Microwave Irradiation Application in Biodiesel Production from Promising Biodiesel Feedstock: Microalgae (*Chlorella protothecoides*)

N. Azcan, O. Yilmaz

***Abstract*—Microwave irradiation effect on transesterification reaction of the new generation biofuel resource, microalgae, was studied. Experiments were conducted in order to evaluate the effects of reaction variables such as catalyst amount (1-1.5% w/w), oil:methanol molar ratio (1:6-1:10), and time (5-20 min) on methyl ester content of biodiesel. A comparative study on heating system was performed to show energy-efficiency of microwave-accelerated transesterification reaction. Suitable transesterification reaction conditions were determined as 65ºC, 1 wt.% KOH, 5 min, 1:8 microalgae oil:methanol molar ratio using microwave heating system. At these conditions fatty acid methyl ester content was determined as 96.54%. The results show that microwave heating has effectively reduced the reaction time from 210 min to 5 min.**

***Key words*—Microwave irradiation, Microalgae oil, Transesterification, Biodiesel**

1. INTRODUCTION

Biodiesel, a common term for long chain alkyl esters, is a renewable, biodegradable, and non-toxic biofuel that shows great promise. It is derived from the transesterification of mono-, di- and tri-acylglycerides (TAGs) [1]. Biodiesel fuel can be produced by transesterification of virtually any triglyceride feedstock. This includes oil-bearing crops, animal fats, and algal lipids. The literature contains hundreds of references of biodiesel production from a wide variety of feedstock's [2]. Raw material availability of raw vegetable oil is being recently a critical issue for the biodiesel production. Most of biodiesel is produced from edible vegetable oils. There is concern that at anticipated future production levels of the use of edible oils for fuel production will compete significantly with food uses. This would result in undesirable increase in food and biodiesel costs, a particularly damaging occurrence in the case of biodiesel, which, even at current prices, cannot compete with petroleum fuel on an economic basis.

Feedstock expense is the major contributor to the cost of biodiesel production. In order to solve this problem, industries use waste vegetable oil and grease and animal fats from poultry to produce biodiesel.

In addition, researchers are developing certain crops with high oil content just for the production of biodiesel or looking for new sources to produce biodiesel [3].

Microalgae have been highlighted as a promising alternative and renewable feedstock source for biofuels (Figure 1) since they have high photosynthesis efficiency, tolerance for poor quality water, biomass productivity, and growth rate when compared with other energy crops [4, 5, 2, 6]. Non-requirement of arable land for microalgal culture makes their growth without conflict with food production [7].

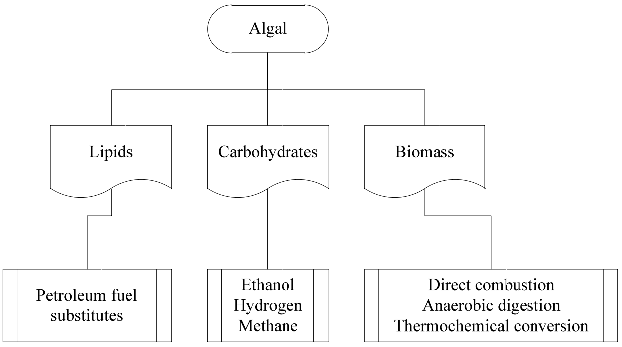

Fig. 1. Five commonly studied algal components or products useful for alternative fuels

Microalgae can produce both biofuels and valuable co-products such as omega-3 and several metabolites of economic interest, such as carotenoids (e.g., astaxanthin, lutein), vitamin E (alpha–tocopherol), and poly unsaturated fatty acids (arachidonic and γ linoleic). Thus, they have a large potential for feed, food, cosmetics, and pharmaceutical industries, which makes their conversion to bio-diesel cost efficient [8, 9].

Various methods have already been used for biodiesel production from microalgae biomass. A process containing of extraction followed by transesterification was performed. Lipid extraction consists of different techniques such as Soxhlet extraction [10], ultrasonification (chloroform, methanol mixture, methanol) [5], supercritical fluid extraction [8]. Transesterification reaction was performed in the presence of different catalyst such as acid [11], alkali and enzymatic [8, 5].

The short reaction times and expanded reaction range that is offered by microwave assisted organic synthesis are

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suited to the increased demand in industry [12]. In general, most organic reactions have been heated using traditional heat transfer equipment such as oil baths, sand baths and heating jackets. These heating techniques are, however, rather slow and a temperature gradient can develop within the sample. In addition, local overheating can lead to product, substrate and reagent decomposition. In contrast, in microwave dielectric heating, the microwave energy is introduced into the chemical reactor remotely and direct access by energy source to the reactor vessel is obtained. The microwave radiation passes through the walls of the vessel and heats only the reactants and solvent, not the reaction vessel itself [12].

Microalgae oil was used in this study in order to obtain biodiesel by transesterification reaction under microwave irradiation which is effective in accelerating the reaction rate. Microwave effect on the transesterification reaction is twofold: (1) enhancement of reaction by a thermal effect, and (2) evaporation of methanol due to the strong microwave interaction of the material [13].

2. EXPERIMENTALS & METHODS

2.1. *Materials*

Microalgae oil, *Chlorella protothecoides*, was provided by Soley Institute (Istanbul, Turkey). Methanol, potassium hydroxide, pyridine and *N*-methyl-*N*-trimethysilyltrifluoroacetamide (MSTFA) were supplied from Sigma-Aldrich. Standards of fatty acid methyl esters were purchased from Accu Standards.

2.2. *Equipment*

Microwave assisted transesterification experiments were conducted at Start S model microwave unit, supplied from Milestone Company-Italy. The system (Fig. 2) was equipped with a reflux condenser, a magnetic stirrer bar and a non-contact infrared continuous feedback temperature system which allows continuous stirring and constant temperature control.

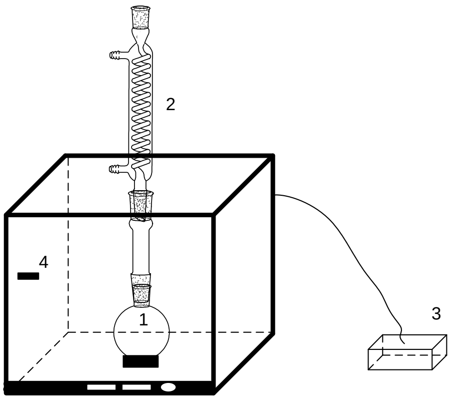

Fig. 2. Microwave synthesis unit; 1) glass reactor; 2) condenser; 3) control unit; 4) infrared temperature sensor

Fatty acid composition of microalgae oil and methyl ester content of biodiesel were determined by Agilent 6890N Gas Chromatography apparatus equipped with flame ionization detector.

2.3. *Experimental Procedure*

Transesterification reactions were carried out using heating system (microwave synthesis unit, water bath as conventional heating) and without heating.

Catalyst was dissolved in methanol. When the oil was heated to desired temperature, prepared solution was added into the reactor. The reaction was captured by immersing the mixture in an ice bath then centrifuged at 4000 rpm for 10 min and the top methyl ester phase was separated from glycerol phase. Upper layer was washed with deionized water in order to remove impurities.

2.3.1. *Transesterification reaction assisted by microwave heating*

Transesterification reactions were conducted at microwave synthesis unit in the presence of KOH (1.0-1.5% by weight of oil) at 65^{o}C temperature. Reaction conditions are given in Table 1.

Table 1. Reaction conditions

Time min	**Oil:methanol molar ratio**	**Catalyst amount wt.%**
5	1:6	1.0
10	1:8	1.5
15	1:10	-
20	-	-

2.3.2. *Reaction at room temperature*

Transesterification reactions were performed at 25^{o}C, using various oil:methanol molar ratio (1:6, 1:8, 1:10) and time (60, 120, 180, 240, 300 min) in the presence of 1wt.% KOH.

Magnetic stirrer bar was used during the reaction.

2.3.3. *Conventional heating system*

Transesterification reactions were done at 65^{o}C, 1:8 oil:methanol molar ratio 210 min in the presence of 1wt.% KOH.

2.4. *Analytical Methods*

2.4.1. *Determination of physicochemical properties of microalgae oil*

Relative fatty acid composition of microalgae oil was determined as methyl esters of fatty acid by gas chromatography analysis using Agilent 6890N gas chromatography apparatus with HP-Innowax column (60 mL × 0.25 mm ID × 0.25 µm film thickness) after converting fatty acids into methyl ester forms using 14% BF_3 in methanol [14]. A necessary procedure associated with this analysis is lipid derivatization. This process changes the volatility of lipid components, and improves peak shape and thus provides better separation [15]. Helium was used as a carrier gas at a flow rate of 1.0 mL/min. Temperature program was started at 60°C, heated at 4°C/min to 220°C and heated to 240°C at 1°C/min, staying at this temperature for 10 min [16, 17].

Relative density, viscosity, saponification number, acid value, peroxide value and iodine value of microalgae oil were determined according to standard methods [14, 18].

2.4.2. Determination of ester content

Biodiesel purity is defined as methyl ester content of biodiesel. The methyl esters were firstly derivatized by N-methyl-N-trimethysilyltrifluoroacetamide (MSTFA) at 25°C, for 15 min which is known as silylation. Silylation is the most common method used to derivate organic compounds containing active hydrogen atoms (e.g. -OH, =NH, $-NH_2$, –SH and –COOH), which results in products with reduced polarity, enhanced volatility and increased thermal and catalytic stability necessary for optimal sensitivity and resolution of various components in mixtures by GC analyses. Therefore the methyl esters obtained from the transesterification of microalgae oil were reacted with MSTFA at 25°C, for 15 min. After silylation, the methyl esters, MG, DG, TG and ester content were identified using gas chromatography (Agilent 6890N) equipped with DB-5HT column (15 m × 0.32 mm ID × 0.10 µm film thickness) and flame ionization detector. Temperature program was started at 50°C, heated at 15°C/min to 180°C and heated to 230°C at 7°C/min, then heated at 10°C/min to 370°C, staying at this temperature for 20 min [16, 17].

2.4.2.1. Fuel properties of biodiesel

Physical properties of biodiesel such as relative density, viscosity, flash point, heating value and ester content were determined using standard test methods according to EN 14214.

2.4.3. Estimation of minimum heat energy consumption

The minimum heat energy consumption during maintaining reaction temperature could be defined to heat dissipation of the reactor to the surrounding air. The heat dissipation was estimated by the lumped capacitance method which may be used to determine the variation of the temperature with time [19, 20, 21]. If there is no external heat supply, because no temperature gradient exists on the material mixture due to strong stirring, transient temperature variation is determined by the heat dissipation as following,

$$-hA_s(T - T_{amb}) = mc\frac{dT}{dt} \tag{1}$$

The left side of equation 1 is the heat dissipation of the reactor. If the constant hA_s is obtained, the heat dissipation can be obtained as the temperatures of reaction and surrounding air. From equation 1, transient temperature variation becomes

$$T = (T_i - T_{amb})\exp\left[-\frac{hA_s}{mc}t\right] + T_{amb} \tag{2}$$

The constant hA_s could be estimated by fitting the experimental result to the equation 2 [19].

3. RESULTS & DISCUSSION

The fatty acid composition of the microalgae oil was determined by gas chromatography. It was found that the fatty acids of the oil were composed primarily of 65.39% oleic acid, 20.89% linoleic acid, 6.23% linolenic acid, 4.99% palmitic acid, 1.66% stearic acid, 0.55% arachidic acid, 0.23% palmitoleic acid, 0.15% lauric acid. Fatty acid composition of microalga is in good agreement with literature [22].

The physicochemical properties of microalgae oil are given in Table 2.

Table 2. Physicochemical properties of microalgae oil

Moisture %	**Relative Density**	**Iodine Index**	**Acid Value**	**Peroxide Value**
0.04	0.9127	115.39	0.22	11.95

Physicochemical properties of microalgae oil are in the range of the literature [22].

Biodiesel conversion (methyl ester content) was determined under different time, catalyst loading, temperature, and oil:methanol molar ratio and heating system in order to minimize the reaction time with a maximum conversion.

3.1. Microwave Heating

Two different catalyst:oil weight ratios (1.0 and 1.5%) were used for transesterification at 65°C, 1:6 oil:methanol molar ratio, 15 min. 1% KOH gave the highest biodiesel purity (96.25%). So that in further experiments 1.0 wt.% KOH was used.

Combined effect of time (5-20 min) and oil:methanol molar ratio (1:6-1:10) was investigated. Experimental results are shown in Fig 3.

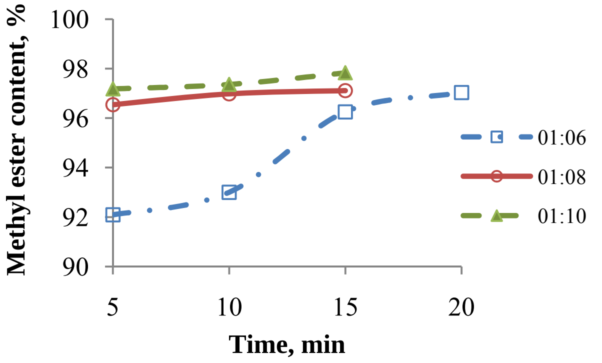

Fig. 3. Effect of time and oil:methanol molar ratio on biodiesel conversion

According to Fig. 3, oil:methanol molar ratio has significant effect on fatty acid methyl ester content of biodiesel (conversion). 96.7% methyl ester content of biodiesel was obtained using 1:6 oil:methanol molar ratio after 20 min reaction time. Similar purity (96.54%) was achieved after 5 min using 1:8 oil:methanol molar ratio. Therefore, suitable time and oil:methanol molar ratio were determined as 5 min and 1:8, respectively.

3.2. *Room Temperature Reactions*

Transesterification reactions were done at room temperature to compare with the results obtained by microwave heating. Reactions were performed at different time (60-300 min) and oil:methanol molar ratio (1:6-1:10) at 25°C, 1%wt. KOH. Experimental results are shown in Fig 4.

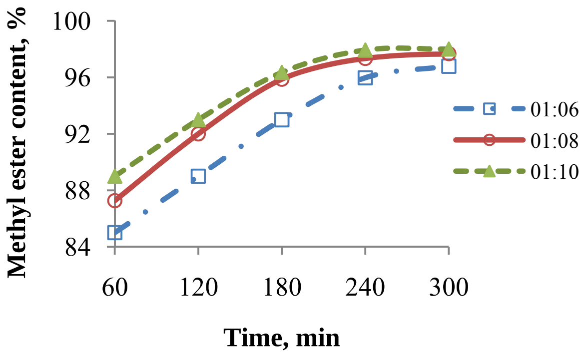

Fig. 4. Effect of time and oil:methanol molar ratio on biodiesel conversion

As it is seen in Fig. 4, conversion increases with time up to 240 minutes than keep constant. Conversion increases from 95.97 to 97.34% with the oil:methanol molar ratio up to 1:8 which is almost the same with 1:10.

97.34% conversion was obtained at 240 min which meet the EN 14214.

3.3. *Conventional Heating*

96.94% methyl ester content was obtained using 1:8 oil:methanol molar ratio, 1wt.% KOH at 65°C and 210 min reaction time.

3.4. *Fuel Properties of Biodiesel*

Comparison of fuel properties of microalgae oil with standard value are given in Table 3.

Table 3. Fuel properties of resulting biodiesel from microalgae oil

Properties	**Biodiesel**	**Standard Values**
Relative density	0.8772	0.86-0.90
Viscosity (mm^2/s, 40°C)	4.51	1.9-6.0
Moisture content (%)	0.08	0.05 (max)
Pour point (°C)	-20	0 (max)
Cloud point (°C)	-4	-
Heating value, J/g	38,339	35,000-40,000

Obtained values are coherent with EN 14214.

3.5. *Microwave Energy Consumption*

Microwave energy consumption was calculated according to method used by Kim *et al*. [19]. The absorbed microwave power is shown in Fig. 5.

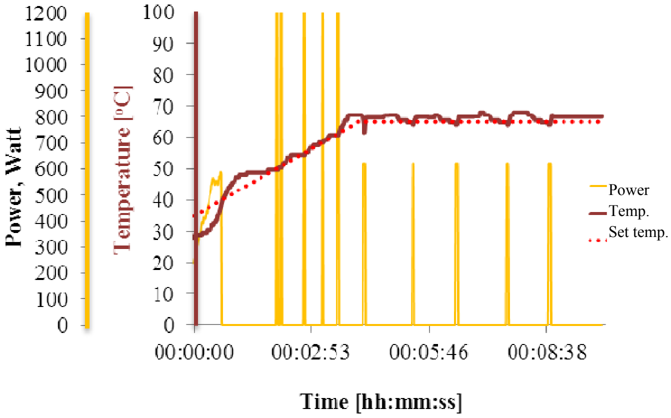

Fig. 5. Absorbed microwave power and temperature profile (65°C, 1 wt.% KOH, 1:8 oil:methanol molar ratio, 5 min)

The energy consumptions were obtained in separated two stages of temperature rise and maintenance for convenience as shown in Table 4.

Table 4. Energy consumption of microwave synthesis unit

	Microwave	**Electricity[a]**	**Minimum Heat Demand**
TR (KJ)	12.19	20.33	7.52[b]
TM (W)	11.76	19.60	6.77[c]
Total (KJ)[d]	15.72	26.20	92.82

[a] Electric energy (or power) consumption for microwave generation: Only 60% electric energy converts to microwave.

[b] Estimated minimum heat energy demand calculated by heat capacities of 29.9922 g-microalgae oil, 9 g-methanol, 0.2961 g-catalyst, 90.2528 g-glass vessel. The initial and final temperatures were 25°C and 65°C, respectively.

[c] Heat loss of the reactor to the surrounding air calculated by the measured heat transfer coefficient of the reactor at 65°C with the ambient temperature of 25°C.

[d] Energy consumption until conversion of more than 96.5% could be obtained; the reaction times of 5 min for microwave heating and 210 min for the conventional heating were used.

The energy consumption at the stage of temperature maintenance (temperature profiles inside the reactor during the synthesis) was shown by the unit of power (watt). Total energy consumption could be determined from the reaction time of the microwave heating. The microwave power for maintaining temperature was averaged of the absorbed microwave power during the reaction [19]. The energy of microwaves comes from electrical energy that is converted by a power supply to high voltages that in turn are applied to the microwave power tube or generator [23]. Therefore, the energy consumption of electricity should be compared with the one of the conventional heating in order to show the energy-efficiency. The electric energy consumption was calculated by dividing the measured microwave energy consumption by 0.60 considering typical energy conversion rates of high-voltage power supply and the magnetron to 0.80 and 0.75, respectively [19].

The estimated minimum heat energy demand for temperature rise was calculated by heat capacities of the reactor composed of oil of 29.9922 g, methanol of 9 g, catalyst of 0.2961 g, and glass vessel of 90.2528 g. The other energy consumptions such as evaporation of methanol, reaction energy and heat loss did not consider here. The minimum heat demand for the temperature maintenance was obtained from a measurement of heat dissipation from the reactor to the surrounding air. Heat transfer constant of hA_s was determined as 0.1708 W/K using equation 2. The heat dissipation rate (minimum heat energy consumption) at the reaction temperature was calculated to 6.77 W.

As a result, the value of microwave energy consumption during temperature rise and maintenance is higher than the estimated minimum heat energy demand because of dielectric property of reaction mixture. A material's heating rate is governed by the amount of microwave power input to it. Power level requirements are based on the properties of the material being heated for a particular throughput and the initial and final temperatures [24]. Another reason can be caused by polarization which takes place when the effective current in the irradiated sample is out of phase with that of the applied field by a difference (termed δ). This difference defines the tangent loss factor, tan δ, often named the dissipation factor or the dielectric loss tangent. The word "loss" refers to the input microwave energy that is lost to the sample by being dissipated as heat [25].

Compared to the conventional heating method, microwave irradiation can reduce reaction time and save energy significantly due to the fast and volumetric heating effect [26]. Reaction time changes according to heating system in order to reach 96.5% conversion such as 5, 210, 240 min for microwave, conventional and room temperature, respectively.

Eventually, the electric energy consumption becomes only 28.22% of the estimated minimum heat demand Table 4.

Magnetic stirrer consumes electrical energy to mix the reactants and 630 KJ was used for 240 min.

IV. CONCLUSION

Transesterification reaction of microalgae oil in the presence of KOH was carried out using different heating systems (microwave, room temperature). The suitable biodiesel conversion (96.54%) was obtained using 1 wt.% KOH, 1:8 oil:methanol at 65°C and 5 min reaction time by using microwave heating system. 97.34% conversion was achieved with 1 wt.% KOH, 1:8 oil:methanol at room temperature (25°C) and 240 min reaction time. 96.94% conversion was found using conventional heating system at 210 min.

While there are many heating techniques such as conventional, ultrasound, water-bath; they require longer reaction times, and are energy- and cost-intensive. Microwave heating shows a promising technique for biodiesel production in a short reaction time with high product yield.

Electric energy consumption for microwave heating in this accelerated transesterification reaction was only 28.22% of estimated minimum heat energy demand of significantly reduced reaction time.

ABBREVATION

TR : Temperature rise
TM : Temperature maintenance
h : Heat transfer coefficient, Wm^2K^{-1}
A_s : Surface area, m^2
m : Mass of the materials, kg
c : Specific heat of the materials, $Jkg^{-}1K^{-1}$
T_i : Initial temperature, K
T_{amb} : Ambient temperature of the surrounding air, K
Temp : Temperature
t : Time
hh : Hour
mm : Minute
ss : Second
tan δ : Tangent loss factor

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