

THE PLACE OF FREE FATTY ACIDS AND WATER IN BIODIESEL PRODUCTION PROCESS FROM WASTE OILS

Mehmet AKÇAY

Department of Mechanical Education, Technical Education Faculty, Pamukkale University, Denizli, Turkey

Yakup SEKMEN

Department of Automotive Engineering, Engineering Faculty, Karabük Üniversitesi, Karabük, Türkiye

İlker Turgut YILMAZ

Automotive Programme, Vocational Collage of Luleburgaz Kırklareli University, Kırklareli, Türkiye

Mustafa GÖLCÜ

Department of Mechanical Education Technical Education Faculty, Pamukkale University, Denizli, Turkey

Hilmi YAZICI

Department of Mechanical Education Technical Education Faculty, Pamukkale University, Denizli, Turkey

Abstract

Biodiesel is a fuel that used in diesel engines produced from various renewable resources (plant, animal fats, waste oils, algae, etc.) and has high potential to be an alternative to standard diesel fuel. Using waste oils which cause significant damages when they are poured to environment should be preferred rather than using edible oils as a raw material in biodiesel production. This situation has a great importance for lowering the cost of biodiesel production, protecting of edible oil source and minimizing damages of waste oils on environment. In this study, importance of used vegetable and animal oils which is specified to be waste oil was evaluated in terms of environment and biodiesel production costs. In addition, it was investigated that, the effect of free fatty acids of waste oils (FFA) and water to the biodiesel production process in the literature.

Keywords: *Waste oil, biodiesel, water, free fatty acid (FFA)*

INTRODUCTION

The facts of dependence to petroleum based fuels increasing rapidly due to rising number of the motor vehicles in the world of late years, environmental damages caused by these fuels and run out of sources, are canalized researcher to search alternative fuel sources. Recently, it is given point to biodiesel momentarily obtained from renewable sources and it is seen an alternative to diesel fuel [1-7].

Biodiesel can be getting from renewable sources as animal fats, vegetable oils and used waste oils. But using the edible oil for producing biodiesel causes rising prices comparing to diesel fuel [8,9]. Biodiesel production costs consist of %84 raw materials, %7 chemicals, %4 using water and electricity and %5 fixed outgoings [10]. It is seen that, raw materials have an important place in biodiesel production

costs. Using non edible and waste oils which are harmful for health, in producing biodiesel make considerable decreases at production costs. Besides of that, for countries like Turkey which production of fatty seed plants is limited and which provide oil needs from importation, using edible oils for biodiesel production is caused an increase at edible oil needs [8,9].

In this study, it is examined that effect of free fatty acids and water to biodiesel production process with literature is scrutinized.

RECYCLING OF WASTE OIL AS AN ALTERNATIVE FUEL IN DIESEL ENGINES

Nowadays, the most important problem of the biodiesel production is costs. Using of edible oils for raw material in biodiesel process causes an increase at costs compared to diesel fuel [8-10]. Therefore, when an eye is given to last

studies it is seen that there is a tendency to oils which are waste and have low prices, are used as raw materials [11-20].

It is estimated that about 3,2x10⁴ tons biodiesel is only produced from animal fats in USA in 2002 [21].

In Turkey, it is about 350 thousands tons animal and vegetable waste oils are occurred in a year. Recovering with these waste oils, about 35 thousands tons biodiesel and glycerin are gained a year. About 3500 thousand tons soaps are produced from glycerin which is obtained from biodiesel process and with biodiesel it is contributed to economy about 480 million Turkish Liras in a year [8,22,23]. With using these waste oils in biodiesel production it is reported that 900 thousand tons greenhouse gases (CO₂) which are thrown to atmosphere, can be reduced [8].

Turkey's diesel fuel consumption was about 12 680 018 tons in 2006 [24]. Biodiesel production with waste oil is so small near diesel fuel needs can be engrossed. But using waste oils in biodiesel production, especially water sources and water quality are protected. Living conditions of the posterities is considered, it is expressed that situation carries weight [25].

BIODIESEL PRODUCTION FROM WASTE OILS

Some features of vegetable and animal fats are developed for using them in diesel engines. With this aim, methods which are used are dilution, microemulsion, proliz and transesterification. Today the most preferred method is transesterification method [26-28].

Oils which are used in process of producing biodiesel with transesterification method are reacted with a reasonable alcohol (for example ethanol, methanol, butanol etc.) chemically [21,29,30]. To accelerate the reaction basic (alkali) (NaOH, KOH), acidic (H₂SO₄, HCl) or enzyme (biological) can be used [21,24,29,31]. New chemical compounds are form at the end of the reaction and they are named methyl esters. These esters which are obtained are known as biodiesels [29]. In general biodiesel is an alternative diesel fuel which is obtained renewable oils as vegetable, animal and used waste oils [8,29,32]. Bio word indicates to renewable and

biological fuel, diesel word indicates to available in diesel engines [21,33].

In transesterification reactions, alkali catalyzers are more referred to acidic catalyzers because alkali catalyzers have high reaction speed (about 10-15 times, require low alcohol, have high ester transformation attainability at room temperature, have low corrosion risk, etc [8,29,34].

It is stated that free fatty acids and water contents of oil which is used as raw material, have an important role in transesterification process [35]. If reaction medium has water and oil's free fatty acid level is high it is not possible using alkali catalyzer [8,33]. For this reason before passing to biodiesel production process with transesterification method, oil's features should be analyzed. In figure 1 it is seen that the effects of free fatty acid and water on transesterification of beef tallow.

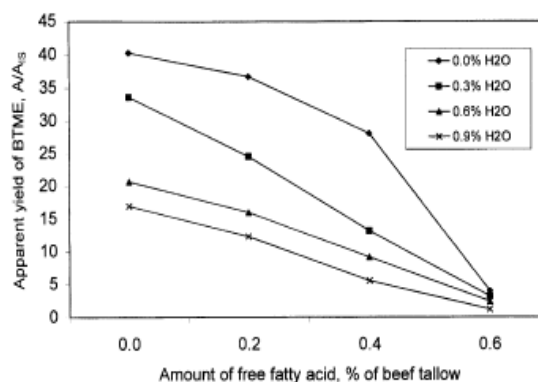


Figure 1. The effects of free fatty acid and water on transesterification of beef tallow [35]

Existence of water has more negative effect than existence of free fatty acid in transesterification process. High rate of water which is in oils is caused to saponified of reaction and decreases activity of catalyzer. Thus before passing to reaction process water content of oil is determined and oil is heated to 100-110 oC to provide water evaporates [12,33,36,37]. In figure 1 it is seen that while water proportion is increasing beef tallow methyl ester (BTME) proportion is decreasing in beef tallow transesterification reaction.

The another negative factor in transesterification process is reaction isn't occurred completely due to alkali catalyzers

reacted with oils which are including free fatty acids at high rates. Oil which has high rate free fatty acid content has a negative effect on reaction like water. Water caused to saponify during reaction and soap which is done decreases reaction efficiency because soap complicates decomposition process of biodiesel with glycerin and wash water [14,37,38]. In figure 1 it is seen that while free fatty acid proportion of oil is increasing beef tallow methyl ester proportion is decreasing in beef tallow transesterification reaction. In figure 2 it is seen that oil which has high rate free fatty acid content reacted with alkali catalyzer and formation of soap.

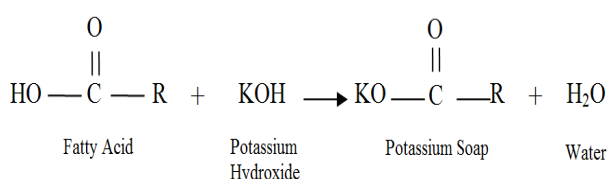


Figure 2. Formation of soap [29]

According to studies which are done by researchers, free fatty acid level of oil must be about under %1 (2 mg KOH/g) to carry out transesterification reactions with alkali catalyzer [39,40,41,42]. Otherwise free fatty acid level of oil must be decreased doing pre-curing with acidic catalyzer [7,8]. In this instance, with using acidic catalyzers (H₂SO₄ or HCl) instead of alkali catalyzers, free fatty acids turn into monoesters and free fatty acid level of oil is decreased [7,8,29,43]. In figure 3 pre-curing reaction is seen.

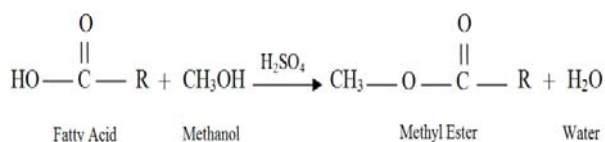


Figure 3. Pre-curing reaction [8,29]

The unit which is used for decreasing acid level at the first stage of the reaction is called pre-process unit and the unit which is used for producing biodiesel is called main process unit [8,26,38]. After free fatty acid levels of vegetable and animal oils are decreased to normal levels (%1) and water is removed from medium, it is turn to come transesterification reaction which is main process, with alkali catalyzer. As alcohol

and catalyzer proportions are determined in transesterification reaction, triglyceride proportion which doesn't reach is considered [8]. Firstly experiments which are on a small scale are done more than one for determining optimum conditions and mixture rates of reaction and it is taught more helpful that on a large scale production is made with knowledge which is obtained these experiments.

CONCLUSION

About 350 thousands tons waste oils which are based on vegetable and animal fats are approved in a year in Turkey. Pouring these waste oils to sewerage causes important damages. As a result of using waste oils as a raw material for biodiesel producing, damages on environment and biodiesel production costs are decreased to minimum.

Transesterification reaction which is done with acid catalyzed is slower than done with alkali catalyzed.

The efficiency of ester transformation in biodiesel production process is affected importantly by free fatty acid and water. Higher free fatty acid content causes to saponification and water and embarrasses ester transformation.

All at of methods can be used for biodiesel production. The most used method is transesterification method in all methods.

The potential of vegetable and animal waste oil is determined over country to use them in biodiesel production and this process is encouraged by government.

It must be taken heed of using waste oils in biodiesel production process instead of edible oils and given weight to developing biodiesel production process.

REFERENCE

- [1] Kansedo, J., Lee, K.T., Bhatia, S. "Biodiesel Production From Palm Oil Via Heterogeneous Transesterification", Biomass and Bioenergy, 33, 271-276, (2009).
- [2] Bhatti, H.N., Hanif, M.A., Qasim, M., Rehman, A. "Biodiesel Production From Waste Tallow", Fuel, 87, 2961-2966, (2008).
- [3] Srivastava, P.K. and Verma, M. "Methyl ester of karanja oil as an alternative renewable source energy", Fuel, 87:1673-1677, (2008).

- [4] Godiganur, S., Murthy, C. S., Reddy, R. P. "Performance And Emission Characteristics Of A Kirloskar HA394 Diesel Engine Operated On Fish Oil Methyl Esters, Renewable Energy, 35:355–359, (2010).
- [5] Reyes, J.F, Sepúlveda, M.A. "PM-10 Emissions And Power Of A Diesel Engine Fueled With Crude And Refined Biodiesel From Salmon Oil", Fuel, 85:1714–1719, (2006).
- [6] Cunha, M. E., Krause, L. C., Moraes, M. S. A., Faccini, C. S., Jacques, R. A., Almeida, S. R., Alves Rodrigues, M. R., Caramão, E. B. "Beef Tallow Biodiesel Produced In A Pilot Scale", Fuel Processing Technology, 90:570–575, (2009).
- [7] Alptekin, E., Çanakçı, M., (2008) "Farklı Hammaddelerden Retilen Metil Ester Ve Gliserinin Bazı Özelliklerinin Belirlenmesi", Gazi Üniv. Müh. Mim. Fak. Der., Cilt 23, No 3, 549-556, (2008).
- [8] Alptekin, E., Çanakçı, M. "Biyodizel ve Türkiye'deki Durumu", Mühendis ve Makine, Cilt: 47 Sayı: 561, (2006).
- [9] Yaşar, B. "Türkiyede Byodizel Üretim Maliyeti ve Yaşanan Sorunlar"ı VII. Ulusal Temiz Enerji Sempozyumu, İstanbul, 197-204, (2008).
- [10] Gui, M.M., Lee, K.T., Bhatia, S. "Feasibility of edible oil vs. non-edible vs. waste edible oil as biodiesel feedstock" Energy, 33, 1646-1653, (2008).
- [11] Demirbas, A. "Biodiesel From Waste Cooking Oil Via Base-Catalytic And Supercritical Methanol Transesterification", Energy Conversion and Management 50 923–927, (2009).
- [12] Gürü, M., Artukoğlu, B.D., Keskin, A., Koca, A. "Biodiesel Production From Waste Animal Fat And Improvement of Its Characteristics By Synthesized Nickel And Magnesium Additive", Energy Conversion and Management 50 498–502, (2009).
- [13] Wiggers, V.R., Wisniewski Jr., A., Madureira, L.A.S., Barros, A.A. C., Meier, H.F. "Biofuels From Waste Fish Oil Pyrolysis: Continuous Production In A Pilot Plant Fuel 88 2135–2141, (2009).
- [14] Gürü, M., Koca, A., Can, Ö., Çınar, C., Şahin, F. "Biodiesel Production From Waste Chicken Fat Based Sources And Evaluation With Mg Based Additive In A Diesel Engine", Renewable Energy xxx 1–7, (2009).
- [15] Tashtoush, G.M., Al-Widyan, M. I., Al-Jarrah, M. M. "Experimental Study On Evaluation And Optimization Of Conversion Of Waste Animal Fat Into Biodiesel", Energy Conversion and Management 45 2697–2711, (2004).
- [16] Öner, C., Altun, Ş. "Biodiesel Production From Inedible Animal Tallow And An Experimental Investigation Of Its Use As Alternative Fuel In A Direct Injection Diesel Engine", Applied Energy, 86:2114–2120, (2009).
- [17] Meng, X., Chen, G. and Wang, Y. "Biodiesel production from waste cooking oil via alkali catalyst and its engine test", Fuel Processing Technology 89, 851-857, (2008).
- [18] Phan, A.N. and Phan, T. "Biodiesel Production From Waste Cooking Oils", Fuel, 87, 3490–3496, (2008).
- [19] Bhatti, H.N., Hanif, M.A., Qasim, M., Rehman, A. "Biodiesel Production From Waste Tallow", Fuel, 87, 2961–2966, (2008).
- [20] Ertaş, M., ALMA, M. H., FİDAN, M. S. "Defne Artıklarından Piroлиз Metodu İle Sentetik Sıvı Yakıt Üretimi", VII. Ulusal Temiz Enerji Sempozyumu, UTES'2008, 17-19 İstanbul, 249-258, (2008).
- [21] Çildir, O., Çanakçı, M. "Çeşitli Bitkisel Yağlardan Biyodizel Üretiminde Katalizör ve Alkol Miktarının Yakıt Özellikleri Üzerine Etkisinin İncelenmesi", Gazi Üniv. Müh. Mim. Fak. Der., Cilt 21, No 2, 367-372, (2006).
- [22] Öztürk, M. "Kullanılmış bitkisel ve hayvansal atık yağlar", Çevre ve Orman Bakanlığı, Ankara, <http://www.cevreorman.gov.tr/belgeler/yaclar.pdf>, (2004).
- [23] Öztürk, M. "Kızartma atık yağları tehlike saçıyor" <http://www.mozturk.net> (Ziyaret Tarihi: 05.06.2010)
- [24] Acaroğlu, M. "Alternatif Enerji Kaynakları", Nobel yayınları, Ankara, (2007).
- [25] Yaşar, B. "Türkiye'de bitkisel hayvansal atık yağlar sorunu ve biyodizel üretimi" Tarım ve Mühendislik, (78-89), 63-64, (2006).
- [26] Doğan Artukoğlu, B. Hayvansal yağlardan biyodizel üretimi ve özelliklerinin geliştirilmesi, yüksek lisans tezi, Gazi Üniversitesi Fen

Bilimleri Enstitüsü, Ankara, 10-44, (2006).

- [27] Altun, Ş., GÜR, M.A. “Bitkisel Yağların Alternatif Yakıt Olarak Dizel Motorlarında Kullanılması”, HR.Ü.Z.F.Dergisi, 9(3): 35-42, (2005).
- [28] Akgün, G., Bayındır, H., Aydın, H., Düz, Z. “Hayvansal yağlardan biyodizel üretimi ve teknik değerlerinin belirlenmesi üzerine bir çalışma” V. Yenilenebilir enerji kaynakları sempozyumu, 131-136, (2009), Diyarbakır
- [29] Gerpen, J.V. “Biodiesel Processing and Production”, Fuel Processing Technology 86 1097– 1107, (2005).
- [30] Keskin, A., Aydın, K. “Tall Yağı Biyodizeli Üretimi ve Bunun Dizel Motor Performansı ve Emisyonları Üzerindeki Etkileri”, Ç.Ü.Müh.Mim.Fak.Dergisi, 20(1):85-94, (2005).
- [31] Keskin, A., Gürü, M., Altıparmak, D. “Tall Yağı Biyodizelinin Dizel Yakıtı İle %90 Oranındaki Karışımının Alternatif Dizel Yakıtı Olarak İncelenmesi” Gazi Üniv. Müh. Mim. Fak. Der., 22(1), 57-63, (2007).
- [32] Haşimoğlu, C., İçingür, Y., Özsert, İ. “Turbo Şarjlı Bir Dizel Motorda Yakıt Olarak Biyodizel Kullanılmasının Motor Performans Ve Egzoz Emisyonlarına Etkisi”, Gazi Üniv. Müh. Mim. Fak. Der., Cilt 23, No 1, 207-213, (2008).
- [33] Çanakçı, M. and ÖZSEZEN, A.N. “Evaluating Waste Cooking Oils As Alternative Diesel Fuel”, G.U. Journal of Science, 18(1):81-91, (2005).
- [34] Canakci, M. and Gerpen, J.V. “Biodiesel Production From Oils And Fats With High Free Fatty Acids”, Transactions of the ASAE, Vol. 44(6): 1429–1436, (2001).
- [35] Ma, F., Clements, L.D., Hana, M.A. “The effect of catalyst free fatty acids and water on transesterification of beef tallow” Transactions of the ASAE, 41(5), 1261-1264, (1998).
- [36] Altun Ş. ve Öner C. “Hayvansal iç yağlardan transesterifikasyon reaksiyonu ile biyodizel üretilmesi”, Doğu Anadolu Bölgesi Araştırmaları, Cilt:6, sayı:3, 116-125, (2008).
- [37] Canakci, M., Van Gerpen, J., “Biodiesel production via acid catalysis” Transactions of the ASAE, 42(5), 1203-1210, (1999).
- [38] <http://eng.ege.edu.tr/~otles/foodwaste-oil.tripod.com/biodizel/id2.html> (Ziyaret tarihi: 20.11.2009).
- [39] Ma, F., Hana, M. A. “Biodiesel production: a review”, Bioresource Technology, 70:1-15, (1999).
- [40] Ramadhas, A.S., Jayaraj, S., Muraleedharan, S. C. “Biodiesel Production From High FFA Rubber Seed Oil”, Fuel 84 335–340, (2005).
- [41] Sharma, Y.C., Singh, B. “Development of Biodiesel: Current Scenario”, Renewable and Sustainable Energy Reviews 13:1646–1651, (2009).
- [42] Liu, K. “Preparation of fatty acid methyl esters for gas–chromatographic analysis of lipids in biological materials” JAOCS, 71(11): 1179–1187, (1994).
- [43] Canakci, M. and Gerpen, J.V., “Biodiesel Production From Oils And Fats With High Free Fatty Acids”, Transactions of the ASAE, Vol. 44(6): 1429–1436, (2001).