e-ISSN: 2458-8156

Journal Homepage: http://dergipark.gov.tr/ejens

EJENS
European Journal of Engineering and Natural Sciences

DergiPark AKADEMİK

CODEN: EJENS

Biodiesel Production Using Wet and Dry Purification Methods

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Publication Info

Paper received:
29 May 2016

Revised received:
15 October 2016

Accepted:
01 March 2017

Abstract

In biodiesel production via transesterification, after removing glycerol from crude biodiesel, purification process must be performed before using biodiesel as a fuel that meets the EN 14214 standard. In the literature, various processes are presented for purification of biodiesel however; dry and wet washing methods are mostly recommended because of their higher efficiencies and easier applicabilities. In this study, methyl esters (biodiesel) derived from waste frying oil (WFO) and sunflower oil were generated using transesterification technique in the presence of KOH and methanol in a novel microwave assisted biodiesel reactor. For purification of crude biodiesel, two different methods; washing with distilled water as wet washing, and with magnesol as dry washing were carried out and compared. According to the results, dry washing method improved biodiesel yield and ester content, it also reduced the purification process time considerably.

Key words

Biodiesel, Transesterification, Purification Techniques

1. INTRODUCTION

The chemical process, transesterification includes a TAG (triglycerides) reaction with a short chain monohydric alcohol in the presence of a catalyst to obtain biodiesel which is defined as fatty acid alkyl esters (FAAE), and by-product glycerol. Three moles of alkyl esters and one mole of glycerol are formed for every mole of TAG that undergoes complete conversion reaction [1]. In transesterification reactions, presence of sufficient amount of methanol is essential to break the glycerol-fatty acid linkages [2]. Methanol is the most commonly used alcohol in commercial biodiesel production via transesterification, since it is generally less expensive than other alcohols. There are different types of catalysts used in chemical reactions, among them; homogenous alkali catalysts (sodium or potassium hydroxide or methoxide etc.) are inexpensive catalysts generally used in commercial biodiesel production from refined or treated oils. Beside of the economic issues and concerns, homogenous alkali catalysts are more preferred than acid catalysts and enzymes due to their high reactivity and short reaction time requirements [1, 3]. Also, another reason for widely using alkali catalyzed biodiesel production techniques is this method's being less corrosive than others [4].

At the end of the alkali transesterification reactions, the by-product glycerol is removed from the crude alkyl ester-glycerol mixture. In addition, crude ester must be purified to obtain high quality biodiesel which must meet international standard specifications (EN14214, ASTMD6751 etc.) by removing excess contaminants (methanol, catalyst etc.) and impurities (soap, wax etc.) [5]. In commercial biodiesel production, purification method is called as washing process, and it is categorized into 2 techniques as: wet and dry washing [6]. Besides these, alternative washing method, membrane extraction has been investigated [7].

1.1. Wet Washing

Wet washing method is more traditional and widely used for removing containing the unreacted oil, excess catalyst and alcohol, salts, soaps, organic impurities etc. from crude biodiesel. In wet washing process, water is used for purification. Water has the ability to provide a means for addition of acid to neutralize the unreacted alkali catalyst. Wet washing

method simplifies removal of the salt products formed in transesterification reaction. The unreacted (excess) alcohol after transesterification should be removed before the washing process to decrease the amount of alcohol in the residual wastewater. Also, some researchers such as Van Gerpen et al. suggest removing process of excess alcohol after the end of wet washing [8, 9]. The researchers prevented precipitation of saturated fatty acid esters using distilled water (≈50-60°C). Emulsion generation is retarded when gentle water washing is applied fostering rapid and complete phase separation [8] The washing with hot distilled water results in the biodiesel purity of 99% [10]. Both of the dry and wet washing methods are used in commercial biodiesel production, however, it is claimed that only wet washing process can purify the biodiesel in desired levels, and the purified biodiesel meets the EN14214 standards [6].

Beside the advantages of wet washing, Low et al. [11] declared that this method has some drawbacks such as long separation time and loss of product yield. The loss of biodiesel yields in the rinsing water increases the formation of polluted liquid effluent [12]**.** In addition, the large amount of biodiesel wastewater formed after wet washing process causes an enormous problem for the biofuel industry and environment. Veljkovi´c et al. [13] reported that the generated biodiesel wastewater was about 28 million m^3 in 2011 in the world.

1.2. Dry Washing

Using absorbents is another method of treating crude biodiesel. Dry washing technique generally uses ion exchangers or a magnesium silicate powder as absorbents [6]**.** These materials are utilized to replace the usage of distilled water in order to remove the impurities and purify crude esters. At the end of the dry washing, filtration is ordinarilycarried out for improving efficiency of the process. The advantages of dry washing can be described as: no waste water is generated and the total surface area coverage of the wash tank is minimized. Besides, this washing method has important advantages such as: strong affinity to polar compounds, easy to install into biodiesel processer plant, dramatically lower washing time, solid waste can be used in various ways, saves space etc. The main preferred absorbents in biodiesel production are defined as magnesol, ion exchange resin, activated carbon, activated fiber etc. [14].

Magnesol is used in many investigations and suggested by the authors. Sabudak and Yildiz[15] made a comparison of hot water washing (50%-V/V and 50°C) and dry washing with magnesol (1 wt%) according to the ester contents of methyl esters. They produced biodiesel from waste cooking oil by 3 different processes. In the event of one step alkali transesterification, they achieved 80.8% and 84.9% ester contents with wet washing and dry washing, respectively. In two step alkali transesterification, 91.0% ester content was obtained by wet washing while 92.3% by dry washing. In the third process (two step acid-alkali transesterification), 95.6% and 96.9% ester contents were measured at the end of the wet and dry washing processes, respectively. As a result, it was found that dry washing enhanced the ester content of crude biodiesel more than wet washing, in addition, only the samples purified by dry washing fulfilled with EN14214 ester content standards (min.96.5%). Berrios and Skelton [6]purified crude biodiesel samples using 0.25, 0.50, 0.75 and 1.00% magnesol concentrations at the temperature of 60 °C. 10 min and 20 min washing time were experimented while standard washing time is known as 30 min. A vacuum filtration and a water ejector were performed in separating process. With the exception of the experiments with 0.25% (wt/wt) magnesol concentration, all the experiments remove in satisfactory way the glycerol content in 10min of reaction. The same happened in the soap removal. They specified that min 0.75% magnesol concentration is needed with a washing time of 10 min; and it is necessary a previous methanol removal to avoid the saturation of the adsorbents. Also, none of the experiments decreased the methanol content below the defined level of the EN14214 Biodiesel Standards, and the best result was obtained using with 1%(wt/wt) magnesol concentration at 60°C temp. Bryan [16] applied dry washing technique in the presence of magnesol (1%) on both soybean and yellow grease crude biodiesels, also he used wet washing technique to compare those two methods clearly. The physicochemical properties of purified methyl esters (soybean&grease based) by dry washing method were fulfilled with EN 14214 and ASTM D6751standards. Moreover, the researcher claimed that magnesol treated sample of yellow grease derived methyl esters met all ASTM standards while the water washed and dried sample did not. The author remarked that magnesol has a strong affinity for polar compounds, thereby actively filtering out metal contaminants, mono and di-glycerides, free glycerin, and excess methanol as well as free fatty acids and soap.

1.3. Objectives

As it is seen in section *1.1.*and*1.2.*, conflicting outcomes exist in the literature about dry and wet washing purification methods. Thereby, the main objective of the study has been determined as comparing the wet washing method with hot distilled water and dry washing method with magnesol based on the obtained ester content amounts and yields of purified biodiesel samples. In the experiments, the biodiesel samples were produced via alkali catalyzed transesterification in various reaction conditions.

2. MATERIAL AND METHOD

2.1. Materials

In the experiments, methanol and KOH were used as an alcohol and a catalyst. The raw materials were determined as waste frying oil (WFO) with an FFA value ≈0.2% which was collected from local restaurants in Balıkesir, Turkey, and sunflower oil was supplied from an oil production plant. Methanol and KOH were purchased from Sigma–Aldrich, and magnesol ($MgO:SiO_2$ (1:2.7)) from Dallas Group of America.

2.2. Equipment

Biodiesel reactor:

The biodiesel processor system has 60 L capacity and it is composed of a reactor tank, a microwave heating system, a mechanic stirrer, a circulation pump, and a PLC circuit and software to control reaction parameters (temp, mixing rate etc.).

Wet washing:

The distilled water was produced from a water distillation system, and the washed crude biodiesel samples were settled in separatory funnels.

Dry washing:

In order to heat crude biodiesel samples filled into the beakers, the magnetic hotplate stirrer (Dragon-MS-H280-Pro) was used. In the filtering process, a vacuum pump and filters (pore sizes: 10 µm and 1.2 µm) were utilized.

2.3. Biodiesel Production

Reaction parameters:

In order to achieve maximum conversions, 6:1 molar ratio of methanol to oil is recommended in the literature[17]. Thereby, 6:1 molar ratio was fixed in all experiments we carried out. The catalyst loadings were defined as 1 wt% KOH for sunflower oil, and 1 wt% and 1.5 wt% for waste cooking oil. Because, the FFA of waste oils are higher than vegetable oils and free fatty acids can react with alkali catalysts to soap and water formation, and saponification consumes alkali catalysts [3]. In all the experiments, reaction temperature was set to 60°C.

Methyl ester formation:

Methyl ester production was realized in our novel microwave assisted biodiesel reactor in the defined production conditions, and two washing methods were performed to the same products after the settling processes. The main steps of biodiesel production are shown in Figure 1.

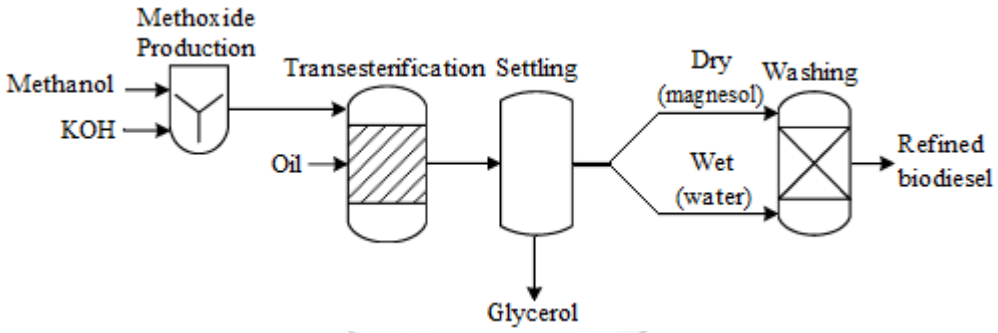


Figure 1. Schematic diagram of the biodiesel productions

Firstly, some physical and chemical properties of oils were determined (Table 1). Fatty acid compositions of oils were analyzed (IUPAC IID19) using Gas Chromatography (GC), and the average molecular weight of oils were calculated. Then the amounts of methanol and KOH were defined for each experiment. The density (EN ISO 3679), kinematic viscosity (EN ISO 3104), and methyl ester content (EN 14103) tests were performed on biodiesel or oils by using a pycnometer, a viscometer (AKV-202-TANAKA), and the ester contents were measured in İnönü University Fuel / Oil Analysis Laboratory in Malatya, Turkey.

Table 1. Some properties of WFO and Sunflower oil

Properties	Unit	WFO	Sunflower Oil
Density (15°C)	g cm^{-3}	0.925	0.921
Viscosity (40°C)	mm^2 s^{-1} 36.47		32.57
Acid value	mg KOH g^{-1}	0.69	0.26
Avr. molecular weight	$g.mol^{-1}$	879.14	879.82

In the first step of methyl ester production, methanol and KOH were added into the methoxide tank and the methoxide solution was formed. Then the methoxide was transferred to the reactor, into the preheated oil. Transesterification reactions were carried out at 60°C and the crude biodiesel samples were taken at different time intervals, and they were placed in the

separatory funnels. After the settling processes, two layers were observed as it is seen in Figure 2 (the upper layer is the biodiesel phase, the lower layer is the crude glycerol), and the glycerol layers were removed. Finally, the crude biodiesel samples were purified by two different methods.

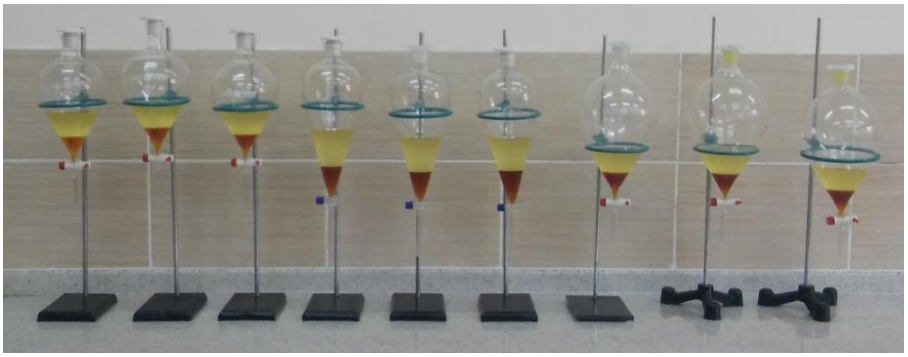


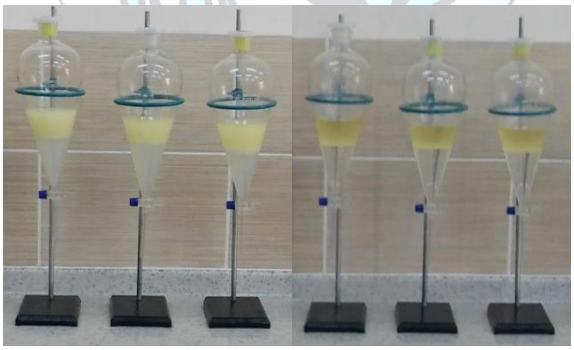
Figure 2. Crude biodiesel and glycerol layers

2.4. Purification Process

As regards previous investigations about biodiesel production from WFO, the optimum result (by wet washing) was achieved with 20 min transesterification reaction while max reaction time was defined as 90 min. However, when sunflower oil was used as raw material, it was observed that the reaction was completed in a very short time, and at the end of the 20 min, 98.30% ester content was achieved. Thereby, the purification techniques were applied to the crude biodiesel samples produced in 20 min and 90 min.

2.4.1. Wet washing (water)

After removing the glycerol layers from the separatory funnels, warm distilled water at 55° C was added into the each crude biodiesel samples, and the water-biodiesel mixtures were gently shaken. Then they were waited for settling, and two layers occurred as it is seen in Figure 3a and Figure 3b (the upper layer is washed biodiesel, the lower layer is waste water). The down layers were removed and the biodiesel layers were washed three times more. In the first three washing processes, the settling time was defined as 60 min while in the final washing the sedimentation time was performed as 360 min to provide the separation exactly. In order to remove undesired components such as the excess methanol or existing water, the washed biodiesel samples were dried at 110 ° C until they were appeared crystal clear. At least, the final products were filtered using filter paper.

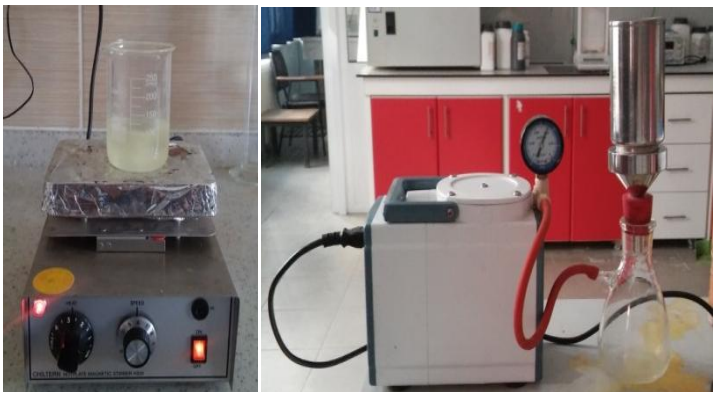


(a) (b)

Figure 3. Biodiesel and wastewater layers: (a)1st wash, (b) 4th wash

2.4.2. Dry washing (magnesol)

In the dry washing processes with magnesol; at first, the glycerol layers were removed from biodiesel layer as same as the section 2.4.1. The crude biodiesel samples were transferred to the beakers and they were heated to 65° C. The magnesol absorbents (1 wt%) were filled into the beakers and the mixtures were stirred for 30 min at constant 65° C (Figure 4a). At the final stage, the mixtures were filtered in two steps (10 µm and 1.2 µm) under vacuum (Figure 4b). The initial and final appearance of used magnesol is shown in Figure 5. In this study, the experiments containing dry washing method, crude biodiesel samples were purified directly, however, one sample was dried at 110° C to evaporate existing methanol and water before the purification process to observe the difference.



(a) (b)

Figure 4. (a) Stirring process of crude biodiesel-magnesol mixture, (b)Filtering process using vacuum pump

Figure 5. The magnesol absorbent before and after the purification process

3. RESULTS AND DISCUSSION

Ester content (purity) is the main biodiesel property to analyze the transesterification efficiency and completion rate. Moreover, the purity level of biodiesel has a strong effect on fuel properties and on engine life. On the other hand, the main goal of transesterification reaction is decreasing the high viscosity value of oil, and density of biodiesel is a significant property affecting combustion process with viscosity. Thereby, these three main biodiesel properties were measured and analyzed, and wet and dry washing techniques were compared according to these values. In table 2 and 3, the differences of fuel properties and product yields related to used washing methods and raw materials are shown clearly.

Table 2. Fuel properties of the WFO based biodiesel samples.

Reaction time	**Purification Processes**	**Density (15^0C)**	**Viscosity (15^0C)**	**Ester content**	**Product yield ($m_{biodiesel}/m_{oil}$)**
		(kg/m^3)	**(mm^2/s)**	**(%m/m)**	**(%)**
20 min	Wet washing	882	4.592	94.41	97.45
20 min	Dry washing	886	4.642	94.51	97.51
20 min *(1.5%KOH)*	Wet washing	874	4.784	94.27	94.64
20 min *(1.5%KOH)*	Dry washing	889	4.845	94.49	96.62
90 min	Wet washing	878	4.568	94.41	94.54
90 min	Dry washing	888	4.852	95.12	94.56
90 min	*2 step process:* 1st Wet washing 2nd Dry washing	870	4.566	95.76	92.31

Table 3. Fuel properties of the sunflower based biodiesel samples.

Reaction time	Purification Processes	Density (15°C)	Viscosity (15°C)	Ester content	Product yield ($m_{biodiesel}/m_{oil}$)
		(kg/m^3)	(mm^2/s)	(%m/m)	(%)
20 min	Wet washing	877	4.628	98.30	96.92
20 min	Dry washing	871	4.611	98.52	96.99
20 min	*2 step process:* 1st Wet washing	868	4.618	98.82	95.17
90 min	Wet washing	875	4.711	96.85	92.14
90 min	Dry washing	880	4.687	98.28	96.06
90 min	Dry washing (*After evaporating methanol*)	873	4.655	99.73	94.63
90 min	*2 step process:* 1st Wet washing	881	4.723	98.63	89.26

According to the results; 20 min WFO based and 90 min sunflower based biodiesel productions, dry washing method using magnesol increased the ester content compared to wet washing at the ratios of 0.22% and 1.43%, respectively. Also, the dry washing method performed after evaporating process gave the best ester content value in all experiments. This method increased the ester content ratios at the range of 1.45% (90 min transesterification) compared to the dry washing method. Absence of methanol and water in crude biodiesel must have contributed to enhance the efficiency of magnesol in absorbing the impurities (soap, glycerol etc.). When these two methods were applied consecutively, the increments in the ester contents were achieved as: ≈1.3% in WFO based biodiesel production (90 min), ≈0.5% in sunflower oil based biodiesel production (20 min) compared to wet and dry washing. In addition, the increments of 1.78% and 0.35% (90 min) were measured compared to wet washing and dry washing in sunflower oil based biodiesel production, respectively. In terms of product (purified biodiesel) yields, dry washing method gave the best results, and the two step purification techniques caused poor yield ratios. Regarding the density and viscosity properties, all the purification methods gave the suitable results according to the EN14214 standards. As seen in Table 2 and 3, the densities varies at the range of 868-888 kgm^{-3}, the viscosity values varies at the range of 4.568-4.726 mm^2s^{-1} while the EN14214 limits are 860-900 kgm^{-3} for density and 3.5-5 mm^2s^{-1} for viscosity of biodiesel.

According to the washing methods' practicability and fastness, dry washing method becomes prominent by reducing purification time dramatically. It minimized the process time up to 30 min from 540 min compared to wet washing method, moreover it does not require a washing tank and a water distiller system.

4. CONCLUSION

As a result of this study, it is observed that dry washing method is a more practical and efficient technique compared to wet washing (water) method. Dry washing method takes about less than 18 times than wet washing method; also it increases ester content and yield of biodiesel. In addition, evaporating methanol and water before dry washing improves purity (ester content) of biodiesel a little more. Applying wet and dry washing processes together increases ester content in comparison to wet washing and dry washing method however, it does not increase the ester content noticeably and it reduces product yield. This study shows that the optimum method for purifying crude biodiesel is dry washing.

ACKNOWLEDGMENT

This work was supported by Scientific Research Projects Coordination Unit of Balikesir University(Project No: 2016/09), and it was presented in International Conference on Environmental Science and Technology (ICOEST 2016), in Belgrade/Serbia (28 September-2 October 2016).

BIOGRAPHY

Veli Gökhan DEMiR graduated from mechanical engineering at Sakarya University in 2008. He has a master degree in mechanical engineering from Balıkesir University and he has been a Ph.D. student since 2011. In his Ph.D. work, he has investigated about production of biofuels and their combustion efficiencies. Currently, he is a research assistant in mechanical engineering at University of Balikesir.

REFERENCES

[1]. B.R. Moser, "Biodiesel production, properties, and feedstocks," *In Vitro Cellular & Developmental Biology-Plant*, 45(3). p. 229-266, 2009.

[2]. M.I. Al-Widyan and A.O. Al-Shyoukh, "Experimental evaluation of the transesterification of waste palm oil into biodiesel," *Bioresource technology*, 85(3). p. 253-256, 2002.

[3]. Y. Zhang, M. Dube, D. McLean and M. Kates, "Biodiesel production from waste cooking oil: 1. Process design and technological assessment," *Bioresource technology*, 89(1). p. 1-16, 2003.

[4]. M. Jayed, H. Masjuki, R. Saidur, M. Kalam and M.I. Jahirul, "Environmental aspects and challenges of oilseed produced biodiesel in Southeast Asia," *Renewable and Sustainable Energy Reviews*, 13(9). p. 2452-2462, 2009.

[5]. N.M. Daud, S.R.S. Abdullah, H.A. Hasan and Z. Yaakob, "Production of biodiesel and its wastewater treatment technologies: A review," *Process Safety and Environmental Protection*, 94. p. 487-508, 2015.

[6]. M. Berrios and R. Skelton, "Comparison of purification methods for biodiesel," *Chemical Engineering Journal*, 144(3). p. 459-465, 2008.

[7]. D.Y. Leung, X. Wu and M. Leung, "A review on biodiesel production using catalyzed transesterification," *Applied energy*, 87(4). p. 1083-1095, 2010.

[8]. I. Atadashi, M. Aroua and A.A. Aziz, "Biodiesel separation and purification: a review," *Renewable Energy*, 36(2). p. 437-443, 2011.

[9]. J. Van Gerpen, B. Shanks, R. Pruszko, D. Clements and G. Knothe, *Biodiesel Production Technology, National Renewable Energy Laboratory Subcontractor Report NREL*. 2004, SR-510-36244.

[10]. F. Karaosmanoglu, K.B. Cigizoglu, M. Tüter and S. Ertekin, "Investigation of the refining step of biodiesel production," *Energy & Fuels*, 10(4). p. 890-895, 1996.

[11]. S. Low, G. Gan and K. Cheong, "Separation of methyl ester from water in a wet neutralization process," *Journal of Sustainable Energy & Environment*, 2(1), 2011.

[12]. S. Kumjadpai, K. Ngamlerdpokin, P. Chatanon, P. Lertsathitphongs and M. Hunsom, "Management of fatty acid methyl ester (fame) wastewater by a combined two stage chemical recovery and coagulation process," *The Canadian Journal of Chemical Engineering*, 89(2). p. 369-376, 2011.

[13]. V. Veljković, O. Stamenković and M. Tasić, "Wastewater management in biodiesel production," *Reporting For Sustainability*. p. 471-475, 2013.

[14]. I. Atadashi, M. Aroua, A.A. Aziz and N. Sulaiman, "Refining technologies for the purification of crude biodiesel," *Applied energy*, 88(12). p. 4239-4251, 2011.

[15]. T. Sabudak and M. Yildiz, "Biodiesel production from waste frying oils and its quality control," *Waste management*, 30(5). p. 799-803, 2010.

[16]. T. Bryan, Adsorbing It All. (2016); Available from: http://www.biodieselmagazine.com/articles/239/adsorbing-it-all.

[17]. R. Turck, *Method for producing fatty acid esters of monovalent alkyl alcohols and use thereof*. 2003, Google Patents;L. Meher, D.V. Sagar and S. Naik, "Technical aspects of biodiesel production by transesterification—a review," *Renewable and sustainable energy reviews*, 10(3). p. 248-268, 2006.