SAMPLE

Biodiesel purification using sorbents

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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 mg_{KOH}/g_{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®
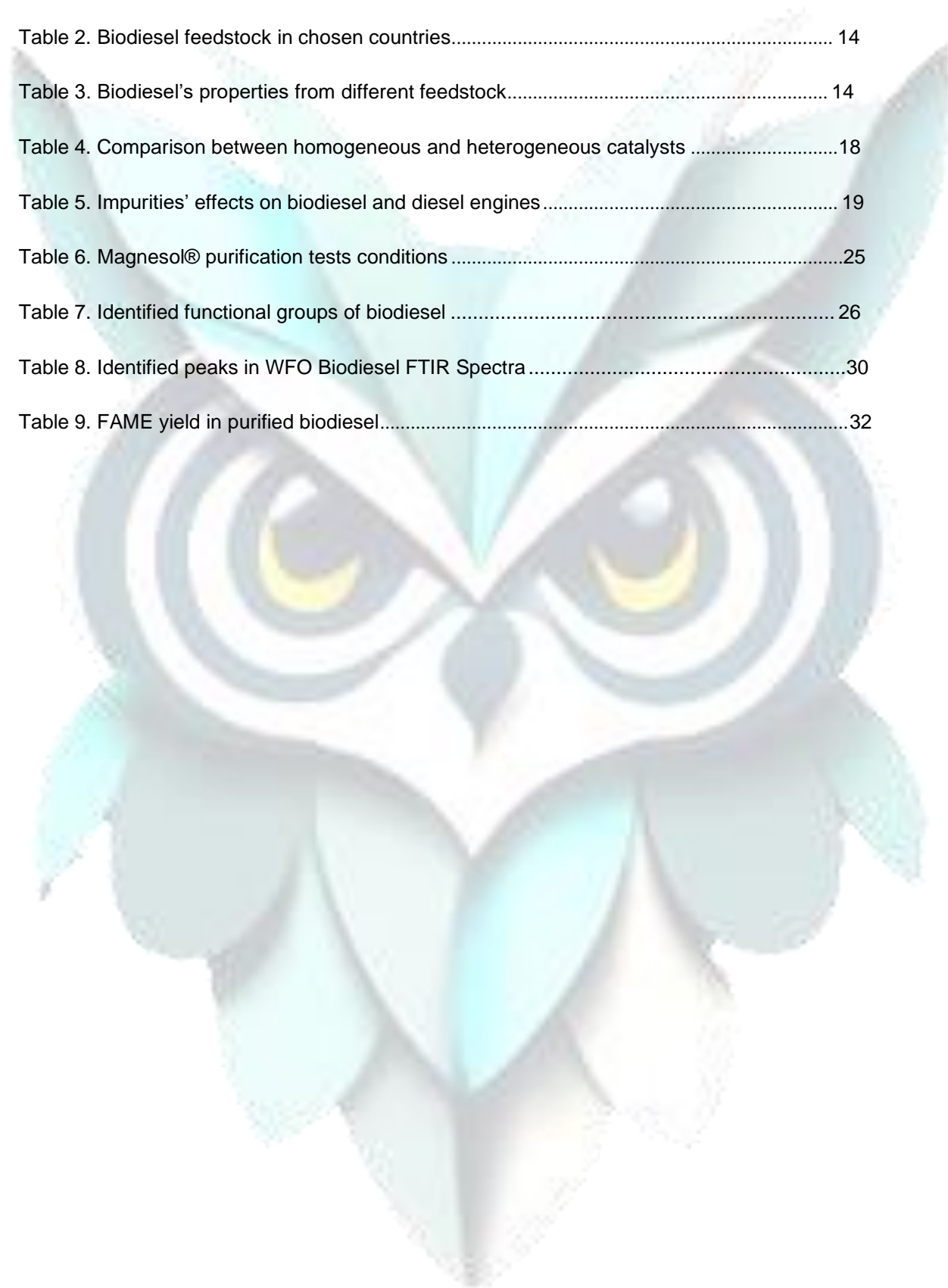
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1. Introduction

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, what shows Figure 1.
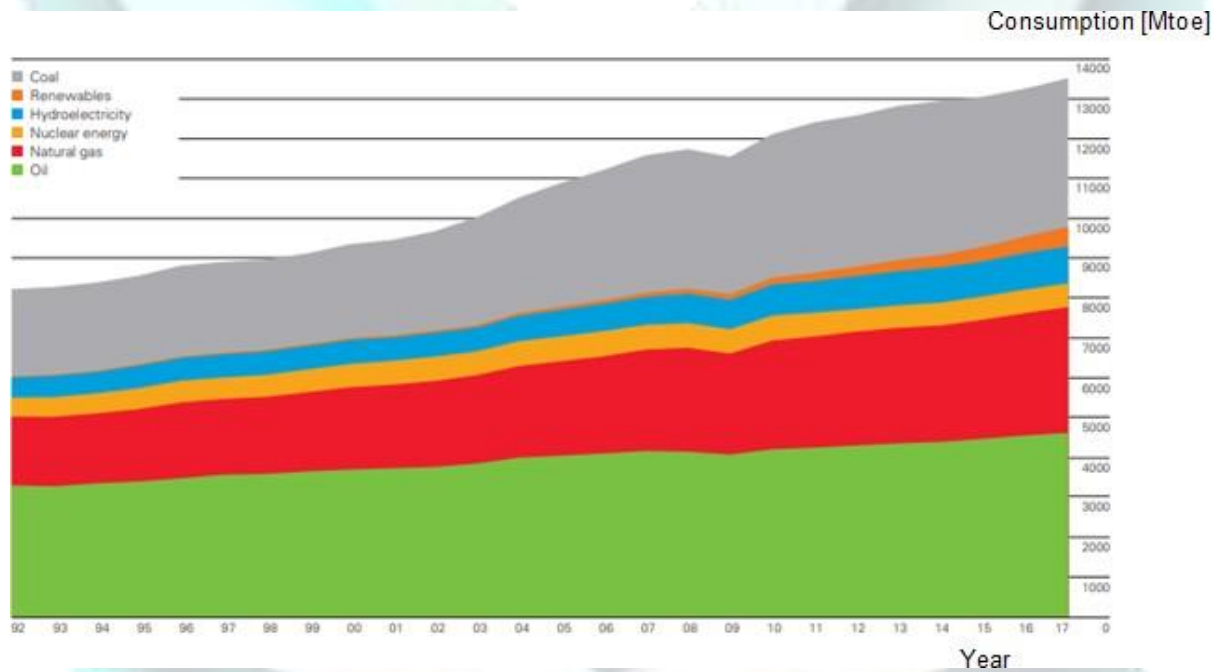
Figure 1. World Energy Consumption by source. Adapted from [1].

It is easily seen that renewable sources grew significantly during the past few years, but to meet the full demand other fossil based fuels also increased, like oil, natural gas or coal. This is also due to developing technology and better efficiency of machines and processes.

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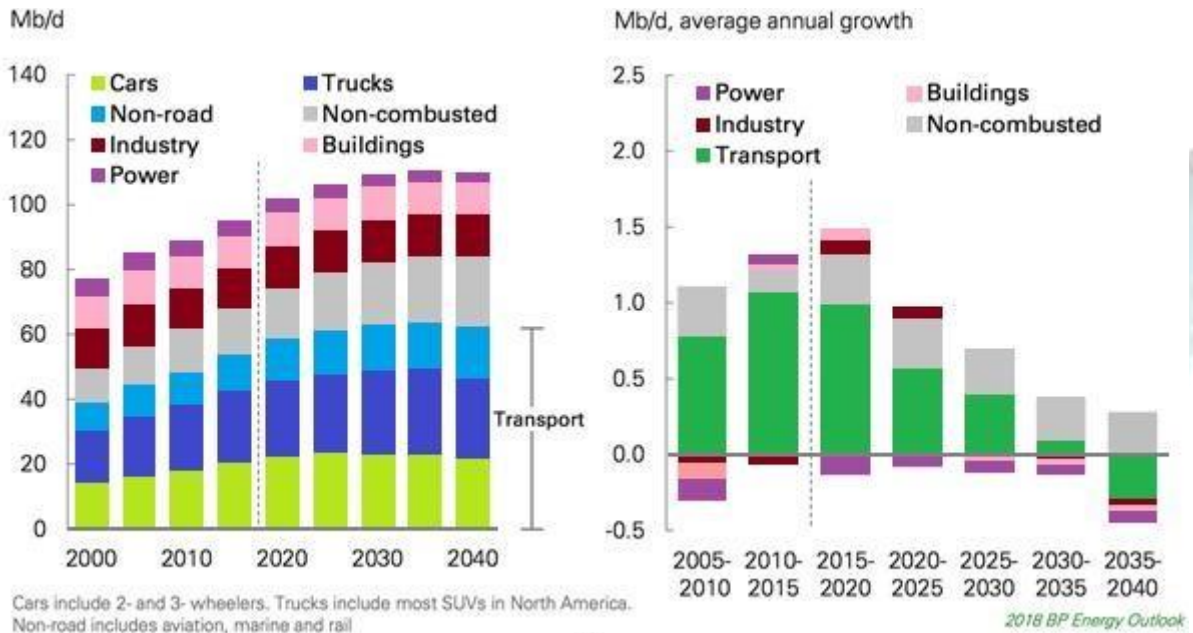
Figure 2. Liquid demand (A) and its growth (B). Adapted from [2].

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.

Biodiesel was divided onto 4 categories based on used feedstock for production. Those are: first generation, second generation, third generation and fourth generation. There are many debates on food versus fuel from edible crops as poverty and starvation is present on the globe and more developed countries want to spend food on fuel generation. This reason was the main drive for newer and more diversified feedstocks for biodiesel production [3, 4, 5]. Those generations present different raw materials, like vegetable oils for first generation or algae for third generation.

All these materials 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 [16].

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. The second method requires water, what puts more costs

into the process, increased production time and the need to dehydrate the biodiesel afterwards. Most commonly used liquids are hot water and a phosphoric acid solution [13]. Additionally, when using with feeds that contain more free fatty acids, emulsions may form due to earlier saponification process [18]. Dry washing method is based on using adsorbents like Magnesol® or activated carbon. The main mechanism is to accumulate impurities on the surface of the sorbent. This method does not produce wastewater what makes it very attractive, but used product has to be landfilled, since there are no much research on regeneration of these sorbents [13].

Biofuels does not only give an alternative fuel or replacements in other industries, because of its decentralised production it can be a future for energy security. European Union (EU) does not have its own oil reserves, they are imported from other continents as shown on Figure 3.
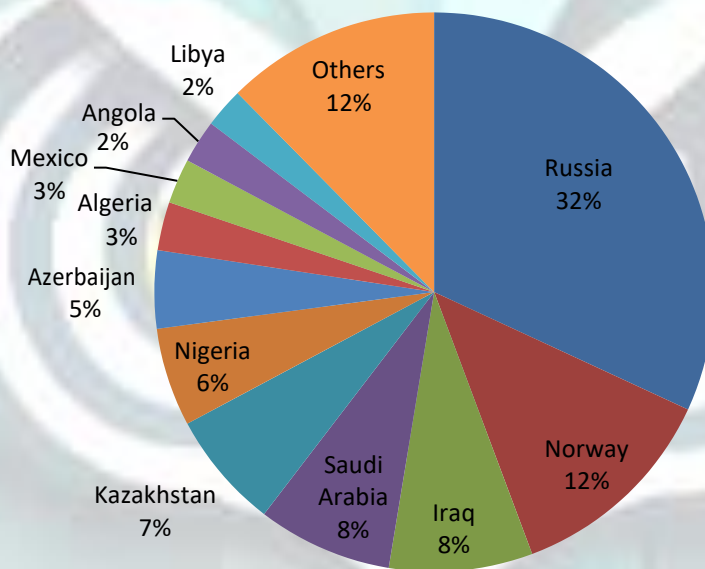
Figure 3. Crude oil imports to European Union by country. Adapted from [6].

European Union is largely dependent on Russia as almost one third of oil import comes from that country. Its political views and international relations are not in favour for cheap and easy going export to EU. Second is Norway which is close compared to other countries and has a stable government, unlike for example Iraq or Libya. Long transport increases costs of oil and after many processes the cost of final product.

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 CO_2 in order to grow, so when burned it releases that compound back to atmosphere making the gross CO_2 increase is much less significant than fossil fuels. 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 [7]. In contrast in study [8] NO_x and smoke emissions were higher than from diesel.

1.1 Thesis Objective

The main goal of this Thesis is to test dry washing purification process on biodiesel produced from waste frying oils and heterogeneous catalyst. Catalyst was obtained by calcination of eggshells, because they contain high amount of calcium, mixed with ammonia carbonate or oxalate to obtain porous structure. Waste frying oil was collected from a local restaurant.

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. The first one is made with only single bond between carbon atoms and the most common one is palmitic (16:0) and stearic (18:0) acids. The latter group has at least one double carbon-carbon bond and there are 3 main fatty acids: oleic (18:1), linoleic (18:2) and linolenic (18:3). These, together with other components, determine the oil's chemical and physical properties, what later is transferred to produced biodiesel [9].

There are many ways of biodiesel production, these include: micro-emulsion, pyrolysis, transesterification and supercritical methanol [23]. Micro emulsion is a colloidal dispersion of immiscible oil and water stabilized by an interfacial film of amphiphile. To create fuel, ethanol is used instead of water creating ethanol-in-oil microemulsion. Main advantage of this process is its simplicity, but there are drawbacks in low quality fuel – viscosity, volatility and stability does not fulfil standards [24].

Pyrolysis is a process where organic matter is decomposed under the influence of temperature. Vegetable or animal oils, fatty acids or methyl esters can be used as material to produce biodiesel. Product has high cetane number, viscosity, sulfur and water content are within acceptable norms, while ash content, pour point and residues are above limits [23]. Additionally costs are higher due to equipment used and high temperatures.

Supercritical methanol is a transesterification process with higher temperature, around 520-560 K, these processes will be discussed later in chapter 2.3 Transesterification.

In order to classify biodiesel, a number of properties were descripted and it's standards, so there are no problems with incorporating it into existing diesel engines. Those engines are called Compression-Ignition (CI) engines, so when the air-fuel mixture is compressed to a certain amount, the increasing temperature allows the gas to self-ignite. In contrast in spark ignition engines there is a

special mechanism to create a spark and inflame the air-fuel mixture. Vegetable oils are not suitable for direct use in diesel engine and cause many problems presented in Table 1.

Table 1. Problems with using vegetable oils directly in diesel engines. Adapted from [25].

Problem	Cause	Solution
Engine knocking	Low cetane number	Fuel preheat, use of higher compression engines
Plugging and gumming of filters	Natural gums and phosphatides in oils	Oil refinery to reduce gums in oil
Cold weather starting	Low flash point, high viscosity	Fuel preheat
Carbon deposits	High viscosity, incomplete combustion	Fuel preheat, increase ester content in oil
Engine wear		Oil additives to inhibit oxidation, fuel preheat, increase ester content in oil
Lubricating oil failure	Polymerization of vegetable oil	

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. As presented in norm the minimum value for both diesel and biodiesel is 51 to prevent negative effects. Though it is reported that low CN also reduces formation of NO_x. Depending on methods and catalysts the values for biodiesel from waste frying oil varies from 54 to 68 [12, 13],

- 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/m^3, while for the latter it's 860 – 900 kg/m^3. From study [13] all tested waste frying oils fulfilled the requirements.

- 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. This condition in studies [13, 14] is met and it's always above 150 °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 [15].

- Kinematic Viscosity – this property of fuel is very important, because it can lead to not complete combustion, increase energy demand from pumps [19].

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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.

European Union set in Renewable Energy Derivative (2009/28/EC) that all countries' transport fuels should be made of at least 10% biofuels by 2020. In order for pure biofuel, B100, to be put into engine there needs to be changes done. Therefore blending biodiesel or ethanol with petrol diesel are a common way to proceed with that requirement [20]. In the EU the most typical fuel blend is B7, blend with 7% of biodiesel [21]. While in the United States of America B5 and B20 are the most commonly used ones. Blending represents a good stability in price, lower emissions of greenhouse gases [22].

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. Together with increase of oil price, demand for food stocks also raised due to surge in biodiesel production and caused a lot of concerns for this processes. To meet this new need new feedstocks have been developed to decrease amount of food used for biodiesel production [3,4].

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 [3,4].

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 [4].

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 rage 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. Table 1. shows biodiesel feedstock in chosen countries.

Table 2. Biodiesel feedstock in chosen countries. Adapted from [25].

Country	Feedstock
USA	Soybean, peanut, waste oil
Germany	Rapeseed
UK	Rapeseed, waste cooking oil
Ireland	Frying oil, animal fats
Indonesia	Coconut, jatropa, palm oil
China	Rapeseed, waste cooking oil, jatropa
India	Jatropa, sunflower, peanut, soybean

Each feedstock also provides biodiesel with different properties, depending on the composition of plants/fats. Table 3 presents chosen feedstocks' physico-chemical characteristics. All these feedstocks have similar high heating value of 38-39 MJ/kg (no data for coconut oil) [25].

Table 3. Biodiesel's properties from different feedstock. Adapted from [23].

Feedstock	Density	Kinematic viscosity	Cetane number	Flash Point	Cloud Point
-	Kg/m^3	Mm^2/s	-	°C	°C
Soybean	913,8	4,08	50,9	131	-0,5
Jatropa	940	4,40	57,1	163	4
Rapeseed	902,6	4,83	52,9	155	-4
Sunflower	916,1	4,60	49,0	183	1
Palm	918	4,71	57,3	135	16

For large production scale, costs should be lowered for economical and feasibility purposes and according to [25] 75% of costs are associated with oil, shown on Figure 4. Because of variety of crops used and availability in many parts of the world transportation costs are minimalized, unlike

natural gas or oil, which only some countries possess deposits of. There is no cost for long intercountry pipelines or special ships to carry the fuel.
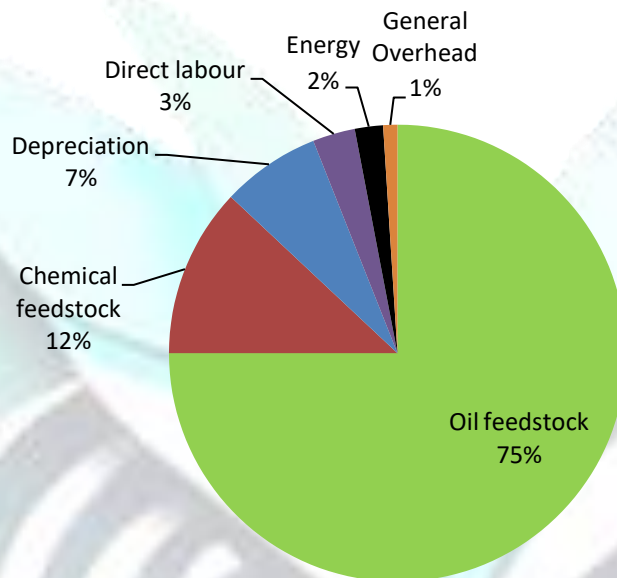

Figure 4. Biodiesel production costs breakdown. Adapted from [25].

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 [26].

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 [26]. 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 Transesterification

Among many biodiesel production processes transesterification reaction seems the most profitable one, promising a good industrial production. Biodiesel or fatty acid methyl ester (FAME), can be obtained during transesterification process between fatty material, like vegetable oil, and an alcohol. Triglycerides react with alcohol in 1 to 3 molar ratio stoichometrically and under temperature and the reaction occurs producing FAME and glycerol. Reaction is made in 3 stages as shows on Figure 5 [27].

Reaction is reversible, so excess of alcohol is used to move the reaction equilibrium towards the product side. It can be catalysed in order to increase the speed of the process. Most commonly used alcohols are methanol and ethanol due to their low costs, high availability, good reactivity [28].

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If the reaction is not catalysed, supercritical methanol process should be installed. This method provides much higher pressure and temperature for the reaction, transferring methanol into its supercritical state, allowing the alcohol for better mixing with biodiesel [29]. Ferobie and Matsumura [29] applied temperature of 270-400 °C, pressure of 20 MPa and methanol to oil ratio 40:1 with continuous reactor. Due to higher parameters needed for this method it is more costly to produce biodiesel, since there is higher energy consumption to create such environment for the reaction.
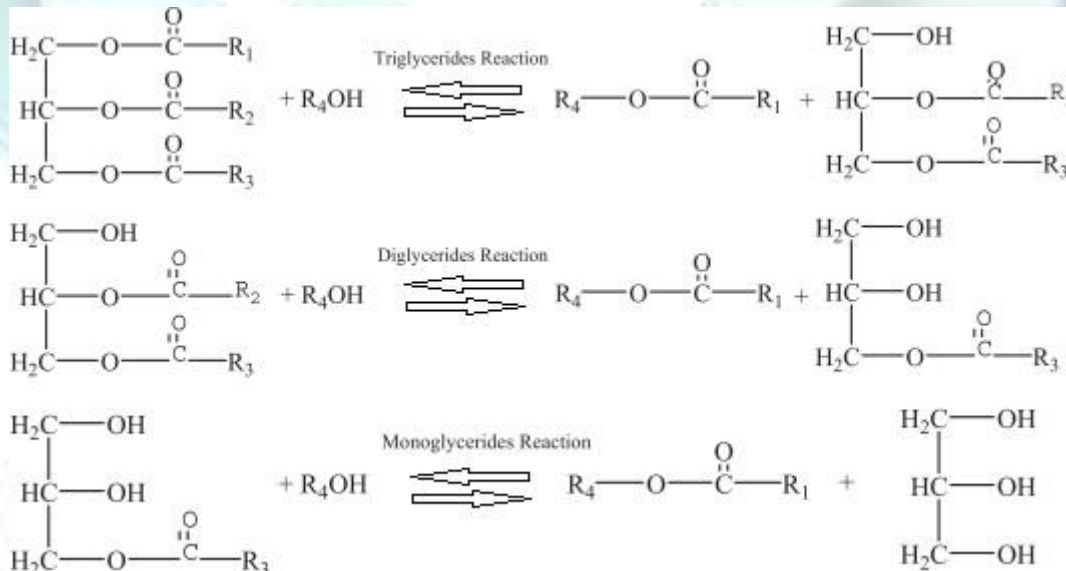

Figure 5. Three steps of transesterification process. Adapted from [27].

Catalysed transesterification uses temperatures in the range of 40-200 °C, but considering commercial use catalysts for higher temperatures are expensive. More research move towards lower temperatures, easily achievable by simple heaters. Pressure in the process stays at atmospheric level, so no additional equipment is needed. Oil to methanol ratio is also smaller then noncatalytic reaction, ranging from 1:5 to 1:20, but best results were obtained with 1:6 or 1:12 ratios, depending on the catalysts [30].

This reaction depends on many factors and parameters such as: oil to alcohol molar ratio, time spent in the reactor, temperature, stirring speed, used catalyst. Each of these contribute to reaction rate, yield, biodiesel's properties and ultimately, to its total cost.

Higher temperature provides better mixing of reactants and thus, better yield, but too high temperature may cause alcohol to evaporate, so if higher temperatures are employed (66°C for methanol or 78°C for ethanol) a proper adjustment in pressure should be made or a cooler, to catch evaporated alcohol and to recirculate it into the reactor. Also saponification process is connected positively with temperature increase, causing lower output in higher temperatures.

Oil to alcohol ratio plays vital role in biodiesel yield, stoichiometrically 1:3 ratio is required for the reaction to reach final stage and achieve equilibrium. Higher ratios provide shifting of the equilibrium towards products, but too much causes lower catalyst concentration and eventually yield is

smaller. Nowadays most commonly used rations are 1:6 and 1:12 due to their high yield (even 97%) [31].

The abovementioned characteristics have impact on reaction time. The main focus is to shorten the reaction time, thus higher temperatures or molar ratio. Too short time will yield too low amount of FAME, since not all triglycerides will have enough time to react with alcohol and too long exposer may result in the backward reaction, causing loss of biodiesel [32].

2.4 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. For example for Fisher-Tropsch synthesis in oil industry there are many different catalysts used, Iron-Manganese (Fe-Mn) or Cobalt-Manganese (Co-Mn) on reduced support with and without alkaline promoters, to name a few [33].

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. Below on Figure 6 there are presented catalyst types for biodiesel production using transesterification process.

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. These and many other characteristics are gathered in Table 4.

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.
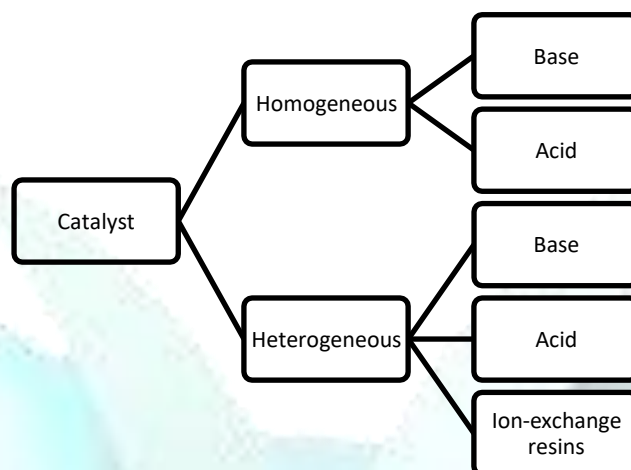
Figure 6. Catalysts types for transesterification process. Adapted from [30].

Table 4. Comparison between homogeneous and heterogeneous catalysts. Adapted from [30].

		Homogeneous Catalysts	Heterogeneous Catalysts
Advantages	Overall	Medium operation conditions	Environmentally friendly, noncorrosive, able to regenerate, longer catalyst life, easier products separation, higher selectivity, fewer disposal problems, Cheaper, May be used in CFBR (Continuous Fixed Bed Reactors)
	Basic	Favourable kinetics: high activity and yield in a short time 4000 times faster reaction than acid catalysed transesterification, Basic methoxides are more effective than hydroxides	-----
	Acidic	-	Simultaneous esterification and transesterification, Insensitive to content of free fatty acids and water
Disadvantages	Overall	Problems with product and waste separation Saponification, emulsion formation Difficulties with catalyst reuse Used only in batch reactors Higher production costs	Lower conversion compared to highly active basic homogeneous catalysts, Requires well mixed state due to presence of 3 phases Oil to alcohol ratio increased, Requires higher pressure and temperature
	Basic	Free fatty acids and water sensitive	Low free fatty acids content and anhydrous condition needed, feedstock with high free fatty acids require pretreatment
	Acidic	Corrosive Low reaction rate Higher oil to alcohol ratio, Higher temperature, Neutralization reaction causes more waste	Low quality of catalysts (site concentration and microporosity), Higher costs compared to basic types

2.5 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 5. Many researchers ([13, 18, 34]) showcase 2 biodiesel purification methods – wet and dry.

Table 5. Impurities' effects on biodiesel and diesel engines. Adapted from [18].

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

2.5.1 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 [17, 35]. Basic principle of this method is presented on figure 7.
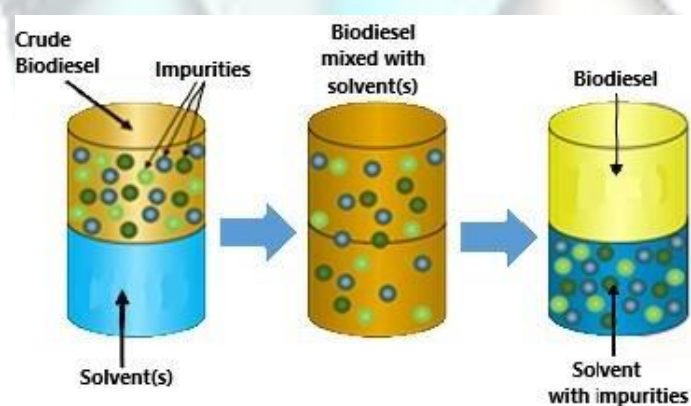

Figure 7. Wet washing method. Adapted from [17].

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 [17, 35].

There are researches being made on other solvents than water, due to its cons. [36] shows ionic liquids and euctectic 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.

Another option is supercritical fluid, like carbon dioxide under high pressure of 30 MPa and medium temperature 40 °C as employed in research [37]. This method allowed purification of above 99% when the contact time reached 90 minutes. Lower temperatures allowed the solvent to obtain higher viscosity and density, and higher pressure granted good solubility.

Beside abovementioned options there is also membrane method. This low water alternative uses filtration membranes, does not 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).
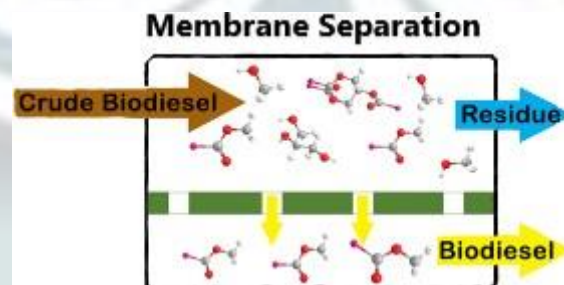
Figure 8. Membrane wet purification method. Adapted from [17].

Besides the obvious difference of composition they differ in properties and ceramic based membranes are more resistant to temperature and pH changes and better efficiency in dealing with base catalysts from transesterification reaction. In both cases glycerol separation is the most important. When it comes to organic membrane increased water content increases glycerol separation [17, 44].

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 [17]. Figure 8 shows this process with impurities infiltrating pores of a solid and adhering to its surface. Beside not generating wastewater, this method does not 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 [38].
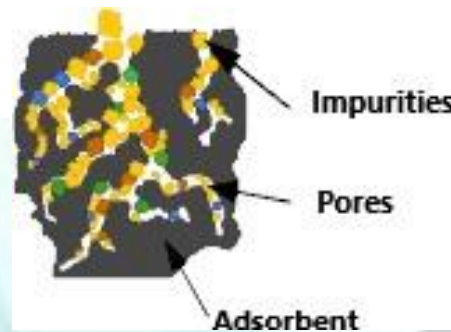

Figure 9. Adsorption process. Adapted from [17].

The most common adsorbents used in industry are based on silica materials – zeolites, gel or molecular sieves. These materials remove effectively glycerol, water and alcohol, that was left after the transesterification reaction. For silica gel amount of alcohol content is very important and it's higher value can decrease the sorption capacity, so alcohol pre-treatment needs to be implemented to obtain satisfactory results [17]. [39, 40] studied silica-gel and at room temperature and results were promising, having high glycerol removal rate. But the industrial beds used to purify biodiesel using silica gel have 1/8 inch silica beads causing mass transfer limitations.

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. [41] 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. Moreover the production of their sorbent is made from natural ingredients making it very environmentally friendly.

Another example of natural adsorbents are cellulose and starch. [43] 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. Additionally like any other natural material it is environmentally friendly and cheaper in production, promising good results for the future.

Another approach has be taken by A. Avinash and A. Murugesan ([52]), who studied cow dung ash for the purpose of biodiesel purification. Their adsorbent was prepared in oven at 500 °C for 2 h. Tested samples were 1,2,3,4 % by weight mixed with biodiesel and then compared with results from wet washing. Results were very promising as the lowest weight ratio adsorbent – biodiesel

showed similar results as the commonly used method. Thanks to this approach there are more ways for wastewaterless methods to purify biodiesel and search for more environmental friendly substances.

Magnesol® is an inorganic matrix of anhydrous sodium sulfate and magnesium silicate. It was shown in [42, 18] 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. Researchers state that higher alcohol removal using higher temperature may be due to its evaporation, rather than silica sorption. Its properties allow it to be used in small ratios with biodiesel, compared to aforementioned natural adsorbents.

Additionally Magnesol®, based on [57], can be regenerated using methanol solvent and reused several times before losing its adsorbance capacity. Regeneration of fumed silica, another sorbent used for biodiesel purification, was studied by [65] and found that alcohols like methanol, isopropanol and acetone. Moreover it is possible to recycle methanol to biodiesel production in order to increase efficiency of unreacted glycerides, absorbed by methanol during sorbent regeneration.

Ion-exchange method is based on electrostatic force between the solid material's surface and crude biodiesel. Basic performance of ion-exchange method was presented on figure 9. 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 [17, 45].
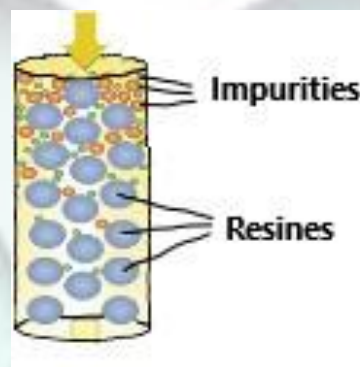

Figure 10. Ion-exchange purification process. Adapted from [17].

3. Materials and methods

3.1 Catalyst preparation

Based on [55] it was decided to make the catalyst from eggshells, that are mainly made of $CaCO_3$ 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. [56] 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. Figure 11 shows prepared eggshell powder (A) and final product of calcination (B).

| A | B |
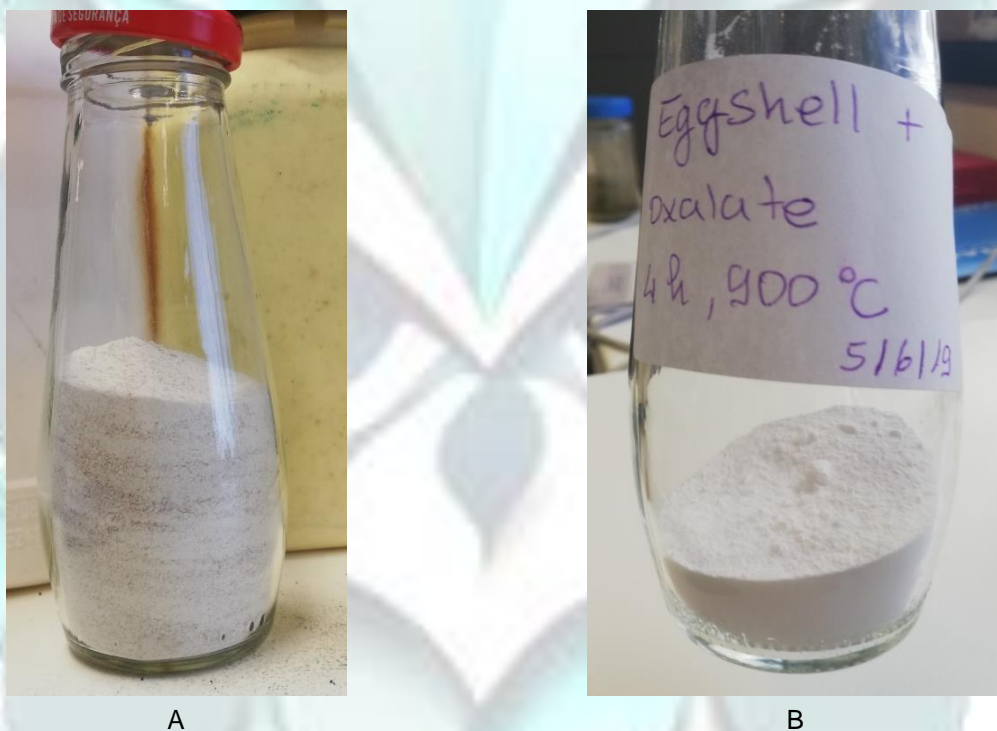
Figure 11 A. Prepared eggshell mixed with ammonia oxalate. B. Eggshell with ammonia oxalate after 4h calcination in 900°C.

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 [47]. 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.

Figure 12. Three-neck round bottom reactor with transesterification reaction taking place.

Reactants stayed in the reactor for 90 minutes with 67 °C and after the elapsed time it was cooled down and by filtration (Figure 4.5 A) the catalyst was removed and the liquid phase was put into a decantation funnel to separate glycerine and biodiesel (Figure 4.5 B).

A
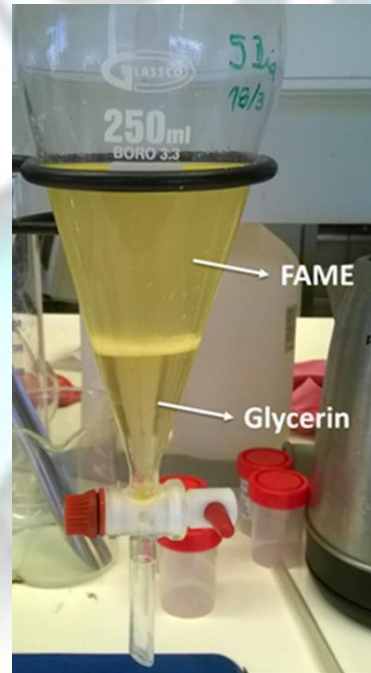
B

Figure 13. A. Vacuum filtration. B. Decantation funnel with products of transesterification reaction.

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 ([18, 42]) the standard washing time is 30 minutes and some researches ([46]) 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 Magneso®l (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). 55 °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. All tests are presented in Table 6.

Table 6. Magnesol® purification tests conditions.

Sample No.	Magnesol® weight [%wt]	Temperature [°C]	Time [min]
1	3	45	40
2	3	45	60
3	3	55	60
4	3	65	20
5	3	65	40
6	3	65	60
7	5	50	30
8	10	65	40

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 [48, 49].

The greatest advantage of FTIR is its simple preparation and research in neutral sample state. The tested material does not need any pretreatment, like heating, addition of special chemicals or polishing. Short time of the examination and easy clean up with ability to quickly change samples for another test also account for this method's pros [49]. However there are problems with detecting weak signals due to spectra noise. It is necessary to use detectors with higher sensitivity as well as more precise setup with optimisation for each sample. [50].

Zhang W.-B. ([51]) reported in his research that FTIR methods for biodiesel properties control show very promising results. Those include kinematic viscosity, density, iodine value and cold filter plugging point. Error obtained with FTIR method was much smaller than the one allowed in European Standards. Fast examination allows to this technique to be used in industrial applications.

As shown in [53], there are many bonds between different elements like carbon, oxygen and hydrogen. They form different molecules and each reacts in a different way for the infrared wavelengths. For example if there is a peak around 3000 cm^{-1} it means there are alkenes bonds between C and H and a peak at around 2924 cm^{-1} gives the information about alkanes. For biodiesel peak around wavelength of 1745 cm^{-2} is very important, because it corresponds to the FAME C=O bonds. the study found that certain functional groups indicate higher FAME content and thus, higher biodiesel content in a blend. Below in Table 7 are presented other important groups and their wavelengths, based on research [53] which studied biodiesel made from peanut oil. In Figure 14 there is also an example of a biodiesel FTIR chart prepared in [54].

Table 7. Identified functional groups of biodiesel. Adapted from [53].

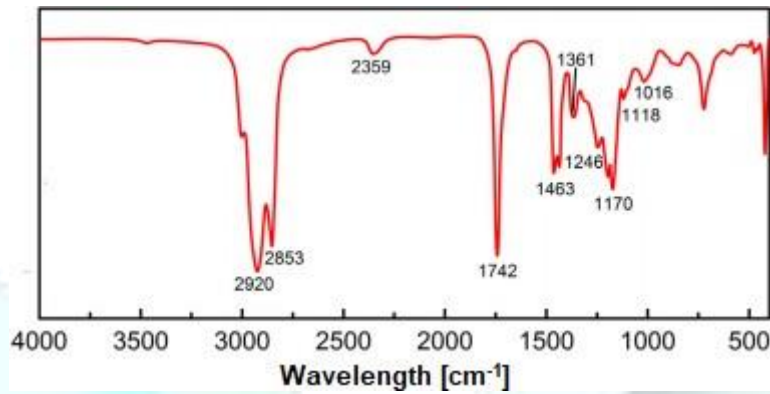| Wavelength [cm^{-1}]	Functional group
3500	O – H (alcohols)
3007, 850	= C – H (alkenes)
2924	C – H (alkanes)
1745	C = O (ester carbonyl in FAME)
1377 - 1465	C – H (methyl of –CH_3)

Figure 14. FTIR results for biodiesel. Adapted from [54].

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 [60].

There were many studies made on biodiesel with thermogravimetry and for example [61] studied oxidation of biodiesel. Figure 15 shows a thermogravimetric curve for a clean biodiesel.
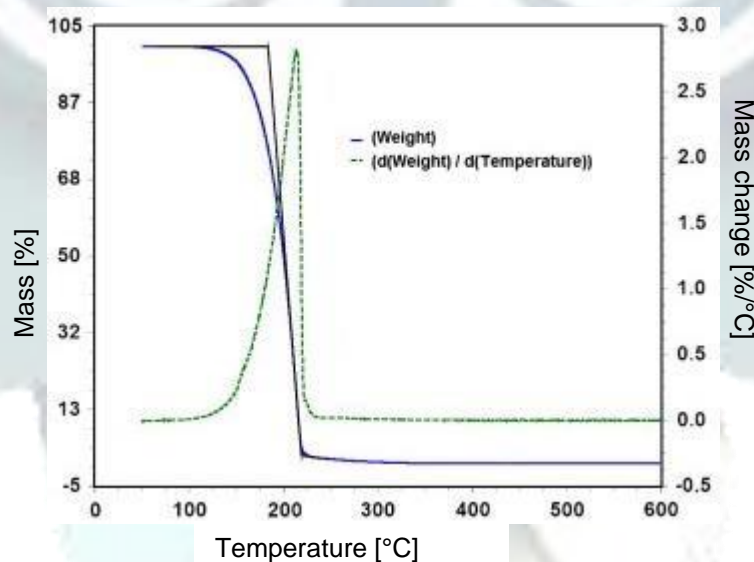
Figure 15. TGA of reference biodiesel. Adapted from [61].

Reference biodiesel was made from 98,5% of FAME, complying with EU standards (at least 96,5%). The changes in mass started to occur around 180 °C, and finish around 210 °C, what was in accordance with biodiesel specifications and dominant methyl esters composition.

TG-DTA/DSC Seteram Labsys was used to perform TGA analysis on post purification Magnesol®. It's interface can be seen in Appendix 2.

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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 [58].

This method uses Bragg's law, shown on Figure 16 and formula 1. A monochromatic photon beam interacts with the sample, thus creating a diffractive ray from a crystal lattice. Each of those reflections have an angular position that depends on a wavelength and material.
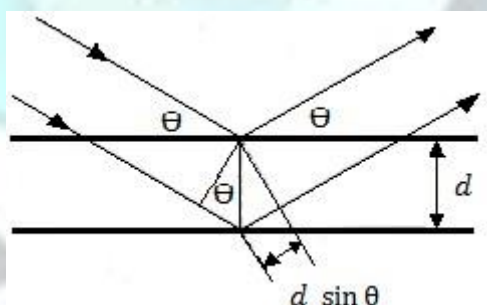

Figure 16. Reflection of a photon beam from two atoms lattices. Adapted from [59].

$$2d \sin(\theta) = n\lambda \tag{1}$$

d – interplanar distance, θ – diffraction angle, λ – wavelength, n – positive integer

Rigaku Geiger flex diffractometer with Cu Kα radiation at 40kV and 40 mA was used to acquire XRD data. Used angle variation was 2°/minute with a range from 5 to 70°. Joint Committee on Powder Diffraction (JCPDS) data were used to identify crystalline phases in the tested material.

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 17 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 ($CaCO_3$, JCPDS 00-001-0837) – calcium carbonate. 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 (CaD). These reactions (2 and 3 accordingly) are shown below. Both calcium hydroxate and diglyceride are good catalysts for transesterification reaction, but the latter is easily soluable in mixture of biodiesel, methanol and glycerine, thus creating one phase with them.

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Because heterogeneous catalyst is leeching into the oil, this compound is another undesirable substance in biodiesel that has to be removed, [62].

$$CaO + H_2O <=> Ca(OH)_2 \qquad (2)$$

$$Ca(OH)_2 + 2C_3H_8O_3 <=> CaD \qquad (3)$$
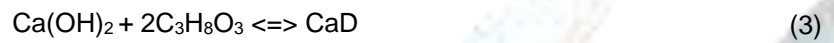
Similar XRD characterization was conducted by [63], confirming existence of those phases. Moreover lime was studied in [64], showing similar behaviour. The latter study shows difference in mud creeper shells, whose XRD shows it is composed of calcium carbonate in the form of aragonite. both calcite and aragonite after calcination created cubic CaO, based on JCPDS files.
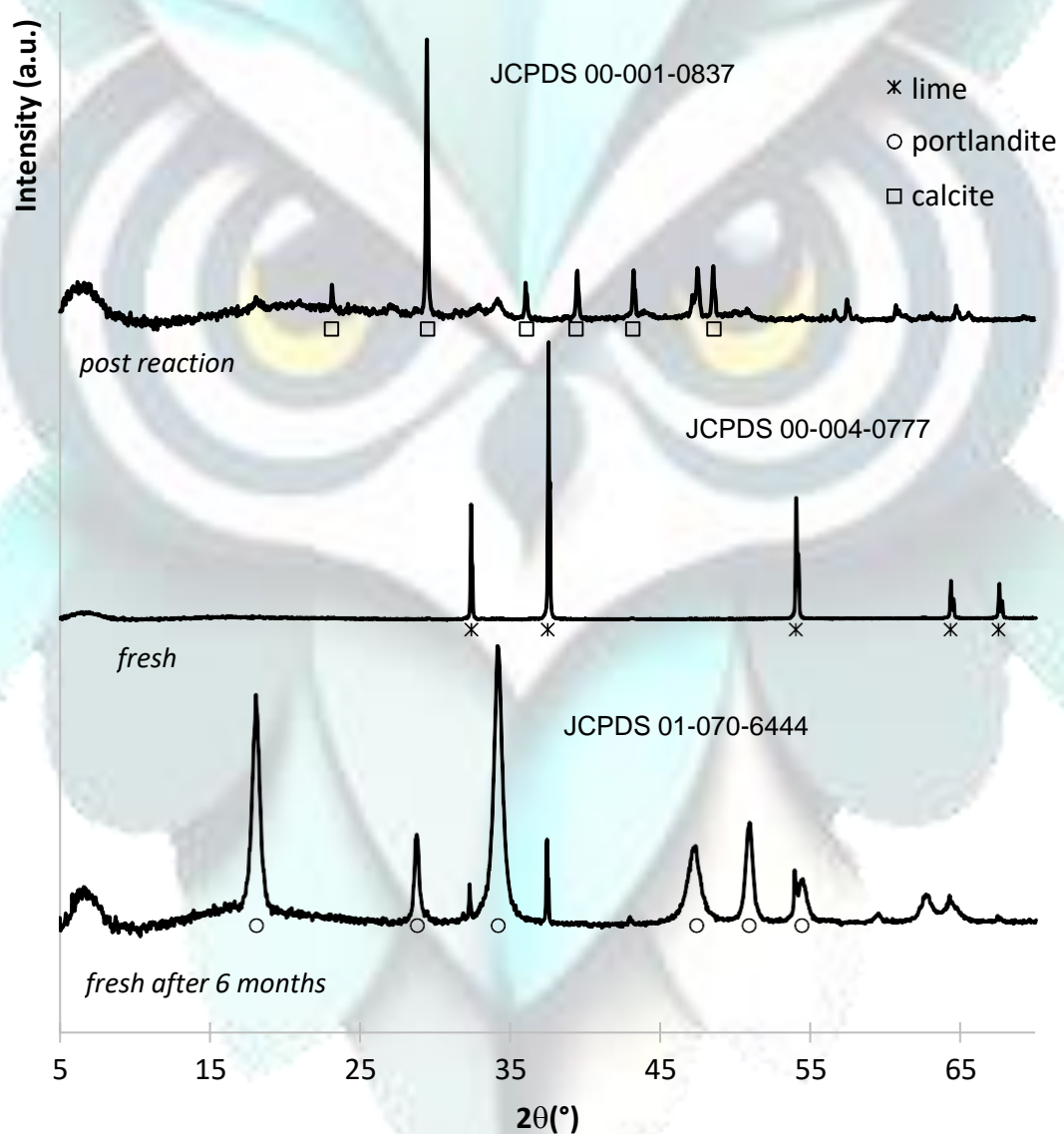
Figure 17. XRD patterns of fresh, post reaction and after 6 months, catalyst.

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 18 shows FTIR spectra and there are clear peaks on some wavelengths. Each peak was assigned a letter that is later described in Table 8.
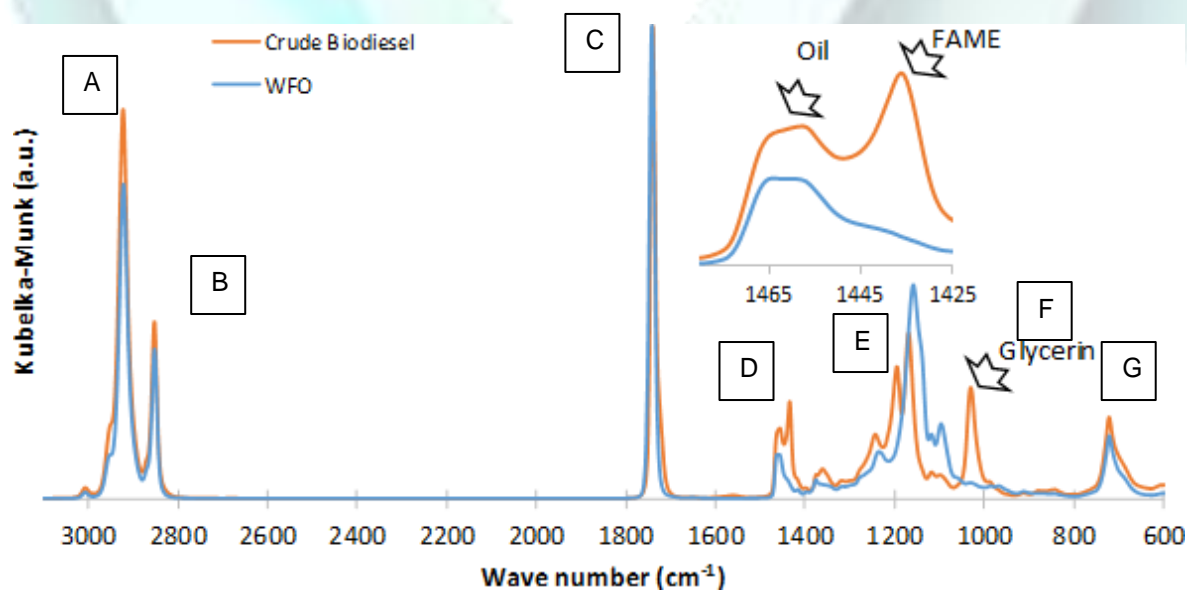
Figure 18. WFO and Crude Biodiesel ATR-FTIR spectra.

Table 8. Identified peaks in WFO Biodiesel FTIR Spectra.

Peak	Wavelength [cm^{-1}]	Description
A	2925	C – H (alkanes)
B	2855	C – H (methylene)
C	1741	C = O (ester carbonyl in FAME)
D	1435	C – H (methyl or –CH$_3$)
E	1172	C – O alkoxy esters
F	1031	C – O – C , ethers, C – O alkoxy esters, glycerine
G	723	= C – H and – (CH$_2$)$_n$ methylene groups

By comparison between the results and [53], biodiesel blends show that with higher FAME content the peaks at 1741 cm^{-1}, 1031 cm^{-1} and 1172 cm^{-1} also intensify, 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 [53]. It means that both biodiesel and fossil diesel contain those groups with similar frequency ranges. Additionally, alkane number relates directly to cetane number, which is very important for diesel fuels.

Comparing the data from FTIR analysis for WFO and the one from study [54], one can see very 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 18 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 Transesterification

50 g samples of crude biodiesel were purified in different conditions (time, sorbent's weight, temperature) and FTIR spectra can be seen on Figure 19. 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 9 there are results for FAME calculations in all purified samples. Calculations are based on literature [67] and [68], and the detailed computation is shown in Appendix 1. 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®.

Table 9. 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; 50°C; 30 min	79.7
	10%W; 65°C; 40 min	88.7
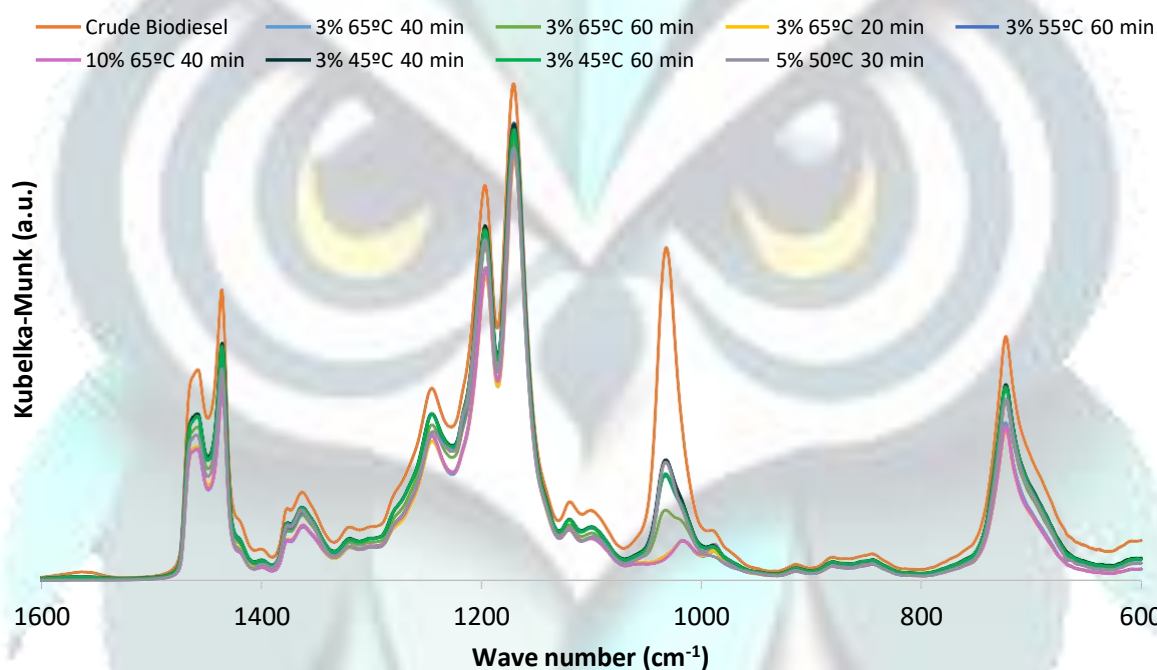
Figure 19. ATR-FTIR spectra of crude and purified biodiesel.

4.4 Magnesol®

Magnesol® was tested before and after purification with FTIR method and thermogravimetry. FTIR curves for all samples are shown on Figure 20. In study [66] 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.
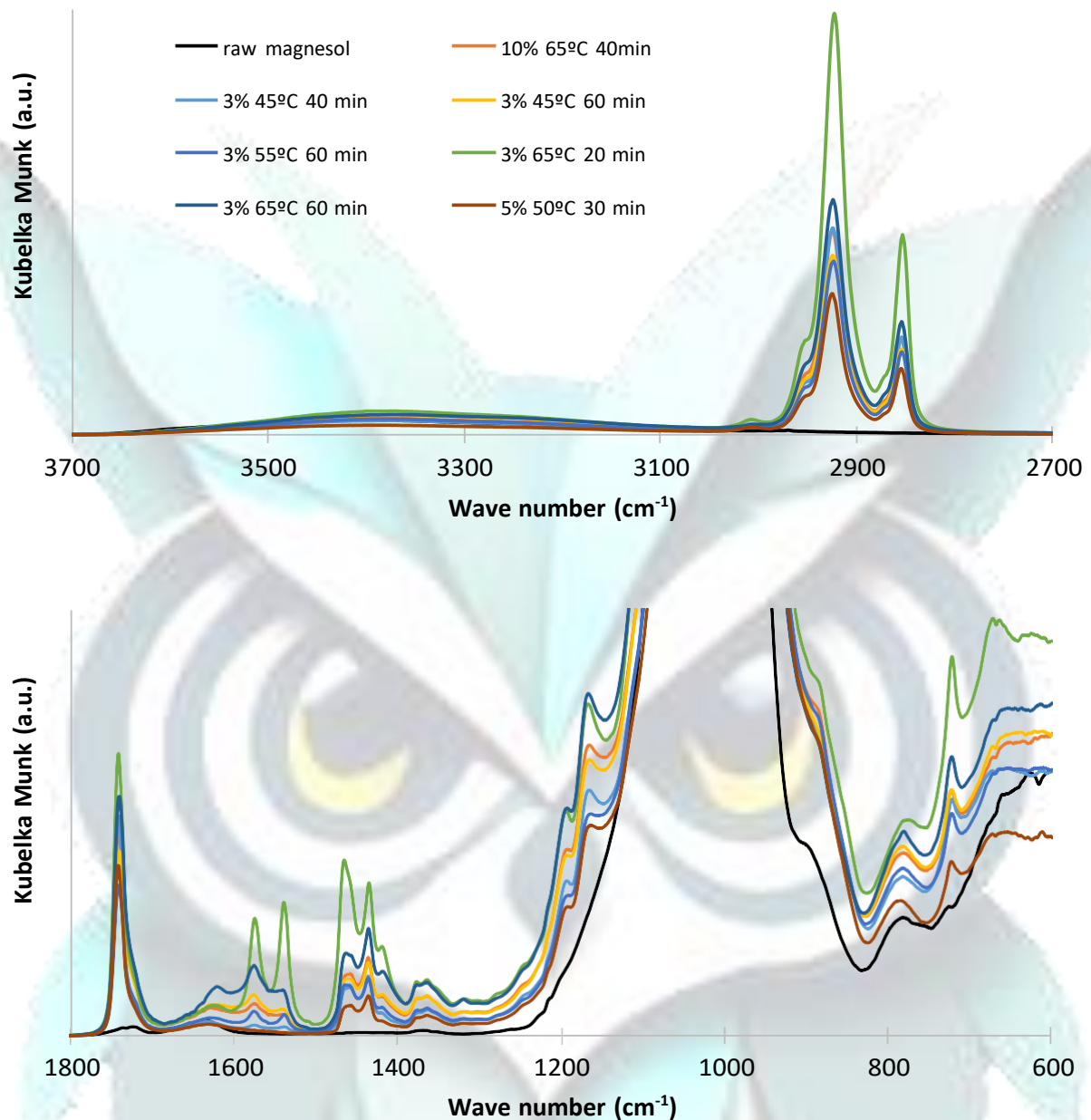
Figure 20. FTIR of fresh and post-purification Magnesol®.

Additionally thermogravimetry tests were conducted on Magnesol®. Figure 21 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 [69]. This sample is the only one to be put in contact with biodiesel for 20 minutes. Moreover this sample doesn't have a peak around 100 °C. That may mean that longer exposure to Magnesol® may lead to displacement of free fatty acids by methanol and water.

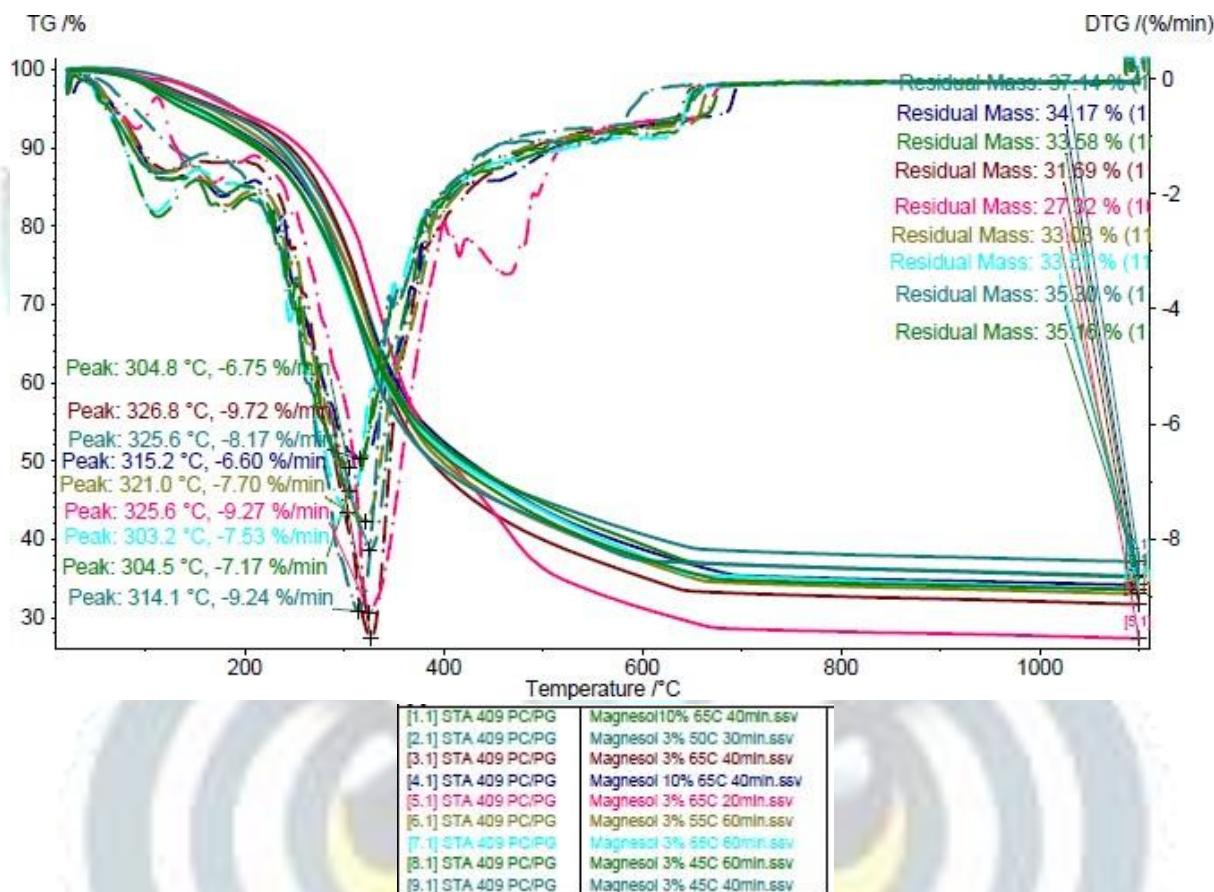|		
[1.1] STA 409 PC/PG	Magnesol10% 65C 40min.ssv	
[2.1] STA 409 PC/PG	Magnesol 3% 50C 30min.ssv	
[3.1] STA 409 PC/PG	Magnesol 3% 65C 40min.ssv	
[4.1] STA 409 PC/PG	Magnesol 10% 65C 40min.ssv	
[5.1] STA 409 PC/PG	Magnesol 3% 65C 20min.ssv	
[6.1] STA 409 PC/PG	Magnesol 3% 55C 60min.ssv	
[7.1] STA 409 PC/PG	Magnesol 3% 65C 60min.ssv	
[8.1] STA 409 PC/PG	Magnesol 3% 45C 60min.ssv	
[9.1] STA 409 PC/PG	Magnesol 3% 45C 40min.ssv	

Figure 21. Thermograms of the post sportion Magnesol® samples.

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.

Biodiesel has many sources, so it is available throughout the world, addressing many users, including less developed countries with no access to fossil fuels. Additionally European Union focuses its energy policies on renewable energy sources and thus, drives the development of biodiesel.

Waste Frying Oil is being considered as one of the feedstock for biodiesel production, especially in a close proximity to large cities, where there are many people, who could provide WFO. This way the costs are lowered, there is no "fuel vs food" problem and CO_2 emissions are lowered.

But the production process also includes purification, because crude biodiesel may not follow international standards and therefore, it needs to be enhanced. There are many unwanted substances that decrease biodiesel's properties, those are for example: leftover catalyst, alcohol from

transesterification , water or free fatty acids. Nowadays there are many methods to purify this green fuel, which can be divided into two groups, dry and wet methods.

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.

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.

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APPENDIX

1. FAME content computation from ATR-FTIR spectra

The ATR-FTIR spectra of WFO, crude biodiesel and purified biodiesel samples were used to quantity the FAME content. The reflectance spectrum of each sample, in the range 1480-1410 cm-1, was deconvoluted using five Gauss curves as described in the literature [67,68]. The band centered at 1436 cm-1 was attributed to fatty acid methyl esters and the weight content of FAME was computed according to:

$$FAME(\%) = \frac{area\ of\ band\ centered\ at\ 1436\ cm^{-1}}{area\ of\ the\ bands\ in\ the\ range\ 1480 - 1410\ cm^{-1}} \cdot 100$$

FTIR spectra bands deconvolution was carried out using Excel software, from Microsoft Office and Gauss curves parameters were optimized using Solver tool. A calibration curve obtained for FAME/soybean oil mixtures with known FAME contents.

In Figure 22 deconvoluted FTIR spectrum of crude WFO biodiesel is displayed as an example of the computations above described. All the analyzed samples presented similar FTIR spectral features.
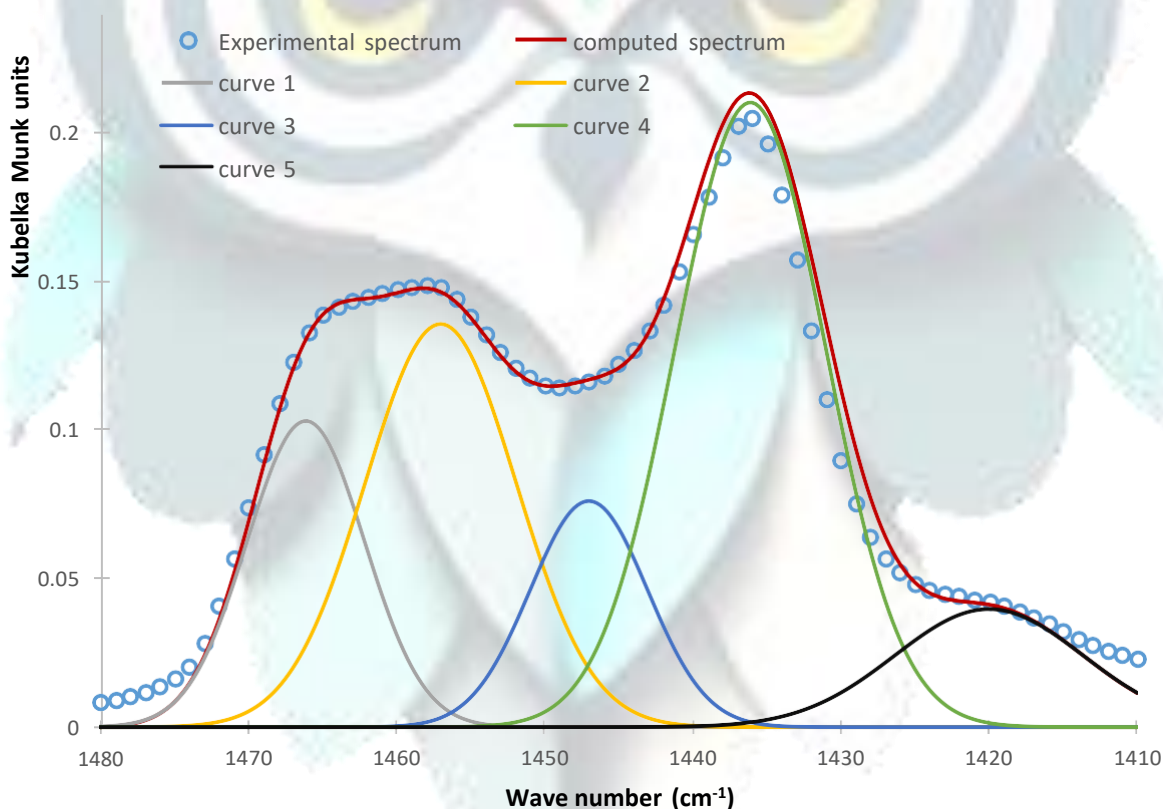

Figure 22. ATR-FTIR spectrum deconvolution to compute the FAME weight content.

2. Thermogravimetry programme.

In Figure 23 there is Thermogravimetry programme interface shown. It was programmed to increase the temperature to 1100 °C with a step of 20 °C/min. The data points to create TG graphs were taken with a frequency of 200 points per minute, what gives 10 points per 1 °C.
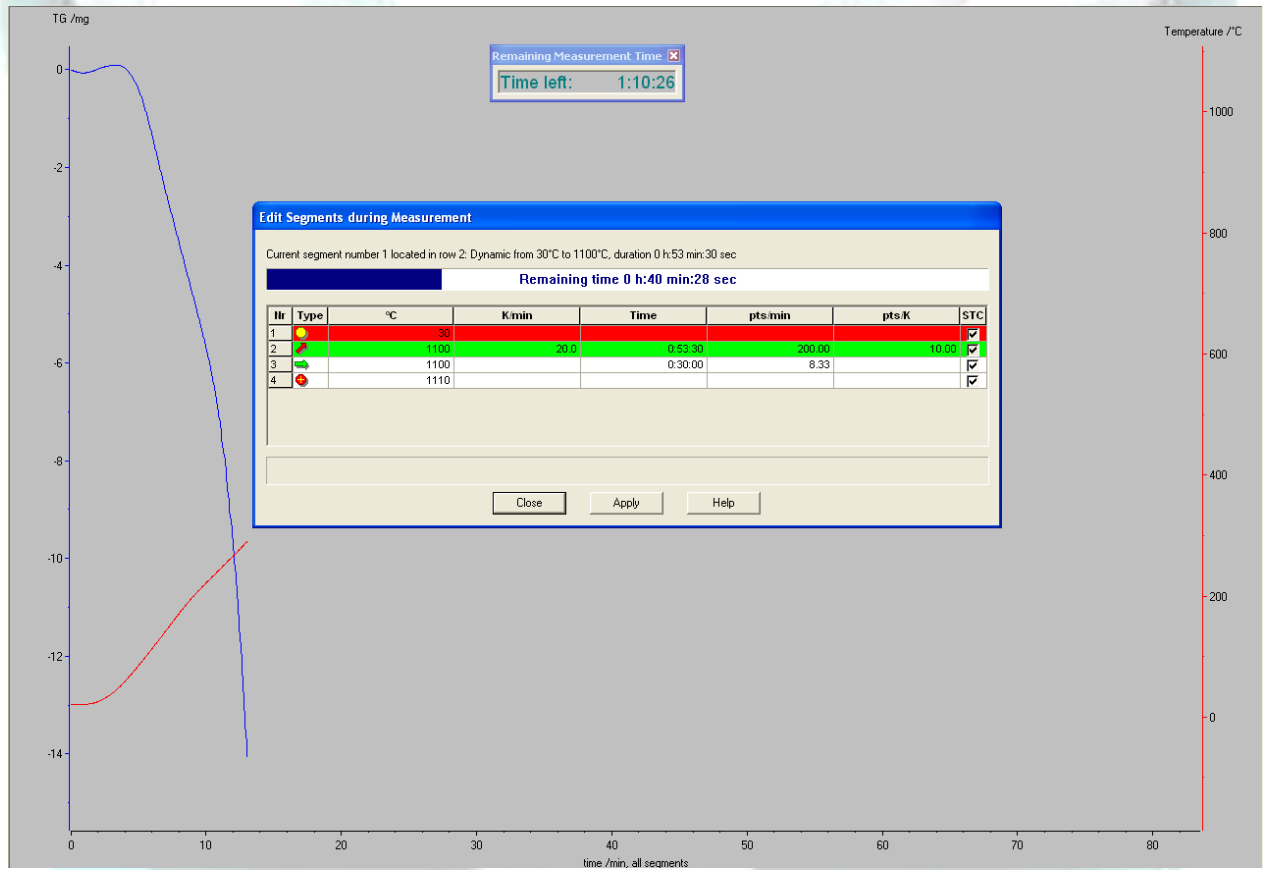

Figure 23. TG programme interface showing the used temperature program.