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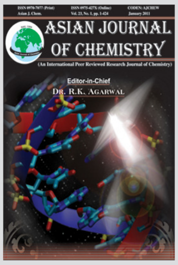

Application of Taguchi Methods to Investigate Factors Affecting the Kinematic Viscosity of Methyl Ester of Tobacco Seed Oil

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Vegetable oils and their esters are alternative renewable fuels for compression ignition engines. One of the main difficulties of using vegetable oils as fuel in diesel engines is their high kinematic viscosity. Transesterification appears to be the most promising technique to reduce the viscosity. Reaction temperature, alcohol/oil molar ratio, type and amount of catalyst, reaction duration and the water content in free fatty acid are the most important parameters in biodiesel production by the transesterification method. One of the most important issues in biodiesel is the viscosity and the factors affecting it for achieving EN 14214 standards. In this study, optimum levels of the variables affecting the viscosity of tobacco seed oil methyl ester were determined using Taguchi's technique at 40, 50 and 60 ºC and 1/4, 1/6 and 1/10 of alcohol/oil molar ratios and addition of 0.5, 1.0 and 1.5 % KOH and NaOH catalysts were chosen as parameters. The Taguchi design method revealed that choosing right catalyst, reaction temperature, alcohol/oil molar ratio and catalyst amount are important factors in view of optimization of kinematic viscosity of tobacco seed oil methyl ester.

Key Words: Tobacco seed oil, Transesterification, Biodiesel, Methyl ester, Taguchi design method.

INTRODUCTION

Increases in prices of petroleum-based fuels and environmental pollution due to exhaust emissions, it has been encouraged studies related to using alternative fuels. Recently, especially non-edible vegetable oils as the price of edible vegetable oils is higher than that of the diesel fuel have been considered as alternative fuels for compression ignition engines. Vegetable oils are renewable, non-toxic, biodegradable and have low emission profiles[1-3]. The best way to use vegetable oil as fuel is to convert it in to biodiesel. Biodiesel is the name of a clean burning mono-alkyl ester-based oxygenated fuel made from natural, renewable sources such as new/used vegetable oils and animal fats. However, some drawbacks have been encountered related to the use of straight vegetable oils in diesel engines primarily due to their high viscosity, lower volatility and lower heat content[4,5]. The high viscosity causes some problems in atomization of injector systems and combustion in cylinders of diesel engines. Also, in long term operations, high viscosity of vegetable oils may lead to ring sticking, formation of injector deposits, development of gumming, as well as incompatibility with lubricating oils[1,6].

Different techniques have been developed to solve their high viscosity and low volatility problems of vegetable oils, such as preheating oils, blending or dilution with other fuels, transesterification and thermal cracking/pyrolysis[1,2,7,8]. Transesterification appears to be the most promising technique which is a chemical process of converting vegetable oil into biodiesel fuel[8,9].

Vegetable oils have to undergo the process of transesterification to be usable in internal Combustion engines. Biodiesel is the product of the process of transesterification. Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. Alcohol combines with the triglycerides to form glycerol and esters. A catalyst is usually used to improve the reaction rate and yield. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially[9,10-14].

The process of transesterification brings about drastic change in viscosity of vegetable oil. The biodiesel thus produced by this process is totally miscible with mineral diesel in any proportion. Biodiesel viscosity comes very close to that of mineral diesel hence no problems in the existing fuel handling system. Flash point of the biodiesel gets lowered after esterification and the cetane number gets improved. Even lower concentrations of biodiesel act as cetane number improver for biodiesel blend. Diesel engine can perform satisfactory for long run on biodiesel without any hardware modifications.

Twenty per cent biodiesel is the optimum concentration for biodiesel blend with improved performance[15].

Catalysts are classified as alkali, acid or enzymes. Alkali-catalyzed transesterification is much faster than acid-catalyzed reaction. However, if a vegetable oil has high free fatty acid and water content, acid catalyzed transesterification reaction is suitable. The alkaline catalyst concentrations in the range of 0.5-1 % by weight yield 94-99 % conversion of vegetable oils into esters. Further increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove the catalyst from the reaction products at the end of the reaction[13-15]. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts.

The conversion rate increases with reaction time. Freedman *et al.*[12] transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5 % sodium methoxide catalyst and 60 ºC. An approximate yield of 80 % was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93-98 %).

In the present study, alkali-catalyzed transesterification process is performed as the free fatty acids of tobacco seed oil are lower than 1 %. Investigation of the effects of parameters which affects the kinematic viscosity of methyl ester of tobacco seed oil is important. Taguchi method is a useful tool for this purpose. Basic principle of Taguchi methods is to develop an understanding of individual and combined effects of variety of design parameters from a minimum number of experiments[16]. There is no study to be appeared in the open literature investigating the important factors which affects the optimum conditions for kinematic viscosity of methyl ester of tobacco seed oil. For this purpose, Taguchi experimental method has been used to investigate the optimum conditions in this study. In the experimental design, the parameters affecting on the kinematic viscosity are chosen as catalyst types (KOH, NaOH) and catalyst amounts (0.5, 1.0, 1.5 %), reaction temperatures (40, 50, 60 ºC) and alcohol/oil molar ratios (1/4, 1/6, 1/10). The conditions providing EN 14214 standards for the kinematic viscosity were investigated.

EXPERIMENTAL

Extraction of tobacco seed oil: The seeds (original Saribaglar-407) used in the study were provided with Aegean Agricultural Research Institute, Menemen districts of Izmir in Turkey. After tobacco seeds were dried for 1 h at 120 ºC, they were ground to fine powders by an electrical mill.

Determination of fatty acid composition: Fatty acid composition of tobacco seed oil was determined by GC analysis. A Hewlett-Packard 5890 series II gas chromatograph, with a SP2340 type column 30 m long and split-splitless injector, was used. The inside diameter was 0.53 mm and film thickness was 1.0 μm. The detector was a FID. An automatic sampler was attached to the HP 5890 GC to automate sample introduction. The sample (tobacco seed oil) amount injected was 0.5 mL/min. The temperature of GC injector was 250 °C. Helium was used as a carrier gas. Split ratio was 1:50. The flame ionization detector temperature was 260 °C. The oven temperature was kept at 150 °C for 3 min. After that, the oven was heated with heat ratio 10 °C/min to 225 °C. The oven temperature was constant for 15 min. The oven temperature was constant for 15 min. The fatty acids of tobacco seed oil were identified and quantified using the AOAC 963.33 and AOAC 963.22 methods. Fatty acid composition of tobacco seed oil is shown in Table-1.

TABLE-1
FATTY ACID COMPOSITION OF TOBACCO SEED OIL

Fatty acids (%)	Reference					Present study
	17	**18**	**19**	**20**	**21**	
Myristic acid (C14:0)	0.09	–	0.17	1.13	0.14	0.13
Palmitic acid (C16:0)	10.96	8.82	8.87	8.72	8.46	8.53
Stearic asid (18:0)	3.34	–	3.49	2.64	3.38	3.21
Oleic acid (C18:1)	14.54	13.72	12.4	13.46	11.24	10.32
Linoleic acid (C18:2)	69.49	75.30	67.75	71.63	75.58	76.12
Linolenic (C18:3)	0.69	1.59	4.20	0.93	1.14	1.67
Acid value	–	–	–	–	–	1.00

Design of experiment: The present experiments were designed to apply the Taguchi's methods to establish the effects of two catalysts, three amount of catalysts, reaction temperature and alcohol/oil molar ratios for the purpose of determining optimal conditions of the kinematic viscosity of methyl ester of tobacco seed oil. The three design parameters (factors) and their levels are given in Table-2. Optimum experimental conditions which minimize the kinematic viscosity were determined by Taguchi's methods.

TABLE-2
DESIGN FACTORS AND THEIR LEVELS

Symbols	Factors	1 Level	2 Level	3 Level
A	Catalyst type	KOH	NaOH	–
B	Catalyst amount (%)	0.5	1.0	1.5
C	Reaction Temperature (ºC)	40	50	60
D	Alcohol/oil molar ratio	1/4	1/6	1/10

Basic principle of Taguchi methods is to develop an understanding of individual and combined effects of variety of design parameters from a minimum number of experiments. Taguchi method uses a generic signal-to-noise (S/N) ratio to quantify the present variation. There are several S/N ratios available depending on the type of characteristics including "lower is better" (LB), "nominal is best" (NB) and "higher is better" (HB). Since the lower kinematic viscosity is vital in the yield of methyl ester of tobacco seed oil, the S/N ratio for the LB characteristics is related to the present study which is given by

$$S/N = -10 \log \left(\frac{1}{n} \sum_{i=1}^{n} y_i^2 \right) \quad (1)$$

where n is the number of repetition in a trial under the same design conditions, y_i represents the measured value and subscript i indicates the number of design parameters in the orthogonal array (OA) which is shown in Table-3. In the Taguchi method, a design parameter (factor) is considered to be significant if its influence is large compared to the experimental error as estimated by the analysis of variance (ANOVA) statistical method given by eqns. 2-6 shown below. If this is the case, the design parameter is a critical factor in determining the optimal solution to the design problem:

$$SS_T = \left[\sum_{i=1}^{N} (S/N)i^2\right] - \frac{T^2}{N} \tag{2}$$

$$SS_A = \left[\sum_{i=1}^{K_A}\left(\frac{A_i^2}{n_{Ai}}\right)\right] - \frac{T^2}{N} \tag{3}$$

$$\nu_{total} = N\text{-}1 \tag{4}$$

$$V_{factor} = \frac{SS_{factor}}{\upsilon_{factor}} \tag{5}$$

$$F_{factor} = \frac{V_{factor}}{V_{error}} \tag{6}$$

where, SS_T is the sum of squares due to total variation, N is the total number of experiments, SS_A represents the sum of squares due to factor A, K_A is number of levels for factor A. A_i stands for the sum of the total ith level of the factor A, n_{Ai} is the number of samples for ith level of factor A. T is the sum of total (S/N) ratio of the experiments, ν_{total} is the degrees of freedom, V_{factor} is the variance of the factor, SS_{factor} represents the sum of squares of the factor and F_{factor} is the F ratio of the factor.

TABLE-3
EXPERIMENTAL LAYOUT

Exp. No.	Factors			
	A	B	C	D
1	1	1	1	1
2	1	1	2	2
3	1	1	3	3
4	1	2	1	1
5	1	2	2	2
6	1	2	3	3
7	1	3	1	2
8	1	3	2	3
9	1	3	3	1
10	2	1	1	3
11	2	1	2	1
12	2	1	3	2
13	2	2	1	2
14	2	2	2	3
15	2	2	3	1
16	2	3	1	3
17	2	3	2	1
18	2	3	3	2

In Taguchi methods, the levels of factors given in the ANOVA are meaningful according to 99 % confidence intervals. Table-4 shows analysis of variance (ANOVA) for the parameters considered. Design of experiments is composed considering these confidence limits. Required the minimum experimental layout according to Taguchi methods are given in Table-3.

TABLE-4
ANALYSIS OF VARIANCE (ANOVA)

	Factors	Sum of squares (SS)	Degree of freedom (f)	Mean of squares	$F_{theoretical}$
Kinamatic viscosity	[A] Catalyst type	4.27	1	4.27	5.43*
	[B] Catalyst amount (%)	0.21	2	0.11	0.13
	[C] Reaction temperature (ºC)	1.25	2	0.62	0.78
	[D] Molar ratio	12.02	2	6.01	7.53*
	Total	17.75	7.00	2.54	
	Error	7.99	10.00	0.80	

*At least 99 % confidence.

RESULTS AND DISCUSSION

In this study, optimum levels of the variables affecting the kinematic viscosity of methyl ester of tobacco seed oil were determined using Taguchi's technique. For comparison, reaction temperatures are chosen as of 40, 50 and 60 ºC and alcohol/oil molar ratio are taken as 1/4, 1/6 and 1/10. The amounts of catalysts are chosen as 0.5, 1.0 and 1.5 % for both NaOH and KOH, respectively.

Amount of oil extracted from tobacco seed using *n*-hexane: The oil yield from tobacco seed was obtained 42 % on a mass base. The higher yield of oil from the ground tobacco seed could be explained by the anatomy of tobacco seed[21,22]. The main amount of oil is located in the thin-wall cells of the endosperm and some of the oil is accumulated in the embryo. But there is no oil in the protective seed coat[21,23]. Hexane is reported as the best solvent in the yield of oil from tobacco seed. The oil yields obtained by some other researchers were 38.8 and 45.2 % using *n*-hexane[21,24], respectively.

Production of methyl ester of tobacco seed oil: Transesterification method was used for producing tobacco seed oil methyl ester (TSOME). The weight of the oil, alcohol and catalyst was measured by 0.0001 g sensitivity. Base catalyst was chosen because free oil levels are found *ca.* 1 % in the oil analyses. Reaction temperature, alcohol/oil molar rate, type and amount of catalyst and reaction duration were chosen as parameters to find out the optimum conditions of reaction for tobacco seed oil. At the same time, the affects of these parameters on the kinematic viscosity was measured.

In experiments, reaction temperatures were chosen as of 40, 50 and 60 ºC and alcohol/oil molar ratio are set as 1/ 4, 1/6 and 1/10. The kinematic viscosity was measured for 0.5, 1.0 and 1.5 % KOH and NaOH levels.

Parametric studies were performed for 1 h reaction duration. Gas chromatograph was used for fatty acids compositions analysis and the molecular weight of oil was calculated as 872 g/mol.

Methyl alcohol in 99 % purity was used for transesterification process. Measured and premixed methyl alcohol and catalyst (KOH and NaOH) mixture were poured on glass beaker, then the catalyst is stirred until all catalyst was completely resolved with alcohol. After tobacco seed oil was heated up to desired temperature, the prepared alcohol-catalyst mixture was added to tobacco seed oil to start the transesterification reaction by using the heating bath and glass baloon (1 L) of Buchi rotary evaporator. The temperature sensitivity of the heating bath was ± 0.1 ºC. For each parametric study, 100 g of tobacco seed oil sample was used. The mixture was stirred for 1 h at 600 rpm with ± 1 rpm sensitivity, then it was taken into the separatory funnel and waited until ester-glycerine separation is taken place.

After the separation process, glycerine which was moved to bottom of the separatory funnel was removed. Hot sterile purified water was added to methyl ester of tobacco seed oil in the separatory funnel for the cleaning process, then the separatory funnel was shaken upside down by repeating 4 times. After this process, methyl ester of tobacco seed oil-water mixture was left to settle for 12 h and then pure water and glycerine glimmers were removed from the separatory funnel. Remaining methyl ester of tobacco seed oil was separated from all of the unwanted particles by using an centrifuge separatory device called NUVE NF400 in 4000 rpm and 3600 RCF for 1 h. Finally, methyl ester of tobacco seed oil sample was dried by heating up to 110 ºC for 1 h.

Viscosity was measured by using AND model device. The device was calibrated in two points before measurement by using purified water and calibration liquid.

The methyl ester of tobacco seed oil samples produced for the optimum conditions were analyzed at TUBITAK Marmara Research Centre. The analysis results are given in Table-5.

TABLE-5
ANALYSIS OF METHYL ESTER OF TOBACCO SEED OIL

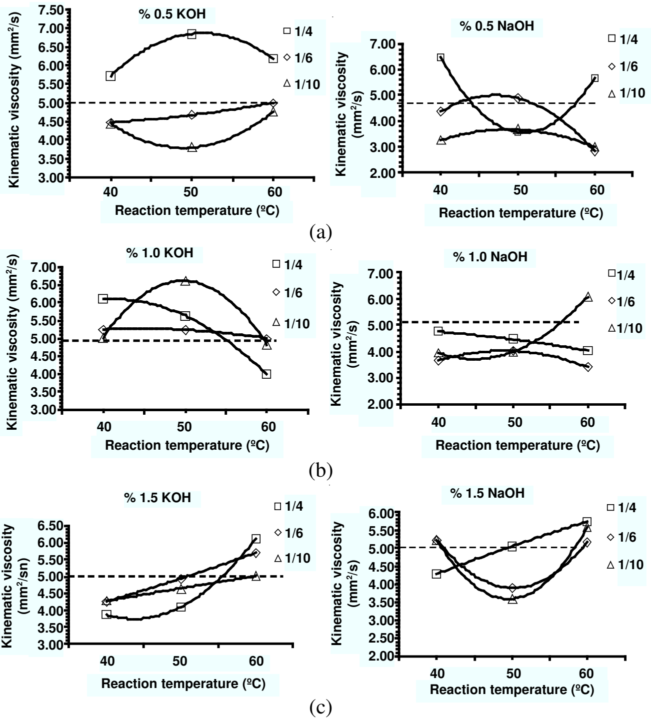
	Method	NaOH	KOH
Ester content (%, m/m)	prEN 14103	96.8	97.1
Carbon residue (%, m/m)	ENISO10370	0.18	0.17
Copper band corrosion (3 h at 50 ºC)	ENISO2160	1.0	1.0
Cold filter plug point (ºC)	EN116	-9.0	-10.0
Water content (mg/kg)	ENISO12937	350.0	320.0
Total contamination (mg/kg)	EN12662	22.0	21.0
Iodine value (g iodine/100 g)	EN1411	117.0	117.0
Methanol content (%, m/m)	EN1410	0.19	0.21
Triglyceride content (%, m/m)	EN1410	0.10	0.10
Diglyceride content (%, m/m)	EN1410	<0.06	0.22
Total glycerol (%, m/m)	EN1410	0.02	0.02
Phosphorus (mg/kg)	EN14107	<3.5	3.5
Monoglyceride content (%, m/m)	EN14105	0.28	0.28
Density (g/cm^3 at 15 ºC)	EN ISO 3675	0.84	0.87
Cetan number	ISO 3104	48.0	53.5
Lower heat value (MJ/kg)	DIN 51900-1	39.12	39.00
Sulphur (mg/kg)	EN ISO 20846	0.0	0.0
Viscosity (mm^2/s)	EN ISO 3104	3.1	4.45
Pour point (ºC)	ASTM D97	-10.0	-9.0
Flash point (ºC)	ASTM D93	145	130

Effects of the parameters on kinematic viscosity: Fig.1 shows the variation of kinematic viscosity of methyl ester of tobacco seed oil after transesterification reaction. The dashed line in the figure shows upper limit of kinematic viscosity regulated by EN14214.

It is seen from Fig. 1a that viscosity of methyl ester of tobacco seed oil obtained with 0.5 % KOH catalyst meets the standards for all conditions except for oil-alcohol molar ratio of 1/4. Minimum value of the viscosity is measured as 3.87 mm^2/s at 50 ºC of reaction temperature and 1/10 of molar ratio. However, the minimum value is obtained at 1/6 of molar ratio and at 50 ºC of reaction temperature as 2.81 mm^2/s for NaOH. It can be seen from Fig. 1a that viscosity of methyl ester of tobacco seed oil obtained with 0.5 % NaOH catalyst meets EN14214 standard for all conditions except for oil-alcohol molar ratio of 1/4 at the reaction temperatures of 40 and 60 ºC.

The viscosities obtained with 1 % KOH catalyst meet EN14214 standard at only 60 ºC reaction temperatures for all oil-alcohol ratios (Fig. 1b). As seen form Fig. 1b, when 1 % NaOH catalyst is used, the viscosity values meet the EN14214 standard for all oil-alcohol molar ratios except for 1/10 molar ratio and 60 ºC reaction temperature condition. All the other viscosity values meet EN14214 for the same parametric conditions.

In the case of 1.5 % KOH, the viscosity meets the EN14214 standard all the conditions except for 1/4 and 1/6 molar ratios at 60 ºC reaction temperature (Fig. 1c). However, for 1.5 % NaOH, viscosities at the conditions of 1/4 molar ratios for 60 ºC are found out of the standard.



(a)

(b)

(c)

Fig. 1. Effects of the parameters on kinematic viscosity

Fig. 1 shows that catalyst amount and alcohol/oil molar ratio heve significant effects on kinematic viscosity for all reaction temperatures.

Determination of optimal conditions for kinematic viscosity by Taguchi method: Optimal conditions were determined by using Taguchi method for kinematic viscosity. As the generated design has not been included in the main experimental layout, the process was re-iterated until the required criteria are satisfied. After confirmations test carried out in 99 % confidence level, the optimum design parameter (factor) combination were found as $A_2B_3C_2D_2$ (NaOH - 1.5 % - 50 ºC - 1/6) for kinematic viscosity. Fig. 2 shows S/N values of factor levels for the kinematic viscosity. Since this combination of design parameter had already been included in the main experimental layout (Table-2) there was no need to carry out an extra confirmation experiment. According to the analysis of variance (ANOVA, Table-4), catalyst type and alcohol/oil molar ratio of methyl ester of tobacco seed oil are meaningful within 99 % confidential level.

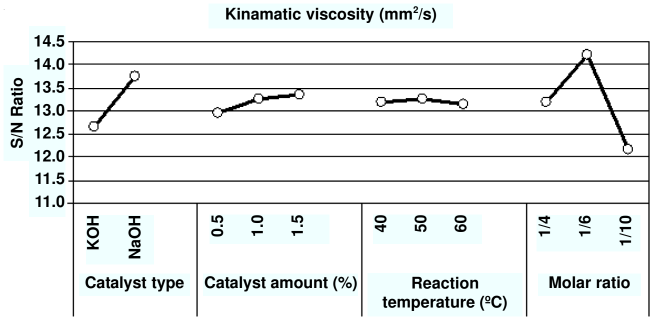


Fig. 2. S/N value of the factors levels for kinematic viscosity

Conclusion

The present study has applied the Taguchi method to investigate the four well known factors on the kinematic viscosity. The conditions which minimize kinematic viscosity were investigated. The conclusion of this study can be summarized as follows:

(1) The Taguchi design method revealed that choosing right catalyst type, catalyst amount, reaction temperature and alcohol/oil molar ratio are important in view of meeting EN 14214 for kinematic viscosity.

(2) Although the effects of catalyst type and molar ratio is meaningful for kinematic viscosity, the effects of amount of catalyst and reaction temperature on kinematic viscosity is found negligibly small.

(3) NaOH is the better catalyst for kinematic viscosity.

(4) Taguchi method is a powerful tool for experimental design so as to minimizing the experiments number which will be conducted. The method gives to a media to find interactions among the factors affecting the kinematic viscosity optimal conditions for the methyl ester of tobacco seed oil.

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