Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2017, 4(10):263-268**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Production of Biodiesel from Microalgae using Acid and Base Catalysts

Mehmet Recai DURGUT*, Erkan GÖNÜLOL, Birol KAYIŞOĞLU

University of Namık Kemal, Faculty of Agriculture, Department of Biosystem Engineering, Tekirdag-Turkey

Abstract Biodiesel is gaining attention as an alternative fuel to diesel engines as it is natural, eco-friendly and alternative diesel fuel which is obtained from renewable resources like animal fats and vegetables oils. In the present study, biodiesel has been produced from microalgae oil using two step catalyzed transesterification reaction acid method followed by base method. Favourable results were obtained for physiochemical analysis (density, flash point, copper strip corrosion test, viscosity, and flow cloud point) of oils in context to biodiesel standards (ASTM). A yield of 86.3% and 91.7% was obtained from microalgae oil by using two step method with a reaction mixture containing 0.5% w/w of H_2SO_4 for acid pre-treatment, 0,4% w/w of KOH.

Keywords Microalgae oil, Transesterification reaction, Biodiesel, Acid catalysts, Base catalysts

Introduction

Biodiesel is an attractive fuel for diesel engines that it can be made from any vegetable oil (edible or non edible oils), used cooking oils, animal fats as well as microalgae oils. Biodiesel, as an alternative fuel, has many benefits. Biodiesel based fuels have received considerable attention because they are renewable, non-toxic and safe to store. Furthermore, because of their oxygen content, the combustion is more complete and consequently carbon monoxide emissions are less.

Vegetable oils are promising feedstocks for biodiesel production since they are renewable in nature, and can be produced on a large scale and environmentally friendly. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel. In order to overcome these disadvantages, many researchers are interested in others feedstocks as microalgae oil.

Biodiesel feedstocks derived from microalgae and macroalgae have emerged as one of the most promising alternative sources of lipid for use in biodiesel production because of their high photosynthetic efficiency to produce biomass and their higher growth rates and productivity compared to conventional crops. In addition to their fast reproduction, they are easier to cultivate than many other types of plants and can produce a higher yield of oil for biodiesel production.

It has been proposed for many years by many researchers to use microalgae as a source of energy long before the day as an alternative energy source [25]. Microalgae, which have been produced as food additives for animal breeding for many years, have begun to be seen as an energy source in the end result of research on biomass energy accelerated by the increasing oil prices in recent years. The studies aiming to use many microalgae, also called third generation biofuels technology, as a source of energy have not been developed technologically in general due to the difficulties stemming from prosest, but limited to laboratory researches, pilot and small scale experiments.

Initially, the Solar Energy Research Institute focused on the use of algal oils as biofuels [14].Working in many countries of the world on the subject of microalgal fat is maintained in confidentiality. In addition to searching for high-fat content, the possibilities for upgrading oil content in existing species are also being explored.

Although microalgae production and harvest are relatively costly, their advantages over land plants and their ability to use water most efficiently increase the interest of researchers. Microalgae production in large volumes can be realized in inefficient places. Functional lipids such as energy source storage products, cell wall components, and fatty acids are components of all plant cells. Lipid synthesis in algae is similar to lipid synthesis in high plants [23].

Most algal oils can be used for biodiesel production. However, it is not economical to spend microalgae used for biodiesel production in the fields of medicine, food, industry, etc, in trace amounts. Microalgae with a particularly high fat content should be preferred for use in biodiesel production [18,19]. Microalgae, depending on their species, are able to produce a large number of different lipids, hydrocarbons and other complex oils [8,13].

For this reason, the project involves determining the factors that will affect the quality of biodiesel to be obtained and the biodiesel obtained from the microalgae in laboratory scale biodiesel facility in accordance with this subject.

Materials and Methods

Panel type photovoltaic reactor has been used in the research because it is easier to clean than other closed systems, ventilation process is easier and costs are lower[17, 22]. The designed panel type photoboreactor has dimensions of 100x50x10 cm [2,21].Mixing is achieved by bubbling air from the air at the bottom of the photovoltaic reactor of compressed air enriched with 1.5 - 2% CO_2 provided by the air pump. Thus microorganism cells will not suffer mechanical damage [4, 17].The water temperature throughout the experiments was kept at 25 °C, the optimum temperature for microalgae cultivation with the help of electric heater [4,27]. The pH value is adjusted to 8.22 by incorporating CO_2 gas [21].The lighting is adjusted to 12 hours of light 12 hours of darkness and is provided by external white fluorescent lamps at a density of 18 w / m^2 for lighting. The lighting panel type photovoltaic reactor was built from both sides. Studies have shown that enlightenment on both sides increases microalgae oil yield by 14%[4,5,20,24].

Nannocholoropsis sp. culture Ege Biyoteknoloji A.Ş. Company. The obtained stock culture was cultured in 250 ml Erlenmeyer flasks and grown in laboratory conditions at 500 ml, 1 L and after 5-liter jars were inoculated, they were grown in a panel-type photobioreactor. Mixing was made by hand in the production made in the Erlenmeyer. Mixing with air aid was provided in the 5 lt replenishment vessel. Nannochloropsis sp. F/2 solution will be used as nutrient medium for microalgin culture [7].

Studies have shown that algal lipid production is in a state of stagnation following the logarithmic growth phase [1,12]. For this reason, it is very important to choose the appropriate time for algae harvesting. Appropriate time was monitored daily after each inoculation to determine the values of pH, optical density (OD) and dry weight. Algae reaching the stagnation phase were centrifuged at 4000 rpm for 10 minutes using Hettich Universal 32-R model centrifuge at the end of the production period and the nutrient media above was removed. After this process, purified water was added to the algal biomass three times and centrifuged three times to clear the remaining traces of nutrient media [3].

To measure optical density throughout the Nannocholoropsissp experiments, cultures were homogenously mixed on a daily basis and then 3 ml samples were taken with a pipette. Scratched samples were placed in quartz tubes and read at a wavelength of 750 nm on a visible spectrophotometer [10]. For each measurement, 4 replicates were applied. Shimadzu UV-1208 spectrophotometer was used to measure the optical density.

The algae, centrifuged for drying, were placed in pre-incubated petri dishes and dried at 100°C for 12 hours [9]. After the drying process, weighed again and the petri dish was removed to find dry weights of the algae.

Dried algae for lipid extraction are placed in Bead-beater tubes. The beads were run for 3 minutes at 4800 rpm in beater to disrupt the algae [9]. Centrifuge tubes were centrifuged at 4000 rpm for 5 minutes by adding hexane as a fat solvent onto algae. As a ratio, 1 g of dry sample was mixed with 6 mL of hexane and allowed to stand for 24 hours, then filtered through filter paper to separate the alum cake from the oil hexane mixture. Hexane and lipid mixture were measured by gravimetric measurement of residual algal lipids by volatilizing hexane at 60 ° C [3].

Figure 1: Harvested and dried algae

Biodiesel from Algae Oil

The basic processes in both methods can be explained as feedstock pretreatment, preparation of methanol and catalyst mixture, adding the mixture to the microalgae oil in the reactor, glycerin removal, washing biodiesel and storage. Two different experiment methods have been applied to compare the effect of catalysts to be used in microalgae oils. The process steps are described in detail below.

A biodiesel unit with a reactor capacity of 500 ml is used to obtain biodiesel from the microalgae oil. The reactor is made of heat resistant Pyrex glass. The reactor is equipped with a temperature control unit that allows the temperature control to be adjusted between -20°C and + 120°C ± 0,1 and a digital controlled mechanical mixer that can be adjustable of speed (200-3000 rpm). The biodiesel production unit is given in Fig.2.

Figure 2: Laboratory scale biodiesel reactor

In order to compare the effect of the catalysts to be used in microalgae oil, two methods have been applied to be acid and base in the production of biodiesel.

Base Method

In this method, KOH was used as the catalyst. The methanol to oil ratio was adjusted to 6: 1 (mol: mol). As a basic catalyst to be used as catalyst, KOH will be 0.4% by weight of the amount of oil used. In this method, the reaction temperature is 60 ^{o}C and the duration is 90 min. Before the reaction, the oil was heated to 65 °C. During the reaction the stirring was maintained at 600 rpm [15].

Acid Method

In this method, H_2SO_4, which is an acidic catalyst as a catalyst, is used, the methanol and oil ratio is set to 9: 1 (mol / mol), the catalyst amount is 0.5% of the oil weight, the reaction temperature is 100 ^{o}C and the reaction time is 8 hours. Mixing speed is 600 rpm. No pre-heating was applied [6].

Properties of Biodiesel

The physical and chemical properties of biodiesel are identified according to standards as follows to compare the quality of biodiesel obtained by two different methods.

- Determination of biodiesel yield: The reaction result will be determined by proportioning the biodiesel and the oil used [26,11]
- Flash point specification
- Determination of kinematic viscosity
- Determination of density

- Flow cloud point
- Copper strip corrosion test

Results and Discussion

As a result of the analysis of the biodiesel samples produced in the study, the data obtained in the two methods are shown in Table-1.

Table 1: Physical and chemical properties of biodiesel produced from algal oil by two different methods

Properties	Unit	European Committe for Standardization		Biodiesel Experiments	
		Min	**Max**	**KOH**	**H_2SO_4**
Efficiency	%	90	-	91,7	86,3
Density,25°C	kg/m^3	860	900	884	893,7
Viscosity, 40°C	mm^2/s	3,5	5,0	4,8	4,65
Flash Point	°C	120	-	172	167°C
Copper Strip Corrosion	50°C'de 3h	-	1	1a	1a
Cloud Point	°C	-	-	4	6
Pour Point	°C	-	-	-2	-3

Efficiency of Biodiesel production is expected to be over 90%.This value was 91.7% (± 0.38) in the first method and 86.3% (± 0.40) in the second method. In terms of yield, the first method appears to be higher than ASTM.

Density is the measure of the fluidity of biodiesel. The density is expected to be between 860-900 kg / m^3. This value was between 884 and 893,7 kg / m^3 in both methods, respectively.

Viscosity is one of the most important characteristics of biodiesel. High viscosity fuel causes poor atomization, bad combustion, clogging of the injectors and carbon buildup in the segments. For biodiesel this value should be between 3.5-6 mm^2/s. This value was 4.8 mm^2/s in the first method and 4.65 mm^2/s in the second method. The viscosity value obtained in both methods can be accepted within the boundary measures. Copper rod corrosion values are at the desired values in both methods.

Flow and Cloud point; the conditions foreseen are the points where the crystal clouds are first seen when the gold liquids are cooled. The cloud point is a critical factor for the diesel fuels for cold air. This creates problems when using very cold conditions of fuels.

The raw material from which the cloud point biodiesel is obtained varies according to the properties of the oil. For example, when measured by ASTM D2500 standards, the temperature of the biodiesel obtained from rapeseed oil is -3 ^{o}C, while the value of food-grade frost is 19 ^{o}C[16]. In this study, where biodiesel was obtained using microalloys, the yield point was -2 ^{o}C and -3 ^{o}C respectively and the cloud point was 4 ^{o}C and 6 ^{o}C respectively.

Conclusion

In this project, biodiesel production from microalgae oil was provided and it was seen that the results of the analyzes made compared to the standards of European Standard Biodiesel of EN 14214 are more suitable to the standard of biodiesel produced by the first method.

The results show that it is possible to use biodiesel obtained by the first method using KOH as a catalyst at certain ratios to diesel fuel.

Acknowledgement

"This work was supported by Research Fund of the Namık Kemal University. Project Number: NKUBAP.00.24.AR.14.07". We thank you to Namık Kemal University

References

[1]. Casadevall, E, Dif, D, Largeau, C, Gudin, C, Chaumont, D and Desant, O. 1985. Studies on batch and continuous cultures of Botryococcus braunii: Hydrocarbon production in relation to physiological state, cell ultrastructure, and phosphate nutrition. Biotechnology and Bioengineering Vol. 27, pp. 286–295.

[2]. Cheng-Wu Z, Zmora O, Kopel R, Richmond A. An industrial-size flat plate glass reactor for mass production of *Nannochloropsis* sp. (Eustigmatophyceae) Aquaculture. 2001; 195:35–49.
[3]. Cirik S, E. Koru, Ş.S. Can, G. Turan, H. Tekoğul, 2011. Mikroalglerden Yenilenebilir Temiz Bir Enerji Kaynağı Olan Biyodizelin Elde Edilmesi, TUBİTAK PROJE NO: 107Y013.
[4]. Dipasmita, P., I. Khozin Goldberg, Z. Cohen and S. Boussiba, 2011. The effect of light, salinity, and nitrogen availability on lipid production by Nannochloropsis sp. Applied Microbial And Cell Physiology (2011) 90:1429–1441. DOI 10.1007/s00253-011-3170-1
[5]. Doan T. Y., B. Sivaloganathan, J.P. Obbard, 2011. Screening of Marine Microalgae for Biodiesel Feedstock. Biomass and Bioenergy, 35 (2011) 2534e2544.
[6]. Goff JM, Bauer SN, Lopes S, Sutterlin RW, Suppes JG. Acid-Catalyzed Alcoholysis of Soybean Oil. J Am Oil ChemSoc 2004;81: 415.
[7]. Guillard, R.R.L. 1975. Culture of phytoplankton for feding marine invertebrates. pp 26- 60. In Smith W.L. and Chanley M.H (Eds.) Culture of Marine Invertebrate Animals. Plenum Press, New York, USA.
[8]. Guschina, I.A. and Harwood, J.L., 2006. Lipids and lipid metabolism in eukaryotic algae. Prog. Lipid Res. 45:160–86.
[9]. Lee, S.L., Yoon, B.D., Oh, H.M., 1998. Rapid method for the determination of lipid from the green alga Botryococcusbraunii. Biotechnology Techniques, Vol. 12, pp. 553–556.
[10]. Liu ZY., Wang GC., Zhou BC., 2007. Effect of Iron on Growth and Lipid Accumulation in Chlorella vulgaris, Bioresour. Technol., 99, (2007) pp.4717–4722.
[11]. Lou W., M. Zong, Z. Duan (2008). Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts, Bioresource Technology (99), 8752-8758
[12]. McGinnis, K.M., Dempster, T.A., and Sommerfeld, M.R., 1997. Characterization of the growth and lipid content of the diatom Chaetoceros muelleri. Journal of Applied Phycology Vol. 9, pp. 19–24.
[13]. Metzger, P. and Largeau, C., 2005. Botryococcus braunii: a rich source for hydrocarbons and related ether lipids. ApplMicrobiolBiotechnol. 66:486–96.
[14]. Neenan, B., Feinberg, D., Hill, A., Mcintosh, R., Terry, K., 1986. Fuels from microalgae: Technology status, potential, and research requirements. Publ. No. SERi/SP-231-2550, Solar Energy Research institute.
[15]. Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil SocChem 1997;74:1457.
[16]. Oğut, H. veOğuz, H., 2006. Biyodizel (Ucuncu MilenyumYakıtı). Nobel Yayınları. 13-24, 169-176.
[17]. Posten, C., 2009. Design principles of photo-bioreactors for cultivation of microalgae. Eng. Life Sci. 2009, 9, No. 3, 165–177.
[18]. Ratledge, C. and Wynn, J.P., 2002. The biochemistry and molecular biology of lipid accumulation in oleaginous microorganisms. Adv. Appl. Microbiol. 51:1–51.
[19]. Ratledge, C., 1993 Single cell oils have they a biotechnological future? Trends Biotechnol 1993; 11:278–84.
[20]. Reichardt T. A., A. M. Collins, O. F. Garcia, A. M. Ruffing, H.D.T. Jones, J.A. Timlin, 2012. Spectroradiometric Monitoring of Nannochloropsis salina Growth. Algal Research 1 (2012) 22–31
[21]. Richmond A., Z. Cheng-Wu, 2001. Optimization of a flat plate glass reactor for mass production of Nannochloropsis sp. Outdoors. Journal of Biotechnology 85 (2001) 259–269
[22]. Richmond, A. and Zou, N., 1999, Effect of light-path length in outdoor flat plate reactors on output rate of cell mass and of EPA in Nannochloropsis sp., J Biotechnol, 70: 351–356p.
[23]. Sawayama, S., Inoue, S., Dote, Y., Yokoyama, S.Y., 1995. CO2 fixation and oil production through microalga. Energy Convers Manag., 36: 729–31.
[24]. Shen Y., Y. Cui, W. Yuan, 2013. Flocculation Optimization of Microalga Nannochloropsis oculata Appl Biochem Biotechnol (2013) 169:2049–2063, DOI 10.1007/s12010-013-0123-4
[25]. Thomsen, L. (2010). "How 'green' are algae farms for biofuel production". Biofuels. 1(4): 515-517

[26]. Zheng S, M. Kates, M.A. Dube, D.D. McLean (2006). Acid-catalyzed production of biodiesel from waste frying oil. Biomass Bioenergy (30), 267–272.
[27]. Zittelli G.C., L. Rodolfi and M.R. Tredici, 2003. Mass cultivation of Nannochloropsis sp. in annular reactors. Journal of Applied Phycology 15: 107–114, 2003.