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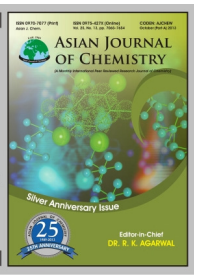

Optimisation of Production Parameters Used in Turning Waste Cooking Oil as Fuel

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In the present study, waste cooking oil with low free fatty acids content was used as feedstock for producing biodiesel. Biodiesel was produced by alkaline-catalyzed transesterification process, which was designed according to the Taguchi method. Molar ratio alcohol/oil, catalyst concentration, reaction temperature and reaction time was chosen as control parameters. Taguchi method was used for optimizing the parameters used in methyl ester production. In experimental study, potassium hydroxide was used as catalyst 0.5 % in volume, molar ratio alcohol/oil (1/10), reaction temperature was 50 ºC and reaction time was 80 min. Catalyst concentration was found the most efficient parameter according to Taguchi method. Finally, the yield of produced waste cooking oil methyl ester was up to 98 % with the optimal conditions of the control parameters which were obtained by Taguchi method. As a result, it is thought that waste cooking oil that has many negative effects in terms of environment can be utilized as an economic and renewable energy source.

Key Words: Waste cooking oil, Biodiesel, Transesterification, Taguchi method.

INTRODUCTION

The energy demand is increasing in the world. According to literature the stock of fossile fuels that complies the 70 % of world energy demand, will be exhausted by 40-50 years. Biomass has the most technical potential in the new and renewable energy sources. Biomass is biological originated, non-fossile organic material mass. Growing population and energy demand brings up some facts like CO_2 emission values are increased to 360 ppm that is far above the obligated values 180-280 ppm. In last 25 years atmospheric CO_2 concentration increased 27 % and that cause 0.5 ºC increase in world temperature[1]. The most important alternative biomass originated diesel engine fuel is biodiesel. Biodiesel is renewable so that it can make CO_2 participate in the photosynthesis circle. By the way the effects of biodiesel fuel on the production of greenhouse gases are minimized.

Oil shortage in food industry all over the world cause difficulties for the necessary oil used for biodiesel production. Therefore non edible oils and waste cooking oil are primarily used in the biodiesel production. Waste cooking oil has ecotoxic properties and they cause pollution in the environment make harmful effects on live. Vegetable or animal originated oils in waste water cause decrease in oxygen of water and defects the live primarily fishes[2]. Discarding the frying oil on time in food processing chain is important for both human health and environment and protection of raw material suitable for biodiesel production. Environmentalist property of biodiesel is based on both transportation and agricultural process. High viscosity cause burning, injection and corrosion in materials on the engine. Several modification techniques used for getting rid of the mentioned problems and the viscosity of the oil was decreased to a lower degree. The modification techniques are dilution, pyrolysis, microemulsion and transesterification[3]. The most common technique was transesterification. The oil used as a raw material in transesterification, esterificates with a monohydric alcohol (methanol, ethanol) and a catalyst and gives fatty acid as main product and glycerine. On the other hand as a byproduct mono and di glycerides and free fatty acids are composed. Alkali catalyzed transesterification is preferred because it is faster and more efficient than acidic catalyzed transesterification[4]. The mechanism of the transesterification process is shown in Fig. 1. Commercial and domestic waste oils are used by conversion to fatty acid esters and their usage as an alternative diesel fuel is an advantage for both human and environment health. The transesterification reaction of waste cooking oil is effected by free fatty acid ratio, water content, chemical structure of alcohol, catalyst type, reaction temperature and reaction time[5].

In this study, biodiesel production with using alkali catalyzed transesterification of waste cooking oil is aimed. Molar ratio alcohol/oil, catalyst concentration, reaction temperature and reaction time was chosen as control parameters. Taguchi experimental design provided optimization in para-

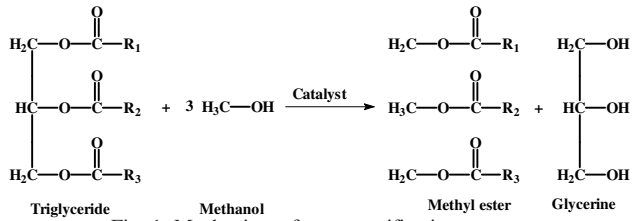

Fig. 1. Mechanism of transesterification process

meters by electing 81 experiments to 9 experiments and the conditions for maximum ester conversion.

EXPERIMENTAL

Waste cooking oil was provided by a local municipality gathered from local restaurants. Dry methanol (Labkim, Istanbul) and potassium hydroxide (Merck, Germany) was used for transesterification. Analytic scale (AND SX-200) was used for scaling. Transesterification process were made in rotary evaporator (Buchi). Produced methyl ester centrifuged by NUVE NF400 centrifugation.

Production of waste cooking oil methyl ester: Some experiments are made to determine the optimum reaction conditions for maximum ester yield from waste cooking oil; 1/8, 1/10 and 1/12 molar ratio alcohol/oil; 50, 55 and 60 ºC reaction temperatures, 0.5, 1.0 and 1.5 % potassium hydroxide; 40, 60 and 80 min reaction time are detected as optimum conditions.

In each experiment, potassium hydroxide with different amounts are solved in suitable amounted methanol and added to 100 g oil put in the flask of rotary evaporator. Heating bath is conditioned to obtained temperature and for the reaction time the rotary evaporator worked at 600 rpm. At the end of the reaction time methyl ester is put into a separating funnel and hold for 12 h. Phase separation was clear and district after the holding time and methyl ester was the upper phase. Glycerin taken out and methanol can be connected to methyl ester is removed at rotary evaporator in 320 mbar vacuum. Furthermore, methyl ester was put again into a separating funnel and washed with warm pure water five times that cause removal of soap and excessive methanol. Excessive water content was also removed in rotary evaporator at 350 mbar vacuum and treated same as soap removal. On the last stage particles hanged in are settled by centrifugation in 4200 rpm for 40 min. Obtained methyl ester was put into glass boxes and hold in cool conditions. Biodiesel analyses are made in TUBITAK Marmara Research Center.

Physico-chemical characteristics: The density was measured with a densimeter. The colour was determined by Lovibond method of AOCS, Cc 13e-92[6] using a glass cell with an optical path length of 153 mm with PFX 880 Tintometer. The pH value was measured with a digital pH meter (Hanna pH 211). Dry matter was determined by oven drying at 105 ºC to the constant weight[7]. FFA content, peroxide value (POV) and iodine value (IV) were determined using AOCS methods, Ca 5a-40[8], Cd 8-53[9] and Cd 1-25[10], respectively.

The degree of unsaturation (DU) was determined as described by Porzucek and Raznikiewicz[11] using the following equation with computed values obtained from GLC after comparison with reference standards:

$$DU = \frac{1\times(\text{wt \% MUFA}) + 2\times(\text{wt \% DUFA}) + 3\times(\text{wt \% PUFA})}{100}$$

where MUFA: represents monounsaturated fatty acid; DUFA: diunsaturated fatty acid and PUFA: polyunsaturated fatty acid.

The refractive index was determined using an Abbe refractometer (WYA Abbe refractometer, Ningbo Yuda Import & Export Co. Ltd., China) at 20 ºC[7].

Fatty acid profile determination: Fatty acid methyl esters (FAMEs) were prepared from the oil samples according to a laboratory protocol described previously[10,12]. Briey, 1 mg of oil was reacted with 0.1 mol/L NaOHeMeOH for 5 min, followed by reacting with 1.1 mol/L HCleMeOH for 5 min at ambient temperature. After adding water to stop the reaction, FAMEs were extracted with iso-octane. GC analysis was conducted with a Shimadzu GC-2010 equipped with a FID and a Shimadzu AOC-20i autosampler (Shimadzu, Columbia, MD). A fused silica capillary column SP™ -2380 (30 m × 0.25 mm with a 0.25 mm film thickness) from Supelco (Bellefonte, PA) was used with helium as the carrier gas at a ow rate of 0.8 mL/min. Injection volume was 1 mL at a split ratio of 10/1. Initial temperature was 142 ºC and increased 6 ºC/min to 184 ºC, held for 3 min and then increased 6 ºC/min to 244 ºC. Individual fatty acid methyl esters were identified by comparing their retention times with those of FAME standards. Area under each fatty acid peak relative to the total area of all fatty acid peaks was used to quantify the fatty acids identified. Results are reported as g fatty acid/100 g total fatty acids[12]. All samples were analyzed in duplicate.

Analysis of waste cooking oil methyl ester: Gas chromatography analysis of waste cooking oil methyl ester was constructed using the gas chromatography (Agilent 6890N). Determination of ester content of biodiesel samples were made according to the standard method DIN EN 14 103 (2003-10). Free and the total glycerol content, mono-di and triglyceride content of the biodiesel samples were determined by gas chromatography apparatus according to the standard method DIN EN 14 105 (2003-10).

Design of experiment for the optimisation of transesterification of waste cooking oil: The design of the experiment *via* the Taguchi method uses a set of orthogonal arrays for performing of the fewest experiments. Performance criteria in Taguchi experimental design is Signal to noise ratio (S/N) and used for evaluating the accuracy. High S/N ratio expresses the clearing off from external factors. S/N ratio calculated according to three standard condition; Larger the better, smaller the better and nominal the best[13].

In this study Taguchi method with orthogonal arrays are embraced and the effects of the parameters below on waste cooking oil methyl ester (WCOME) catalyst concentration, molar ratio of alcohol to oil, reaction temperature and reaction time are detected. Four parameters and three levels for the experimental study is listed in Table-1.

RESULTS AND DISCUSSION

Physico-chemical properties of waste cooking oil: Physico-chemical properties of waste cooking oil are listed in Table-2.

TABLE-1
DESIGN EXPERIMENTS WITH FOUR PARAMETERS AT THREE-LEVEL FOR THE PRODUCTION OF WASTE COOKING OIL METHYL ESTERS

Parameters	Levels		
	1	2	3
(A) Catalyst concentration (wt %)	0.5	1	1.5
(B) Molar ratio alcohol/oil	1/8	1/10	1/12
(C) Reaction time (min)	40	60	80
(D) Reaction temperature (ºC)	50	55	60

TABLE-2
PHYSICOCHEMICAL PROPERTIES OF WASTE COOKING OIL

	Waste cooking oil
Density (g/mL)	0.825
Colour, 5,25"	6.2R-70.0B
pH	6.14
Free fatty acid (g/100 mL)	0.7
Peroxide value (kg O_2)	680
Kinematic viscosity (mm^2/s)	37.56
Acid value (mg KOH/g)	1.4
Refractive index	1,472

Density of waste cooking oil was 0.825 g/mL. Free fatty acid content was about 0.7 g/100 mL in terms of oleic acid. Refractive index value of oil was 1.472. pH values were determined as 6.14 and peroxide value was about 680 kg O_2. Kinematic viscosity of waste cooking oil was also determined as 37.56 mm^2/s.

Fatty acids composition of waste cooking oil: Vegetable oils are composed of saturated and unsaturated fatty acids. The fatty acid composition of the waste cooking oil used in this study was given in Table-3.

TABLE-3
FATTY ACIDS COMPOSITION OF WASTE COOKING OIL

Fatty acids	Fatty acid composition (wt %)
Palmitic (C16:0)	5.76
Stearic (C18:0)	3.12
Behenic (C22:0)	0.66
Palmitoleic (C16:1)	0.37
Oleic (C18:1)	47.22
Linoleic (C18:2)	41.68
Gadoleic (C20:1)	0.19
Others	1

After the fatty acid composition analysis, waste cooking oil was found as composed from saturated 10.39 % and unsaturated fatty acids 89.61 %. Oleic acid (C18:1) was the most abundant unsaturated fatty acid and was found at amounts of 47.22 %, linoleic acid (C18:2) was the follower as amount *ca.* 41.68 %. In terms of saturated fatty acids the most dominant acid was palmitic acid (C16:0) at amount of 5.76 %. In waste cooking oil some saturated fatty acids was found less amounts such as, margaric (C17:0), arachidic (C20:0) and lignoseric acid (C24:0). On the other hand as unsaturated fatty acid palmitoleic acid (C16:1), linolenic acid (C18:3) and erucic acid (C22:1) were also found in little amounts.

Analysis of waste cooking oil methyl ester: Fatty acid methyl esters (FAME) of waste cooking oils produced in optimum conditions are given in Table-4.

TABLE-4
COMPOSITIONS AND FAMEs CONTENTS PRODUCED UNDER THE OPTIMAL CONDITIONS

FAME	Composition (%)
Myristic acid methyl ester (C14:0)	0.23
Palmitic acid methyl ester (C16:0)	4.76
Margaric acid methyl ester (C17:0)	17.62
Stearic acid methyl ester (C18:0)	2.78
Oleic acid methyl ester (C18:1)	38.25
Linoleic acid methyl ester (C18:2)	34.03
Linolenic acid methyl ester (C18:3)	0.08
Arachidic acid methyl ester (C20:0)	0.22
Gadaloic acid methyl ester (C20:1)	0.20
Behenic acid methyl ester (C22:0)	0.28
Erucic acid methyl ester (C22:1)	0.56
Nervonic acid methyl ester (C24:1)	0.21
Lignoceric acid methyl ester (C24:0)	0.36
Total	100.00
FAME contents (%)	97.0

After the fatty acid methyl ester analysis oleic acid methyl ester (C18:1) was the most abundant unsaturated fatty acid methyl ester and was found at amounts of 38.25 %, linoleic acid methyl ester (C18:2) was the follower as amount about 34.03 %. In terms of saturated fatty acid methyl ester the most dominant acid was palmitic acid methyl ester (C16:0) at amount of 4.76 %. In waste cooking oil some saturated fatty acid methyl ester was found less amounts such as, margaric acid methyl ester (C17:0), arachidic acid methyl ester (C20:0) and lignoseric acid methyl ester (C24:0). On the other hand as unsaturated fatty acid palmitoleic acid methyl ester (C16:1), linolenic acid methyl ester (C18:3) and erucic acid methyl ester (C22:1) were also found in little amounts.

Determination of optimal experimental condition by Taguchi method: The experiment was based on the Taguchi orthogonal array (OA) L9 method. Four variables (catalyst concentration, molar ratio alcohol/oil, reaction temperature and reaction time) at three levels were used to design the experiment in MINITAB 15. Taguchi method based on OA reduces variance for the experiment with optimum setting of the control parameters. To identify the combined effect of catalyst concentration, molar ratio alcohol /oil, reaction temperature and reaction time on yield, the S/N ratio of the Taguchi method, (which is log functions of desired output) was used for data analysis and prediction of optimum parameters. High ratio of waste cooking oil conversion is preferred so that the "larger the better" S/N ratio was chosen[14].

According to the analysis for the case of 'larger-the-better', the mean squared deviations (MSD) of each experiment were evaluated using the following eqn. 1:

$$MSD = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{1}{y_i}\right)^2 \quad (1)$$

where, n is the number of repetitions of each experiment and y_i is the yield of waste cooking oil methyl ester. The S/N is used to calculate the performance statistics values and contribution ratios of each parameter. Thus the combination of design of experiments with optimisation of control parameters to obtain best results is achieved in the Taguchi method. Then, the S/N ratio was evaluated using the following eqn. 2:

$$\frac{S}{N}\text{ratio} = -10\log(\text{MSD}) \quad (2)$$

The contribution of an experimental parameter was calculated from the maximum difference in the values between the mean S/N ratios at each level. The order of influence of the parameters in terms of the yield of waste cooking oil methyl ester was; A(catalyst concentration) > B(molar ratio alcohol/oil) > C(reaction time) > D(reaction temperature).

The effect of individual parameters at different levels on the yield of waste cooking oil methyl ester is shown in Fig. 2. A larger mean S/N ratio indicates a greater effect of the control parameter at that level on the yield of waste cooking oil methyl ester; the catalyst concentration was the most influential parameter on the yield of waste cooking oil methyl ester. The greatest increase in the S/N ratio on the yield of waste cooking oil methyl ester was achieved from 0.5 to 1.0 wt % for the sample level further increases were not significant above the 1.5 wt % sample level. The numerical value of the maximum point in each graph indicates the optimum range of the experimental conditions. Therefore, the optimum conditions for the greatest yield of waste cooking oil methyl ester were $A_1B_2C_3D_1$. In order words, based on the S/N ratio, the optimal parameters were A (catalyst concentration) at level 1 (0.5 wt %), B (molar ratio alcohol/oil) at level 2 (1:10), C (reaction time) at level 3 (80 min) and D (reaction temperature) at level 1 (50 ºC).

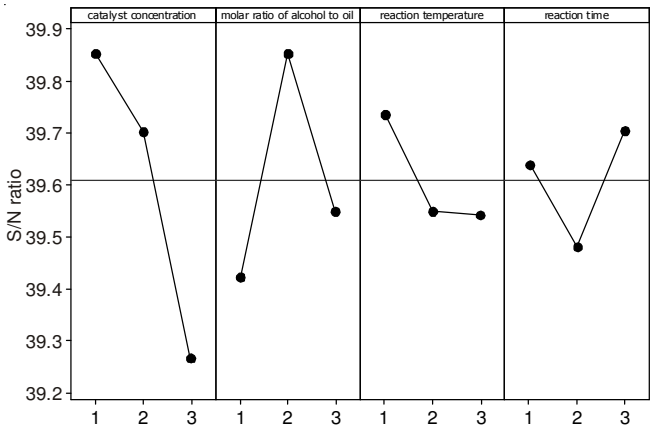

Fig. 2. Effects of each parameter at different levels on the yield of waste cooking oil methyl ester

A better feel for the relative effect of the different welding parameters (catalyst concentration, molar ratio alcohol/oil, reaction time and reaction temperature) on the waste cooking oil methyl ester was obtained by decomposition of variance, which is called analysis of variance (ANOVA)[13]. The relative importance of the welding parameters with respect to the waste cooking oil methyl ester was investigated to determine more accurately the optimum combinations of the welding parameters by using ANOVA. According to ANOVA results catalyst concentration was the most effective factor on fatty acid methyl ester yield, reaction temperature was the least effective factor. The best experiment that made the maximum conversion ratio in obtained fatty acid methyl ester was $A_1B_2C_3D_1$. The confirmation experiment that made in same condition showed a conversion ratio *ca.* 98 %. As seen in Fig. 3 the differences between 1 and 2 level catalyst concentration was little and usage of 1 % for the 0.5 % showed similar optimum results.

Conclusion

In this study, the maximum waste cooking oil methyl ester production with the help of Taguchi experimental design and ANOVA variance analysis was provided and the importance level of each parameter was determined. The catalyst concentration, molar ratio alcohol/oil and reaction time were found to be significant parameters affecting the production of waste cooking oil methyl ester. The contribution of the catalyst concentration on the production process was larger than that of any other parameter. Reaction temperature parameter was the least effective parameter. Parameters selected for the waste cooking oil methyl ester production and their effective levels are used for production and maximum methyl ester conversion was performed. Using waste cooking oil in biodiesel production in terms of economic value has advantages such as: preventing the illegal and unhealthy places, being equipment for the fight against global warming. In terms of biodiesel production being low cost raw material constitutes advantage for waste oil. Providing continuous supply to the biodiesel production plants, waste cooking will cause continuous production in biodiesel industry.

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