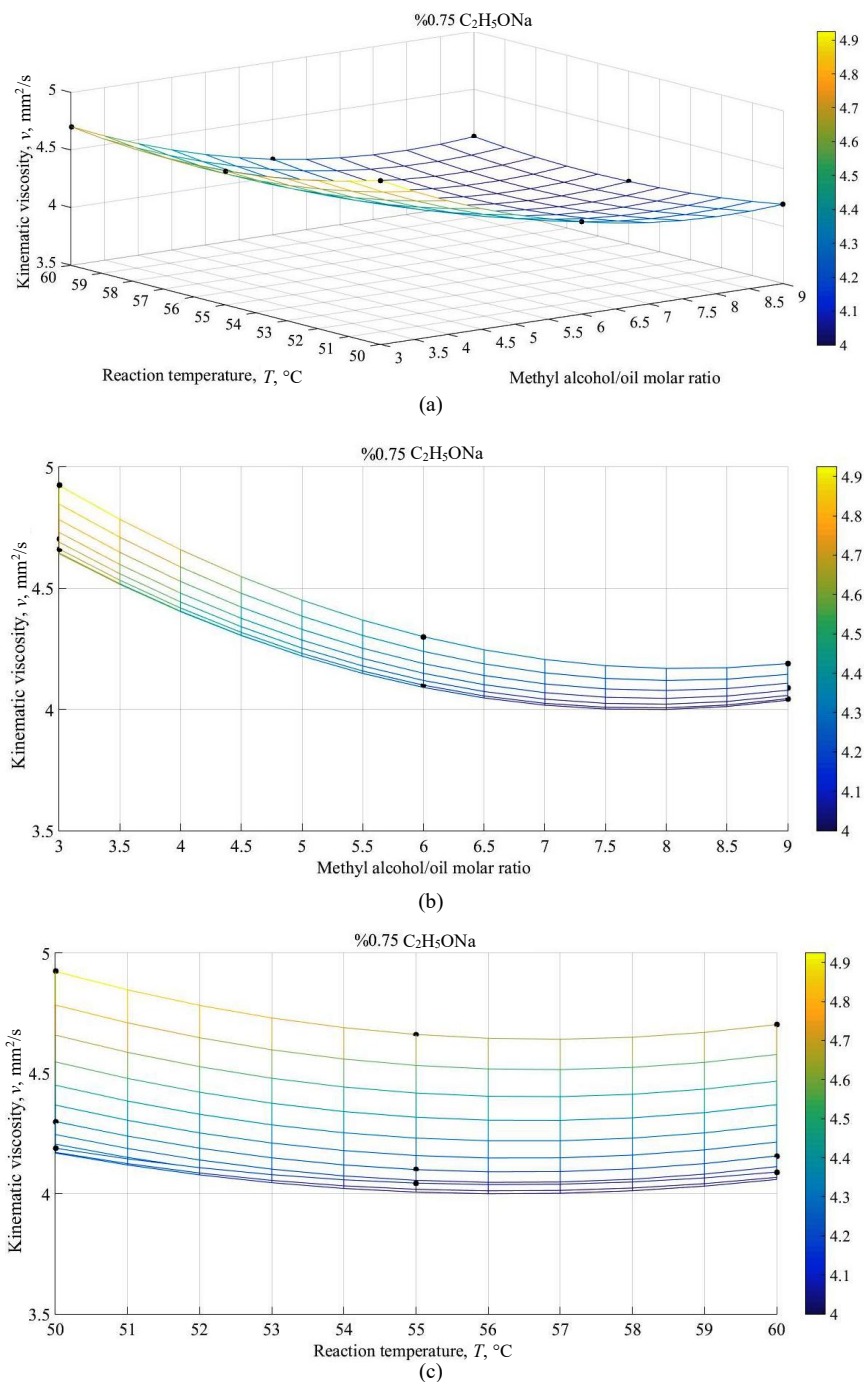
Fig. 1. Change of methyl ester viscosity (a) vs. reaction temperature and alcohol/oil molar ratio simultaneously;
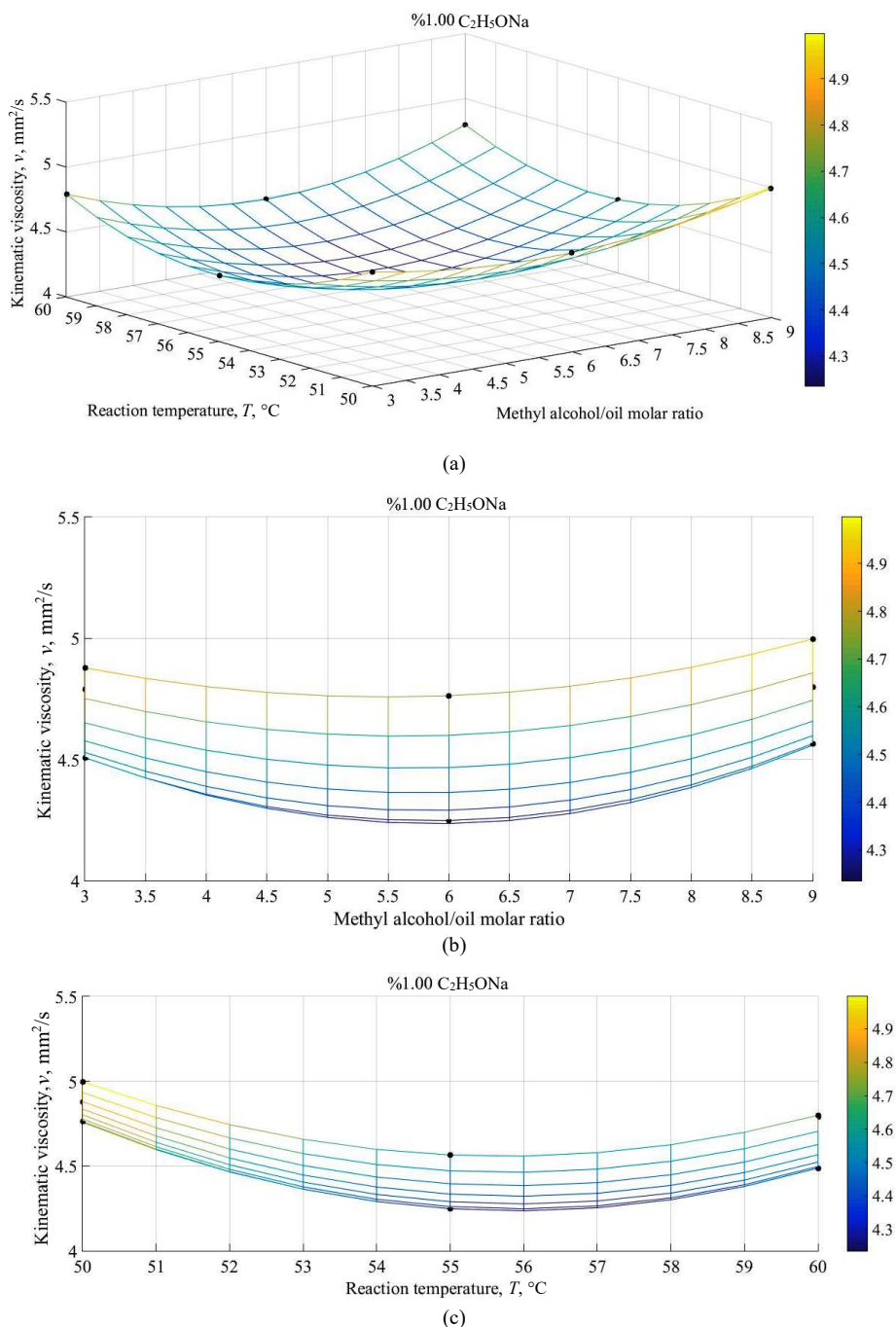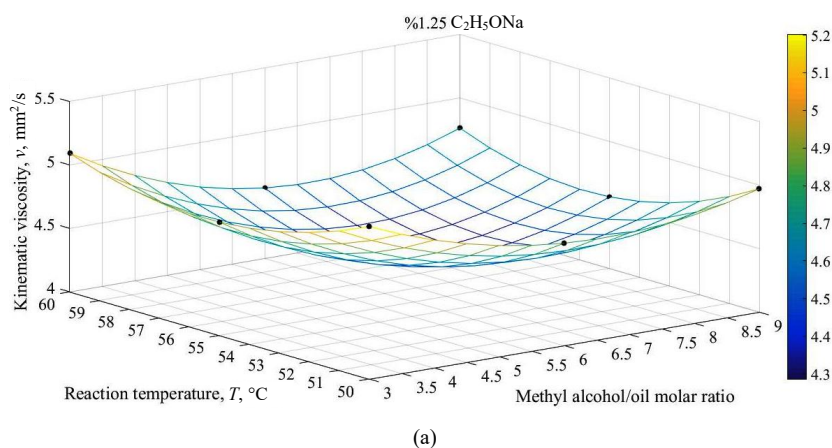(b) alcohol/oil molar ratio; (c) reaction temperature for the catalyst concentration of 0.75 %.

(a)

(b)

(c)

Fig. 2. Change of methyl ester viscosity (a) vs. reaction temperature and alcohol/oil molar ratio simultaneously; (b) alcohol/oil molar ratio; (c) reaction temperature for the catalyst concentration of 1.00 %.

In this study, 2D Fig. 1–6(b, c) were also given to illustrate the individual effects of reaction temperature and alcohol to oil molar ratio on viscosities of methyl and ethyl esters for the use of different catalyst concentrations (0.75 %, 1.00 % and 1.25 %). As shown in 2D Fig. 1–6(b), since the adequate biodiesel yield from transesterification is not obtained, viscosities of methyl and ethyl esters produced at lower alcohol ratios (such as 3:1 or 9:1) take higher values. As the molar ratio is increased, the transesterification, as an equilibrium reaction, shifts to ester side (i.e. reaction yield improves), viscosities decrease and take estimated minimum values of 3.9998 mm^2/s, 4.2356 mm^2/s and 4.2862 mm^2/s at 8:1, 6:1 and 6.5:1 methyl alcohol to oil molar ratios; and 4.4562 mm^2/s, 4.3930 mm^2/s and 4.4040 mm^2/s at 13:1, 12:1 and 12:1 ethyl alcohol to oil molar ratios for 0.75 %, 1.00 % and 1.25 %, respectively. However, the higher alcohol to oil molar ratios (e.g. 9:1 for methanolysis and 15:1 for ethanolysis) result in increase in viscosities of methyl and ethyl esters because of deactivation in catalyst activity, emulsifier effect of OH^- group, decrease in transesterification yield and increase in the solubility of glycerol in the ester phase. The viscosity values of methyl esters generally change in a narrower range in case of using 0.75 % catalyst concentration, compared to 1.00 % and 1.25 %, as shown in 2D Fig. 1–3(b). Moreover, viscosity values of ethyl esters change with respect to alcohol to oil molar ratio in a wider range at lower molar ratios (9:1) while vice versa at higher molar ratios (12:1 or 15:1) in case of using the catalyst concentration of 0.75 %, as shown in Fig. 4 (b). However, the change of viscosity vs. ethyl alcohol to oil molar ratio occurs in the about constant range for catalyst concentration of 1.00 %, as shown in Fig. 5(b), while it occurs in the firstly narrower, then wider, and finally again narrower ranges as molar ratio increases for catalyst concentration of 1.25 %, as shown in Fig. 6(b).
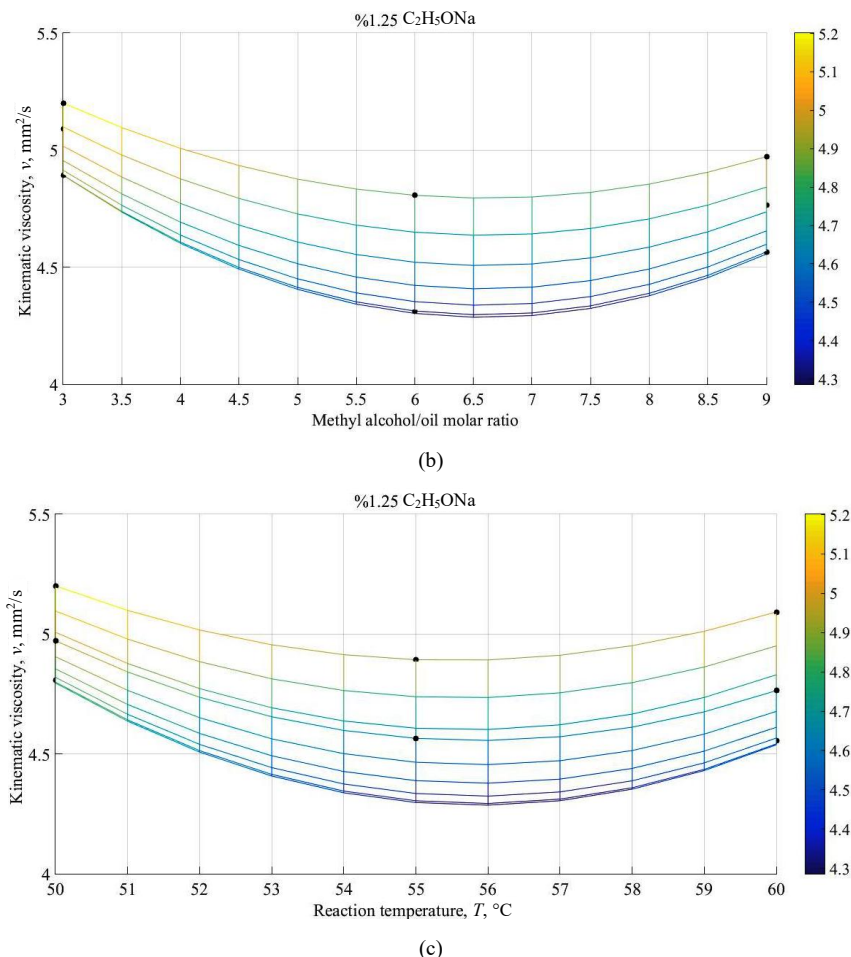

(a)

(b)

(c)

Fig. 3. Change of methyl ester viscosity (a) vs. reaction temperature and alcohol/oil molar ratio simultaneously; (b) alcohol/oil molar ratio; (c) reaction temperature for the catalyst concentration of 1.25 %.

The change of methyl ester viscosity is more clear in case of using 1.00 % and 1.25 % catalyst concentrations. In other words, variation in viscosity of methyl ester is slighter for catalyst concentration of 0.75 % then 1.00 % and 1.25 %, as seen in Fig. 1–3(a). In addition, variation in catalyst amount does not significantly affect the behavior of change in ethyl ester viscosity with respect to reaction temperature and alcohol/oil molar ratio simultaneously, as seen in Fig. 4–6(a). In other words, the similar characteristics in the viscosity change of ethyl esters were obtained for different catalyst amounts (0.75 %, 1.00 % and 1.25 %). As shown in these figures, methyl and ethyl esters having higher viscosity were produced at lower reaction temperatures (e.g. 50 °C for methanolysis and 60 °C for ethanolysis) and alcohol/oil molar ratios (e.g. 3:1 for methanolysis and 9:1 for ethanolysis). However, as temperature and molar ratio are increased until the specific parametric values, viscosity decreases and lowers to a minimum. However, after these parametric values, when temperature and molar ratio continue to increase, viscosity tends to increase as well.
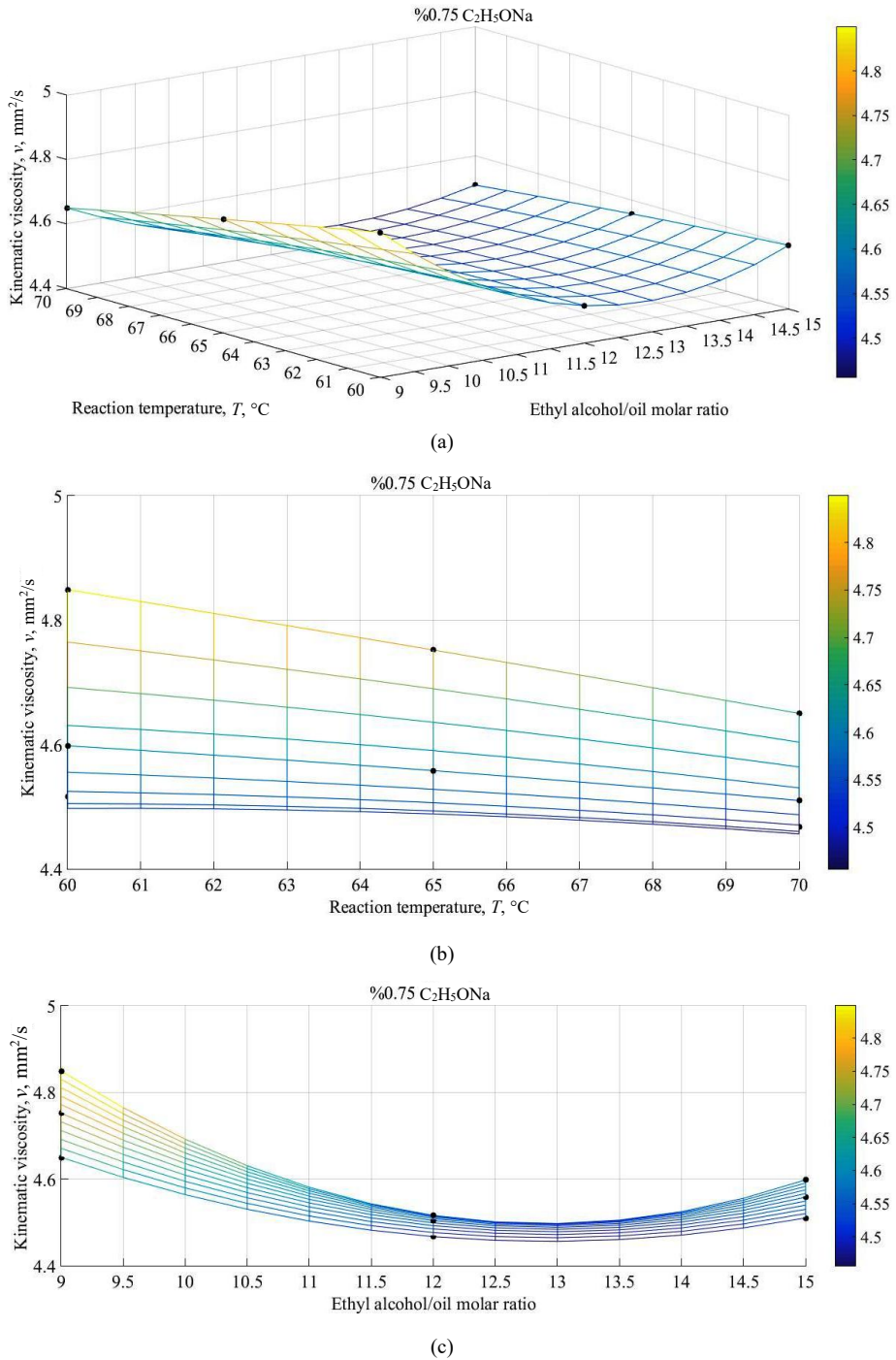
(a)

(b)

(c)

Fig. 4. Variation in ethyl ester viscosity (a) vs. reaction temperature and alcohol/oil molar ratio simultaneously; (b) alcohol/oil molar ratio; (c) reaction temperature for the catalyst concentration of 0.75 %.
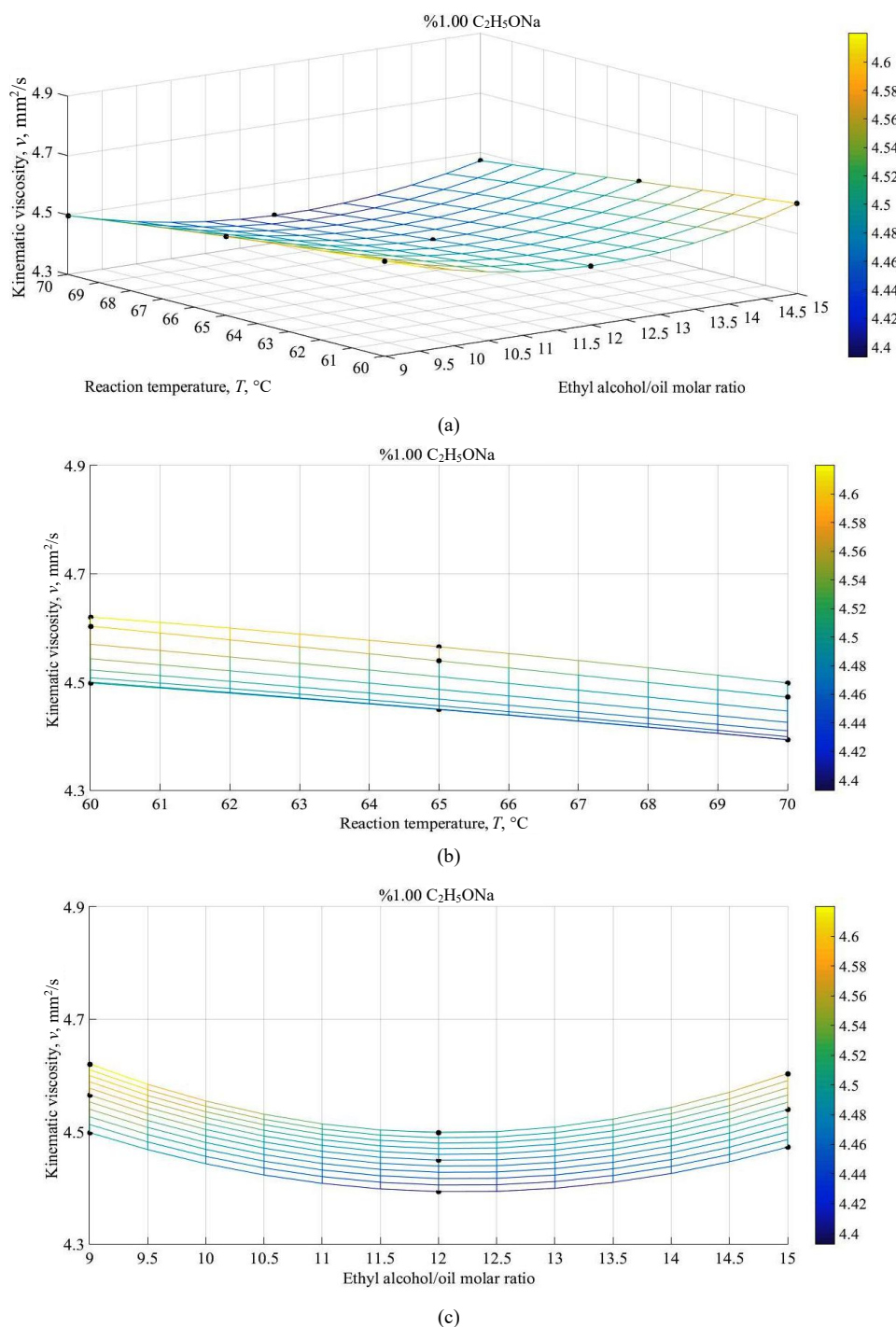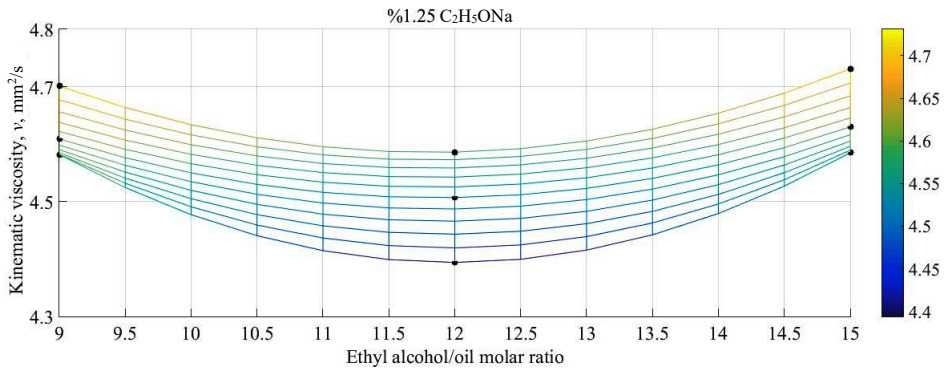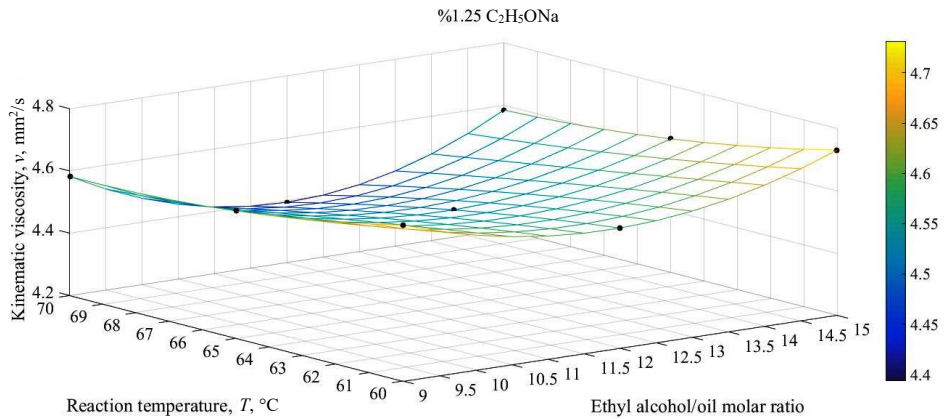
(a)

(b)

(c)

Fig. 5. Variation in ethyl ester viscosity (a) vs. reaction temperature and alcohol/oil molar ratio simultaneously;
(b) alcohol/oil molar ratio; (c) reaction temperature for the catalyst concentration of 1.00 %.

2D Fig. 1–6(c) show the individual effect of reaction temperature on viscosities of methyl and ethyl esters produced using different catalyst concentrations (0.75 %, 1.00 % and 1.25 %). As reaction temperature is increased, the transesterification, as an endothermic reaction, shifts to ester side (i.e. conversion yield to biodiesel increases), and viscosities of methyl and ethyl esters diminish until 56 °C and 70 °C at which the values reach minimums, given above for all catalyst concentrations, respectively. However, higher reaction temperatures than 56 °C and 70 °C cause a decrease in the reaction yield because of evaporation of alcohol from the reaction medium, saponification and decomposition, resulting in the increase in viscosities of methyl and ethyl esters. The variation in viscosities of methyl esters with respect to reaction temperature occurs in a more narrow range when the catalyst concentration of 1.00 % is used, compared to 0.75 % and 1.25 %, as seen in 2D Fig. 1–3(c). In addition, the interval of variation in viscosity values of ethyl esters vs. reaction temperature nearly remains for 1.00 % and 1.25 % while the interval decreases for 0.75 % catalyst concentration as the reaction temperature is raised, as seen in Fig. 4–6(c).
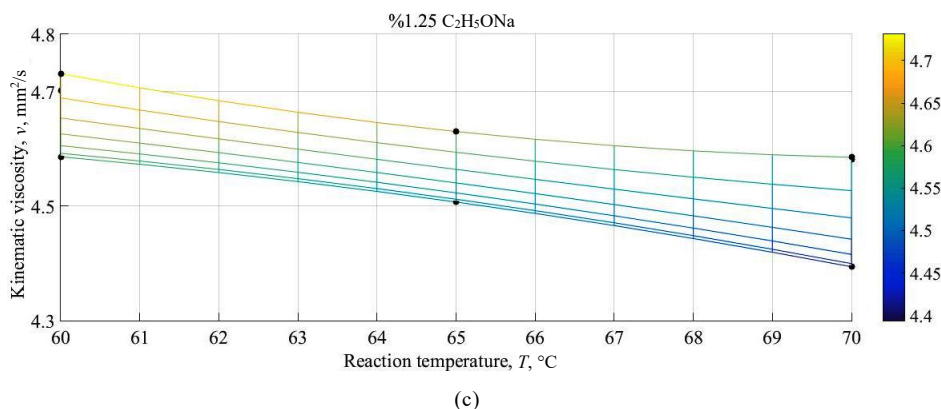

(a)

(b)

Fig. 6. Variation in ethyl ester viscosity (a) vs. reaction temperature and alcohol/oil molar ratio simultaneously; (b) alcohol/oil molar ratio; (c) reaction temperature for the catalyst concentration of 1.25 %.

In summary, in accordance with the aim of the study mentioned in the introduction section, according to experimental viscosity data (Appendix Table 1), the methyl ester having the lowest viscosity of 4.044 mm^2/s was produced with the reaction parameters: 0.75 % catalyst concentration, 9:1 methyl alcohol to oil molar ratio, 55 °C reaction temperature and 90 minutes reaction duration. However, by means of cubic spline interpolation, optimum reaction parameters providing estimated viscosity value of 3.9998 mm^2/s even lower than experimental value of 4.044 mm^2/s were determined as: 0.75 % catalyst concentration, 8:1 methyl alcohol to oil molar ratio and 56 °C reaction temperature, as mentioned above. According to the optimum reaction parameters obtained from spline interpolation, safflower oil methyl ester was synthesized and the viscosity value was obtained as 3.989 mm^2/s, which is very close to the estimated value (3.9998 mm^2/s) and lower than the experimental value of 4.044 mm^2/s. Further, the ethyl ester having the lowest viscosity of 4.393 mm^2/s was synthesized by means of transesterification carried out at 70 °C, alcohol to oil molar ratio of 12:1 and by using catalyst concentration of 1.00 % for 120 minutes, as seen in Appendix Table 2. It was noted here that the ethyl ester having a viscosity of 4.467 mm^2/s was produced via the reaction parameters: 70 °C, 0.75 % and 12:1 (Appendix Table 2), although, according to results of cubic spline interpolation, the lower viscosity of 4.450 mm^2/s than the experimental value of 4.467 mm^2/s was also obtained with the same parameters except for the higher alcohol to oil molar ratio (13:1). This value is very close to the value of 4.4562 mm^2/s estimated from spline interpolation, as shown in Fig. 4(b), showing the results obtained from cubic interpolation are highly reliable and accurate.

4. CONCLUSIONS

Kinematic viscosity is the key fuel property influencing spray characteristics, engine performance and exhaust emissions. The high viscosity of biodiesel causes poor atomization, incomplete combustion and increase in exhaust emissions. Therefore, the importance of this study is to produce the lowest viscosity safflower oil methyl and ethyl esters for solving the high viscosity problem, thus increasing the use of biodiesel in the world. For this, (1) an experimental optimization of methanolysis and ethanolysis reactions was carried out by investigating the effects of catalyst (sodium ethoxide) amount, reaction temperature and alcohol (methyl or ethyl) to oil

molar ratio on viscosity of produced biodiesel as a full factorial design, and (2) dynamic viscosities and densities of biodiesels were measured in accordance with ISO 4787 and DIN 53015 standards, respectively. In addition, it is thought that this study has the scientific importance since parametric works such as this on production of the lowest viscosity methyl or ethyl ester are rarely performed in existing literature, although, there are many studies on optimization of transesterification reaction parameters giving the highest methyl or ethyl ester yield. Moreover, the use of safflower oil with high potential and low-cost in biodiesel production shows the practical importance of this study. The following conclusions can be drawn from the study:

− Viscosities of methyl esters produced using catalyst concentration of 1.25 % generally take the highest values, compared to 0.75 % and 1.00 %, as seen in Appendix Table 1;
− Viscosities of ethyl esters produced using catalyst concentration of 1.00 % are generally the lowest, compared to 0.75 % and 1.25 %, as seen in Appendix Table 2;
− Viscosity values of methyl and ethyl esters decrease and lower to a minimum at certain parametric values as reaction temperature or alcohol molar ratio increases. However, when reaction temperature and molar ratio are again increased, the reaction yield decreases and viscosities again tend to increase;
− The catalyst concentration of 0.75 %, alcohol to oil molar ratio of 8:1, reaction temperature of 56 °C and reaction duration of 90 minutes provide the lowest viscosity safflower oil methyl ester of 3.989 mm^2/s;
− The lowest viscosity safflower oil ethyl ester of 4.393 mm^2/s was produced by means of the parameters: 1.00 % catalyst concentration, 12:1 alcohol to oil molar ratio, 70 °C reaction temperature and 120 minutes reaction duration.

APPENDIX

TABLE 1. VISCOSITY DATA OF METHYL ESTERS PRODUCED
ACCORDING TO DIFFERENT PARAMETRIC VALUES

Catalyst concentration	Methyl alcohol/oil molar ratio	Reaction temperature T, °C	Kinematic viscosity v, mm²/s
0.75 %	3:1	50	4.924
		55	4.662
		60	4.703
	6:1	50	4.300
		55	4.100
		60	4.157
	9:1	50	4.189
		55	4.044
		60	4.090
1.00 %	3:1	50	4.878
		55	4.507
		60	4.790
	6:1	50	4.763
		55	4.248
		60	4.488
	9:1	50	4.997
		55	4.545
		60	4.799
1.25 %	3:1	50	5.201
		55	4.893
		60	5.092
	6:1	50	4.807
		55	4.313
		60	4.555
	9:1	50	4.972
		55	4.575
		60	4.764

TABLE 2. VISCOSITY DATA OF ETHYL ESTERS PRODUCED
ACCORDING TO DIFFERENT PARAMETRIC VALUES

Catalyst concentration	Ethyl alcohol/oil molar ratio	Reaction temperature T, °C	Kinematic viscosity N, mm^2/s
0.75 %	9:1	60	4.849
		65	4.752
		70	4.650
	12:1	60	4.516
		65	4.504
		70	4.467
	15:1	60	4.598
		65	4.558
		70	4.510
1.00 %	9:1	60	4.620
		65	4.565
		70	4.498
	12:1	60	4.509
		65	4.449
		70	4.393
	15:1	60	4.603
		65	4.539
		70	4.472
1.25 %	9:1	60	4.701
		65	4.609
		70	4.582
	12:1	60	4.586
		65	4.507
		70	4.404
	15:1	60	4.731
		65	4.630
		70	4.585

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