

Determination of biodiesel quality parameters for optimization of production process conditions

Zakir Taghizade

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Prof. Paulo Brito
Prof. Antonio Ribeiro
Prof. Helder Gomes

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ABSTRACT

According to many scientists third industrial revolution has already began and this primarily means the transition to renewable energy sources. Energy requirements are increasing rapidly due to fast industrialization and the increased number of vehicles on the roads. Massive consumption of fossil fuels leads to environmental pollution, therefore, biofuels are offered as an alternative. For example, the application of biodiesel in diesel engines instead of diesel results in the proven reduction of harmful exhaust emissions. One of the most important technologies, which has been already explored at the commercial level, is the production of a liquid biofuel applicable in compression-ignition engines (or diesel engines), from biomass rich in fats and oils. This biofuel is generically referred as biodiesel, and consists essentially of a mixture of FAME's (fatty acid methyl esters). This current work describes modern approaches of biodiesel production from vegetable oil and subsequent analysis of produced biodiesel main characteristics such as density, acidity, iodine value and FAME content.

Keywords : biodiesel, synthesis, quality characterization

RESUMO

De acordo com muitos cientistas, a terceira revolução industrial já começou, e implica necessariamente a transição para fontes de energia renováveis. As necessidades de consumo energético aumentam significativamente, devido à rápida industrialização e ao aumento do número de veículos nas estradas. O grande consumo de combustíveis fósseis conduz a poluição ambiental, e deste modo, os biocombustíveis apresentam-se como uma alternativa viável. Por exemplo, a aplicação do biodiesel em motores diesel em substituição do gasóleo resulta na redução comprovada de emissões de gases de escape nocivos. Assim, uma das tecnologias mais importantes, já explorada a nível comercial, consiste na produção deste biocombustível líquido, aplicável em motores de ignição por compressão (ou motores diesel), a partir de biomassa rica em gorduras e óleos. Este biocombustível é genericamente conhecido como biodiesel e consiste essencialmente de uma mistura de FAME's (ésteres metílicos de ácidos gordos). Assim, este trabalho descreve as abordagens modernas de produção do biodiesel de óleo vegetal e a posterior análise da qualidade do biodiesel produzido através da monitorização das principais propriedades tais como densidade, acidez, valor de iodo e conteúdo em FAME's.

Palavras-chave: biodiesel, síntese, caracterização da qualidade

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1. INTRODUCTION

Energy problem and sustainability have been challenging problems since the industrial revolution. Scientists from all over the world work hard find reliable, secure, clean, affordable and sustainable energy resources. Energy sources can be classified into three main groups: fossil fuels, renewable, and fissile. Fossil fuels are formed during millions of years, and in some cases can be even more than 650 million years by anaerobic decomposition of deep organisms [1]. There are mainly six types of fossil fuels: petroleum, coal, bitumens, natural gas, oil shales, and tar sands. The term fissile refers to nuclear energy sources and fissile energy sources include uranium and thorium. The most prospective recourse of energy is renewable energy sources and it includes biomass, hydro, wind, solar (thermal and photovoltaic), geothermal, marine, and hydrogen. Every year the importance of renewable sources increases and by 2040 according to scientists forecasts almost half of world's energy supply will be from renewable sources, meanwhile, 80% of total world's electricity production will be from renewables [2,3]. Table 1 shows world energy reserves in terms of fissile and fossil fuels, Fig. 1 compares global energy consumption in 5 different categories as petroleum, coal, natural gas, nuclear and renewables.

Table 1. World energy reserves [4]

Deuterium	Uranium	Coal	Shale oil	Crude oil	Natural gas	Tar sands
7.5×10^9	1.2×10^5	320.0	79.0	37.0	19.6	6.1

Each unit = 1×10^{15} MJ = 1.67×10^{11} bbl crude oil.

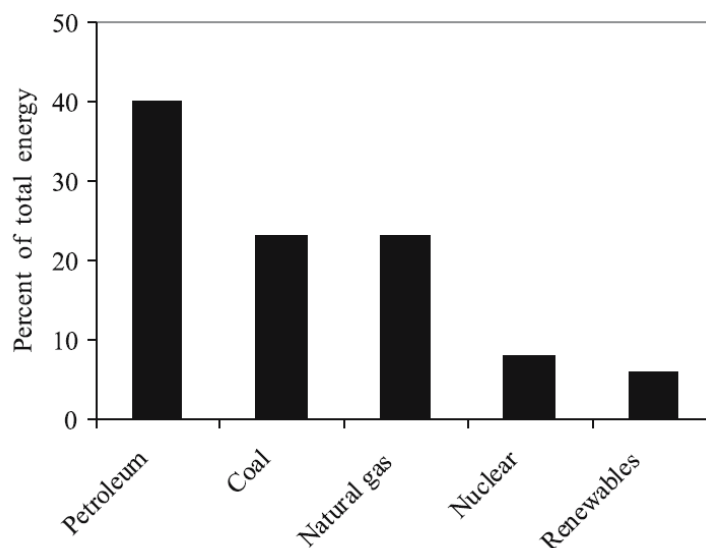


Figure 1. Worldwide fossil, nuclear and renewable energy consumption (2005)

This article will mainly cover topics concerning biofuels and particularly will discuss the use of biodiesel. Biodiesel is the type of biofuel and it can be produced by transesterification process from vegetable oil or animal fat. Biodiesel production grew rapidly starting from 2002 to 2006 with 40% increase annually [5]. The world's major share of biodiesel production falls on the US and EU. According to the United States Environmental Protection Agency (EPA) total demand for diesel in the US and EU is 147 billion gallons. Table 1.2 shows biodiesel summary for consumption and production in the US [6]. As can be seen from the table production rates are increasing every year and the target for 2020 is set by EPA to ramp up production to 12 billion gallons in USA.

Table. 2 Biodiesel summaries, 2009-2011 (million gallons) [6]

	2009	2010	2011
Biodiesel			
Consumption	326	263	878
Consumption Consumption (Percentage of Distillate Fuel by Volume)	0.6	0.5	1.5
Production	516	343	967
Gross Imports	77	23	36
Gross Exports	266	105	73

1.1 BACKGROUND AND MOTIVATION

The motivation behind this work is precise and simple. Searching for a renewable low cost replacement for fossil fuels is the need of the hour. As, fossil fuels are depleting at a larger pace, and the gasses emitted by using such fuels are environmentally unfriendly, there is an immense need for an alternative strategy. Therefore, biodiesel with all the required qualities in efficiency to replace fossil fuels and with comfortable economical productivity is considered elsewhere as an option of highest priority. Biodiesel is biodegradable, non toxic, has low emission profiles. It has become an alternative strategy because of these characters and its renewability. The cost of biodiesel is the main hurdle for the commercialization of the product. The research thus is necessary in this field for future greener generations.

1.2 MAIN OBJECTIVES

The main objectives of this work are: biodiesel production at laboratory scale, with commercial vegetable oils and waste cooking oils, through systematic and reproducible procedures, testing different process conditions (temperature, catalyst, reagents, etc.); implementation of biodiesel characterization methods, according to the quality parameters and the methods of analysis established in the EN14214 standard; qualitative and quantitative characterization of the biodiesel produced and determination of relationships between the quality of biodiesel produced and the corresponding process conditions; and monitoring of the evolution of the characteristics of biodiesel stored over time.

1.3 OUTLINE OF THE REPORT

In the first chapter of this thesis work is presented the introduction to biodiesel with indicating the main objective of this study. Chapter 2 describes biodiesel parameters and standards. The experimental procedure detailed explained in Chapter 3, then results discussed in Chapter 4 with further conclusions and suggestions for the future work in Chapter 5.

2. FOSSIL FUELS AND BIOFUELS

According to the US Energy Information Centre (EIA) in 2007 86.4% of global energy consumption comes from fossil fuels. In the first place of this chart is petroleum with 36%, then coal and natural gas with 27.4% and 23% respectively [7]. More than 70% of world's dwindling oil reserves are in Middle East and Russian Federation [8]. Fig. 2 shows world oil production scenarios based on the current production. It is clearly showed that today is the peak of oil production and during next decades oil production will fall drastically [8].

The word petroleum comes from the Latin roots *petra*, which means rock and *oleum* means oil. In the petroleum there is wide range of hydrocarbons in different states like gases, liquids and solids. The physical properties of petroleum could be different depending on place and conditions of the exploration. Crude oil and natural gas are the most important forms of petroleum. [9]

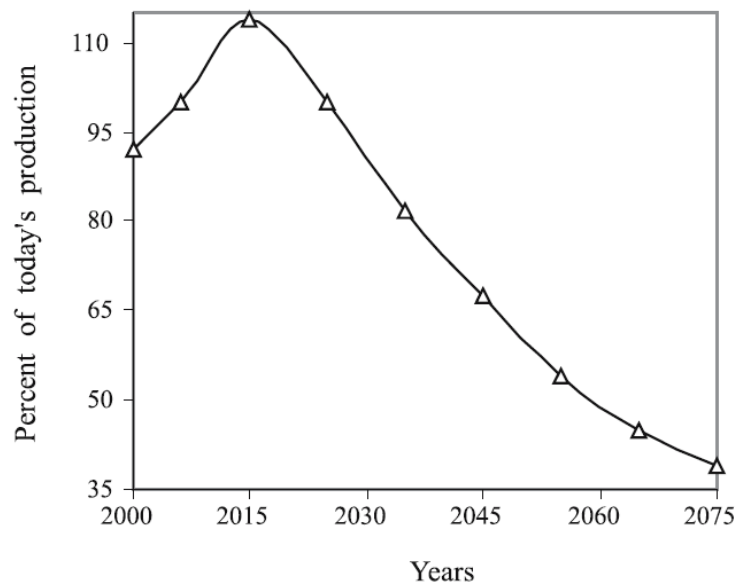


Figure 2. Global oil production scenarios based on current production (2005) [8]

Crude oil is a complex mixture of mainly hydrocarbons from 50% to 95% by weight. Most of world's crude oil reserves are not conventional. Crude oil contains alkanes (paraffins), naphthenes, aromatics, asphaltics with different percentages by weight depending on place and conditions of exploration. Figure 3 shows world oil reserves in 4 different categories with relative percentages. The first step in refining process is separation of crude oil into useful products by using distillation process. Table 3 shows the number of individual products in 17 different classes [10]. According to survey conducted by American Petroleum Institute there are

more than 2000 products that made by different petroleum refineries and petrochemical plants [11]. The most important fraction of oil distillation is gasoline, which is used mainly in transportation purposes. Therefore, more than 60% of the crude oil is used to produce gasoline, while, 30% of it is refined for diesel fuel production [10]. Gasoline is the complex mixture of hydrocarbons having typical boiling point from 38 C to 205 C as determined by the ASTM method. The most important characteristic of gasoline is its antiknock performance. Quality of the gasoline depends on crude oil, method of refining, various blends and additives.

Total World Oil Reserves

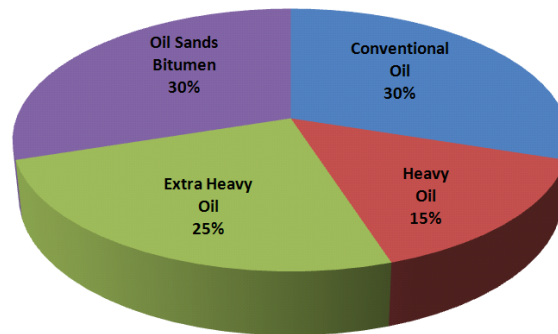


Figure 3. Global Oil reserves [10]

Table 3. Products made by the U.S. Petroleum Industry [11]

Class	Number
Fuel gas	1
Liquefied gases	13
Gasolines	40
Motor	19
Aviation	9
Other (tractor, marine, etc.)	12
Gas turbine (jet) fuels	5
Kerosines	10
Middle distillates (diesel and light fuel oils)	27
Residual fuel oil	16
Lubricating oils	1156
White oils	100
Rust preventatives	65
Transformer and cable oils	12
Greases	271
Waxes	113
Asphalts	209
Cokes	4
Carbon blacks	5
Chemicals, solvents, miscellaneous	300
Total	2347

Another important fraction of crude oil is a diesel fuel, which is a liquid fuel used in diesel engines. It is also used mainly in transportation such as automobile, railroad, aircraft and military vehicles. The diesel fuel ignites by compression in the engine, which was invented by Rudolf Diesel, with the air and fuel mixture without spark ignition in contrast to gasoline engines [12]. The diesel engines become more popular since they are more efficient and cheaper than gasoline engines. Predominantly automotive diesel fuel contains C₁₀ to C₁₅ hydrocarbons with boiling range from 182 C to 316 C and is used in high speed engines in automobiles, trucks, and buses. The principal quality index of diesel fuel is cetane number, which shows the ignition quality of the fuel. In addition volatility, viscosity, sulfur content, percent aromatics, and cloud point are also important properties of diesel fuels.

Natural gas is the fastest growing primary energy source in the world. Today 25% of global energy consumption falls to natural gas [13]. Natural gas consists of lightweight alkanes, such as methane, ethane, propane, butane, isobutene and pentane. Most of the natural gas is methane with 80% and is used as a refinery fuel, but can also be used as a hydrogen feedstock [8,10].

Coal as the one of the most ancient energy resource has been used as a primary energy source for heating, electricity production and metal refining industry. Worldwide coal consumption was 7.99 billion short tons in 2010 and it increased more than 35% in comparison with 1998. According to Energy Information Administration it increased more than 40% over 12 years from 1999 to 2011 and was 14,416 million tons.

Renewable energy is a promising alternative solution for fossil fuels because it is clean and environmentally friendly. According to the forecast of European Renewable Energy Council (2006) in 2040 almost half of the global energy demand will be observed from renewable energy sources. Table 4 shows the global energy scenario by 2040.

Table 4 Global renewable energy scenario [15]

	2001	2010	2020	2030	2040
Total consumption (million ton oil equivalent)	10,038	10,549	11,425	12,352	13,310
Biomass	1,080	1,313	1,791	2,483	3,271
Large hydro	22.7	266	309	341	358
Geothermal	43.2	86	186	333	493
Small hydro	9.5	19	49	106	189
Wind	4.7	44	266	542	688
Solar thermal	4.1	15	66	244	480
Photovoltaic	0.2	2	24	221	784
Solar thermal electricity	0.1	0.4	3	16	68
Marine (tidal/wave/ocean)	0.05	0.1	0.4	3	20
Total renewable energy sources	1,365.5	1,745.5	2,694.4	4,289	6,351
Renewable energy source contribution (%)	13.6	16.6	23.6	34.7	47.7

As can be derived from the table the most prospective renewable energy source is Biomass. Biomass has been recognized as a major world RES (Renewable Energy Source) to supplement declining fossil fuel resources [15]. Biomass is the name given to all Earth's living organisms. The term biomass refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, biogases, industrial residues, waste paper, municipal solid waste, sawdust, bio-solids, grass, waste from food processing, aquatic plants and algae animal wastes, and a host of other materials. Biomass is the name given to the plant matter that is made by photosynthesis process where sun's energy converts CO₂ and water converts to organic material. The application of biomass as a primary source of energy will have positive impact on the greenhouse gas emissions because CO₂ emissions during the combustion and removal of CO₂ during photosynthesis process are the same.

Biomass can be used as an energy source after different conversion processes. Fig. 4 shows the main biomass conversion processes [8].

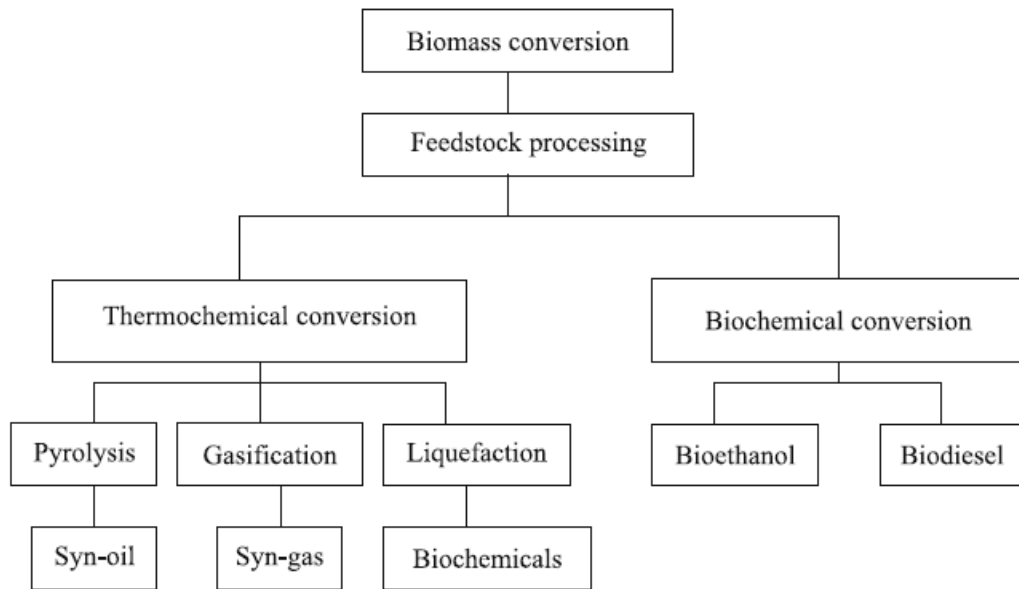


Figure. 4 Biomass conversion processes [8]

Biomass can be converted by biochemical process to the Bioethanol and Biodiesel and by thermochemical processes products like Syn-oil, Syn-gas and biochemicals can be produced. Biofuels can be also classified as first and second generation depending on ease of extraction by conventional technology. Biofuels made from sugars and vegetable oils are considered to be first generation.

Bioethanol is produced by microbial fermentation process from sugars, starches or cellulose. In 2011 global ethanol production reached 84.6 billion litres. World's largest bioethanol producers are the U.S. and Brazil with 62% and 25% respectively. [16]

Biodiesel is the most popular biofuel in European countries. In most developed countries there are strict policies for setting minimum percentages for biodiesel application. For example, in Germany and France this rate is 8% [17]. It is used mainly in automobile engines but also is applied in railway, aircraft and heating purposes.

During anaerobic respiration of organic matters different mixtures of gases are produced. The term Biogas refers to this gas mixture that was produced by advanced waste treatment technologies. Biogas is mainly consists of methane about 55%-75% and could be used in electricity generation, cogeneration gas engines and fuel cells. [18]

2.1 WHAT IS BIODIESEL?

Biodiesel is an alternative diesel, which can be produced from renewable biological sources such as vegetable oils. It is biodegradable and nontoxic, has low emission profiles and therefore, is environmentally beneficial [19]. The strongest motivation for increasing of production and

consumption of biodiesel is environmental issues. Petroleum consumption reaches its maximum every year and this trend will continue at least 10-15 years. As a result high petroleum consumption leads to local air pollution and global warming problems caused by CO₂. Significant investigations has been conducted on vegetable oils as diesel fuel. During these researches different types of oils such as palm oil, soybean, sunflower, coconut, rapeseed and tung oils are tested as a diesel fuel. Additionally, oil from algae, bacteria and fungi also have been researched [20]. Microalgae has been examined as source of methyl ester diesel fuel [21]. Biodiesel mainly is used as a blend to the diesel fuel. The letter B is used to indicate biodiesel contamination of the diesel blend and usually 4 types of blends are used in diesel engines: B100, B20, B5 and B2 where numbers refer to the biodiesel percentage [22]. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel [23].

2.2 BIODIESEL AS A RENEWABLE ENERGY SOURCE

Vegetable oil methyl esters, commonly referred to as biodiesel. Vegetable oils can be converted into their (m)ethyl esters via a transesterification process in the presence of a catalyst. Methyl, ethyl, 2-propyl, and butyl esters have been prepared from vegetable oils through transesterification using potassium and/or sodium alkoxides as catalysts [24]. The purpose of the transesterification process is to lower the viscosity of the oil. Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of bio-oils into smaller, straight-chain molecules of the type required in regular diesel combustion engines [25]. There several advantages and disadvantages of biodiesel in comparison with diesel oil. The main fuel and physical parameters are density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility. Biodiesel generates slightly less power and expend more fuel in comparison with No.2 diesel fuel. Nevertheless, biodiesel is better diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability [26]. Most of the biodiesel currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However, there are large amounts of low cost oils and fats such as restaurant waste and animal fats that could be converted into biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be converted into biodiesel using an alkaline catalyst [27].

2.3 FATS AND OILS

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats.

Biodiesel is produced from high free fatty acid feedstocks such as recycled oils and fats.

Vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule [25]. Table 5 shows main groups and types of oils that could be used in biodiesel production [25].

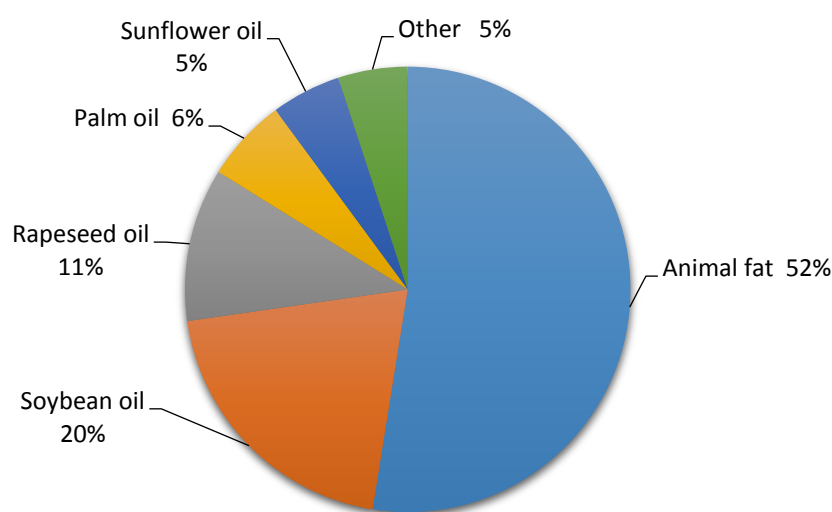
Table 5 Oil species for biofuel production [25]

Group	Source of oil
Major oils	Coconut (Copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), sunflower, sesame, soybean, and sunflower
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (<i>Acrocomia sclerocarpa</i>), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, (<i>Caryocar brasiliensis</i> seed), pine nut, poppyseed, prune kernel, quinoa, ramtil (<i>Guizotia abyssinica</i> seed or Niger pea), rice bran, tallow, tea (camellia), thistle (<i>Silybum marianum</i> seed), and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatropa or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall

Vegetable oils are a renewable and potentially inexhaustible source of energy with energy content close to diesel fuel. Refined oils and fats contain large amounts of free fatty acids [28]. The advantages of vegetable oils as diesel fuel are liquidity, ready availability, renewability, lower sulfur and aromatic content, and biodegradability [29]. The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains [25].

Figure 5 shows oil and fat feedstock distribution in top ten developed countries with self-sufficiency potential in 2006 [25].

Figure 5 Oil and fat feedstock [25]



Today, the world’s largest producer of soybeans is the USA.

Vegetable oils are recovered from plants by chemical extraction using solvent extracts. The most common extraction solvent is petroleum-derived hexane. Physical extraction supercritical carbon dioxide effectively extracts vegetable oils and fats [30].

2.4 IMPORTANCE OF BIODIESEL IN BIOFUELS FIELD

The need of the hour today with regard to renewable energy sources is to overcome the problem of depletion of fossil fuel reserves. It is also a major interest to reduce the green house gas emissions which directly or indirectly are the causes of global warming. Therefore, there is an utmost need to find alternative sources for fossil fuels instead of oil and its derivatives. Several research studies have led us to an opinion that of all the possible alternatives, biodiesel plays a very significant role of interest for various reasons. They are less toxic and highly biodegradable. No major modifications are required when used as a replacement of diesel fuels

in boilers and other combustion engines. Most important with respect to environmental concerns is their zero emissions of sulphates, aromatic compounds and few other chemical compounds that can cause a negative impact on the environment. On the other hand, this biodiesel production can help many rural un-employees and directly help in the rural economic development.

It is in the beginning of 1980s the use of biodiesel has taken up its gear. This is a gift from 1900s by Sir Rudolf Diesel, using vegetable oil as an alternative. His forward thinking about renewable energy sources had made us take a stand on present research [31].

2.5 CURRENT TECHNOLOGIES IN BIODIESEL PRODUCTION

There are many current technologies or procedures employed in the production of Biodiesel. The viscosities of animal fats and vegetable oils are reduced in order to use them as diesel engine fuels. The procedures involved in these processes vary as mentioned below:

1. Direct use and blending
2. Micro-emulsions
3. Pyrolysis of vegetable oil
4. Transesterification

1. Direct use and blending: Crude vegetable oils are found not much encouraging to be used directly as diesel engine fuels. Hence, crude vegetable oils are mixed directly or diluted with diesel fuel to improve the viscosity and to be used for diesel engines. Energy consumption in the case of these oils are found equivalent to diesel fuel. The ratios of oil to diesel 1:10 – 2:10 was found successful [32]. But at the end, the use of direct oils or blend of oils was not satisfactory with regard to direct or indirect usage as diesel fuels. Polymerisation during storage and combustion, carbon deposits and lubricating oil thickening are the problems encountered generally [33].

2. Micro-emulsions of oil: The fuels of this kind are also termed as hybrid fuels. The problem of high vegetable oil viscosity can be overcome by micro-emulsification. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions in the range of 1–150 nm, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles [33]. They exist as three components

namely an oil phase, an aqueous phase and a surfactant. The maximum viscosity limitation required for diesel engines can be met by micro-emulsions with butanol, hexanol and octanol [34].

3. Pyrolysis of Oils: Pyrolysis is the conversion of an organic compound into another organic compound by means of heat with the help of catalyst. Animal fats, vegetable oils, natural fatty acids or methyl esters of fatty acids can be used as pyrolyzed material. In the case of animal fats and vegetable oils conversion, triglycerides play an important role and thus the thermal cracking reactions. It is a promising technology for biodiesel production. The pyrolysis reactions can be divided into catalytic and non-catalytic reactions. The points to be considered are the expensive equipment for the process and all possibilities of more gasoline production than diesel fuel [35].

4. Transesterification of oils: The most important and effective current technology for biodiesel production is the transesterification of oils with alcohol to give biodiesel as main product and glycerine as by product.

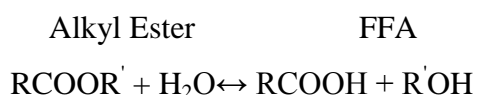
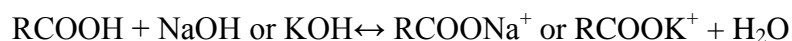
The current technologies in use for production of biodiesel are catalytic and non-catalytic transesterification methods.

1. Catalytic: The transesterification of vegetable oils by heating with an alcohol and using a catalyst is carried out in this process. Two types of catalysts are used in catalytic technique, one is by homogenous catalysts and the other one by heterogeneous catalyst. In the catalytic methods the selection of suitable catalyst is more important to reduce the cost of production.

a) The homogenous catalytic methods are again sub divided into two methods, one is homogenous base catalytic transesterification and the other, homogenous acid catalytic transesterification.

i) **Homogenous base catalytic transesterification:** At present, this process is the most employed in commercial sectors. It uses homogenous catalysts such as an alkaline metal alkoxides and hydroxides, as well as sodium or potassium carbonates [36]. In the method of basic methanolysis, almost in all the cases sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4% to 2% w/w of oil. The reasons these catalysts preferred are best operative conditions, high conversion rate in minimum time, good catalytic activity and economical. The limitations of this process are detailed in the equations below:





Equation 1. Side reactions in biodiesel production procedure.

ii. **Homogeneous acid catalytic transesterification:** An acid catalyst is used for the processing of triglycerides for biodiesel production. Sulphuric acid, sulphonic acid and hydrochloric acid are used as acid catalysts. The process starts by mixing the oil directly with the acidified alcohol, and then the separation and transesterification occur in one step, with the alcohol acting both as a solvent and as an esterification reagent [37].

iii. **Heterogeneous catalytic transesterification:** These catalysts can act in different phases which can help in easy separation. The expensive method of homogeneous catalysts has called for heterogeneous methods. No soap formation takes place in heterogeneous processes. The whole is shown in the figure below.

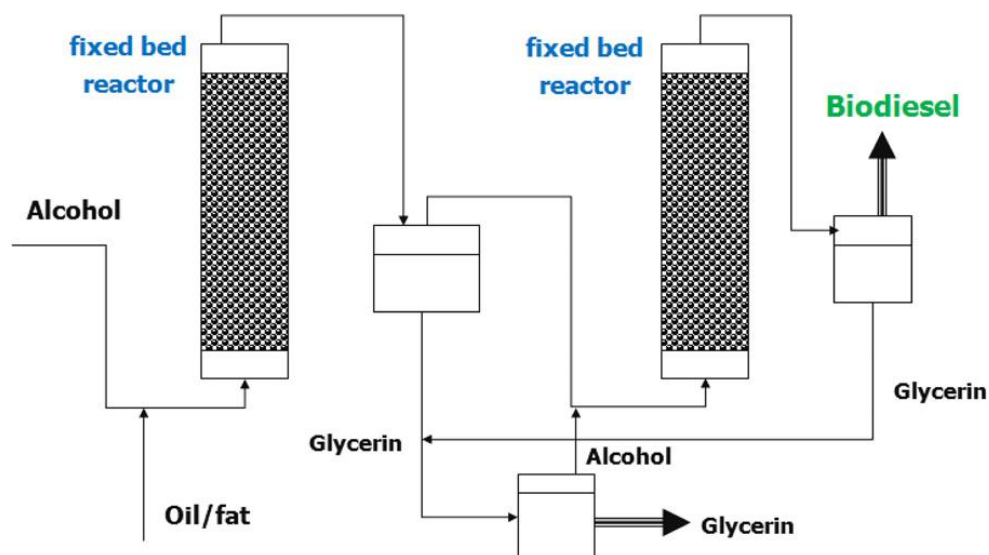


Figure 6 Heterogeneous catalytic transesterification [38]

There are two more divisions in heterogeneous catalyst run reactions, they are heterogeneous solid base catalysts and heterogeneous solid acid catalysts. The former catalysts are base or basic oxides coated over large surface area. Solid-base catalysts are more active than solid-acid catalyst. The most common solid-base catalysts are Basic zeolites, alkaline earth metal

oxides and hydrotalcites. Solid base can lead to the heterogeneous catalytic process, which promises the cost reasonable biodiesel production [38].

Heterogeneous solid acid catalysts have different acid sites with varying strengths of Bronsted or Lewis acidity, compared to the homogeneous acid catalysts. Heterogeneous solid acid catalysts, such as Nafion-NR50, sulphated zirconia and tungstated zirconia have been chosen to catalyze biodiesel forming transesterification due to the presence of sufficient acid site strength [39].

2. Non catalytic: There are few non catalytic methods too. These processes render production of biodiesel through a conventional transesterification system complicated, thus giving a reason to investigate the production of biodiesel from triglycerides via non-catalytic reactions. Super critical alcohol esterification, and BIOX co-solvent transesterification are included in the non catalytic processes [40].

2.6 EUROPEAN NORMS

SCOPE

The European standards states requirements and test methods for fatty acid methyl esters (FAME) to be used as automotive fuel or diesel engines fuels at 100% concentration. It also specifies an extender for automotive fuel for diesel engines with the requirements of EN 590. At 100 % concentration it is applicable to fuel for use in diesel engine vehicles designed or subsequently adapted to run on 100 % FAME [41].

2.7 BIODIESEL REQUIREMENTS AND RELATED TEST METHODS

- a) **Dyes/Markers:** Use of dyes or markers is allowed.
- b) **Additives:** The appropriate fuel additives without known harmful side effects are recommended. This can help to avoid deterioration of driveability and emissions control durability. So, as to improve the performance quality, additives are allowed.
- c) **Stabilizing agents:** these are added to the product to stabilize FAME on a long term idea. In order to improve the long term stability of FAME, it is recommended that stabilizing agents should be added to the product immediately after its production, at least before its eventual blending into a mixture with petroleum based diesel fuel.
- d) Generally applicable requirements and test methods are depicted in the table below [41].

Table 6. Biodiesel requirements and test methods [41]

Property	Limits		Test method
	minimum	Maximum	
Fame content, % (m/m)	96.5	-	EN14103
Density at 15°C, kg/m ³	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40°C, mm ² /s	3.50	5.00	EN ISO 3104
Flash point, °C	101	-	EN ISO 2719 EN ISO 3679
Sulfur content, mg/kg	-	10.0	EN ISO 20846 EN ISO 20884
Carbon residue, wt % (on 10% distillation residue)	-	0.3	EN ISO 10370
Cetane number	51	-	EN ISO 5165
Sulfated ash content, %	-	0.02	ISO 3987
Water, mg/kg	-	500	EN ISO 12937
Total contamination, mg/kg	-	24	EN ISO 12662
Copper strip corrosion (3h at 50°C), rating	Class 1		EN ISO 2160
Oxidation stability, 110°C, hours	6	-	prEN 15751 EN 14112
Acid value, mgKOG/g	-	0.5	EN 14104
Iodine value, g iodine/100g	-	120	EN 14111
Linolenic acid methyl ester, % (m/m)	-	12.0	EN 14103
Polyunsaturated (≥ 4 double bonds) methyl esters, % (m/m)	-	1	
Methanol content, % (m/m)	-	0.20	EN 14110
Monoglyceride content, % (m/m)		0.80	EN 14105
Diglyceride content, % (m/m)	-	0.2	EN 14105
Triglyceride content, % (m/m)	-	0.2	EN 14105
Free glycerol, % (m/m)	-	0.02	EN 14105 EN 14106
Total glycerol, % (m/m)			
Group I metals (Na+K). mg/kg	-	5	EN 14108 EN 14109 EN 14538
Group I metals (Ca+Mg). mg/kg	-	5	EN 14538
Phosphorous content, mg/kg	-	4	EN 14107

2.8 PROPERTIES OF BIODIESEL FROM VARIOUS SOURCES

The viscosity, density and flash point of the raw materials used for production of biodiesel are lowered in the process. The chemical composition of the biomass used is directly related to some important properties of the diesel oil, such as viscosity, melting point, thermal stability and cetane index. Therefore, it is possible to assume the property values of biodiesel produced from a specific vegetable oil. The study by, evaluated the properties of biodiesel oils from varieties of biomass sources such as castor, soybean, cotton and canola [42] .

In another study by, high amounts of free fatty acids determine the quality of biodiesel to be produced. Oils containing hydroxyl group compounds possess high viscosity due to the presence of hydrogen bonding. The physico-chemical properties of Jatropha and castor oils were assessed for their potential in biodiesel. This research study has shown that high amounts of Free fatty acids in oils has produced low quality diesel oil and vice versa. In both the cases of jatropha and castor oils, the FFAs are neutralized to improve the quality of biodiesel [43].

One more research study on evaluating different materials for biodiesel production by [43], has given a clear idea on the properties of the oils and the respective produced biodiesel properties. The below tables provide the information on the same.

Table 7. Oil properties [44]

Properties	Units	Jatropha oil	Palm oil	Soybean oil	Waste cooking oil
Kinematic viscosity at 38°C	Mm ² /s	49.93	39.6	32.6	36.4
Cetane number	-	40-45	42.0	37.9	49.0
Heating value	MJ/kg	-	-	39.6	-
Flash point	°C	240	267	254	485
Cloud point	°C	-	31.0	-	-
Density	g/mL	0.9186	0.9180	0.9138	0.8830
Carbon residue	wt%	0.10	0.23	0.25	0.46

Table 8. Biodiesel properties [44]

Property	Jatropha	Soybean	Oil palm	WCO	Biodiesel standards		
					ASTM D 6751-02	DIN EN 14214	Diesel fuel
Density at 20°C, kg/m ³	880	885	880	884	870-900	875-900	850
Viscosity at 40°C, mm ² /s	2.37	4.5	5.7	4.5	1.9-6.0	3.5-5.0	2.60
Cloud point, °C	-	1	13	1	-	-	4
Flash point °C	135	178	164	180	130	120	68
Pour point	2	-7	12	-5.0	-15 to 10	-15 to 10	-20
Water, %	0.025	-	-	0.4	0.03	0.05	0.02
Sulfur, PPM	-	-	-		50	50	500
Carbon residue, wt %	0.2	-	-	0.3	-	0.3	0.17
Cetane number	61	45	62	57.2	48-60	49	49
Calorific value, Mj/kg	39.2	33.5	33.5	32.9	-	-	42

2.9 IMPROVEMENT OF BIODIESEL PROPERTIES

The properties of a biodiesel fuel that are determined by the structure of its component fatty esters include ignition quality, heat of combustion, cold flow, oxidative stability, viscosity and lubricity[45]. Among them cold flow property is very important one. Because of having some advantages as higher cetane number, reduced emissions of particulates(NO_x, SO_x,CO) and hydrocarbons, reduced toxicity, improved safety and lower lifecycle CO₂ emissions at the same time low temperature property is the main disadvantage of biodiesel [46]. Robert O. Dunn reported that field studies on cold weather performance are scarce, there is evidence that soybean oil fatty acid methyl esters (SME) develop operability issues as ambient temperatures approach 0-2°C. In contrast, petrodiesel develops similar problems at a significantly lower temperature range, typically between -16 and -20°C. Blending biodiesel with petrodiesel may be advantageous for mitigating the poor cold flow properties of biodiesel from many lipid feedstocks. On the other hand, blending at higher ratios may compromise cold flow properties [47].The other way of improving properties of biodiesel is using additives such nickel and magnesium [48]

3. Experimental Section

3.1 Chemical and solvents

In this work were used three types of vegetable oils: new vegetable oil, waste cooking oil and old vegetable oil. The waste cooking oil was collected from university canteen. The transesterification reaction used NaOH as a catalyst and methanol (99.9% purity) as a reactant. The acid number of biodiesel calculated through volumetric titration with standard KOH solution with diethyl ether/ ethanol solvent obtained from Panreac Quimica (Spain) and Fischer Scientific (UK) and phenolphthalein as pH indicator. Iodine content was determined by volumetric titration with $\text{Na}_2\text{S}_2\text{O}_3$ using cyclohexane/acetic acid as solvent purchased from Riedel-de Haen and Fluka (Germany) and Wijs reagent was used as indicator.

3.2 Production of Biodiesel

For the biodiesel production experiments there were used the following reference quantities of reactants and catalyst: 200ml of vegetable oil, 40 ml methanol and 1g NaOH.

At the first step of the experiment NaOH was added into the methanol, and stirred until all NaOH dissolved.

Then, 200 ml of vegetable oil was measured using a measuring cylinder and heated until 55-60°C. After reaching the desirable temperature, NaOH/Methanol mixture was added to the continuously mixed-heated oil (Figure 7) and the reaction was carried out in 1 hour. After reaction finished, the reaction mixture was allowed to rest.



Figure 7. Vegetable oil mixing with NaOH/Methanol solution

3.3 Determination of the production yield

After the reaction, the reaction mixture was let to decantate until the biodiesel light layer completely separated from the glycerin heavy layer. It took one day to glycerin and biodiesel layers separated (Figure 8).

The biodiesel layer was separated by removal of the glycerin layer. Afterwards, the biodiesel was prepared to the washing procedure.

For the washing process, 50% (related the biodiesel volume) of water was added to the biodiesel in order to extract contaminants. The mix was allowed to separate, forming a top biodiesel layer and a bottom aqueous layer, due to difference in densities and immiscibility. After complete separation, the aqueous layer is removed and the extraction process is repeated until the aqueous layer shows no contamination.

The next step is the drying process. The drying process occurs by heating the biodiesel sample to a temperature range of 105-110°C. Temperature should not be less than 105°C and higher than 110°C. Biodiesel was heated during about 30 minutes until all the water evaporated and separated from the sample.



Figure 8. Washing process

3.4 Biodiesel acid value

Titration

Titration process is used determine how much FFA is present and how much extra lye (basic) is required to drive the biodiesel reaction to completion.

As a solvent for titration is used 1/1 Ethanol/Diethyl Ether mixture and standard solution of KOH with concentration 0.008285 M. Phenolphthalein pH indicator will show a color change when the end point is reached.

Procedure

1. Measure 50mL of Ethanol/Diethyl Ether solvent in a 250mL Erlenmeyer flask using a graduate beaker and add 5 drops of phenolphthalein.
2. Add some drops of KOH solution using micro-burette in order to neutralize the solvent until color changed into light pink.
3. Measure 10g of biodiesel and add to neutralized solvent.
4. Repeat the titration until reaching desired color.

Acidity of biodiesel calculated with following formula

where ,

AV is the acid value of biodiesel (mg KOH/g biodiesel)

V is needed volume of KOH (mL)

C is KOH concentration (mol/L)

m is the biodiesel mass used for determination (g)

56.1 is the molar mass of KOH (g/mol)

3.5 Biodiesel density (picnometer)

1. To calculate density of biodiesel, firstly should measure three masses : mass of empty pycnometer, mass of picnometer with ultra pure water, mass of picnometer with biodiesel sample.

During measuring mass of picnometer with ultra pure water and mass of picnometer with biodiesel, temperature should be measured at the same time

2. Calculation of impulsion suffered on the weighting plate of the environment by picnometer (A in g) using following formula

(2)

3. Calculation of pycnometer's volume (V_t in cm^3)

where,

m_1 is the mass of empty picnometer

m_2 is the mass of picnometer with ultrapure water

4. Calculation of biodiesel density at room temperature g/cm^3

(4)

where,

m_3 is the mass of picnometer with biodiesel

5. Correction factor to calculate density at 15°C (g/cm^3)

3.6 Biodiesel density (hydrometer)

Determination of biodiesel density at 15°C using hydrometer

Hydrometer is a graduated glass tube filled with air and fitted with a weight which used to measure density of biodiesel.

1. Add 90ml of biodiesel sample in a graduate beaker, measuring room temperature using a thermometer.
2. Drop hydrometer inside the beaker with biodiesel and wait until the hydrometer stop to move.
3. Read the value in the hydrometer scale.

3.7 Biodiesel iodine value

The iodine number is a measure for the number of double bonds in a sample. It specifies the amount of iodine in g that are consumed by 100 g of the biodiesel sample under the given conditions. The determination of the iodine number by titration with a solution of sodium thiosulfate is described by the European standard EN 14111.

The amount of iodine present is determined by titrating with sodium thiosulfate using starch indicator.

Procedure

1. Prepare solvent by mixing equal volumes (200mL) of cyclohexane and acetic acid.
2. Prepare 250 mL Erlenmeyer flasks and accurately weight 0.13-0.15 g of biodiesel samples. Dissolve samples with biodiesel using 20mL of prepared solvent and add 25mL of Wijs reagent (0.1 mol/L) using precision pipette and stopper. Place the flasks in the dark and leave for 1h.
3. Prepare blank solution : 20mL of solvent with 25mL of Wijs reagent, without adding biodiesel sample.
4. At the end of 1h, add 20mL of potassium iodide solution and 150mL of ultra pure water and titrate with standard sodium thiosulfate solution $\text{Na}_2\text{S}_2\text{O}_3$ with concentration 0.1013 mol/L. Continue titration until reaching yellow color, then add 8 drops of starch solution and titrate until reaching light grey color.
5. Repeat the same procedure with another 12 samples

Calculation of iodine value

The iodine value, expressed in g of I/100g of biodiesel calculated with the following formula:

where,

c is the exact concentration of standard volumetric sodium thiosulfate solution, (mol/L)

V_1 volume of standard sodium thiosulfate solution used for blank test, (mL)

V_2 volume of standard sodium thiosulfate solution used for sample titration (mL)

m is the mass of the biodiesel (g)

12.69 is molar mass of biodiesel

3.8 Biodiesel FAMES content

All biodiesel samples were analyzed using Varian 3800 GC equipment equipped with an Supelcowax 10 (30m \times 0.25mm \times 0.25 μ m). Injector temperature is 250°C. Oven:50°C(2 min); 4°C/min until 220°C(total running time:80 min). Sample volume: 1 μ L. Injector split ratio is 1:20.

Prepare the sample:

1. Measure 250 mg of biodiesel to a 10 ml flask.
2. Add 5 ml of heptane.
3. Shake the solution and let it stand for 1 min.
4. Dry the solution adding a micro-spatula of anhydrous sodium sulfate. Shake and let the solution stand until clarification. (near 5 min)
5. Analyse the solution by GC using the operating conditions described before.

Obtained from chromatogram FAME peaks were identified and confirmed by comparing their retention times to those of known standards. Table 9 lists the retention times of all compounds, presented in Supelco 37 Compound Mix [50], using the similar column package like was used for the following experiment.



Figure 9. Varian 3800 GC equipment

Table 9. Identified 37 FAME compounds, presented in standard solution, obtained from Supelco 37 Compound Mix

Peak ID	Acid Methyl esters	Time (min)
1	C4:0 (Butyric)	5.880
2	C6:0 (Caproic)	10.987
3	C8:0 (Caprylic)	17.305
4	C10:0 (Capric)	23.498
5	C11:0 (Undecanoic)	26.416
6	C12:0 (Lauric)	29.208
7	C13:0 (Tridecanoic)	31.876
8	C14:0 (Myristic)	34.433
9	C14:1 (Myristoleic)	35.382
10	C15:0 (Pentadecanoic)	36.880
11	C15:1 (cis-10-Pentadecenoic)	37.803
12	C16:0 (Palmitic)	39.232
13	C16:1 (Palmitoleic)	39.858
14	C17:0 (Heptadecanoic)	41.482
15	C17:1 (cis-10-Heptadecenoic)	41.878
16	C18:0 (Stearic)	43.652
17/18	C18:1n9c (Oleic)/ C18:1n9t (Elaidic)	44.118
19/20	C18:2n6c (Linoleic)/ C18:2n6t (Linolelaidic)	45.149
21	C18:3n6 (γ -Linolenic)	45.884
22	C18:3n3 (α -Linolenic)	46.721
23	C20:0 (Arachidic)	48.437
24	C20:1n9 (cis-11-Eicosenoic)	49.089
25	C20:2 (cis-11,14-Eicosadienoic)	50.682
26	C20:3n6 (cis-8,11,14-Eicosatrienoic)	51.690
30	C21:0 (Henicosanoic)	52.111
27	C20:3n3 (cis-11,14,17-Eicosatrienoic)	52.623
28	C20:4n6 (Arachidonic)	53.174
29	C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic)	55.476
31	C22:0 (Behenic)	55.828
32	C22:1n9 (Erucic)	56.922
33	C22:2 (cis-13,16-Docosadienoic)	59.600
35	C23:0 (Tricosanoic)	61.171
36	C24:0 (Lignoceric)	68.174
34/37	C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic) /C24:1n9 (Nervonic)	70.104

4. Results and Discussion

4.1 Biodiesel production

The amount of NaOH used for biodiesel production of waste cooking oil, was calculated by adding to the reference value above, a specified quantity, assessed by the estimation of the oil sample acidity. This was done by titration with a NaOH solution using isopropanol as solvent (Table 10).

Table 10. Quantity of NaOH solution used for titration

Run	NaOH solution used for titration (ml)
1	1.20
2	1.30

Average value of NaOH solution used for titration is 1.25 ml. For biodiesel production 200 ml of oil, 40ml of methanol and 1.125 g NaOH should be taken (Sample 3).

During experimental work five biodiesel samples were produced. For the preparing Sample 1 was used new vegetable oil, for Sample 2 old vegetable oil, and for other samples were used waste cooking oil.

Reaction parameters and production yield are presented in Table 11.

Table 11. Operating conditions and obtained production yield

Sample	mNaOH (g)	V oil (mL)	V methanol (mL)	Produced volume of biodiesel (mL)
1	1.0051	200	40	160
2	1.0645	200	40	120
3	1.1075	200	40	120
4	1.0579	200	40	120
5	2.1470	400	80	352.5

4.2 Density

There are presented two ways to determine the density of produced during experimental work five biodiesel samples : determination of density with picnometer and hydrometer.

4.2.1 Determination of biodiesel density at 15°C using picnometer.

Firstly, density was determined with picnometer, according to the procedure and conditions described in section above. The table below represents the results obtained with the picnometer.

Table 12. Determination of biodiesel density at 15°C

Sample № 1		
Impulsion data		
A _{1,1}	A _{1,2}	A _{1,3}
0,011370	0,011368	0,011362
Volume data (V, cm³)		
V _{t,1}	V _{t,2}	V _{t,3}
9.5097	9.5086	9.5032
Density data (g/ cm³)		
0.885240	0,885300	0,886203
Density of biodiesel at 15°C (g/ cm³)		
0.891169	0.891229	0.892132
Sample № 2		
Impulsion data		
A _{1,1}	A _{1,2}	A _{1,3}
0.010829	0,010818	0,010833
Volume data (V, cm³)		
V _{t,1}	V _{t,2}	V _{t,3}
9.0578	9.0483	9.0604
Density data (g/ cm³)		
0.897782	0,898259	0,896763
Density of biodiesel at 15°C (g/ cm³)		
0.903711	0.904188	0.902692
Sample № 3		
Impulsion data		
A _{1,1}	A _{1,2}	A _{1,3}
0.011909	0,011910	0,011700
Volume data (V, cm³)		
V _{t,1}	V _{t,2}	V _{t,3}
9.9613	9.9618	9.9532

Density data (g/ cm³)		
0.887827	0,887642	0,888749
Density of biodiesel at 15°C (g/ cm³)		
0.893683	0.893498	0.894605
Sample № 4		
Impulsion data		
A _{1,1}	A _{1,2}	A _{1,3}
0.011804	0,011790	0,011822
Volume data (V, cm³)		
V _{t,1}	V _{t,2}	V _{t,3}
9.8726	9.8615	9.8882
Density data (g/ cm³)		
0.891225	0,892906	0,890093
Density of biodiesel at 15°C (g/ cm³)		
0.897154	0.898907	0.896094
Sample № 5		
Impulsion data		
A _{1,1}	A _{1,2}	A _{1,3}
0.010069	0,010049	0,010046
Volume data (V, cm³)		
V _{t,1}	V _{t,2}	V _{t,3}
8.4217	8.4047	8.4025
Density data (g/ cm³)		
0.885186	0,886902	0,886789
Density of biodiesel at 15°C (g/ cm³)		
0.891187	0.892903	0.892862

Operating conditions for density determination process are presented in Appendix A, Table A1.1

4.2.2 Determination of biodiesel density at 15°C using hydrometer

Another way to determine biodiesel density it is determination using hydrometer.

Determined density values represented in Table 13.

Table 13. Density value of hydrometer at room temperature

Sample 1	
Temperature (°C)	Density (kg/m ³)
18.5	887.5
Sample 2	
Temperature (°C)	Density (kg/m ³)
18.4	898
Sample 3	
Temperature (°C)	Density (kg/m ³)
18.4	890
Sample 4	
Temperature (°C)	Density (kg/m ³)
18.5	891
Sample 5	
Temperature (°C)	Density (kg/m ³)
18.5	887

Calculation of the biodiesel density at 15°C using following formula

$$\text{_____} \quad (6)$$

Results represented in Table 14

Table 14. Calculated density data

(kg/m ³)	(kg/m ³)	(kg/m ³)	(kg/m ³)	(kg/m ³)
887.6	898.1	890.1	891.1	887.1

The experimental results obtained for the density using the hydrometer presented in table 14, vary from 887.1(sample5) to 898.1. These results are between the minimum (860 kg/m³) and the maximum (900 kg/m³) values referred in the EN14214 (see Table 6, page 18)

Although, obtained density results at 15°C with both methods are approximately the same, comparing methods, picnometer method is more precisely and accurate, because hydrometer is

affected by many things (like temperature, that causes the change in density; present of alcohol in biodiesel) that makes readings not accurate.

4.3 Acid Value

The acid number of all obtained biodiesel samples was measured using titration methodology described in section 4.4.1. Obtained results are represented in Table 15

Table 15. Acidity data

Sample 1					
Mass of biodiesel (g)		V KOH (mL)		Acidity (mg KOH/mg biodiesel)	
m_1	m_2	V _{initial}	V _{final}	AV ₁	AV ₂
10.1592	9.6633	1.30	4.60	0.15	0.16
Sample 2					
Mass of biodiesel (g)		V KOH (mL)		Acidity (mg KOH/mg biodiesel)	
m_1	m_2	V _{initial}	V _{final}	AV ₁	AV ₂
10.0018	10.0000	1.30	11.65	0.48	0.48
Sample 3					
Mass of biodiesel (g)		V KOH (mL)		Acidity (mg KOH/mg biodiesel)	
m_1	m_2	V _{initial}	V _{final}	AV ₁	AV ₂
10.0364	10.0130	1.30	7.85	0.30	0.30
Sample 4					
Mass of biodiesel (g)		V KOH (mL)		Acidity (mg KOH/mg biodiesel)	
m_1	m_2	V _{initial}	V _{final}	AV ₁	AV ₂
10.0254	10.0029	1.30	7.40	0.28	0.28
Sample 5					
Mass of biodiesel (g)		V KOH (mL)		Acidity (mg KOH/mg biodiesel)	
m_1	m_2	V _{initial}	V _{final}	AV ₁	AV ₂
10.0218	10.0166	1.30	4.45	0.15	0.15

V initial - volume of KOH needed for neutralize solvent

V final -volume of KOH needed for titration of biodiesel

m_1, m_2 - mass of biodiesel

4.4 Iodine Value

Iodine values, calculated with formula mentioned above, represented in Table 16

Table 16. Iodine value

№ of samples	m _{biodiesel} (g)	Iodine values (g _{iodine} /100g _{biodiesel})
1.1	0.1305	134.9
1.2	0.1523	123.2
2.1	0.1348	136.4
2.2	0.1474	125.6
3.1	0.1405	122.6
3.2	0.1381	114.5
4.1	0.1366	132.7
4.2	0.1392	125.6
5.1	0.1420	133.1
5.2	0.1445	122.8

4.5 Biodiesel characterization through FAMES analysis

GC investigations of content and distribution of fatty acid methyl esters (FAMES) in biodiesels were carried out. Five samples of biodiesel produced with new, old and waste cooking oil were subjected to determine FAMES compositions.

All obtained biodiesel samples were analyzed by qualitative methodology using FAMES areas (%). In order to analyze the quantity and areas of the FAMES in biodiesel, an injection of the biodiesel produced from waste cooking oil (Sample 3) was carried out. The chromatogram of selected sample presented in Figure 10.

The ester content is calculated from the area of all peaks between C14 and C24 methyl esters.

The used GC integration parameters are : a minimum chromatographic area = 6000 and signal noise (s/n)=5.

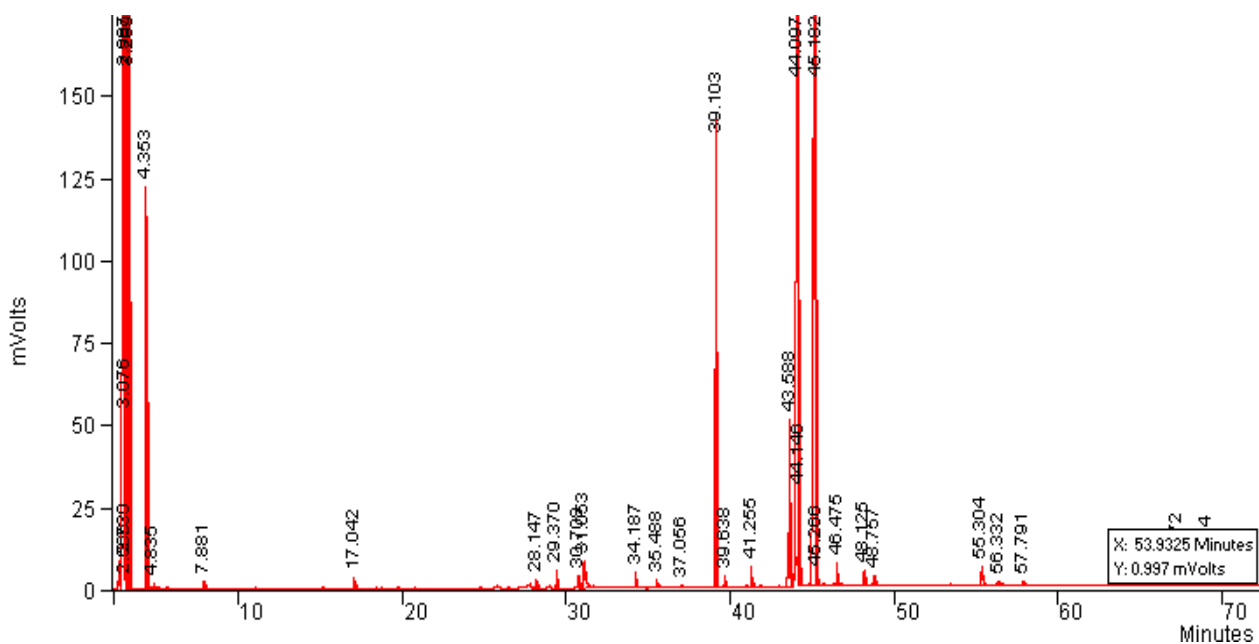


Figure 10. Analyzed chromatogram of selected biodiesel sample [49]

In Table 17 represented the qualitative analysis of all identified FAMES of the selected biodiesel sample. According to this obtained data, the methyl ester content integrated between C14:0 to C24:1n9/C22:6n3. The total area of identified FAMES is 99%, which the major area (49.9%) corresponding to C18:2n6c (Linoleic) and C18:2n6t (Linolelaidic) methyl esters, which in turn represents 2 FAMES. The retention time of methyl Linoleic/ Linolelaidic standard is lower (45.149min) than peak correseponding in analyzed sample (45.182).

Table 17. Identified FAMES content analyzing using Varian GC gas chromatograph

	Components	Time	Area (%)	Ai (%)
1	Not Identified	31.053	72620	1,13
2	C14:0 (Myristic)	34.187	12888	0,20
3	C14:1 (Myristoleic)	35.488	10128	0,16
4	Not Identified	37.056	6098	0,09
5	C16:0 (Palmitic)	39.103	713187	11,09
6	C16:1 (Palmitoleic)	39.638	10947	0,17
7	C17:0 (Heptadecanoic)	41.255	18761	0,29
8	C18:0 (Stearic)	43.588	251178	3,90
9	C18:1n9c (Oleic)/C18:1n9t (Elaidic)	44.097	2022397	31,44
10	Not Identified	44.146	28013	0,44
11	C18:2n6c (Linoleic)/C18:2n6t (Linolelaidic)	45.182	3215528	49,99
12	C18:3n6 (γ -Linolenic)	45.266	8524	0,13
13	C18:3n3 (α -Linolenic)	46.475	24999	0,39
14	Not Identified	48.125	18913	0,29
15	C20:0 (Arachidic)	48.757	8912	0,14
16	C20:5n3 (cis-5,8,11,14,17- Eicosapentaenoic)	55.304	39285	0,61
17	C22:1n9 (Erucic)	56.332	16888	0,26
18	Not Identified	57.791	9827	0,15
19	Not Identified	67.172	13395	0,21
20	C24:1n9 (Nervonic)/C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic)	69.014	6161	0,10
21	Total FAMES area %		6432403	99.0

According to the obtained results, analyzing biodiesel sample (Sample 3, Run 3) was identified 15 FAMES.

The plot presented below, represent the total percentage of FAMES calculated by qualitative method.

Table 18. Total FAMES area of studied samples

Sample	FAMES area (%)
1	100
2	100
3	98.97
4	100
5	100

5. Conclusions and future work

5.1 Conclusions

Before biodiesel can be sold as a fuel or blending stock, it must first meet a defined standard to ensure the fuel does not damage engine components. Therefore, the quality control of biodiesel is a necessity for the successful commercialization of this fuel and its blends.

In this work studied biodiesel production by transesterification reaction using new, old and waste cooking oil as raw material and sodium hydroxide as a catalyst. After obtaining product, according to European Standards quality parameters of biodiesel like: acid value (EN 14104), iodine value (14111), density using pycnometer and hydrometer (EN ISO 3675, EN ISO 12185), FAME content (10103) were studied. GC 3800 Varian Gas Chromatograph provided an appropriate method for analyzing FAME in biodiesel product.

During the experiment, five biodiesel samples were produced. As a result of experimental work, the results of density of biodiesel samples determined using pycnometer and hydrometer does not have significant difference (Table 19).

Table 19. Density values determined with picnometer and hydrometer.

Sample	Density value using pycnometer (g/cm ³)	Density value using hydrometer (g/cm ³)
1	0.891	0.887
2	0.903	0.898
3	0.893	0.890
4	0.897	0.891
5	0.892	0.887

Despite these results, determination of biodiesel density using pycnometer can be considered more precisely, because hydrometer is affected by many things (like temperature, that causes the change in density; present of alcohol in biodiesel) that makes readings not accurate.

Comparing this results with European Standards (according to Standards minimum value is 860 kg/m³ and maximum is 900 kg/m³), obtained results can be considered successful.

Making Biodiesel, it's important to know what the acid level in the oil is. This is because when Biodiesel is produced, one of the chemicals used will be a strong base. Biodiesel samples produced from different raw materials has different values.

The minor acid value (0.15 mgKOH/mgbiodiesel) was obtained for biodiesel produced from new oil (Sample 1) and for waste cooking oil (Sample 5), while the major value (0.48 mgKOH/mgbiodiesel) was for biodiesel sample produced from old oil. This values comply with the value mentioned in European Standards value (0.5 mgKOH/mgbiodiesel)

The investigated biodiesel samples has minimum value of 114.5 (giodine/100gbiodiesel) and maximum value of 136.4 (giodine/100gbiodiesel), thus meets the requirements of EN 14214 with a permitted maximal value of 120 grams of iodine per 100 grams of sample.

Analyzing FAMES content of the obtained products, was observed the percentage of FAMES in biodiesel around 99%.

As all obtained results consisting with European Standard Norms, obtained during experiment results can be considered successful.

5.2 Future work

In this work biodiesel quality parameters (density, acid value, iodine value, FAME content) were studied. But the experimental procedure adopted in present research work can be extended.

Thus further experiments of fuel analytics could be done to get other fuel properties as flash point, cloud point, cetane number, etc. and the further emission testing could be done on different engines using the biodiesel fuel to get results that show the reduction of emissions when using biodiesel fuel.

Used catalyst could be further optimized, however, it might in fact bring benefits in biodiesel production, by improving product quality as well as reducing purification steps and associated wastes.

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Appendix A Biodiesel density

Sample № 1								
m₁ mass of empty picnometer (g)			m₂ mass of picnometer with water (g)			m₃ mass of picnometer with biodiesel (g)		
m_{1.1}	m_{1.2}	m_{1.3}	m_{2.1}	m_{2.2}	m_{2.3}	m_{3.1}	m_{3.2}	m_{3.3}
11.8376	11.8375	11.8374	21.3121	21.3109	21.3054	20.2446	20.2441	20.2478
Sample № 2								
m₁ mass of empty picnometer (g)			m₂ mass of picnometer with water (g)			m₃ mass of picnometer with biodiesel (g)		
m_{1.1}	m_{1.2}	m_{1.3}	m_{2.1}	m_{2.2}	m_{2.3}	m_{3.1}	m_{3.2}	m_{3.3}
14.3638	14.3639	14.3641	23.3883	23.3789	23.3912	22.4849	22.4808	22.4783
Sample № 3								
m₁ mass of empty picnometer (g)			m₂ mass of picnometer with water (g)			m₃ mass of picnometer with biodiesel (g)		
m_{1.1}	m_{1.2}	m_{1.3}	m_{2.1}	m_{2.2}	m_{2.3}	m_{3.1}	m_{3.2}	m_{3.3}
16.9969	16.9968	16.9968	26.9213	26.9217	26.9133	25.8289	25.8274	25.8310
Sample № 4								
m₁ mass of empty picnometer (g)			m₂ mass of picnometer with water (g)			m₃ mass of picnometer with biodiesel (g)		
m_{1.1}	m_{1.2}	m_{1.3}	m_{2.1}	m_{2.2}	m_{2.3}	m_{3.1}	m_{3.2}	m_{3.3}
16.6748	16.6749	16.6749	26.5111	26.5001	26.5267	25.4617	25.4685	25.4645
Sample № 5								
m₁ mass of empty picnometer (g)			m₂ mass of picnometer with water (g)			m₃ mass of picnometer with biodiesel (g)		
m_{1.1}	m_{1.2}	m_{1.3}	m_{2.1}	m_{2.2}	m_{2.3}	m_{3.1}	m_{3.2}	m_{3.3}
16.2316	16.2316	16.2315	24.6223	24.6054	24.6031	23.6763	23.6757	23.6727

Table A1.1

