Hands-on Training the Engineering Students on Biodiesel Production using Waste Vegetable Oils

Goutham Chinni, Israel Belachew and Ramazan Asmatulu*

Department of Mechanical Engineering, Wichita State University 1845 Fairmount, Wichita, KS 67260-0133, USA *Email: <u>ramazan.asmatulu@wichita.edu</u>

Abstract

Energy is playing a vital role in human life and mainly produced from the fossil fuels worldwide. Due to the extensive usage of energy obtained from fossil fuels, alternative sources of energy should be sought for the future demands. Biodiesel can be one of the alternative energy sources to replace the fossil fuels because of the lower emissions and lower harmful exhaust gases. Biodiesel can be directly used or blended with other diesel products to manage some of the pollution and emission problems. In today's conditions, the optimum blend of biodiesel to the diesel seems to be about 10 wt. % (or B10). The emissions and particulates can be adjusted after appropriate blends of biodiesel into the petroleum-based diesel. During the present study, the undergraduate engineering students were trained on biodiesel from the waste vegetable oil. The major goals of this study were to extract the biodiesel from the waste vegetable oil, improve biodiesel properties and train the undergraduate engineering students on the renewable energy systems for their future careers.

Keywords: Waste Vegetable Oil, Transesterification, Biodiesel, Byproducts, Renewable Energy, Student Training.

1. Introduction 1.1 General Background

In order to meet the economic challenges and sustainable developments, many countries have been seeking low cost energy sources [1-3]. During the past half century, the demand for oil, gas and coal all around the world tremendously increased with the increasing population and economic growths. The United States, Russia and China together produce about 31% of the world's energy, but consuming 41% of the produced energies. Biodiesel is one of the options to meet the growing demands of the energy [4-15]. Figure 1 shows the chart for the contributions of the biodiesel productions in 2008 in the world [16]. This chart explicitly reveals that among all countries US holds the largest productions and consumptions of the biodiesel. Figure 2 shows the comparison of ethanol and biodiesel usage from years 2000 to 2015 [17]. After year of 2006, the ethanol and biodiesel usages were considerably increased because of the oil prices and larger demands on the new oil sources.



Figure 1: The chart showing the contributions of the biodiesel productions in the world [16].



Figure 2: The graphic showing the comparison of ethanol and biodiesel usage from the years 2000 to 2015 [17].

Biodiesel can be an alternative fuel for diesel engines that has been receiving a great attention worldwide. Not only can it be obtained from living plants, such as soy oil, sunflower seeds and vegetable oil, but also from our everyday domestic waste, the waste cooking oil and animal fats. In the recent years, biodiesel, containing esters of fatty acids with short chain

alcohols (mainly methanol), gained an important position as an environmentally friendly substitute of petroleum-based diesel fuel. It is biodegradable, non- inflammable, non-toxic, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons when compared to the petroleum-based diesel products. In addition to these advantages of biodiesel over the diesel fuel, the most important advantages of the biodiesel include the reduction of greenhouse gas effects and emissions from exhaust gas of a combustion [1]. Although it attracts the most attention because of its renewable nature, it can be used either pure or in blends with diesel fuel in unmodified diesel engines, and reduces some of the exhaust gas pollutants. It is also attractive because it can be produced easily from common feedstock of waste oils and animal fats.

1.2 Transesterification of Vegetable Oils

Transesterification is the process of separating the fatty acids from their glycerol backbone of oil to form fatty acid esters (FAE) and free glycerol [18-20]. Biodiesel, also known as fatty acid esters, can be produced in a continuous and batch scale by trans-esterifying triglycerides in vegetable oil and animal fats and other organic waste which has lower molecular weight in the presence of a base or acid as a catalyst. Figure 3 shows the transesterification process of converting vegetable oils into biodiesel (methyl ester) [20]. The "R" groups in the chart are the fatty acids, which are usually 12 to 22 carbons in length. A successful transesterification reaction is identified by separation of the ethyl ester (biodiesel) and glycerol. The by-product glycerol settles down and once purified it can be used in different industries for cosmetics and detergent purpose. The reaction taking place between the oil and the alcohol is a chemically reversible process.

н	Catalyst	H	
H - C - OOR		H - C - OH	ROOCH,
H - C - OOR' +	зсн,он 🔫	H - C - OH +	R'OOCH,
$H - C - OOR^3$		н – с – он	R'OOCH,
н		H	
Vegetable Oil + M	ethyl Alcohol —	➤ Glycerol +	Methyl Ester

Figure 3: The transesterification process of converting vegetable oils into biodiesel (methyl ester) [14].

Figure 4 shows the trend of ester yielding / conversion from an oil as a function of time [19]. The esterification yield was very fast in first 10 minutes, and then the maximum yield was reached within 20 minute of the esterification time. After this time, the esterification reaction is leveled off. The average overall conversion achieved this reaction was 94.5%. Issariyakul et al. obtained an ethyl ester conversion of waste cooking oil up to 97% [8]. Leung et al. also reported that the conversion of a waste cooking oil using sodium hydroxide catalysts was approximately 86% [9].



Table 1 gives the physical and chemical properties of the oil feedstock [9].

Figure 4: The graphic showing the trend of ester yield / conversion as a function of time [19].

Property	Waste cooking oil	Neat canola oil				
Acid value (mg KOH/g)	2.1	<0.5				
Kinematic viscosity at 40°C (cSt)	35.3	30.2				
Fatty acid composition (wt%)						
Myristic (C14:0)	0.9	0.1				
Palmitic (C16:0)	20.4	5.5				
Palmitoleic (C16:1)	4.6	1.1				
Stearic (C18:0)	4.8	2.2				
Oleic (C18:1)	52.9	55				
Linoleic(C18:2)	13.5	24				
Linolenic(C18:3)	0.8	8.8				
Arachidic (C20:0)	0.12	0.7				
Eicosenic (C20:1)	0.84	1.4				
Behenic (C22:0)	0.03	0.5				
Erucic (C22:1)	0.07	0.4				
Tetracosanic (C24:0)	0.04	0.3				
Mean molecular wt (g/mol)	856	882				

Table 1: The physical and chemical properties of the oil feedstock [9].

Zheng et al. proved that methyl ester conversion of waste cooking oil in acid catalyzed transesterifications could reach up to 99% [10]. This process was performed using a high methanol to oil ratio of 250:1. Transesterification was carried out using 0.4%, 0.6%, 0.8%, 1.0% and 1.2% of catalyst concentration. With 0.4 % of catalyst concentration, no reaction was observed as there was no separated layer of ester and glycerin in the system [10]. Figure 5 shows the conversion efficiency of ester under different catalyst concentration. With 1.2% catalyst concentration, a complete soap formation was observed because the larger amount of catalyst caused a soap formation in the reaction vessel [11-15].



Figure 5: The conversion efficiency of ester under different catalysts concentrations [11].

1.3 Separations, Washing and Characterization of Biodiesel

After the transesterification process, the reaction products are allowed to cool down and separate based on the gravity values of the products. The clear separation layer can be observed after 12-24 hours of settlement time [1]. After the biodiesel processing is completed, it is very important to wash the final ester products prior to the commercial marking. With the help of DI water, the ester (mainly biodiesel) was washed several times through creating mists on the top with the use of spray nozzle. The recent study reported that the fine mist washing requires a less agitation, resulting in less soap formation and more biodiesel [6]. Washing can be improved by using hot wash water of 50-60° C onto biodiesel [7]. According to the ASTM Biodiesel Fuel Quality Assurance Standard Tests, the biodiesel and byproducts can be characterized using various techniques to determine the physical and chemical properties of the products. Table 2 provides the summary of test methods, the standard limit as recommended by ASTM standards and the expected test results for the waste cooking oils [9].

Test name	Test Method	Standard Limit	Result	European EN14214
Free Glycerin (mass %)	ASTM D6584	Max 0.020	0.022	
Monoglycerides (mass%)	ASTM D6584	NA	0.293	0.8
Diglycerides (mass %)	ASTM D6584	NA	0.19	0.2
Triglycerides (mass%)	ASTM D6584	NA	0.061	0.2
Total Glycerin (mass%)	ASTM D6584	0.024	0.566	
Flash Point, Closed cup (°C)	ASTM D93	Min 130	164	
Phosphorous (ppm)	ASTM D 4951	Max 10	2	
Calcium+Magnesium (ppm)	EN 14538	Max 1	1	
Sodium+potassium (ppm)	EN 14538	Max 5	66	
Water+Sediment (vol%)	ASTM D 2709	Max 0.05	0	
Sulfur by UV (ppm)	ASTM D 5453	Max 15	2	
TAN (mgKOH/g)	ASTM D 664	Max 0.80	0.29	
Viscosity @ 40°C mm ² /sec	ASTM D 445	1.9-6.0	5.03	
Sim.Dis., 90% recovery (°C)	ASTM D 2887	Max 360	366	
Cetane Index	ASTM D 976	Min 47	61	
Cloud Point (°C)	ASTM D 2500	NA	-1	
Pour Point (°c)	ASTM D 97	NA	-16	
Density @15ºC g/cm3	-	NA	0.87	0.86-0.90

Table 2: The summary of test methods, the standard limits and the expected test results for the waste cooking oils [9].

2. Experimental

2.1 Materials

Isopropyl alcohol, potassium hydroxide (as a catalyst), phenolphthalein (pH) solution, and methanol were purchased from the Fisher Scientific. The polymer and solvents were used during the student experiments without any modifications or purifications. The waste vegetable oil was by-product of a household, and filtered with a vacuum filter to remove the access particles accumulated during the cooking / frying. Figure 6 show the waste vegetable oil before and after the filtering process.



Figure 6: The photographs showing the waste vegetable oil a) before and b) after the filtering process.

2.2 Methods

Prior to the biodiesel process, titration tests were performed on the waste vegetable oil to determine amount of catalyst and alcohol. A syringe, small beakers for titration, a 250 ml jar and conical flask with a stopper were used during the titration. Titration solution was prepared using 1 g of KOH pellets into 1 L of DI water. The titration solution was stirred until KOH pellets were completely dissolved in DI water. 1 ml of the waste oil was placed in the beaker, and 10 ml of isopropyl alcohol was added into the same beaker. While stirring, 2-3 drops of phenolphthalein was added in this solution, which was then mixed for a few minutes. The titration solution was added dropwise to the previous mixture by means of a syringe. The titration process was continued until the solution color was changed from light yellow to complete pink. After repeating this process 3-4 times, average titration solution was found to be 3.0 ml. Figure 7 shows the titration process for the biodiesel production using the waste vegetable oil. Based on the calculations, we found that 0.4 g of KOH catalyst and 8 ml of methanol would be necessary to convert 40 ml of filtered waste vegetable oil into biodiesel and glycerin. After the titration process, biodiesel was produced from the waste vegetable oil using the procedures described earlier [1].



Figure 7: The titration process for the biodiesel production using the waste vegetable oil. The titration process was continued until the pink color was clearly seen.

3. Results and Discussion3.1 Producing Biodiesel from Waste Vegetable Oil

In the biodiesel production tests, 0.4 gr of KOH pallets (catalysts) were dissolved in 8 ml of methanol in an Erlenmeyer flask under constant stirring for 5-10 minutes. 40 ml of the filtered oil was heated up to 135 F (57 °C) in a flask on a hotplate, and the catalyst solution (KOH and methanol) was slowly added into the heated oil. After mixing vigorously with the magnetic bar at 600 rpm for about 10-15 minutes, the color of the solution became a dark red, indicating that the chemical reactions took place to produce a biodiesel. The mixed solution of the flask covered with a rubber stopper was kept in the fume hood overnight (10-12 hrs). This duration completed the reactions and separated the biodiesel (top light layer) and glycerin (bottom dark layer). Figure 8 shows the photographs of the biodiesel (top light layer) and glycerin (bottom dark layer) as a by-product.

Separating the top layer from the bottom layer will yield the biodiesel. Washing the biodiesel with a top water at 50:50 ratio or air bubbling into the biodiesel removes the impurities / contaminants in the biodiesel for the commercial use. The fatty acid composition of final biodiesel esters was determined by gas chromatography and found that the waste cooking oil contains mainly oleic acid and other compounds in the final products. The biodiesel was characterized for its physical and fuel properties using the ASTM standard methods for the biodiesel fuel quality assurance [12].

2015 ASEE Zone III Conference (Gulf Southwest – Midwest – North Midwest Sections)



Figure 8: The photographs showing a) the biodiesel (top light layer) and glycerin (bottom dark layer) as a by-product, and b) the clean biodiesel.

3.2 Training Undergraduate Engineering Students

Renewable energy has been gaining much attention worldwide because of the environmental and health concerns of the fossil fuels, and biodiesel can be one of the major sources of the renewable energies available in the world. Undergraduate students in the Department of Mechanical Engineering at WSU were involved in every step of the present study, learned many new techniques and gained a lot of new skills and knowledge about titration, filtration of waste oil, extraction of oil, washing and conversion into biodiesel during the experimental studies. Some of the students joined our group used these research activities as their own Engineer of 2020 requirements in the College of Engineering. One of the students (Mr. Israel Belachew) is also a co-author of the present study and made a lot of contributions during the experiments (Figures 7 and 8). We believe that these studies and new experiments will enhance the knowledge of many BS engineering students to perform more detail studies in these fields for their higher level educations.

4. Conclusions

Because of the shortages in economically producible fossil fuels, global economic crises, and environmental and health problems, many researchers and scientists have been focused on the renewable energy sources in the world. Biodiesel is one of the greater sources of the renewable energies available in the world. It can be directly used or as a blend of petroleum-based diesel to increase the life time of the energy sources, and provide sustainable developments. In this study, biodiesel was successfully produced from the waste vegetable oil collected from a local home using transesterification process. Throughout the experiments, the students gained an understanding of the biodiesel processes (e.g., titration, transesterification, thermal liquefaction, separation, and clean biodiesel), and how the biodiesel and its byproducts were used for different applications. It is believed that these activities will motivate the undergraduate engineering students to do further studies in these fields for their MS and PhD degrees.

Acknowledgement

The authors greatly acknowledge the Wichita State University for the financial and technical supports of this study.

References

- 1) G. Phal, *Biodiesel: Growing a New Energy Economy*, 2nd Edition, Chelsea Green Publishing, 2008.
- 2) H. Prankl, "Standardization of biodiesel", Final Report, Federal Institute of Agricultural Engineering (BLT), Austria, 2000.
- 3) S. Prasad, A. Singh, H.C. Joshi, "Ethanol as an Alternative Fuel from Agricultural, Industrial and Urban Residues," *Resources Conservation and Recycling*, 2007, Vol. 50, pp. 1-39.
- 4) D.S. Barry, R. B. Justin, and E.H. Kathleen, "Grain and Cellulosic Ethanol: History, Economics, and Energy Policy," *Biomass and Bioenergy*, 2007, Vol.31, pp. 416-425.
- 5) S. Caro, Z. Mouloungi, and G. Vaitilingom, "Interest of Combining an Additive with Diesel-Ethanol Blends of Use in Diesel Engines," *Fuel*, 2001, Vol.80, pp. 565-74.
- 6) W.H. Kemp, Biodiesel Basics and Beyond. A Comprehensive Guide to Production and Use for the Home and Farm, Aztext Press: Ontario, Canada, 2008, 18 pages.
- 7) R. Rywotycki, "The Effect of Fat Temperature on Heat Energy Consumption during Frying of Food," *Journal of Food Engineering*, 2002, Vol. 54, pp. 257-261.
- T. Issariyakul, M.G. Kulkarni, A.K. Dalai, N.N. Bakhshi, "Production of Biodiesel form Waste Fryer Grease using Mixed Methanol/Ethanol System," *Fuel Processing Technology*, 2007, Vol. 88, pp. 429- 436.
- 9) <u>http://file.scirp.org/Html/5-6401269_33407.htm,</u> accessed in July 20, 2015.
- 10) P. Kwanchreon, A. Luengnaruemitchai, S. Jai-in, "Solubility of a Diesel Biodiesel Ethanol Blend its Fuel Properties, and Its Emission Characteristics from Diesel Engine" *Fuel*, 2007, Vol.86, pp. 1053-1061.
- 11) S. Zheng, M. Kates, M.A. Dube, and D.D. McLean, "Acid-catalyzed Production of Biodiesel from Waste Frying Oil," *Biomass and Bioenergy*, 2006, Vol. 30, pp. 267-272.
- 12) http://www.crimsonrenewable.com/biodiesel-specifications.pdf
- 13) L. Attanatho, S. Magmee, and P. Jenvanipanjakil, The Joint International Conference on Sustainable Energy and Environment, Huan Hin, Thailand, 2004.
- 14) A.C. Hansen, Q. Zhang, P.W.L. Lyne, "Ethanol-diesel Fuel Blends Review," *Bioresource Technology*, 2005, Vol.96, pp. 277-85.
- 15) http://www.ag.ndsu.edu/pubs/ageng/machine/ae1240w.htm, accessed in July 25, 2015.
- 16) R. Asmatulu, Nanotechnology Safety, Elsevier, Amsterdam, The Nederland, August, 2013.
- 17) <u>http://circoloippicolevalli.it/foto/photos/index.php?p=84</u>, accessed in July 4, 2015.
- 18) <u>http://www.mdpi.com/2077-0472/2/4/414/htm</u>, accessed in July 13, 2015.
- 19) <u>http://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1212&context=usepapapers.</u>, accessed in July 9, 2015.
- 20) https://en.wikipedia.org/wiki/User:Rataguera/draft, accessed in July 14, 2015.

Biographical Information

Goutham Chinni

Mr. Goutham is a MS student in the Department of Mechanical Engineering at Wichita State University (WSU), and has been working on the biodiesel related projects. He will graduate in May 2016.

Israel Belachew

Mr. Israel is a BS student in the Department of Mechanical Engineering at WSU, and has a strong interests in the renewable energy systems. He will graduate in May 2015, and will join the MS program at WSU.

Ramazan Asmatulu

Dr. Ramazan Asmatulu received his Ph.D. degree in 2001 from the Department of Materials Science and Engineering at Virginia Tech. After having the postdoc experiences, he joined the Department of Mechanical Engineering at WSU in 2006 as an assistant professor, and received his tenure and promotion to be associate processor in 2012. He is currently working with 13 M.S. and 8 Ph.D. students in the same department. Throughout his studies, he has published 76 journal papers and 166 conference proceedings, edited two books, authored 33 book chapters and 4 laboratory manuals, received 35 funded proposals, 15 patents and 34 honors/awards, presented 91 presentations, chaired many international conferences and reviewed several manuscripts in international journals and conference proceedings. To date, his scholarly activities have been cited more than 1050 times, according to the web of science.