

Biodiesel purification using sorbents

Sebastian Zborowski

szboro@interia.pl

Instituto Superior Tecnico, Unoversidade de Lisboa, Portugal

December 2019

Abstract

Climate change, believed to be induced by anthropogenic carbon emissions, motivates the demand for renewable fuels. European legislation requires that by 2020 a minimum of 10% of renewable fuels be incorporated into transportation sector fuel. Only 7% of the incorporated biofuels can be produced using refined or semi-refined vegetable oils, which prompts the research on the use of low-grade fats on biodiesel production.

Biodiesel production from waste frying oils ($0,6 \text{ mg}_{\text{KOH}} / \text{g}_{\text{oil}}$) was studied over a heterogeneous basic catalyst prepared by calcination (4h at 900°C) of eggshells mixed with ammonium oxalate. X-ray diffraction pattern showed for fresh catalyst features belonging to lime. The biodiesel produced by methanolysis at 67°C (5g catalyst / 100g oil; methanol/oil molar ratio = 12 and 90 minute reaction time) had only 77.6% methyl esters (FAME) which were far below the European standard (EN14214) required content (96.5% by weight).

Dry purification of biodiesel was accomplished using a commercial magnesium silicate (Magnesol®, synthetic amorphous magnesium silicate). Adsorption tests were accomplished using less than 10% of solid (Magnesol®/biodiesel weight) for less than 60 minutes at temperatures in the 45°C - 65°C range. Infrared spectra of the purified biodiesel samples showed that Magnesol® was effective for glycerine removal but less effective for removing non-transesterified fats. Under the best conditions tested, the purified biodiesel sample contained only 88.7% FAME which indicates that the conditions of the purification process must be optimized.

Keywords: Biodiesel; Waste frying oils; Methanolysis; Calcium oxide; Dry purification; Magnesol®

1. Introduction

Nowadays the energy consumption is growing and conventional fuels were always there to meet the demand, but they will diminish in near future leading to higher prices. Additionally the World's population is more and more concerned about climate change and environmental protection [1]. That is why renewables and alternative fuels are being researched and developed and their growth is significant in the previous years and is predicted to further accelerate in the future.

But apart from energy many liquids, like oil are used in other industries, like pharmacy or chemistry and bio-based liquids will have to also take these branches of industry as the level of excavated oil will decrease.

The growth in oil based liquids demand in the next 20 years is expected what is shown on Figure 2. It is easily seen that transport sector is the one that requires the most liquids, that includes diesel and petroleum, takes over 50% of the trade. Power generation contributes the least, followed by building and industry requirements.

When it comes to electricity production there are many alternatives – solar, wind, geothermal, biomass to name a few. But transportation fuels are still focused on fossil sources and there are not many mass scale other options that are more environment friendly. For many years the research has been done in biodiesel field and there have been many different solutions proposed to where to get renewable material as well as production process itself. Biofuels also, by replacing conventional fuels, can decrease the pollution

production of greenhouse gasses. Climate concerns are one of the most important ones nowadays on international scale and biodiesel shown huge prospects in that regard. Used feedstock consumes CO₂ in order to grow, so when burned it releases that compound back to atmosphere making the gross CO₂ increase is much less significant than fossil fuels.

All materials from which biodiesel is produced have to undergo the same process of transesterification in order to obtain final product, which is biodiesel. During this reaction an alcohol reacts with oils with present catalyst, resulting in methyl esters and glycerol. This chemical process may result in up to 99,9% yield of esters, depending on amount of reactants, catalyst and conditions during the reaction – temperature, residual time and pressure [5].

After biodiesel production process it needs to be purified from reactants and other impurities that may decrease biodiesel properties. Those include: unreacted alcohol and free fatty acids, catalyst, soaps. These may cause corrosion, low properties of fuel for example: low flash point, out of standard viscosity and density and increased emissions. There exist many ways to clean biodiesel and they can be divided into two categories: dry and wet.

2. Literature review

2.1 Biodiesel

Biodiesel is counted as renewable energy source as it is made from waste materials or feedstock that will regrow during our lifetime, like plants, crops or animal fats. Those are composed of triglycerides – fatty acid esters with glycerol. Fatty acids can be divided into two groups: saturated and unsaturated. These, together with other components, determine the oil's chemical and physical properties, what later is transferred to produced biodiesel [8].

There are many ways of biodiesel production, these include: micro-emulsion, pyrolysis, transesterification and supercritical methanol [9].

There are several standards for fuel to fulfil before it is allowed to be used in those engines. European Union forced certain properties and its values to be met in EN 590:2009 Automotive fuels - Diesel - Requirements and test methods, and EN 14214 Biodiesel standard [10, 11]. The most important ones are:

- Cetane Number (CN) – this value corresponds to ignition qualities, like no knocking or start-ability. Low number means longer ignition delay as there are comparatively more fuel gathering before proper combustion.
- Density – it's the measure of mass per unit of volume. It differs for diesel and biodiesel, for the first one it can vary from 820 to 845 kg/m³, while for the latter it's 860 – 900 kg/m³.

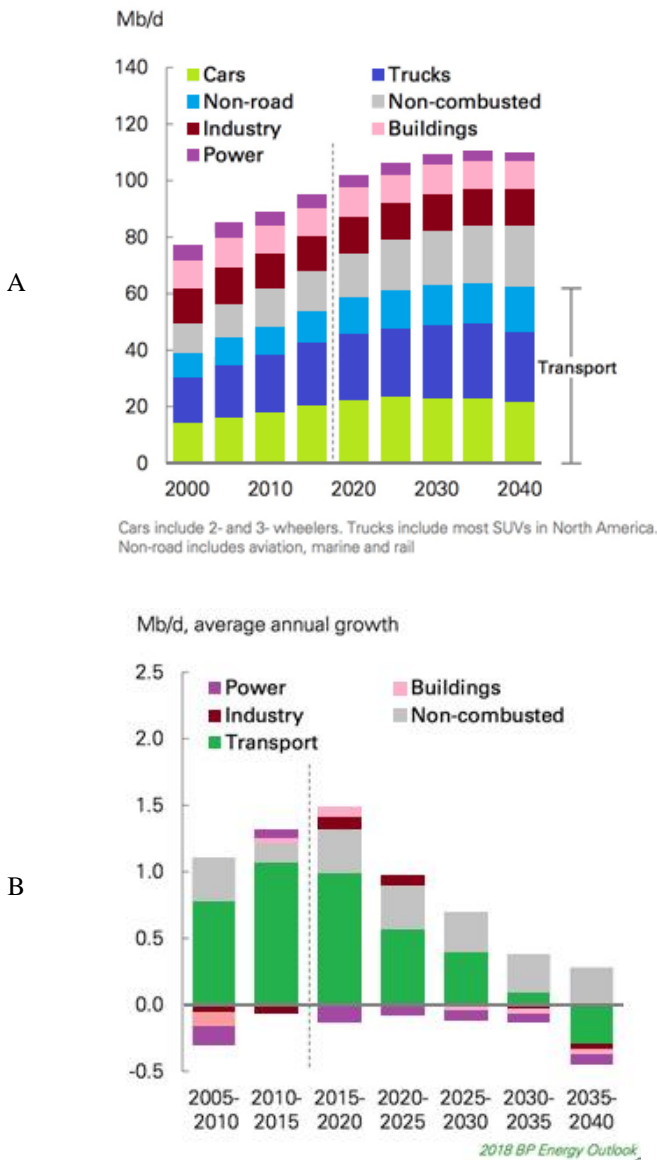


Figure 2. Liquid demand (A) and its growth (B). Adapted from [2].

Additionally biodiesel produces less CO as its composition allows for better total combustion, the same applies to reduced emission of unburnt hydrocarbons. It is important to remember that there are many sources of biodiesel, presented earlier, and emissions from each may differ what was shown in study [3]. In contrast in study [4] NO_x and smoke emissions were higher than from diesel.

- Flashpoint – it's the lowest temperature, that after adding an ignition source, the volatile material ignites and the flame does not stay when the ignition source is removed. In diesel this value is stated at minimum 55 °C, while for biodiesel it's almost twice more, 101 °C.

- Oxidative Stability – describes the tendency of the fuel reacting with oxygen at ambient temperatures. It is a very important factor for long term storage [12].

- Kinematic Viscosity – this property of fuel is very important, because it can lead to not complete combustion, increase energy demand from pumps [13].

There are many other parameters that are needed for fuel to be fulfilled, but are not described in detail in this work for example: sulphur content, glycerine content, water content, pour point, cold filter plugging point.

Nowadays biofuels are divided into 4 categories: first generation, second generation, third generation and fourth generation. First generation biofuels' feedstock are mostly food crops, like sugar cane, corn, vegetable oils like soybean, rapeseed, or peanut crops. This leads to many debates fuels versus food, because of the poor countries and hunger around the world, that more developed countries process food for their own purposes.

Second generation biofuels are based on non-edible crops, wood waste, forest residues and municipal waste and its organic fraction. Thus, many drawbacks of 1st generation biofuels, like arable land use or using food crops, are not a problem when it comes to 2nd generation. Unfortunately waste materials may not be enough to meet the demand in the future, since there are limited amounts of such materials, so additional fast growing wood crops are needed to fulfil increasing needs [15,16].

Third generation biofuels are fuels made from algae and microalgae. There are many advantages to use these kind of feedstock instead of conventional food crops or wastes. Algae grow fast and they do not need very good agricultural land that can be used for food crops. Additionally it is possible to cultivate algae the whole year, unlike other seasonal crops, making it a constant feedstock for industry. The main drawback would be that the final product has high water content that needs to be removed [16].

Lastly the fourth generation biofuels, which are the newest development in this industry. They use genetically modified algae to increase their growth

factors through improved photosynthesis process or increased light penetration. There are still concerns about the environmental friendliness of genetic engineering [5].

2.2 Biodiesel Feedstock

Main advantage of biodiesel is its variety of feedstock. Due to its wide range it can be produced almost in every part of the world as a decentralised fuel source. Availability depends on a couple factors like: location and climate, soil and agricultural conditions. Depending on country, different feedstock is used, for example in USA the most used is soybean or peanut, while in UK or China it is rapeseed. In Indonesia and India jatropha crops are very common. Each feedstock also provides biodiesel with different properties, depending on the composition of plants/fats.

For large production scale, costs should be lowered for economical and feasibility purposes and according to [14] 75% of costs are associated with oil. In the USA in July 2015 the price for diesel was 2,93 \$, while biodiesel was at 3,55\$ per gallon, at the same time fresh soybean oil cost 2,61 \$/gal, showing accordance to the presented Figure 4. In order to become more competitive feedstock expenditures must be decreased [17].

Waste Frying Oil (WFO) seems like a reasonable solution for this problem. It is estimated that Europe produces from 2 to 3 million litres of WFO per day [17]. Converting this amount of oil into biodiesel would highly impact the market. As a waste, WFO, is cheap and can be collected locally, especially in large cities with many restaurants and habitants. There have been many studies considering WFO as feedstock for biodiesel production.

2.3 Catalysts

Catalysts are substances, materials that allow a reaction to proceed faster, increasing its chemical reaction rate, by decreasing activation energy. After the reaction the catalyst is not consumed and should stay the same without chemical changes.

Nowadays catalysts are commonly used in industry, with complicated and refined structure and composition.

Basic properties of catalysts are as follows:

- selectivity – describes the direction of the reaction preferred by the catalyst,
- activity – chemical reaction speed,

- stability – performance during operation and regeneration,
- temperature – shows when the catalyst works with highest efficiency and best results.

Catalysts can be divided based on their contact type with the reaction compounds, in the same phase, liquid or gas called homogeneous, or in different phases, called heterogeneous. Also by catalyst properties if it is basic or acidic.

Each type has its advantages and disadvantages. Heterogeneous catalysts does not cause corrosion, it is possible for their regeneration, easier to remove from the final product, acidic catalysts are able to catalyse transesterification and esterification at the same time regardless of water content and free fatty acids. But they also come with cons, which include the need for well mixing due to another phase or high oil to alcohol ratio.

Basic homogeneous catalysts have high advantage in kinetics, having high activity and yield in shorter time than heterogeneous, but they come with many cons, like sensitivity to water and free fatty acid content or higher saponification and emulsion formation.

There are many aspects to consider when picking the right catalyst, including their reactions with reactants, efficiency, properties of oil they can be used with, reactor type and price.

2.4 Purification

Before reaching to the final customer biodiesel has to meet certain characteristics and regulations. Density difference between glycerol and biodiesel are enough to separate them using standard gravitational settling or centrifugation. But after this process biodiesel is still not ready for market purposes. It is contaminated with free glycerides, soap, remainings of reactants – oils, alcohol, water and catalyst. Those affect final product causing different effects and losses in quality, listed in Table 1. Many researchers ([6, 7, 18]) showcase 2 biodiesel purification methods – wet and dry.

2.4.1 Wet purification

Wet purification consists of adding deionized water, organic solvents or mineral acid with water to crude biodiesel. By this action it is possible to remove soluble impurities from the biodiesel. This simple method allows easy and effective glycerol and methanol removal. This process requires large amounts of water and therefore the mixture after the

purification needs to be dried, for example by molecular sieves and then by filtration or hot gas stripping, vacuum flash evaporation [15, 19].

Efficiency of this method is high, but it also comes with disadvantages, like possibility of free fatty acids formation, loss of biodiesel yield due to emulsion formation and most importantly this method produces a lot of wastewater that needs to be treated in order to be released back to environment. It was reported that water used may be from 3 to 10 times larger in volume than crude biodiesel for purification. Moreover due to deionized water, biodiesel drying after purification and treatment of wastewater, energy costs are increasing [15, 19].

Table 1 Impurities' effects on biodiesel and diesel engines. Adapted from [7].

Impurity	Effect
Water	Corrosion Free fatty acids formation through hydrolysis Filter blockage due to bacteria growth
Free Fatty Acid	Lower oxidation stability Corrosion
Alcohol	Lower viscosity and density Lower flash point Corrosion
Glycerides	Higher viscosity Crystallization Carbon residue in injectors
Metals soap catalyst)	Carbon residue in injectors Filter blockage due to ashes
Glycerol	Increased emissions Settling problems

There are researches being made on other solvents than water, due to its cons. [20] shows ionic liquids and eutectic solvents to be used. Those green solvents have a series of advantages, like non-flammability, environment friendly, biodegradability and reusability. These make them promising substitution for water, but their costs are increased, limiting their applications.

Beside abovementioned options there is also membrane method. This low water alternative uses filtration membranes, doesn't produce wastewater, lowering industrial costs. depending on feedstock membranes may have finer sieves 0,1 µm up to 1 nm.

There are two types of membranes: polymeric (organic) and ceramic (inorganic).

2.5.2 Dry purification

An alternative option for biodiesel purification is dry washing. This method is based on adsorption process between biodiesel and an absorbent material, or by applying ion-exchange resin bed and passing crude biodiesel through it. Adsorption means that atoms, molecules or ions adhere to the surface of a solid material [15]. Impurities infiltrate pores of a solid and adhering to its surface. Besides not generating wastewater, this method doesn't require large purification tanks compared to wet methods. Moreover lower time, ability for easy retrofit of biodiesel plants, recyclability of used material make it a very competitive way to purify biodiesel [21].

There have been many products developed for industry, such as Magnesol® and activated carbon. Due to their basic and acidic sites on surface they attract glycerol and alcohols, and in consequence they have high efficiency. [22] prepared activated carbon from spent tea waste and compared its effectiveness with other methods, silica gel and wet purification on a biodiesel produced from waste cooking oil. Their research showed that activated carbon yields better results than other tested methods due to its composition and surface oxygen groups that help with adsorption.

Another example of natural adsorbents are cellulose and starch. [23] made a research on different starch (corn, potato and cassava) and eucalyptus bleached kraft cellulose. The experiments used sunflower oil and purification process was carried out in 25°C and stirred for 10 minutes. The test samples were 1, 2, 5, 10 by weight %. Best results were obtained with 5% or more to decrease acidity index, indicating free fatty acids left in biodiesel, combined alkalinity, showing catalyst concentration (NaOH), glycerine and turbidity.

Magnesol® is an inorganic matrix of anhydrous sodium sulfate and magnesium silicate. It was shown in [7, 24] that Magnesol® has very high efficiency in water, methanol and soap removal from biodiesel. Those studies used different oils, Faccini made biodiesel from soybean oil, while Skelton used industrial refined and used cooking oil. Soap was removed in 96%, alcohol in 90% and water content in 60%. Their researches were made with 0,25-1 weight % displaying its adsorbance capabilities and effectiveness. Best results were obtained with 60 °C and 60 minutes of stirring after Magnesol® powder was added to preheated biodiesel.

Ion-exchange method is based on electrostatic force between the solid material's surface and crude biodiesel. There are many industrial used resins, like Lewatit GF202 or PD206, BD10. The last two were not capable of removing alcohols to a satisfactory level, but GF202 fulfilled this standard as well as glycerol and soap removal. there are a series of properties to consider when picking ion-exchange resin: porosity, size, stability, density and charge [15, 25].

3. Materials and methods

3.1 Catalyst preparation

Based on [31] it was decided to make the catalyst from eggshells, that are mainly made of CaCO₃ and by basic calcination process they can be turned into CaO, creating an active, heterogeneous catalyst. Eggshells were first cleaned with tap water and left to dry. Then they were grinded in a mortar and mixed with ammonia oxalate. This nitrogen compound turns into gaseous state during calcination process and improves the morphology of the final catalyst. [34] studied the calcination process and found that the best temperature to obtain high amount of calcium oxide is 900 °C. The samples were left under this temperature for 4h. Final product was a heterogeneous catalyst.

3.2 Biodiesel production

Huge methanol to oil ratio 12:1 was used to increase the pace of the reaction. Before combining the reactants, 5% by biodiesel weight catalyst was mixed with alcohol at 65 °C for 1 h, what also has positive effect on the final transesterification reaction as mentioned in the study [35]. Oil was also preheated before adding it to the reactor – three-neck round bottom flask. The setup is shown on Figure 4.4. After 1 h of alcohol preheat, oil was added to the reactor. Reactants stayed in the reactor for 90 minutes with 67 °C and after the elapsed time it was cooled down and by filtration the catalyst was removed and the liquid phase was put into a decantation funnel to separate glycerine and biodiesel.

3.3 Purification process

For purification stage after biodiesel production from WFO it was decided to use dry method with Magnesol® adsorbent. Purification was carried out on the same station as biodiesel production, in a three-neck round bottom flask.

There were two parameters measured during these experiments. Contact time to check if longer exposer of biodiesel to adsorbent will increase its

parameters. As presented in literature ([16]) the standard washing time is 30 minutes and some researches took up to 1 hour. Tested time stamps were 20, 40 and 60 minutes. Another important aspect is the amount of adsorbent added to the biodiesel. Aforementioned studies ranged from 0,25 – 3 weight % of Magnesol® (biodiesel based) added to biodiesel. For the purpose of this study a weight of 3% biodiesel mass was used, as it expressed highest purification. Second parameter tested was the temperature of purification. Based on literature the best temperature of the washing is around 60-70 °C and the beforementioned washing times and weight ratios 65 °C was tested. Additionally Magnesol® was tested in 45 °C with 2 longer exposure times (40 and 60 minutes). 50 °C was acquired in order to see the trend of increasing adsorption with temperature and an extra test was carried out with 10% of Magnesol® and 65 °C.

3.4 FTIR

Infrared spectroscopy analyses the interaction between matter with infrared light emitted and directed at a sample. Under this beam molecules vibrate and absorb certain wavelengths of infrared light. Due to this absorbance and spectra one can determine chemical composition of the sample and structural information. It is a non-destructive, surface technique that allows for liquid or solid substance examinations. The sample is placed on a crystal that is infrared transparent, so all absorbed wavelengths belong only to the tested material [26, 27].

3.5 Thermogravimetry

Thermogravimetry (TGA) is a very common method for studies including adsorption, absorption, thermal decomposition etc. Basic principle of this technique is to measure mass change in time or with increasing temperature. obtaining data about mass change gives valuable information about the sample, as different compounds decompose, evaporate in different conditions and it is easy to determine what substance changed its state based on temperature of weight change and additionally to evaluate the sample's stability and composition [32].

3.5 X-Ray Diffraction

X-ray Diffraction (XRD) is a non-destructive method used for identification, quantification and characterization of a sample. It can be used even with small amounts of material and allows for bulk examination of a material. The only flaw of this technique is that it can only detect crystalline material, so amorphous materials will not

be examined [33]. It uses well known Bragg's law and allows for detail inspection of a sample.

4. Results and discussion

4.1 Catalyst

Produced catalyst from eggshells was characterized using XRD. The material was tested 3 times, freshly made after calcination, after reaction with oil and methanol, and after 6 months of not-usage. For results interpretation JCPDS XRD files were used to identify crystal structures in the catalyst. In Figure 3 is can be observed that fresh catalyst consists mainly from lime (CaO, JCPDS 000-004-0777), showing calcination process was made with high efficiency and material will fulfil its role as a catalyst. Post reaction catalyst is made mostly from calcite (CaCO₃, JCPDS 00-001-0837) – calcium carbonate.

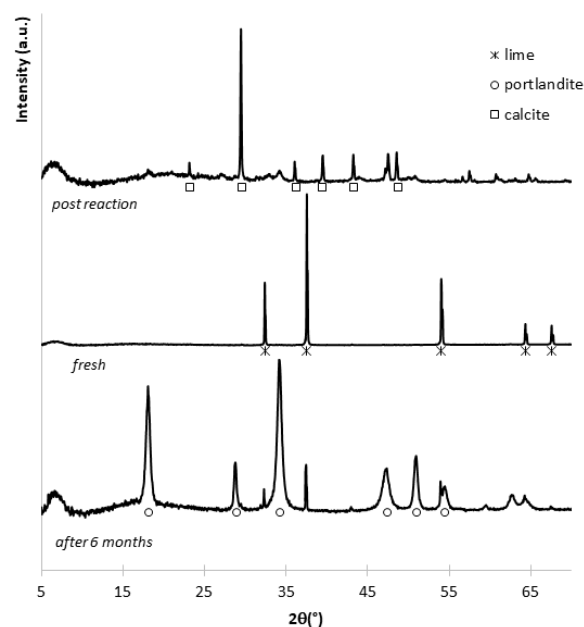


Figure 3. XRD patterns of fresh, post reaction and after 6 months, catalyst.

In the XRD for sample after 6 months there are mainly peaks associated with portlandite (Ca(OH)₂, JCPDS 01-070-6444) – calcium hydroxate. It shows hydrophilic affinity of lime. For the reaction of transesterification it is very important, because methanol, air and WFO may contain moisture. Thus calcium hydroxate may be forming during the reaction and by contact with glycerine it may form calcium diglyceroxide.

4.2 Produced biodiesel

Produced biodiesel and WFO were put into FTIR testing in order to find bonds and to determine the compounds that are dissolved in the mixtures. Figure 4

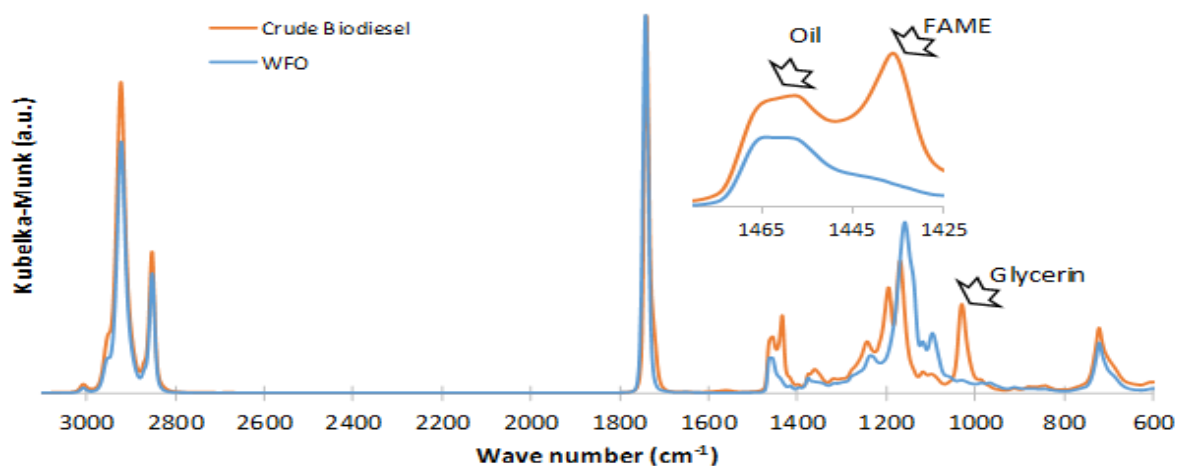


Figure 4. WFO and Crude Biodiesel ATR-FTIR spectra.

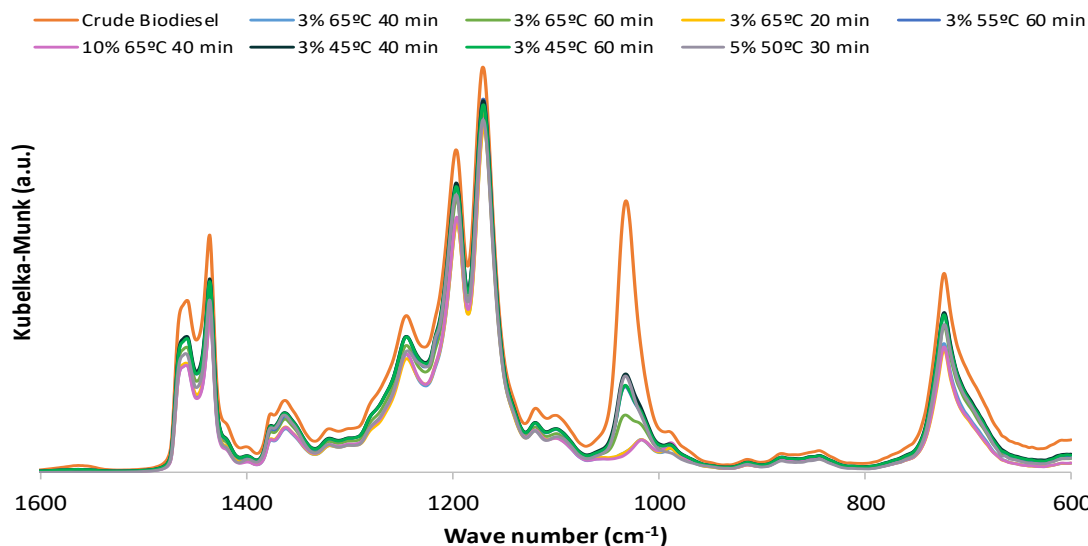


Figure 5. ATR-FTIR spectra of crude and purified biodieses

Table 4. FAME yield in purified biodiesel.

Conditions		FAME content (% W/W)
Biodiesel purified with Magnesol®	3%W; 45°C; 40 min	80.1
	3%W; 45°C; 60 min	83.1
	3%W; 55°C; 60 min	84.6
	3%W; 65°C; 20 min	86.2
	3%W; 65°C; 40 min	86.4
	3%W; 65°C; 40 min	86.6
	5%W; 55°C; 30 min	79.7
	10%W; 65°C; 40 min	88.7

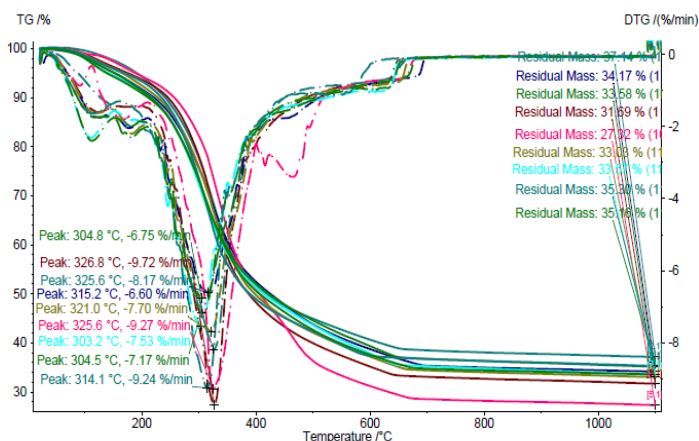


Figure 6. TG graph for purified Biodiesel.

shows FTIR spectra and there are clear peaks on some wavelengths.

By comparison between the results and [28], biodiesel blends show that with higher FAME content the peaks at 1741 cm⁻¹, 1031 cm⁻¹ and 1172 cm⁻¹ also intensity, implying that FAME is an indication of biodiesel content in a blend with petroleum diesel. The same relationship has been found with peaks appearing at 723 cm⁻¹, indicating that they are also correlated.

Peaks found at higher wavelengths 2855 cm⁻¹ and 2925 cm⁻¹ didn't follow that pattern in the study [28]. It means that both biodiesel and fossil diesel contain those groups with similar frequency ranges.

Comparing the data from FTIR analysis for WFO and the one from study [29], one can see many similarities. Peaks appear in the same wavelengths in the given range of testing. The cited study had a more broad range of the spectra, since it was able to go down to 400 cm⁻¹, while this work finished FTIR on 600 cm⁻¹. Thus, Huang, et. al. was able to find another peak at around 420 cm⁻¹.

High peak on Figure 4 on 1031 cm⁻¹ shows high amount of glycerine in crude biodiesel. That may be caused by incomplete separation in decantation funnel or by unideal mechanical separation when the glycerine was poured down from decantation funnel. In that case some glycerine may have stayed in funnel and got mixed with biodiesel again, thus being difficult to detect with naked eye.

Based on two samples taken from crude biodiesel the average FAME content was calculated and it was equal to 77,6 % by weight.

4.3 Biodiesel after purification

50 g samples of crude biodiesel were purified in different conditions (time, sorbent's weight, temperature) and FTIR spectra can be seen on Figure 5. The biggest change occurred in glycerine band, what can be observed as the peak at 1031 cm⁻¹ has decreased significantly compared to crude biodiesel. Magnesol® has been found to remove glycerol partially and the best results were obtained for conditions: 10% weight, 65°C and 60 minute contact time.

In Table 4 there are results for FAME calculations in all purified samples. Best results were obtained with 10% weight of Magnesol® (biodiesel based). On other results it can be seen that with increasing time of

contact between the sorbent and crude biodiesel, the FAME content grows.

Even with best conditions applied, Magnesol® was not able to increase FAME content to 96,5%, which is minimum amount for biodiesel as stated in European Biodiesel Standard EN 14214 [11]. High affinity to glycerine may be affected by hygroscopic properties of Magnesol®.

4.4 Magnesol®

Magnesol® was tested before and after purification with FTIR method and thermogravimetry. FTIR curves for all samples are shown on Figure 7. In study [36] magnesium silicate at 1016 cm⁻¹ represents a vibrational band, this band is also seen in conducted raw Magnesol® FTIR. During purification because of glycerine adsorption peak has shifted towards 1031 cm⁻¹ what was earlier described to be associated with glycerol bands. Additionally it can be seen that Magnesol® adsorbed water and alcohols, what shows by increased peaks at around 3500 and 2900 cm⁻¹. Bands around 1470-1430 cm⁻¹ show that some of the unreacted WFO and FAME were also adsorbed.

Additionally thermogravimetry tests were conducted on Magnesol®. Figure 6 shows TG graphs for given samples. All show a high peak near 300 – 330 °C, what corresponds to glycerine decomposition. The different temperatures are the result of different amount of glycerine adsorbed by Magnesol®. Early peak around 110 °C may be associated with methanol and water evaporation. Peak at 460 °C is observed only for one of the samples and may show carbon combustion. Literature describes this peak for combustion of monounsaturated fatty acids [30].

5. Conclusions

The demand for energy in the world requires to find new sources of energy. Together with changing climate, limited fossil resources and new laws, there are many studies towards green, renewable sources, like wind, solar or hydro. In order to decrease the usage of conventional fuels used in transport, new alternative is being developed in the form of biodiesel. This product is biodegradable, less toxic to the environment and has a comparable performance to its fossil counterpart.

The main objective of this study was to see the capabilities of WFO as a biodiesel feedstock and ways to enhance the fuel by purification. The results show that biodiesel produced from WFO with heterogeneous catalyst are lower than from other sources, like

soybean oil. Thus it is necessary to improve its properties by purification.

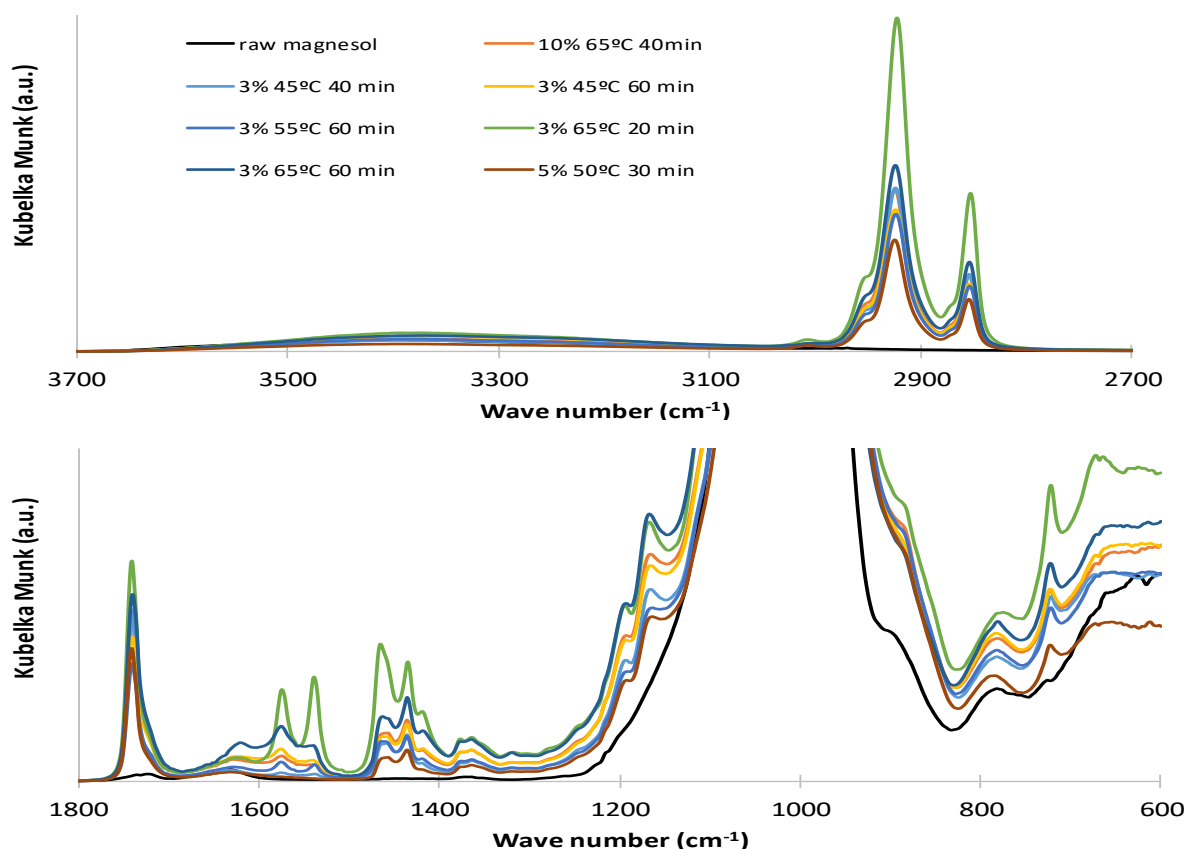


Figure 7. FTIR of fresh and post-purification Magnesol®.

Magnesol® was used to purify produced biodiesel. It has been found to remove impurities like: glycerol, water, methanol and fatty acids. All conditions for purification allowed for purification of 2 to 11%. Best conditions for that were 10% Magnesol® weight, 65°C of contact temperature and 60 minutes of contact time.

Further studies should be made in order to quantify the amounts of absorbed impurities in Magnesol®. Additionally more studies on temperature and weight ratio variations should be conducted in order to deepen the knowledge of Magnesol® as a biodiesel purification sorbent.

References

- [1] BP Statistical Review of World Energy, June 2018
- [2] J. Pyper, BP Forecast, Shared, *Autonomous EVs Will Help Drive to Peak Oil Before 2040*, February 2018, <https://www.greentechmedia.com/articles/read/bp-forecast-autonomous-electric-vehicles-peak-oil#gs.gnjadu>, available: 06.06.2019
- [3] K. A. Abed, M. S. Gad, A. K. El Morsi, M. M. Sayed, S. Abu Elyazeed, *Effect of biodiesel fuels on diesel engine emissions*, Egyptian Journal of Petroleum, March 2019, vol. 28
- [4] L. Anantha Ramana, B. Deepanraj, S. Rajakumar, V. Sivasubramanian, *Experimental investigation on performance, combustion and emission analysis of a direct injection diesel engine fuelled with rapeseed oil biodiesel*, Fuel, June 2019, vol. 246, p. 69-74
- [5] Gerhard Knothe, Jon Van Gerpen, *Biodiesel Production, The Biodiesel Handbook*, 2010, p. 31-96
- [6] J. M. Fonseca, J. G. Teleken, V. de Cinque Almeida, C. da Silva, *Biodiesel from waste frying oils: Methods of production and purification*, March 2019, Energy Conversion and Management, vol. 184, p. 205-2018
- [7] Monica Berrios, Robert L. Skelton, *Comparison of purification methods for biodiesel*, Chemical Engineering Journal, 2008, vol. 144, p. 459-465
- [8] J. M. Marchetti, *A summary of the available technologies for biodiesel production based on a comparison of different feedstock's properties*, Process Safety and Environmental Protection, May 2012, vol. 90, p. 157-163

- [9] L. Lin, Z. Cunshan, S. Vittayapadung, S. Xiangqian, D. Mingdong, *Opportunities and challenges for biodiesel fuel*, Applied Energy, 2011, vol. 88, p. 1020-1031
- [10] EN 590:2009 Automotive fuels - Diesel - Requirements and test methods
- [11] EN 14214 Biodiesel standard
- [12] James Pullen, Khizer Saeed, *An overview of biodiesel oxidation stability*, Renewable and Sustainable Energy Reviews, 2012, vol. 16, p. 5924-5950
- [13] Luis Felipe Ramirez Verduzco, *Density and viscosity of biodiesel as a function of temperature: Empirical models*, Renewable and Sustainable Energy Reviews, 2013, vol. 19, p. 652-665
- [14] A.E. Atabani, et al., *A comprehensive review on biodiesel as an alternative energy resource and its characteristics*, Renewable and Sustainable Energy Reviews, 2012, vol. 16, p. 2070-2093
- [15] S. N. Naik, Vaibhav V. Goud, Prasant K. Rout, Jay K. Dalai, *Production of first and second generation biofuels: A comprehensive review*, Renewable and Sustainable Energy Reviews, 2010, vol. 14, p. 578-597
- [16] Hayder A. Alalwan, Alaa H. Alminshid, Haydar A. S. Aljaafari, *Promising evolution of biofuel generations. Subject Review*, Renewable Energy Focus, March 2019, vol. 28, p. 127-139
- [17] I. J. Duti, M. Maliha, S. Ahmed, *Biodiesel Production from Waste Frying Oil and Its Process Simulation*, Journal of Modern Science and Technology, vol. 4, p. 50-62
- [18] I.M. Atadashi, *Purification of crude biodiesel using dry washing and membrane technologies*, Alexandria Engineering Journal, 2015, vol. 54, p. 1265-1272
- [19] I. J. Stojković, et al., *Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification*, Renewable and Sustainable Energy Reviews, 2014, vol. 32, p. 1-15
- [20] H. Zhao, G. A. Baker, *Ionic liquids and deep eutectic solvents for biodiesel synthesis: a review*, Journal of chemical Technology and Biotechnology, 2013, vol. 88, p. 3-12
- [21] V. G. Demir, H. S. Soyhan, *Biodiesel Production Using Wet and Dry Purification Methods*, European Journal of Engineering and Natural Sciences, 2017, vol. 2, p. 137-143
- [22] A. B. Fadhi, M. M. Dheyab, Abdul-Qader Y. Abdul-Qader, *Purification of biodiesel using activated carbons produced from spent tea waste*, Journal of the Association of Arab Universities for Basic and Applied Sciences, 2012, vol. 11, p. 45-49
- [23] M. G. Gomes, D. Q. Santos, L. C. de Morais, D. Pasquini, *Purification of biodiesel by dry washing, employing starch and cellulose natural adsorbents*, Fuel, 2015, vol. 155, p. 1-6
- [24] C. S. Faccini, et al., *Dry washing in biodiesel purification: a comparative study of adsorbents*, Journal of the Brazilian Chemical Society, 2011, vol. 22, p. 558-563
- [25] M. Berrois, J. Siles, M. Martin, A. Martin, Ion Exchange in: S. Ramaswamy, H. J. Huang, B. V. Ramarao, (Eds.), *Separation and purification technologies in biorafineries*, John Wiley and Sons, 2013
- [26] S. E. Glassford, B. Byrne, S. G. Kazarian, *Recent applications of ATR FTIR spectroscopy and imaging to proteins*, Biochimica et Biophysica Acta (BBA) - Proteins and Proteomics, 2013, p. 2849-2858
- [27] K. Sahil, et al., *Interpretation of Infra-Red Spectra*, International journal of pharmaceutical and chemical sciences, 2012, vol. 1, p. 174-200
- [28] A. Y. Oyerinde, E. I. Bello, *Use of Fourier Transformation Infrared (FTIR) Spectroscopy for Analysis of Functional Groups in Peanut Oil Biodiesel and Its Blends*, British Journal of Applied Science and Technology, 2016, vol. 13, p. 1-14
- [29] Y. Huang, et al., *Investigation on fuel properties and engine performance of the extraction phase liquid of bio-oil/biodiesel blends*, Renewable Energy, 2020, vol. 147, p. 1990-2002
- [30] J. C. O. Santos, I. M. G. dos Santos, A. G. De Souza, S. Prasad, *Thermal Stability and Kinetic Study on Thermal Decomposition of Commercial Edible Oils by Thermogravimetry*, Journal of Food Science, 2002, vol. 67, p. 1393-1398
- [31] Y. C. Wong, R. X. Ang, *Study of calcined eggshell as potential catalyst for biodiesel formation using used cooking oil*, Open Chemistry, 2018, vol. 16, p. 1166-1175
- [32] S. Loganathan et al., *Thermogravimetric Analysis for Characterization of Nanomaterials, Thermal and Rheological Measurement Techniques for Nanomaterials Characterization*, 2017, p. 67-108
- [33] Giovanni Perego, *Characterization of heterogeneous catalysts by X-ray diffraction techniques*, Catalysis Today, 1998, vol. 41(1-3), 251-259
- [34] R. Mohadi, K. Anggraini, F. Riyanti, A. Lesbani, *Preparation Calcium Oxide From Chicken Eggshells*, Srivijaya Journal of Environment, 2016, p. 32-35
- [35] A. Kawashima, K. Matsubara, K. Honda, *Acceleration of catalytic activity of calcium oxide for biodiesel production*, Bioresource Technology, 2009, vol. 100, p. 696-700
- [36] Iyad Rashid, et al., *Magnesium Silicate*, in: Harry G. Brittain, *Profiles of Drug Substances, Excipients and Related Methodology*, 2011, vol. 36