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Biofuels from transesterification of used oils

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From,

Ziad Guerfi.

List of figures

Chapter I:

Chapter II:

Chapter III:

Chapter IV:

List of tables

Chapter I:

Chapter II:

Chapter III:

Chapter IV:

List of abbreviations

Chapter I:

W.W.I	World War one
KPa	Kilo-Pascal
PPM	Parts Per Million or (milligrams per liter (mg/L))
ISO	International Organization for Standardization
ASTM	American Society for Testing and Materials
Wt%	Weight Titration
TAG	Triacylglycerols
DAG	Diacylglycerols
MAG	Monoacylglycerols
FFAs	Free Fatty Acids
ABE	Acetone-Butanol-Ethanol
IEA	International Energy Agency
LCA	Life Cycle Analysis
U.S	United States
C.O.F.E	Canola Oils Ethyl Ester

Chapter II:

TG	Triacylglycerols
g/cc	Gram per Cubic Centimeter
cSt	Unit Centistokes
UV	Ultra-Violet
EPA	Environmental Protection Agency
PV	Peroxide Values

Chapter III:

IR	Infrared radiation
AGL	Acids Glycerol
Δt	Time difference
FT-IR	Fourier Transform Infrared
AJR	Recommended daily allowance

Chapter IV:

A%	Acidity %
FAME	Fatty Acids Methyl Esters
BIO.D	Biodiesel
F	Frying oils
et al	And others
Bx	Blends of Biodiesels with Gasoline
DS	Date Seeds
EN	European Nations

Summary

Chapter I: Biofuels

Chapter II: Characterization of oils, used oils and frying oils

Chapter III: Experimental and Practical Studies

Chapter IV: Discussion of Results

General Introduction

General Introduction

Biofuels are drawing increasing attention worldwide as substitutes for petroleum-derived transportation fuels to help address energy cost, energy security and global warning concerns associated with liquid fossil fuels. The term biofuel is used here to mean any liquid fuel made from plant material that can be used as a substitute for petroleum-derived fuel. Biofuels can include relatively familiar ones, such as ethanol made from sugar cane or diesel-like fuel made from soybean oil **[1]**.

Interest in liquid biofuels production and use has increased worldwide as part of government policies to address the growing scarcity and riskiness of petroleum use, and, at least in theory, to help mitigate adverse global climate changes. Biomass energy or bioenergy is the key focus for agriculture. Biofuels have become a popular way to use renewable biomass energy and have emerged as a potentially major alternative to gasoline and diesel transportation fuels derived from petroleum. Interest has been growing in the large-scale application of biofuels to address the twin global challenges of global climate change, and shifting away from increasingly scarce and environmentally and politically risky petroleum supplies **[2]**.

Biofuels generally refer to liquid transportation fuels such as bioethanol and biodiesel. Their production and use has the potential to decrease global greenhouse gas emissions. Moreover, their use as additives can decrease our dependence upon petroleum based fossil fuels. And also can improve the local employment opportunities for farmers. In contrast to the other renewable energy sources, biomass can be converted directly into biofuels. Ethanol (ethyl alcohol) is most commonly made by fermenting any carbohydrate (sugar, cellulose or starch) rich biomass. At present, the efforts needed in bioenergy are substantially lesser than that needed for making biofuel/bioenergy as an important platform for various activities ultimately leading towards growth in sustainable manner **[3]**.

Chapter I clarifies on serval important points as brief history with different inventions throughout centuries started from Stone Age with fire to Industrial Revolution Age with Rudolph diesel and his compression ignition diesel. Also, in this chapter defines biofuels, its types with showing different feedstocks to produce these types by major methods of production. Illustrate high hints of facts on advantages and its improvements. At the end of chapter I, it shows major different comparison of gasoline, diesel and biodiesel fuels with its characterizations for each type. Also facts about biodiesels to be substitute energy for gasoline and diesel fuels.

Chapter II discusses characterization of oils and its types as vegetables oils like sunflower oil, olive oil, palm oils and also non-edible oils like Jatropha oils, Karanja oils and algae oils. Wherever, this chapter talks also about characterization of used oils and how to recycle it. Moreover, it talks too about characterization of frying oils with showing its chemistry like quality changes of oils and with chemicals changes involved in frying oils process.

Chapter III represents the experimental works. It gives information about materials and products that they used in laboratory works with examining the physical chemical studies of oils and frying oils as well as biodiesels by such indexes like acid index, viscosity speed measurement, refractive index and relative density also with IR spectroscopy. At the end, with transesterification reaction for each type of oils to produce biodiesels derived from them.

Chapter IV reviews some of different types of marketed oils in Algeria and its chemical composition of Elio oil. Also, it shows characterization of new oils from brand Elio by spectrum of FT-IR. The most important part in this chapter, it focuses on results that obtained during experiments works in laboratory with acid index, refractive index, viscosity speed measurement and density relative of Elio oil, frying oils and biodiesels. All these results are tabulated in tables and illustrated in different figures for each type of index for each type of oils. Therefore, it explains about different and characterization between of oils and biodiesels by indexes that was mentioned before. At the end, it highlights on opinions, thoughts and researches examples about biodiesels in Algeria.

Chapter I

Biofuels

Chapter I: Biofuels

I.1. A brief history

Biofuels in the solid form has been in use ever since man discovered fire. Wood was the first form of biofuel that was used even by the ancient people for cooking and heating. With the discovery of electricity, biofuel has been used since a very long time for the production of electricity. This form of fuel was discovered even before the discovery of the fossil fuels, but with the exploration of the fossil fuel like gas, coal and oil, the production and use of biofuel suffered a severe impact. With the advantages placed by the fossil fuels, they gained a lot of popularity especially in the developed countries [4]. During the early stages of the industrial revolution, biofuels powered the first lamps and internal combustion engines. Forms of liquid energy derived from renewable plant material were well known and widely used for many thousands of years. By the early 1700s, lamps fueled by vegetable oils and fats lit up the major streets in European and American cities as shown in Figure (**I.1**) . New kinds of lamps such as Ami Argand's 1783 with whale oil. It designs contributed to be better streets and home lighting [5].

Figure I.1: Vegetable oils and fats lit up streets in London **[6]**

An exhibit developed in Germany around 1900s, it was devoted to alcohol-powered automobiles, farm machinery and a wide variety of lamps, stoves, heaters, laundry irons, hair curlers, coffee roasters and every conceivable household appliance and agricultural engine powered by alcohol [7]. Strong interest in biofuels continued with enthusiastic endorsements by scientists and engineers. Typical there was a statement by inventor Alexander Graham Bell who wrote in National Geographic in 1917 that ethanol makes a beautiful, clean and efficient fuel that can be manufactured from corn stalks and in fact from almost any vegetable matter capable of fermentation. He also said that we need never fear the exhaustion of our present fuel supplies so long as we can produce an annual crop of alcohol to any extent desired. That alcohol in some form will be a constituent of the motor fuel of the future [8]. The French, British and German biofuels laws and researches had a worldwide impact. Engineers in Asia and Latin America who studied in European universities took home ideas about national self-sufficiency, fuel improvement and agrarian support that would form the basis of biofuels programs in their own countries during the 1930s and into the 1970s [9].

German inventor Rudolph Diesel also designed his compression ignition 'diesel' engine for heavy fuels from oil but he also found that groundnut, castor and palm oils worked quite well. He wrote 'One cannot predict what part of these vegetables oils will play in the colonies in the future. In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes even when all our natural stores of solid and liquid fuels are exhausted' [10].

The American engineer Henry Ford thought that biofuels is "the fuel of the future". Ford's vision of mass biofuel consumption began with his Model T Ford during the WWI oil shortage motivated him to design it. Starting in 1908, the Model T propelled Ford Motor Company to become the largest producer of automobiles at the time for it low price that make it affordable to almost all middle class Americans. By 1918, over half the cars in America were model T is giving Ford little reason to change the car's design in its nearly 20 years on the road. From the original design, the Model T ran on ethanol as well as petroleum. Ford believed ethanol would become the most commonly used fuel source. As early as 1925, he envisioned an America that would grow its own fuel, making it out of everything from potatoes, apples to sawdust and weeds with more people willing to consume agricultural goods. He believed farmers produce would have more market value [11, 12].

Brazil's ethanol industry had huge success in the 1930s, with more sugar than it could use. The government directed sugarcane into ethanol production and made the addition of ethanol to gasoline compulsory. The first major alcohol fuel plant was built in Recife. As alcohol production grew and proved profitable, Brazil contemplated a national fuel program. In 1931, gasoline cost about 41 cents per gallon while alcohol was less than half the cost. Fuel alcohol production rose from one hundred thousand liters in 1933 to 51.5 million liters in 1937 [9].

In 1819, French chemist Henri Braconnot discovered that a sulfuric acid treatment could convert straw, wood or cotton into glucose. Another French chemist Anselme Payen isolated and purified cellulose in 1838. As polymer chemistry came better understood, a variety of inventors found ways to use it in billiard balls, shirt collars and camera film in the 1870s and 1880s. Cellulose seemed even more useful when around 1900 scientists analyzed the composition of cellulose and understood that it could be broken down into glucose molecules and converted into a wide variety of chemicals and fuels **[13]**. Around the early 20th century, news articles about cellulose as a feedstock for biofuels were common, reflecting not only advances in science but also hope for alternative biofuels in the face of a possible oil shortage. The Washington Post, for instance it said: “One of the most important of recent discoveries is that ethyl alcohol is so remarkably cheap that it can be obtained from ordinary sawdust and seems destined to solve the problem of motor fuel wood, then in place of petroleum is to be for auto drivers the future source of supply” **[14]**.

I.2. Biofuels

I.2.1. Definition

Biofuels are fuels that obtained from organic materials. They include wood, straw, sugarcane residue, animal wastes, landfill gas, biodiesel, ethanol, municipal waste, black liquor, switchgrass and a variety of synthetic gases derived from plant and animal matter. Biofuels are distinct from fossil fuels in that they are in some sense renewable. There are so many biofuels and they are derived from so many sources. Biofuels have the potential to leapfrog traditional barriers to entry because they are liquid fuels compatible with current vehicles and blend able with current fuels **[15]**.

I.2.2. Major types of biofuels

I.2.2.1. Bioethanol

Bioethanol produced from cheap feedstocks. Traditionally, it produce from cellulose and starch rich crops. For example, we have potato, rice, and sugar cane. Starch can be converted to glucose by commercial enzymes, subsequently fermented and saccharomyces cerevisiae to ethanol. Use of abundant and cheap wastes such as lignocellulosic. Food waste has been explored as alternative substrates for ethanol production **[16]**.

The various biomass feedstocks that can be used for bioethanol production are divided into two major groups: first generation feedstocks and second-generation feedstocks. First generation feedstocks include sugar, sugar cane, sugar beet and starch crops like corn, wheat and barley. The second-generation feedstocks belong wood, grasses, forestry residues and other lignocellulosic materials as new more sophisticated conversion technologies are developed to enable the production of bioethanol from cellulosic feedstocks. The woody biomass used in many ways such as fuel pellet production for combustion and electricity production and lignocellulosic materials have been used for many years in paper mills **[17]**.

I.2.2.2. Biobutanol

Biobutanol is often described as a new fuel. It is a biogasoline colorless, flammable alcohol. It comes as a safer and more competitive alternative to bioethanol or biodiesel. The physico chemical properties of butanol (n-Butyl alcohol) are presented in Table (**I.1**). It is produced using biomass feedstock and can alternatively be used as a gasoline additive for fuel blend in an internal combustion engine. It also acts as an industrial solvent **[18]**.

Table I.1: Physico-chemical properties of butanol.

Physico-chemical property	**Value**
Melting point	-89.9 °C
Boiling point	117.6 °C
Relative density	0.809 to 0.811 g/cm^3
Vapor pressure	0.56 KPa at 20°C
Water solubility	77g/l at 20°C
Partition coefficient n-octanol/water (log value)	0.88
Odor Threshold	15 ppm (average)

Biobutanol in comparison with bioethanol. It is chemically more analogous to regular gasoline with about 90% of its energy content where the energy content of ethanol to that of regular gasoline is only 50%. Researches for alternative fuel production were necessary and one had a choice between ethanol and butanol for a subsidized alternative fuel. However, it was felt like that the production of butanol via fermentation was too expensive along with the difficulty in recovering butanol. However, after years of recent technological developments in biobutanol production and the rising cost of petroleum products. Biobutanol has become more competitive. It is safer to use and is environmentally friendly with 85%

less carbon emissions than regular gasoline. Then, biobutanol is emerging as a safer and more competitive alternative to gasoline and bioethanol. It is a better alternative biofuel for internal combustion engines. It is promising new generation alternative biofuel that offers a range of advantages as a liquid fuel for transportation. It is a four carbon alcoholic biofuel, which has been commercially used as an industrial solvent and as a precursor for the synthesis of different types of organic chemicals **[19]**.

I.2.2.3. Biomethane

Since today's infrastructure for transport is based on liquid fuels, the introduction of gaseous fuels into the transport sector is slow and challenging for future transport strategies. Nevertheless, there are exists already a market for vehicles which use gaseous fuels in place of liquid fuels. Today, most of them run on natural gas, many automotive manufacturers already offer pure or bivalent natural gas vehicles as standard models. One of the promising future options for sustainable transport fuels is the subsidization of natural gas by biomethane. Biomethane is used for the final gaseous fuel after digestion of biomass and purification. It contains more than 95% methane. Biomethane is the most efficient and clean burning biofuel which is available today, it can be produced from nearly all types of biomass including wet biomass. The raw material for the production of biomethane is biogas, which can be processed from various feedstock sources. For biogas production, it is much more different feedstock sources can be used than for common liquid biofuels. The origin of the feedstock can be vary ranging from livestock waste, manure and harvest surplus to vegetable oil residues. Energy crops are becoming more and more practice as feedstock source for biogas production **[20]**.

I.2.2.4. Biodiesel

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feedstocks such as vegetable oil or animal fats for use in compression ignition engines. The concept of using biodiesel as a transportation fuel goes back to the first demonstration of the diesel engine for which Rudolph Diesel used biodiesel made from corn oil in 1893 with the increasing interest and use. Biodiesel has physical properties very similar to conventional diesel. It was characterized by its physical and fuel properties including; density, viscosity, high heating value, cetane number, cloud point, pour point and flash points according to ISO norms. In general, biodiesel compares well to petroleum-based diesel as shows in Table (**I.2**) **[21]**.

Table I.2: Specifications of Diesel and Biodiesel Fuels.

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	Hydrocarbons (C_{10}-C_{21})	Fatty acid methyl esters (C_{12}-C_{22})
Kin. viscosity (mm^2/s) at 313 K	1.9 to 4.1	1.9 to 6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (K)	333 to 353	373 to 443
Cloud point (K)	258 to 278	270 to 285
Pour point (K)	238 to 258	258 to 289
Carbon, wt%	87	77
Cetane number	40 to 55	48 to 60

Today a production capacity of almost 30 million tons of biodiesel exists worldwide. On the other hand, there is a total annual production of vegetable oils with approximation 110 million tons per year, which is mainly used for food purposes. As the production of vegetable oils cannot be increased in such a way as there is the demand for biodiesel and competition with the food market. In addition, concern on unsustainable production of oil plants like palm oil has led to extensive discussions leading to the search for non-edible oil seeds. All vegetable oils and animal fat can be used as feedstock for biodiesel production. Most of these oils and fats have a similar chemical composition; they consist of triglycerides with different amounts of individual fatty acids [22].

The major fatty acids are those with a chain length of 16 and 18 carbons where the chain could be saturated or unsaturated. Methyl esters produced from these fatty acids have very similar combustion characteristics in a diesel engine because the major components in fossil diesel fuel are also straight chain hydrocarbons with a chain length about 16 carbons (hexadecane). The major feedstocks for the biodiesel production today are rapeseed oil (Canola), soybean oil and palm oil. In addition, a series of other vegetable oils has quite similar fatty acid distribution, it can be used as blend. Only coconut oil and palm kernel oil have fatty acids with 12 or 14 carbons as major components [22].

I.3. Major methods of production for biofuels

I.3.1. Fermentation chemistry

Fermentation represents the first or second chemical process to be exploited deliberately by humankind. The other contender is combustion for example controlled use of fire. Fermentation of sugars particularly glucose produces ethanol. Ethanol was probably the first organic chemical to be produced on a large scale. Ethanol's importance in fuel chemistry lies in its use as a liquid transportation fuel either blended with or as a replacement for gasoline. Fermentation begins with enzyme-catalyzed hydrolysis of a polysaccharide to glucose. Starches tend to be easier to hydrolyze than cellulose. Consequently, starches are preferred feedstock for ethanol production. Conversion of glucose into pyruvate is called glycolysis. In terms of chemical composition, it converts one molecule of $C_6H_{12}O_6$ to two molecules of $C_3H_4O_3$. Since the total product is hydrogen deficient relative to the starting material, this conversion must be an oxidation reaction [23]:

$$C_6H_{12}O_6 + 2.O \longrightarrow 2.C_3H_4O_3 + 2.H_2O$$

The sequence of sugar synthesis depended on electron-transfer reduction reactions. It is reasonable to expect that the chemical decomposition of sugar molecules depend on oxidation chemistry. Pyruvic acid is having two functional groups, carboxyl and carbonyl. In first step pyruvic acid decarboxylate to acetaldehyde as shown in Figure (**I.2**). Then finally, acetaldehyde reduced to ethanol as shown in next Figure (**I.3**) [23]:

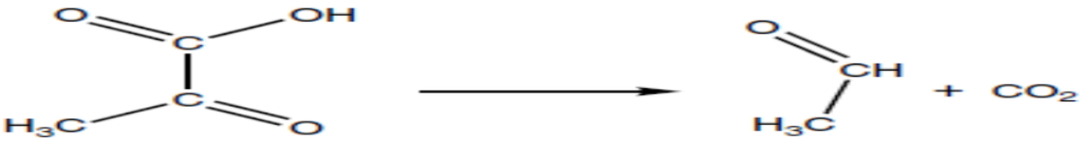


Figure I.2: Pyruvic acid decarboxylate to acetaldehyde reaction.

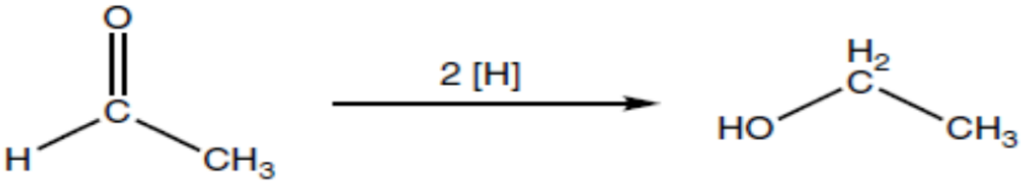


Figure I.3: Reaction of acetaldehyde reduced to ethanol

I.3.2. General Transesterification

The general transesterification reaction for acid or base catalyzed conversion of oils consisting primarily of neutral triacylglycerols (TAG) in reaction with alcohols to form alkyl esters as shown in Figure (**I.4**). The alkyl esters produced depend on the alcohol used where methanol (R=CH_3) and ethanol (R=CH_2CH_3) are most common. The catalysts for transesterification include KOH, NaOH or H_2SO_4. Excess alcohol with adequate catalyst generally forces the reaction equilibrium toward the products of biodiesel esters and glycerol with bio-based oils typically containing mostly TAG. The stoichiometric relationship requires three moles of alcohol per mole of TAG (3:1). The reaction usually requires excess amounts of alcohols ranging from 6:1 up to 20:1 and depending on the reaction chemistry for base-catalyzed transesterification and as high as 50:1 for acid transesterification **[24]**.

The reaction for base catalyzed systems will occur rapidly at room temperature although higher temperatures of 50°C are often employed to reduce initial viscosity of oils while increasing reaction rates. Acid catalysed transesterification is often reacted at higher temperatures from just below the boiling point of the alcohol to 120°C in pressurized vessels. The transesterification reaction of TAGs takes place in three steps where TAG is first converted to a diacylglycerol (DAG) and one fatty acid ester. Then the DAG converted to monoacylglycerol (MAG) liberating an additional fatty acid ester and finally the MAG converted to glycerol liberating the final fatty acid ester **[24]**.

$$\text{TAG} + \text{Alcohol} \xrightarrow{\text{Catalyst}} \text{Fatty Acid Ester} + \text{Glycerol } (C_3H_5(OH)_3)$$

Figure I.4: Transesterification of triacylglycerols to fatty acid esters.

I.3.3. Transesterification of waste frying and cooking

Vegetable oils has too high a viscosity for use in most existing diesel engines for a straight replacement fuel oils. One of the most common methods used to reduce oil viscosity in the biodiesel industry called transesterification process. High viscosity means more difficulty for motor engine to injection and lowers the volatility characteristics of any oil to be replacement for fuels and gasoline. In transesterification reaction, the triglyceride component of oil reacts with the alcohol in the presence of catalyst to give ester and glycerol. Used vegetable oil is reacted with alcohol, in most of the cases methanol is used because of better efficiency. However, ethanol and isopropyl alcohol can also be used. Ethanol is use for animal fats **[25]**.

I.3.4. General Esterification

The esterification process is a reversible reaction where free fatty acids (FFA) are converted to alkyl esters via acid catalysis (HCl or more commonly H_2SO_4). When oils are high in free fatty acids as common in waste cooking oils. The simultaneous esterification and transesterification reactions via acid catalysis is advantageous to potentially obtain nearly complete conversion to biodiesel. The esterification process follows a similar reaction mechanism of acid catalyzed transesterification. The reactants including FFA and alcohol are catalyzed by acid to create the alkyl ester and water as shown in Figure (**I.5**).

It used 2% ferric sulfate as catalyst and to conduct esterification pretreatment step before transesterification, and obtained 97% conversion of waste cooking oil high in FFA **[26]**.

$$\mathrm{RCOOH} \quad + \quad \mathrm{R'OH} \quad \xrightarrow{\text{Catalyst}} \quad \mathrm{RCOOR'} \quad + \quad \mathrm{H_2O}$$

Figure I.5: Acid-catalyzed esterification.

I.3.5. ABE Fermentation to Biobutanol

Biobutanol is obtained from fermentation of biomass feedstocks using specific strains of clostridium acetobutylicum. A flow diagram for its production using acetone-butanol-ethanol (ABE) fermentation is given in Figure (**I.6**). The biomass feedstock contains carbohydrates (sugars) that are broken down and converted to various alcohols including acetone, butanol and ethanol. However, alcohol production is limited owing to the toxic effects of these alcohols at increased concentrations. Technological developments like application of DNA technology has resulted in isolation, improvement and selection of efficient microbial strains that are tolerant to high concentrations of alcohol. Furthermore, newer modifications, genes, and enzymes are constantly researched which can improve the bioproduction of butanol **[27]**.

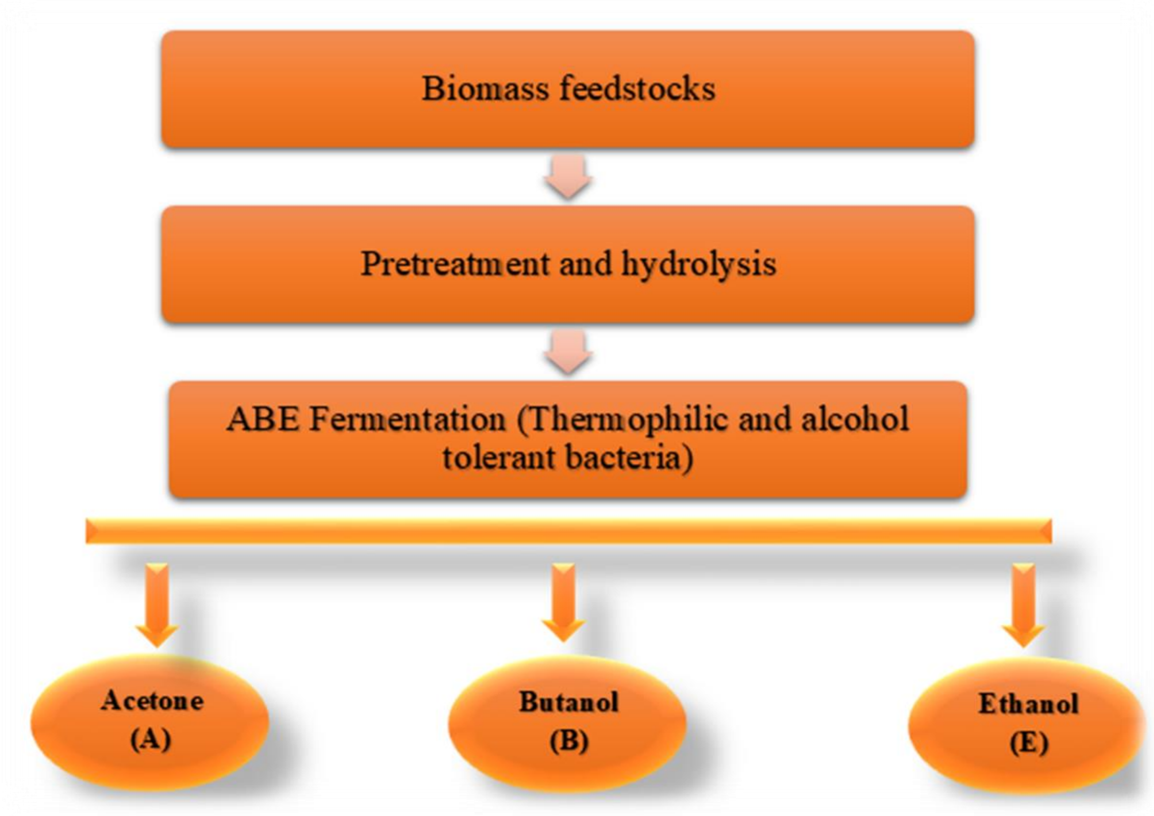


Figure I.6: A general schematic of biobutanol production via ABE fermentation.

I.4. Advantages

I.4.1. Cost

The overall cost benefit of using them is much higher. They are cleaner fuels, which mean they produce fewer emissions on burning. Biofuels are adaptable to current engine designs and perform very well in most conditions. This keeps the engine running for longer requires less maintenance and brings down overall pollution check costs. With the increased demand of biofuels, they have a potential of becoming cheaper in future as well. According to the IEA, the costs of ethanol production in new plants in Brazil are the lowest in the world at \$0.20 per liter and \$0.30 per liter of gasoline. This subsequently declined even further to \$0.18 per liter. Transportation and blending and distribution costs can add some \$0.20 per liter to the retail price. In China are between \$0.28 and \$0.46 per liter depending on the price of the feedstock. Production of biodiesel from palm oil costs around \$0.70 per liter where biodiesel produced from rapeseed oil may cost up to \$1.00 per liter with soybean diesel in between. The cost of biodiesel production in China mainly from used cooking oil ranges from \$0.21 to \$0.42 [28].

I.4.2. Easy to Source

Gasoline is refined from crude oil, which happens to be a non-renewable resource. Although current reservoirs of gas will sustain for many years, they will end sometime in near future. Biofuels are made from many different sources such as manure, waste from crops and plants grown specifically for the fuel. Unlike other renewable energy sources, biomass can be converted directly into liquid fuels called biofuels to help meet transportation fuel needs. The two most common types of biofuels in use today are ethanol and biodiesel both of them represent the first generation of biofuel technology **[28]**.

I.4.3. Renewable

Most of the fossil fuels will expire and end up in smoke one day. Since most of the sources like manure, corn, switchgrass, soybeans, waste from crops and plants are renewable and are not likely to run out any time soon making the use. Ethanol is an alcohol. It is made by fermenting any biomass high in carbohydrates (starches, sugars, or celluloses). Ethanol is mostly used as a fuel additive to cut down a vehicle's carbon monoxide and other smog causing emissions. Biodiesel is made by combining alcohol usually methanol with vegetable oil, animal fats or recycled cooking greases. It can be used as an additive to reduce vehicle emissions typically 20% or in its pure form as a renewable alternative fuel for diesel engines. Biodiesels are vegetable oil or animal fats based diesel fuels that can be used in standard diesel engines. Since they use plant and animal matter for production. They qualify as a renewable source of energy. They used as an additive in diesel fuels and can be used in diesel-powered without requiring any modifications in the engine design or type **[28]**.

I.4.4. Reduce of greenhouse gases

Fossil fuels when burnt. It produce large amount of greenhouse gases, for example carbon dioxide in the atmosphere. These greenhouse gases trap sunlight and cause planet to warm. The burning of coal and oil increases the temperature and causes global warning. To reduce the impact of greenhouse gases, people around the world have to use biofuels. Studies suggests that biofuels reduces greenhouse gases up to 65% **[28]**.

I.4.5. Lower levels of pollution

I.4.5.1. CO_2 and toxics emissions

Since biofuels can made from renewable resources. They cause less pollution to the planet. However, that is not the only reason why the use of biofuels is being encouraged. They release lower levels of carbon dioxide. The emissions produced on combustion of biofuels are significantly lesser than those produced from fossil fuels. CO_2 emissions from bioethanol and biodiesel combustion are up to nine times lesser than from gasoline combustion. According to a technique called Life Cycle Analysis (LCA) first generation biofuels save up to 60% and second-generation biofuels save up to 80% of carbon emissions as compared to other fossil fuels **[28]**.

I.4.5.2. Spills and Surface Contamination

Biofuels are not 100% safe, but they are much safer than fossil fuels. Biofuels are biological molecules and this means they are biodegradable. Bacteria and other organisms that live naturally in the soil and water are able to use biofuel molecules as energy sources and break them down into harmless products. This means that even though concentrated biofuel spills can kill things like plants and smaller animals, they will not persist in the environment and cause damage or make an area uninhabitable for long periods **[28]**.

I.4.5.3. Sulphur and Atmospheric Contamination

One of the major problems to arise from burning fossil fuels especially coal, it is acid rain that comes from the high sulphur content of these fuels. Biofuels can be produced in ways that completely eliminate sulphur and thus can eliminate this component of acid rain. On the other hand, biofuels tend to contain high levels of nitrogen, which can form compounds that also lead to acid rain and atmospheric contamination. Overall, the net impact on acid rain production is usually negative meaning biofuels can reduce acid rain. Importantly, biofuels can produced to ensure that contamination is as low as possible giving them an edge over fossil fuels because it is easier to avoid contamination in the production phase than it is to remove contaminants during refining **[28]**.

I.3. Gasoline, Diesel and Biodiesel comparison

I.3.1. Gasoline

I.3.1.1. Definition

Gasoline or petroleum is a fossil fuel, because it was formed from the remains of tiny sea plants and animals that died millions of years ago and sank to the bottom of the oceans. This organic mixture was subjected to enormous hydraulic pressure and geothermal heat. Over time, the mixture changed with breaking down into compounds made of hydrocarbons by reduction reactions. This results in the formation of oil saturated rocks. The crude oil rises and gets trapped under nonporous rocks that are sealed with salt or clay layers **[29]**.

I.3.1.2. Characterizations of Gasoline

Octane Number is the ability of a fuel to resist autoignition during engine operation is a key motor gasoline quality parameter. The autoignition resistance of a motor gasoline fuel quantified by its octane number. Although density is included in motor gasoline specifications, it is not an important property for engine operation or protection. However, it has an influence on the energy value of the fuel and therefore on vehicle performance and fuel economy. In a refinery, the real importance of fuel density is one of economics. Fuel is sold on a volumetric basis and marketing a fuel with the lowest possible density is advantageous to the refiner least mass sold for the highest income. In practice, density is a consequence of the refinery design rather than the converse being true **[30]**.

Before combustion, gasoline is a very volatile mixture of natural hydrocarbons and other organic chemicals derived from crude oil. Producers add other chemicals to gasoline to improve octane, increase combustion efficiency, protect engine and exhaust components. Gasoline usually contains more than 150 chemicals. Gasoline can also have negative effects on our health, both before and after burning. We usually exposed to gasoline fumes and gasoline engine exhaust when we breathe but it is also possible to absorb it through the skin or ingest it **[31]**.

I.3.2. Diesel fuels

I.3.2.1. Definition

Diesel fuel is made from petroleum. All petroleum are crude oils composed primarily of hydrocarbons of the paraffinic, naphthenic and aromatic classes. Each class contains a very broad range of molecular weights. Out of the ground, crude oil can be as thin and light colored or as thick and black as melted tar. Thin crude oils have relatively low densities. In the U.S, light crudes called high gravity crude oils. Conversely, thick and heavy crude oils with relatively high densities are low gravity crude oils. Outside of the U S, light crude refers to a low-density crude oil and heavy crude to a high-density crude oil **[32]**.

I.3.2.2. Characterization of Diesel fuels

Cetane number rates a diesel fuel's quality of ignition. However, it is actually a measure of the fuel's ignition delay, which means period between start of the injection of fuel and start of the combustion of fuel. It is different to the octane number seen on a retail gasoline dispenser that it is a measure of ability to resist auto ignition referred to as pre-ignition, knocking or pinging. In general, a higher cetane fuel will have a shorter ignition delay period than a lower cetane fuel. A higher cetane number leading a shorter ignition time means; more complete combustion of fuel, quicker starting, improved fuel efficiency, a reduction harmful emission and quicker pumping of protective lubricating fluids throughout the system **[33]**. The cetane number uses to assess the self-ignition capacity of a diesel fuel on a scale of 0 to 100. It measures the ability of the oil to ignite under the effect of pressure. More cetane number is higher that leads the fuel is easily flammable **[34]**.

I.3.3. Biodiesel to be substitute energy for Gasoline and diesel

I.3.3.1. Biodiesel from triglycerides via Transesterification

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high a viscosity for use in most existing diesel engines as a straight replacement fuel oil. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. It is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield because the reaction is reversible. Excess alcohol is used to shift the equilibrium to the product side. To achieve a high yield of the ester that means alcohols must be used in excess **[35]**.

Along with density, it is an important parameter for fuel atomization and distribution. Density measurement is useful for determining fuel quantity and quality. Biodiesel density is related to methyl esters content to methanol quantity **[35]**.

I.3.3.2. Concluding remarks

- ✓ Gasoline and diesel are two types from the refining of crude oil. They differ in their chemical characteristics as well as the type of engines they power. Gasoline is composed of a mixture of light hydrocarbons mainly heptane (C_7H_{16}) while diesel is made of heavier hydrocarbons distributed around cetane ($C_{16}H_{34}$). They are both produced from crude oil. The components of which are extracted in different cuts by distillation **[36]**.
- ✓ Gasoline and diesel are used in different types of engines. Cars that run on gasoline have atmospheric engines, generally operating between 1 and 40 bar, the ignition of which generated by an electric spark. Diesel used in diesel engines that do not have ignition, this fuel being injected at very high pressure up to 2,000 bar and exploding by compression. In 2011, almost (3/4) of new vehicles sold in France were fitted with diesel engines **[37]**.
- ✓ Diesel engines can run on diesel blended with up to 20% biodiesel by volume with almost no effect on vehicle performance. Biodiesel is typically blended with diesel at rates of 2%, 5%, or 20%, and the resulting fuel is called B2, B5, or B20 respectively. As the chemical composition of biodiesel differs from that of conventional diesel, the use of a fuel mixture like B20 in a diesel engine will generate emissions somewhat different from that of conventional diesel. For example, studies have shown that exhaust emissions of particulate matter, carbon monoxide, hydrocarbons and polycyclic aromatic hydrocarbons are generally lower for biodiesel than for regular diesel **[37]**.
- ✓ Biodiesel fuels have been recently stood out due to some important advantages such as requiring little or no modification for use in diesel engines. They are non-toxic, they have higher biodegradability and contain almost no sulphur. The molecular structure of biodiesel is similar to diesel fuel, and it contains additional oxygen, which is useful to reduce unburned HC, CO, and smoke opacity in the exhaust. Table (**I.3**) shows the some fuel properties of canola-oil-ethyl-ester (C.O.F.E) and diesel fuel **[38]**.

Table I.3: Fuel properties of biodiesel and diesel fuel.

Properties	Diesel	C.O.F.E
Density (kg/m3) at 15°C	837	870
Viscosity (mm2/s) at 40°C	3.9	5.2
Calorific Value (kJ/kg)	43300	39600

Chapter II

Characterization of oils, used oils and frying oils

II.1. Oils

II.1.1. Definition

A hydrocarbon liquid substance that is greasy to the touch and is formed by natural resources or the breakdown of fats. Oil comes in many forms as diverse as crude oil and vegetable oil, which serve very different purposes as shown in Figure (**II.1**) types of oils and animal fats. Products consisting of oil are insoluble when added to water, but will dissolve in organic substances which are those acquired from living organisms **[39]**.

Figure II.1: Types of oils and fats **[40]**.

II.1.2. Types of oils

Seed, oilseeds and animal fats occupy an important place in agricultural products and for industrial products to produce fuel. It is the first product to extract and manufacture oils. Now it is interested in all the stages through which the product passes, starting from the raw material, through the manufacturing stages and the manufacturing process, including manufacturing devices and tools. In order to know the characteristics of these products, it is necessary to know the chemistry of these fatty substances. Therefore, fatty substances cannot be explained without reference to their origin. Where oils can be classified:

II.1.2.1. Vegetables oils

Vegetable oils are triglycerides of fatty acids generally extracted from plants. Vegetable oils are mostly consist of natural esters of fatty acids which are triglycerides. The chemical skeleton structure of the natural esters is based on a glycerol backbone, to which three naturally occurring fatty acid groups and where both saturated and unsaturated are bonded.

Again, these fatty acids may be the same or different as shown in Figure (**II.2**). Plants produce these natural esters as part of their natural growth cycle. Although many plant parts may yield oil commercially, oil is extracted primarily from seeds. They are stored in the seeds and can provide a valuable high calorific foodstuff when harvested [41].

Figure II.2: Chemical structure of Triglyceride (natural esters)

In addition, vegetable oils have different chemical structures than diesel. Vegetable oils contain fatty acids that are linked to a glycerin molecule with ester linkages called a triglyceride. The fatty acids are in their carbon chain length and in numbers of double bonds. As can be seen in Table (**II.1**) that palmitic (16:0) and stearic (18:0) acids are two of the most common saturated fatty acids found in every vegetable oil. Similarly, oleic (18:1) and linoleic (18:2) acids are the most common unsaturated fatty acids. Many of the oils also contain some linolenic acid (18:3). Also, we have of both Figure (**II.3**) and Figure (**II.4**); they are showing types of vegetable oils with sunflower oils and cottonseed oils. [42].

Table II.1: Fatty acid composition of vegetable oils.

Fatty acid (xx:y) *	16:0	18:0	18:1	18:2	18:3	Others
Palm	42,6	4,4	40,5	10,1	0,2	1,4
Soybeans	11,9	4,1	23,2	54,2	6.3	0,3
Sunflower seed	6,4	2,9	17,7	72,9	0	0,1
Cottonseed	28,7	0,9	13,0	57,4	0	0
Olive	5,0	1,6	74,7	17,6	0	0,8

*xx is the number of carbon atoms and y is the number of carbon-carbon double bond in the fatty acid.

Figure II.3: Sunflower Oil **[43]**.

Figure II.4: Cottonseed oil **[44]**.

II.1.2.1.1. Soybean oils

A variety of vegetable oils available in nature among them soybean oil. It is the prominent bio-based fluid extracted from soybean seeds (Glycine max). Soybean oil is mainly consists of unsaturated fatty acid. The most abundantly available unsaturated fatty acids in soybean oil are polyunsaturated α-linolenic acid (7 to 10%), linoleic acid (51%) and monounsaturated oleic acid (23%). It is also comprises of saturated fatty acids (stearic acid 4%) and palmitic acid (10%). Soybean oil as shown in Figure (**II.5**) is a major bio-source with abundant applications in the current scenario and it is categorized as linoleic acid oil because it comprises of highly consists of unsaturated linoleic acid **[45]**. Soybean oil is used as both edible oil and transportation fuel. However, oxidative instability and cold flow in northern climates have limited usefulness of a soybean oil derived biodiesel. Implementing the tools of biotechnology to modify the fatty acid profile of soybean for locale performance enhancement may increase the attractiveness of biodiesel derived from this commodity crop **[46]**.

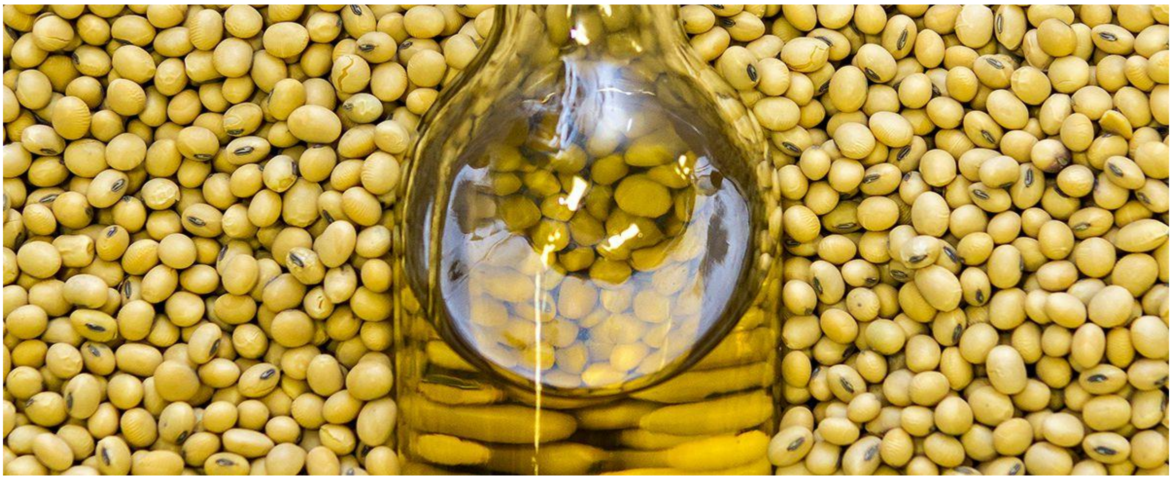


Figure II.5: Soybeans Oil [47].

II.1.2.1.2. Olive oils

Olive oil as shown in Figure (**II.6**), it is a major component of the diet of the countries surrounding the Mediterranean Sea. For the people living in this region, olive oil is the main source of fat in their cuisine. Olive oil is obtained from the fruits of the olive tree (Olea europaea) by mechanical or other physical means under conditions that do not cause any changes in the oil. The oil is first released from the olives by crushing in pressure systems. Olive oil is primarily a mixture of triacylglycerols with some free fatty acids, mono- and diacylglycerols and non-glyceridic constituents (0.5 to 1.5%). The free fatty acid content varies with the type of olive oil (extra virgin, fine virgin, ordinary, mixture of refined with virgin) and it is an important quality criterion in fixing the grade. The fatty acid composition of olive oil ranges from (7.5 to 20%) palmitic acid, (0.5 to 5%) stearic acid, (0.3 to 3.5%) palmitoleic acid, (55 to 85%) oleic acid, (7.5 to 20%) linoleic acid and (0.2 to 1.5%) linolenic acid. Myristic, heptadecanoic and eicosanoic acids are found only in trace amounts [48].

Figure II.6: Olive oil [49].

II.1.2.1.3. Palm oils

Palm oil as shown in Figure (**II.7**), it is a reddish color derived from the fruit of a palm tree with higher saturated fat content. It is available in semisolid state at room temperature. Various types of palm oils are available. The basic major component of palm oil is triacylglycerol (TG). The 95% of palm oil contains glycerol components with three fatty acids. In normal condition, palm oil is a semisolid state and viscosity of palm oil is high **[50]**. Palm oil has a balanced configuration of unsaturated and saturated fatty acids. Palm oil based natural esters are a better substitute for mineral oil to be used as a transformer insulating oil. Palm oil is a good substitute for mineral oil as a liquid insulator in power equipment **[51]**.

Neutralization value of palm oil is comparably higher to vegetable fluids. In order to ensure the performance, additional investigations on oxidation stability of several types of palm oils are essential in present scenario. Further investigations are required to improve the fire safety performance of palm oil. Typical characteristics of palm oil esters and comparison with mineral oil are presented in Table (**II.2**) **[51]**.

Table II.2: Comparison of palm oil esters vs mineral oil properties.

Properties	Palm oil ester	Mineral oil
Density (g/cc) at 15°C	0.86	0.88
Kinematic viscosity, cSt at 40°C	5.06	8.13
Flash point (°C)	186	152
Pour point (°C)	-32.5	-45
Neutralization value (mg of KOH/g)	0.005	<0.01
Dielectric constant	2.95	2.2
Volume resistivity (Ohm.cm^{-1})	7.1	7.6
Breakdown voltage (kV)	81	70 to 75

Figure II.7: Palm Oils [52].

II.1.2.2. Non-edible oils

The main nonedible oil resources include Jatropha, ratanjot, or seemai-kattamankku (Jatropha curcas), karanja) or honge (Pongamia pinnata), rubber seed tree (Hevea brasiliensis), silk cotton tree (Ceiba pentandra), babassu tree, algae and so on. Jatropha as shown in Figure (**II.8)** and karanja also shown in Figure (**II.9**) found in India, they have a high oil content (25 to 30% of seed). In fact, Jatropha oil was used as a diesel fuel substitute during World War II [53]. Plant for rubber seed oil (20% to 30% of seed) is found mainly in Indonesia, Malaysia, Liberia, India, Sri Lanka and Thailand. Oil palms with Elaeis guineensis and Elaeis oleifera are found in Africa and Central/South America. Jojoba oil is produced from the seed of the jojoba plant. It is a shrub native to Southern Arizona, Southern California and Northwestern Mexico. The silk cotton tree has great economic importance for both domestic and industrial uses in Nigeria and its oil is a good source for biodiesel production [54].

Figure II.8: The Jatropha tree [55].

Figure II.9: The Karanja tree [56].

Algae shows in Figure (**II.10**) can grow in practically any place where there is enough sunshine, including areas with saline water. The most significant difference from the oil crop is the yield of algae oil. According to some estimates, the per acre yield of oil from algae is more than 200 times of the yield from the best performing vegetable oil plant. About 19 tons of oil over a year can be produced from diatom algae. A type of fast growing microalgae that can complete an entire growing cycle every few days. However, the production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale and its oil production may be less. Some algae produce up to 50% oil by weight with fatty acid composition of 36% oleic (18:1), 15% palmitic (16:0), 11% stearic (18:0), 8.4% iso-heptadecanoic acid (17:0), and 7.4% linoleic (18:2) acid. The high proportion of saturated and monounsaturated fatty acids in this algae is considered optimal from a fuel. In that fuel polymerization during combustion would be substantially less than what would occur with polyunsaturated fatty acid derived biodiesel [57].

Figure II.10: The algae is harvested from waste streams [58].

II.1.3. Characteristics of oils

II.1.3.1. Physical characteristics

It is known that the fatty substances are either liquid or solid at normal temperature and the glycerides increase in strength with increasing saturation and molecular weight. Their melting point increases as the number of carbon atoms increases and decreases as the number of unsaturated bonds increases. The degree of its hydrolysis in organic solvents decreases with increasing number of carbon atoms and decreases with increasing number of unsaturated bonds. The refractive index increases as the number of carbon atoms increases and increases as the number of unsaturated bonds increases **[59]**.

As for the spectral field, the fatty chains are characterized by the following characteristics: There is absorption of adjacent multiplexed chains in the UV field at wavelength ʎ=350um. In the absence of pigment materials, there is no absorption in the visible radiation field at wavelength ʎ= [380um to 782um]. With absorption in the infrared field, that distinguishes the functional group of the double chain at wavelength ʎ= [10um-10.5um] **[59]**.

II.1.3.2. Chemical characteristics

It has one acidic function, straight and branched chains and chains with double number of carbon atoms. Acids are divided into: **(a).** Saturated, chemically inert, generally citric acid. **(b).** Unsaturated, they accept oxidation reactions and can contain mono-bonding bonds such as oleic acid, binary as nucleic acid and ternary as linolinic acid. **(c).** Stelenic acids with triple bonds, closed-loop cyclic fatty acids and acids with saturated chain **[59]**.

II.2. Used oils

II.2.1. Definition

United States Environmental Protection Agency (EPA) defines used oil, which as shown in Figure (**II.11**). It is any oil that has been refined from crude oil or any synthetic oil that has been used and as a result of such use is contaminated by physical or chemical impurities. Simply but, used oil is exactly what its name implies as any petroleum based or synthetic oil that has been used. During normal use, impurities such as dirt, metal scrapings, water, or chemicals can be mixed in with the oil. Therefore, that in time the oil no longer performs well. Eventually, this used oil must be replaced with virgin or re-refined oil to do the job at hand **[60]**.

Figure II.11: Used Oils before recycling **[61]**.

II.2.2. Recycled used oils

Once oil has been used, it can be collected, recycled and used repeatedly. An estimated 380 million gallons of used oil are recycled each year in United States as shown in Figure (**II.12**). Recycled used oil can sometimes be used again for the same or it can be take on completely different task. For example, used motor oil can be re-refined and sold at the store as motor oil or processed for furnace fuel oil. Used oil can be recycled in the following ways:

a). Reconditioned on site; which involves removing impurities from the used oil and using again. While this form of recycling might not restore the oil to its original condition but it does prolong its life.

b). Inserted into a petroleum refinery; which involves introducing used oil as a feedstock into either the front end of the process or the coker to produce gasoline.

c). Re-refined; which involves treating used oil to remove impurities so that it can be used as a base stock for new lubricating oil. Re-refining prolongs the life of the oil resource indefinitely. This form of recycling is the preferred option, because it closes the recycling loop by reusing the oil to make the same product that it was when it started out and therefore uses less energy and les virgin oil.

d). Processed and burned for energy recovery; which involves removing water and particulates so that used oil can be burned as fuel to generate heat or to power industrial operations **[62]**.

Figure II.12: Used Engine Oil Refining Machine [63].

II.3. Frying oils as a special used oils

II.3.1. Definition

Frying oils defined as a process of drying and cooking of food by immersing food in oil at a high temperature (usually 165 to 190°C) as shown in Figure (**II.13**). During the process, the heat and simultaneous mass transfer of food, oil and air promote a variety of physical and chemical changes such as water loss, oil uptake, crust formation, color change, flavor development, starch gelatinization and oil oxidation. These changes lead to the development of golden brown color, attractive fried aroma, savory flavor, crispy texture and juicy taste in fried products and improve the overall palatability of the products. Oil is subject to high heat, oxygen (from either air or food) and moisture (from food) for extended periods. It resulting in a complex series of reactions involving oxidation, hydrolysis, and polymerization. These reactions give rise to deterioration of oil composition and subsequent generation of a wide variety of volatile and nonvolatile compounds [64].

Figure II.13: Fried potatoes with frying oils for making Biofuels [65].

II.3.2. Chemistry of frying oils

II.3.2.1. Quality change of oils and products

Frying is a complex process in which many physical and chemical changes occur together in hot oil and food fried in it. Blumenthal established a theory incorporating five stages that describe the relationship between quality changes of food and oil during the frying process:

a). Break-In Oil stage: when the oil first meets the food. The new oil is completely hydrophobic while food surface is hydrophilic. Therefore, the interaction between food and oil is very poor. At this stage, the food is basically raw, the surface is not crispy, the starch at the center is not gelatinized and cooked flavors or colors have not developed.

b). Fresh Oil stage: as triacylglycerols break down, small amounts of free fatty acids are released. These fatty acids serve as surfactants that increase the contact between the oil and the food. Cooking improves at this stage, resulting in crisping of the surface, partial gelatinization of the center, slight browning in color and increased absorption of oil.

c). Optimum Oil stage: As frying progresses, higher levels of free fatty acids provide sufficient surfactancy for oil to fully contact food surfaces. Heat transfer is most efficient at this point and heat progresses evenly from oil to surface to center of food. Crispiness and golden color is developed on the surface while the center is fully cooked; favorable frying flavors are produced and oil absorption is at optimum amount at this point. Positive secondary reactions dominate such as oxidation and scission reactions generate flavor compounds and colors.

d). Degrading Oil stage: High heat and extended heating hours increase hydrolysis to the point that negative secondary reactions become dominant. Degrading oil quality results in corresponding deterioration of food characteristics, including darkening and hardening of surface and excessive absorption of oil. Off-flavors and odors begin to develop at this point.

e). Runaway Oil stage: As the oil degrades still further, the food surface burns, the food becomes very greasy from excessive oil and sharp flavor off-notes are produced [66].

II.3.2.2. Chemical changes involved in thermal degradation of oils

Three major types of reactions have been documented during frying process which they are hydrolysis, oxidation and polymerization.

II.3.2.2.1. Hydrolysis

Hydrolysis reactions under normal frying conditions lead on contact with water vapor to the formation of free fatty acids; monoglycerides, diglycerides, or even glycerol as shown in Figure (**II.14**). These compounds are then very sensitive to reactions oxidation, polymerization reactions and the products are responsible for the main taste or odor defects. As they degrade, fatty substances are more and more volatile and oil begins to smoke. The smoke point is the temperature at which the reaction smokes regularly and signals a continuous and significant degradation of the fats. The usual fatty substances have smoke points initially between 180°C and 230°C. The degradation of fatty substances leads to a significant lowering of the point of smoke with 170°C and below, increases the viscosity of the oils and surfactants increases the content responsible for forming foam on the surface and lowering the surface tension between the essentially aqueous foods and oils. Hydrolysis is the cutting of ester bonds. It develops mainly under the action of heat and humidity **[67]**.

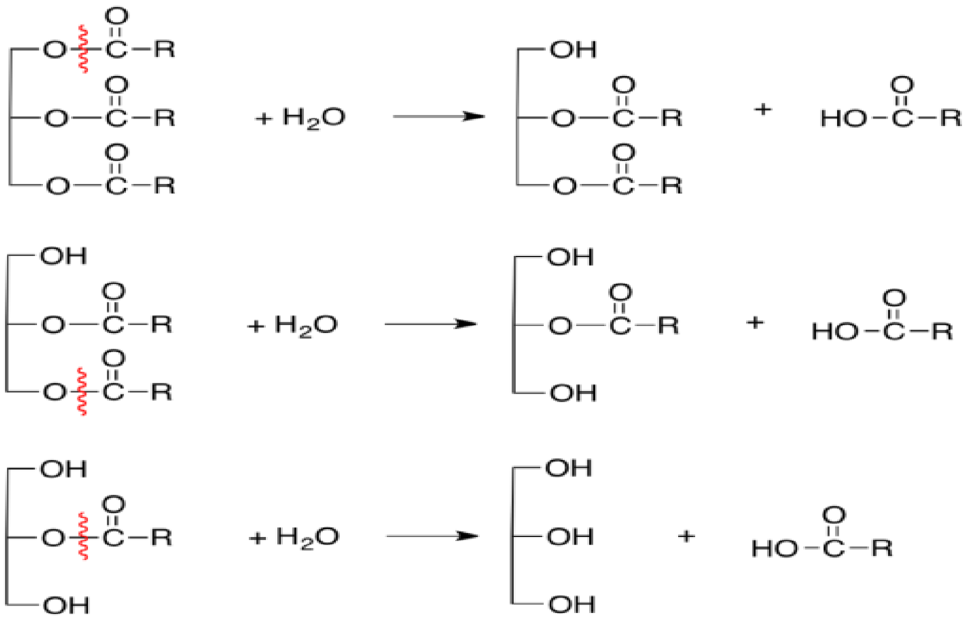


Figure II.14: Formation of free fatty acid and diacylglycerols by hydrolysis **[68]**.

II.3.2.2.2. Oxidation

On contact with oxygen in the air, they cause aromas and color changes often undesirable in frying oils. These unwanted oxidation compounds are derived from hydroperoxides which is the primary oxidation compounds. The chain reactions responsible for their formation are self-catalyzed because they are initiated by the appearance of radical compounds, themselves resulting from the oxidation of triglycerides in the bath. Metal cations such as iron or copper can also initiate and accelerate oxidation reactions [69].

II.3.2.2.3. Polymerization

Polymerizations are particularly facilitated by high temperatures. Dimerization and polymerization occurs in three ways:

a). Radical recombination: When oxygen is limited, allylic radicals recombine with each other to produce mixtures of dimers. The formation of acyclic dimers from oleate is shown in Figure (**II.15**). When sufficient oxygen is present, allylic radicals recombine with alkoxyl and peroxyl radicals, forming ether linkages and peroxide linkages [70].

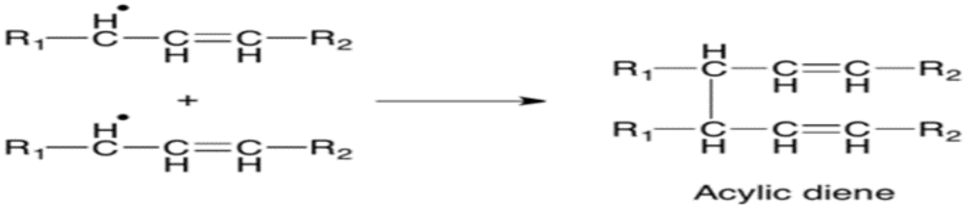


Figure II.15: Radical recombination reactions forming dimers in oleic acid

b). Addition of radicals to double bonds: Addition of radicals to double bonds yields dimeric radicals, which then may either abstract hydrogens or attack other double bonds to form either acyclic or cyclic compounds. Figure (**II.16**) shows the dimerization of linoleic acid by radical additions to double bonds [71].

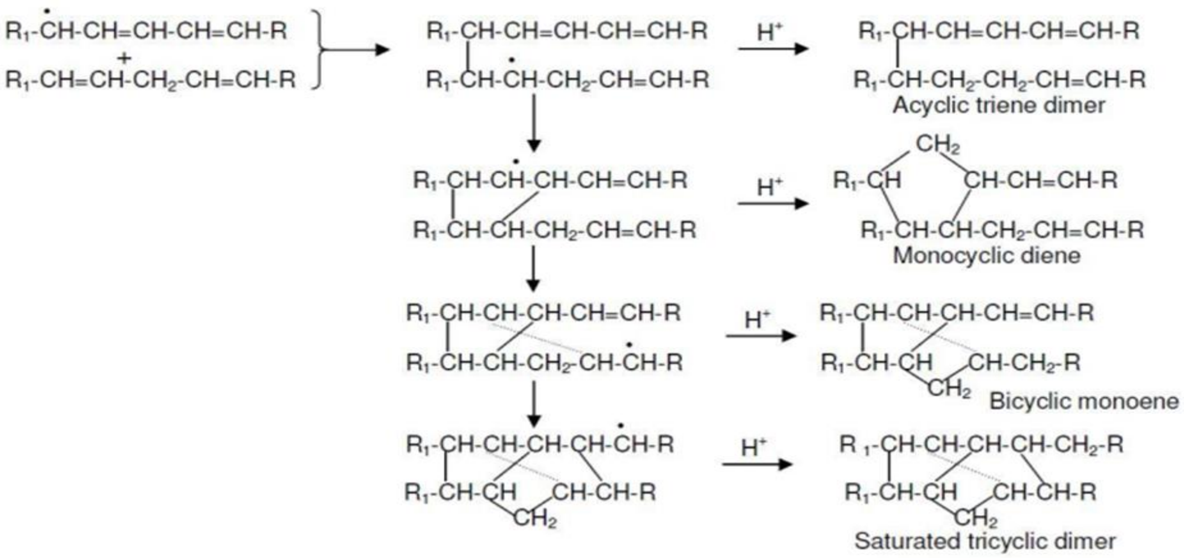


Figure II.16: Dimerization of linoleic acid

c). Diels-Alder addition: Oxidation of polyunsaturated fatty acids yields conjugated diene structures. A special form of cyclic dimers is formed by the addition of conjugated dienes to other double bonds to yield intramolecular or intermolecular substituted cyclohexene products. This special form is shown in Figure (**II.17**) [71].

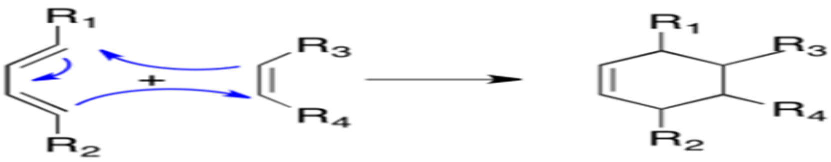


Figure II.17: Diels-Alder reaction

II.3.3. Factors affecting frying oil quality

Although relatively little research has focused on mechanisms of thermal degradation directly. Numerous studies have investigated the effects of various catalytic and antioxidant factors on oil quality in deep-frying. These factors cover a wide range from composition of the oil to components of the food and from conditions of the frying to the type of fryers.

II.3.3.1. Fatty acid composition

The common sense notion that oils composed of polyunsaturated fatty acids have lower frying stability than those composed of monounsaturated and saturated fatty acids [72].

II.3.3.2. Frying conditions

Long time frying results of a wide range of oxidation products including free fatty acids, polar compounds, dimers and polymer most at high levels. The effect of frying time becomes more significant in used oils that already have some degradation products and surfactants. For example, peroxide values (PV) and free fatty acids (FFA) of used palm oil were significantly increased with only 3 minutes increase in frying time **[73]**. High temperatures also accelerate oil degradation and affect fried food quality. When frying temperature was increased, acid value and polymerization increased notably and oil color became darker **[74]**.

II.3.3.3. Oxygen

Effects of oxygen on frying quality of oils have been studied for decades. Rates of change in viscosity and titratable acidity were found to be directly proportional to the degree of exposure of fat surface to oxygen. Oxygen originally dissolved in oil also affects stability. **[75]**.

II.3.3.4. Water

Foods complicate the frying process in several ways. One of the most important aspects is continuous release of water from food into oil. The released moisture agitates the oil and promotes hydrolysis. Moisture also catalyzed production of off-flavors in different kinds of frying oils **[76]**. However, adding lower amounts of water (0.7%) was protective. This protection was attributed to formation of a blanket above the surface of the oil by the steam evolved during frying (or from added water) reducing the amount of oxygen available for oxidation **[77]**.

II.3.3.5. Minor components

Minor components in frying oil include fatty acids, phospholipids, metals, peroxided compounds and naturally occurring and intentionally added antioxidants. Levels of these components are reduced after oil refining. Naturally occurring antioxidants such as tocopherols can provide great protection against oxidation for polyunsaturated fatty acids **[78]**. Free fatty acids are believed to be the first degradation products formed during frying. Many publications note the physical effect of free fatty acids to produce smoke, which may lead to a fire hazard. Fewer publications address fatty acid effects on chemical alterations. Free fatty acids degrade faster than parent triacylglycerols and their presence has been shown to catalyze further hydrolysis and oxidation **[79]**.

Chapter III

Experimental and Practical Studies

Chapter III: Experimental and Practical Studies

III.1. Materials and products

Through this experimental chapter, we will be examining the physical and chemical studies of oils and frying oils as well as biodiesel. By defining characterization and indexes such as relative density, refraction index, viscosity in term of speed and acid index. In addition, characteristics by IR spectroscopy we will also study oils, type of oils and biodiesels. We will see how to synthesize through the traceable steps; starting with transesterification reaction, phase separation, washing step until the end with the distillation step. Then we will do tests again over biodiesels types. The raw materials used to carry out this work represent a normal brand oil (elio) which contains of 80% soybeans and 20% sunflower. After frying process, we have also six types of frying oil as shown in Figure (**III.1**) and list of equipment that we used in our study as shown in Table (**III.1**) and different reagents used for our experiments are 95% methanol and 95% ethanol, potassium hydroxide KOH, Potassium permanganate $KMnO_4$ and colored indicator (phenolphthalein).

Figure III.1: Six types of frying oil

Table III.1: List of equipment that we used in our study

List of Equipment

- 500 ml flask and Bath Marie
- Separating funnel
- Graduated cylinders
- Universal support,
- Stopwatch
- Funnel and Thermometer
- Reflux refrigerant, Column for distillation
- Beakers of different volumes and Balance
- Burette of different volumes
- Erlenmeyer of different volumes
- Hotplate and Magnetic bar

III.2. Physical and chemical Characterization

III.2.1. Acid index

This is the number that expresses in milligrams the amount of potassium hydroxide needed to neutralize the free acids present in 1g of substance. It measures the deterioration state of an oil or the quality of refining [80]. It is also about dissolving the fat in neutralized ethanol, then titrate the AGL using a standard solution of KOH in the presence of phenolphthalein as indicator [81].

- **operating mode:**

❖ Weigh 1g of an oil in a 250ml Erlenmeyer flask.
❖ Take 10ml of ethanol and add them to the Erlenmeyer flask, and mix them well.
❖ Add a few drops of phenolphthalein to the solution as a color indicator.
❖ Titrate with the KOH solution (0.1M) until pink coloring as shown in Figure (**III.2**).
❖ Record precisely the volume of KOH.

- **Method of calculation:**

$$I_A = V_{KOH} * M_{KOH} * C_{KOH} / m_{oil}$$

I_A: Acid index (%) - V_{KOH}: Volume of solution KOH

M_{KOH}: 56.1g/mole - C_{KOH}: Concentration of solution KOH (0.1M)

Figure III.2: Mixed solution of new oil before titration and after titration.

III.2.2. Refraction Index

The refraction index of oils varies according to their establishment measured by the prism depends on the modification of the speed of light. This modification will therefore allow having a more or less precise idea [81]. In addition, it is the ratio of the sine angle of incidence and the sine angle of refraction of a light ray of determined wavelength passing from air into oil at constant temperature [82]. Using a refractometer the angle of refraction is observed directly at the limit of total refraction, the oil being maintained under conditions of isotropism and transparency. Figure (**III.3**) shows refractometer used.

Figure III.3: Refractometer used {Princeton instruments, model 24AJ, serial}.

- **Determination of the refraction index:**

The refraction index is determined according to the following protocol:

- Turn on the refractometer then adjust the distance between the eyepieces to have a clear view of the reticle and the scale of refractive index reading.
- Then add sufficient liquid using a pipette to the horizontal side of the refractometric prism.
- We turn the knurled knob and we try to obtain a maximum of contrast between the two areas and a dividing line as sharp as possible.
- We look in the eyepiece of scale and we read the value of the refractive index as shown in Figure (**III.4**) [81].

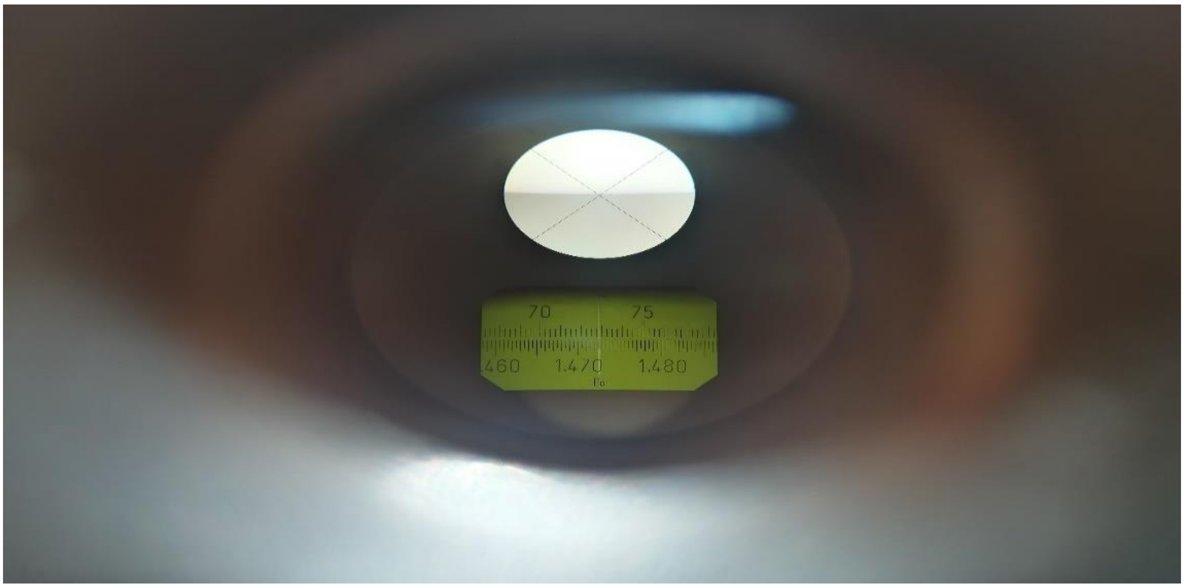


Figure III.4: An experimental example for measuring refraction index for new oil.

III.2.3. Viscosity measurement

Viscosity is the most important characteristic of a fluid. It is defined as the ratio of the shear force and the thickness of the oil. In this experiment, we will investigate how the speed of a sphere falling through a viscous liquid depends on the size of the sphere and measure the viscosity of oils and biodiesel at room temperature [83]. Viscosity is defined as the uniform flow resistance without turbulence occurring in the mass of a material. We will now determine the viscosity of our biodiesel formed as well as that of oil. To do this, you need to determine the rate of fall of a drop of potassium permanganate in oil then in biodiesel. We can deduce the viscosity [84].

- **operating mode:**

✓ Fill a graduated cylinder as much as possible with oil.

✓ Using a dropper drop, a drop of potassium permanganate into the oil then in biodiesel as shown in Figure (**III.5**).

✓ We start the stopwatch when the drop has fallen into oil. Then we stop it when the drop reaches the final graduation.

✓ Note the time it took for the drop to travel this distance (Δt).

✓ We measure the distance (d) in meter travelled by the drop with a ruler on the burette.

✓ We calculate the speed of the drop in ($m.s^{-1}$).

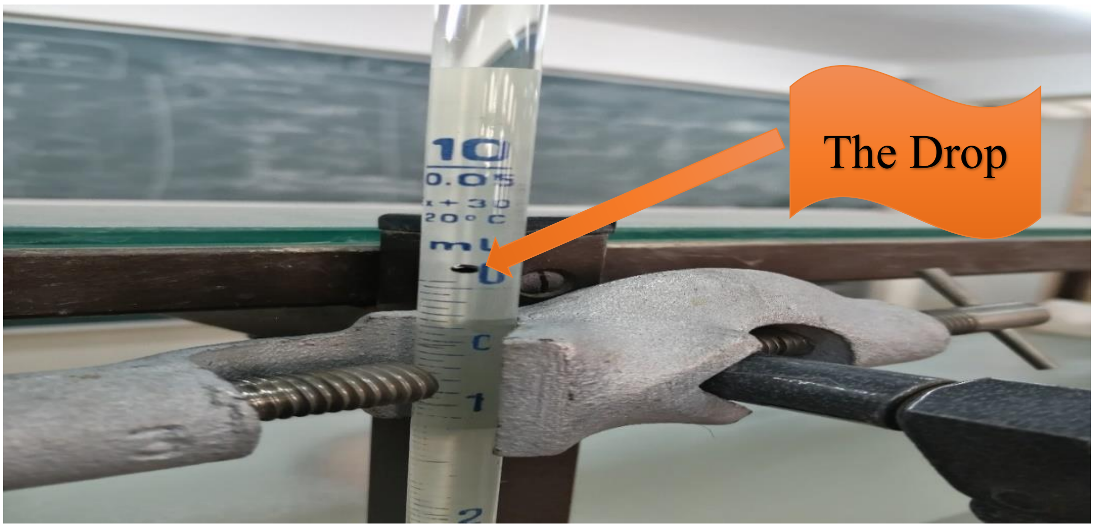


Figure III.5: An experimental example for measuring viscosity of New Oil.

III.2.4. Density calculation

Density is a dimensional quantity defined as the ratio of the mass of a volume of oil (or biodiesel) to that mass of the same volume of water.

- We weighed 10ml of our oil (or biodiesel) as shown in Figure (**III.6**) and we calculated the density: **p= m/V**,   with m: the mass of the oil and V =10ml.

-Then to calculate the density. So, we have: **d = d (biodiesel/oils) / d (water)**,

With water density = 1000g/L

Figure III.6: An experimental example for measuring mass of 2nd frying oil.

III.3. Characteristics by FT-IR Spectroscopy

III.3.1. Introduction

Infrared spectroscopy can be described as the use of instrumentation in measuring a physical property of matter and the relating of the data to chemical composition. The instruments used are called infrared spectrophotometers and the physical property measured is the ability of matter to absorb, transmit, or reflect infrared radiation. Infrared analysis can be used for almost any type of sample as long as the material is composed of or contains compounds (rather than pure elements) **[85]**.

III.3.2. Definition and Principe

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission. FT-IR can provide information such as identify unknown materials, determine the quality or consistency of a sample, determine the amount of components in a mixture. With modern software algorithms, infrared is an excellent tool for quantitative analysis **[86]**.

III.3.3. Sample Analysis Process

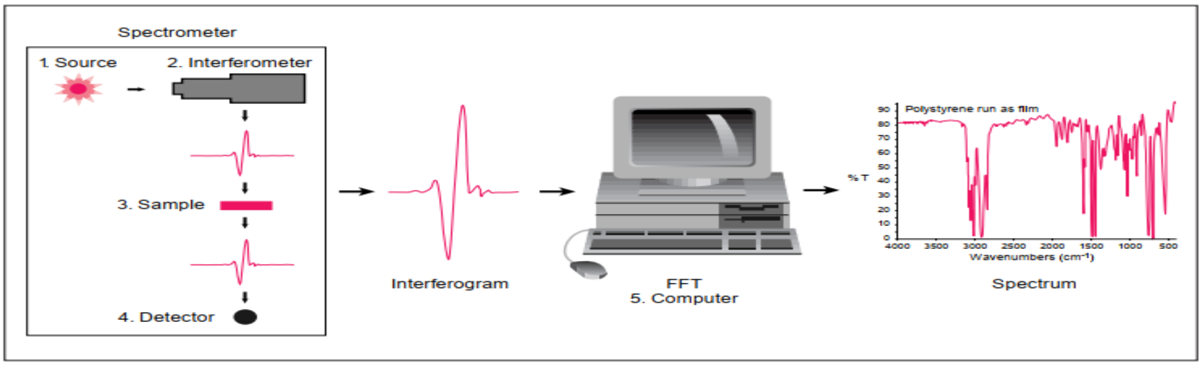


Figure III.7: Introduction to Fourier Transform Infrared Spectrometry

The normal instrumental process follows:

- **The Source:** Infrared energy is emitted from a glowing blackbody source. This beam passes through an aperture which controls the amount of energy presented to the sample and ultimately to the detector.

- **The Interferometer:** The beam enters the interferometer where the spectral encoding takes place. The resulting interferogram signal then exits the interferometer.
- **The Sample:** The beam enters the sample compartment where is transmitted through or reflected of the surface of the sample. It is depending on the type of analysis being accomplished.
- **The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.
- **The Computer:** The measured signal digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation [86].

III.3.4. Region of IR

Now remember that the IR region of the spectrum includes the region of wavelength between about 0.78 and 1000 µm (or wavelength from 12,800 to 10 cm^{-1}). It is useful, both in terms of applications and in terms of instrumentation, to divide this area of the spectrum into three regions:

(a). near infrared: 12,800 to 4,000 cm^{-1}.

(b). medium infrared: 4000 to 200 $cm-^{1}$.

(c). far infrared: 200 to 10 cm^{-1}.

Let us also note now that the most interesting area on the analytical level is between 4000 and 1000 cm^{-1} [87].

III.4. Biodiesel's protocol of synthesis

III.4.1. Introduction of our oils

We are using oils of brand oil (ELIO) which contains 20% sunflower and 80% soybean. These oils are made up of acids: Linoleic acids, oleic acids, palmitic acids, stearic acid and linolenic acid. Elio is recommended for frying, whitewash, food cooking, pastry and seasoning. The maximum advised temperature while used is 180°C. The characteristics of brand oil 'Elio' as we have in Table (**III.2**) for a 100g of Elio oil [88]:

Table III.2: Characteristics of brand oil ‘Elio’

Characteristics	
Energy	900KCAL/3700KJ
Lipids	100g with Saturated fatty acids 15g Monounsaturated fatty acids 25g Polyunsaturated fatty acids 60g
Cholesterol	None
Proteins	0g
Carbohydrates	0g
Vitamin E	100mg (833%AJR)

III.4.2. Brute formula of the corresponding triglyceride

- linoleic sunflower oil: $C_{57}H_{98}O_6$
- Soybean oil: $C_{57}H_{106}O_{10}$

So, we know that our brand Elio’s oil is contained of 80% of soybean oil and 20% of sunflower oil. Therefore, we will have the mass of Elio’s oil is:

$$M=0.8\times M_{Soybeans}+0.2\ M_{Sunflower} \longrightarrow M= 943.6 g/mole$$

III.4.3. Calculating masses of chemical reagents for biodiesel synthesis

Biodiesels or methyl esters are obtained by the transesterification reaction of triglycerides with methanol according to Figure (**III.8**). We have one mole of triglyceride and three moles of methanol then we will produce three mole of mixture of fatty esters and one mole of glycerin [89]:

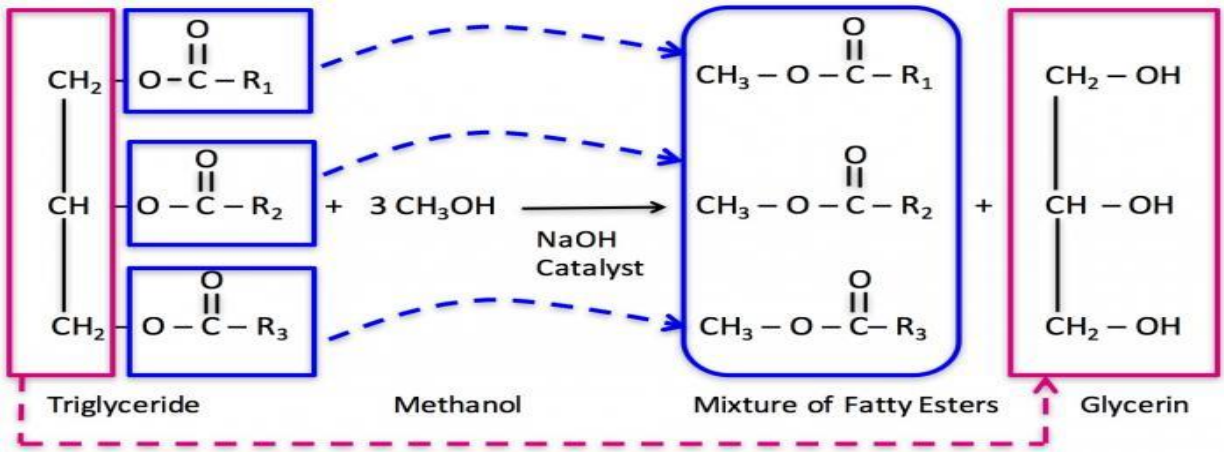


Figure III.8: Chemistry of Biodiesel production.

- **Quantities of reagents used:**

- We took the ratio (1:10) for good performance:

We have:

n (methanol) = ratio × n (oil) = 10 × n (oil)

n (oil) = 250/943.6=0.265 mole

n (methanol) = 10 × 0.265 mole = 2.65 mole

- We know that the molar mass of methanol is 32.04 g/mole.

So, we should say:

m (methanol) = M (methanol) × n (methanol)

m (methanol) = 32.04 g/mole × 2.65 mole = 85 g

- Also, we will consider of catalyst KOH's quantity:

We have KOH 1% mass of oil then: **m (catalyst) = 2.5 g**

III.4.4. Synthesis of Biodiesel

Synthesis of biodiesel passes with the successive steps for production which are;

III.4.4.1. Reaction Transesterification

Transesterification is one of the most important methods used to transform vegetable oils into diesel fuel. It is a process in which vegetable oils, animal fats or oils based on micro-algae. They are mixed with an alcohol ethanol or methanol in the presence of a catalyst **[35]**. We use a catalyst to improve the reaction rate and yield. The purpose of this reaction is to lower the viscosity of oil **[90]**.

- ✓ **Operation mode:**

a). Dissolve the catalyst in methanol, which requires stirring the mixture and heating very slightly as shown in Figure (**III.9**):

Figure III.9: The mixture of methanol and Catalyst KOH

b). Pour the solution obtained in oil and shake vigorously, heating the reaction medium slightly between 40 and 55°C. All the tests were carried out with a process heating circuit. The reaction setup was very simple. It is a 500mL flask equipped with a Refrigerant, agitation is ensured by a stirrer and magnetic bar. The ball is immersed in a water bath. As shows in Figure (**III.10**) [91]:

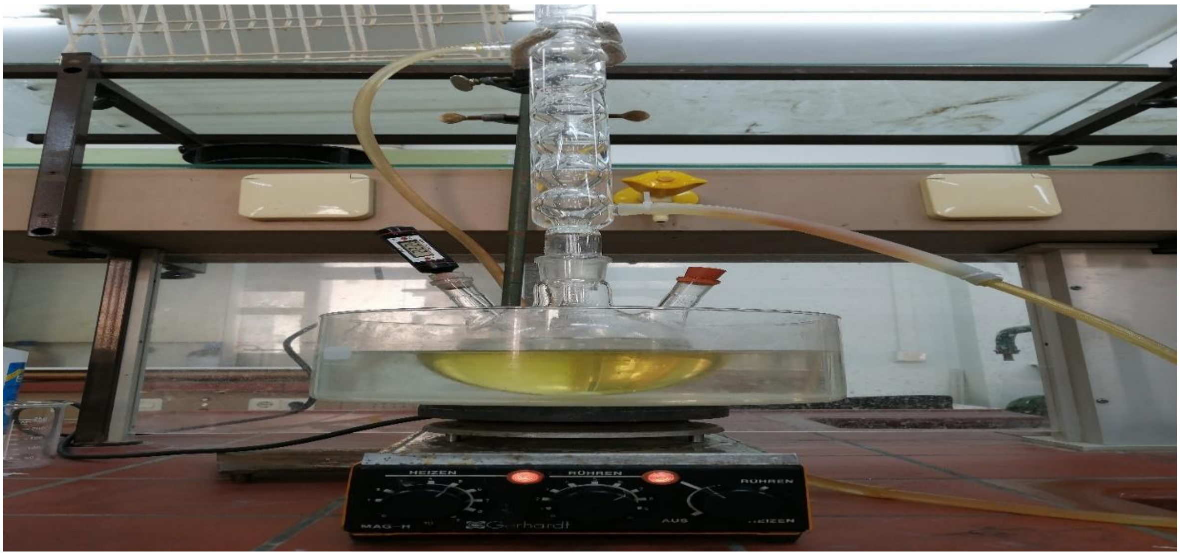


Figure III.10: Experimental example of process heating circuit with mixture of new oil with methanol.

III.4.4.2. Decantation step with separation of phases

After 120 minutes of stirring, allow the mixture to stand for separation to take place. You should know that decantation is very long you must wait at least half a day or 24h. The success of a transesterification reaction is materialized by the presence of two phases (ester and glycerol). The glycerol has a higher density than the ester. It is located at the bottom of the ampoule and decanted after 24h of decantation as shown in Figure (**III.11**) [90].

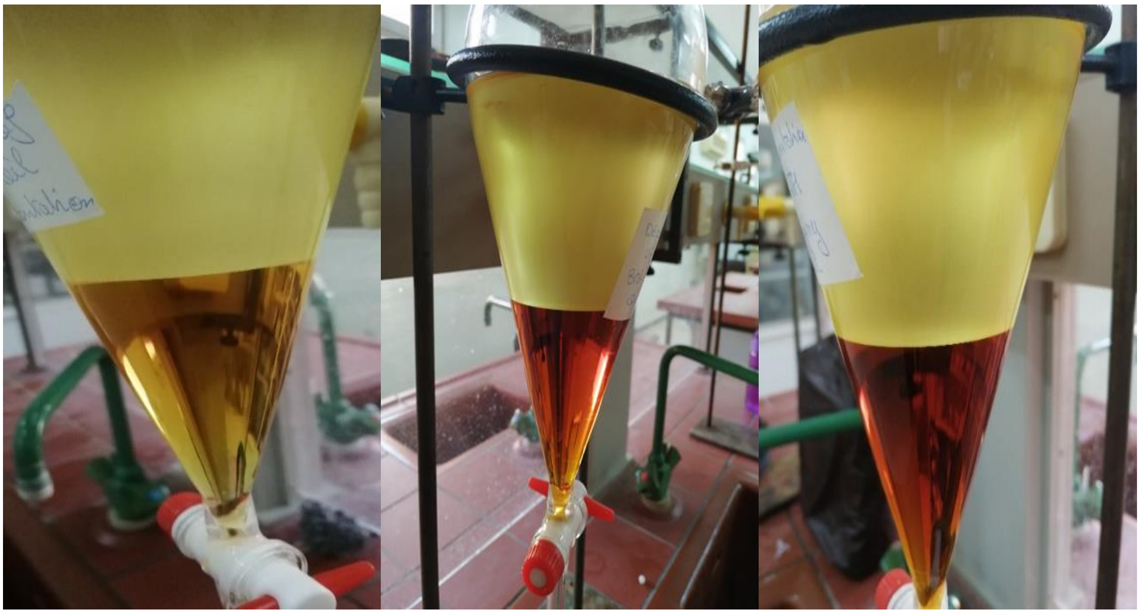


Figure III.11: Experimental examples of decantation step with new oil, 3rd frying oil and 6th frying oil.

III.4.4.3. Washing up step

The biodiesel obtained must be washed to remove excess alcohol and catalyst. Place the biodiesel in a separating funnel and slowly pour the water for rinsing. This operation is delicate; it must be carried out very gently with the least possible agitation because the agitation causes the formation of an emulsion, which decreases the yield of the synthesis. Leave it to settle again for around 24 hours then recover the biodiesel as shown in Figure (**III.12**) [90].

Figure III.12: Experimental examples of washing up step with biodiesel new oil, biodiesel 3rd frying oil and biodiesel 6th frying oil

III.4.4.4. Distillation step

Distillation is the final step where allowing the removal of excess water and methanol from biodiesel. Distillation is one of the oldest and most common method for chemical separation. Historically one of the most known application. It is the process of heating a liquid solution or a liquid vapor mixture to derive off a vapor. The purpose is typically the removal of a light component from a mixture of heavy components, or the other way around the separation of a heavy product from a mixture of light components as shown in Figure (**III.13**) [92].

Figure III.13: Experimental example of distillation process with Biodiesel 5th frying oil

At the end of all this process, we will obtained different types of biodiesel oils as shown in Figure (**III.14**):

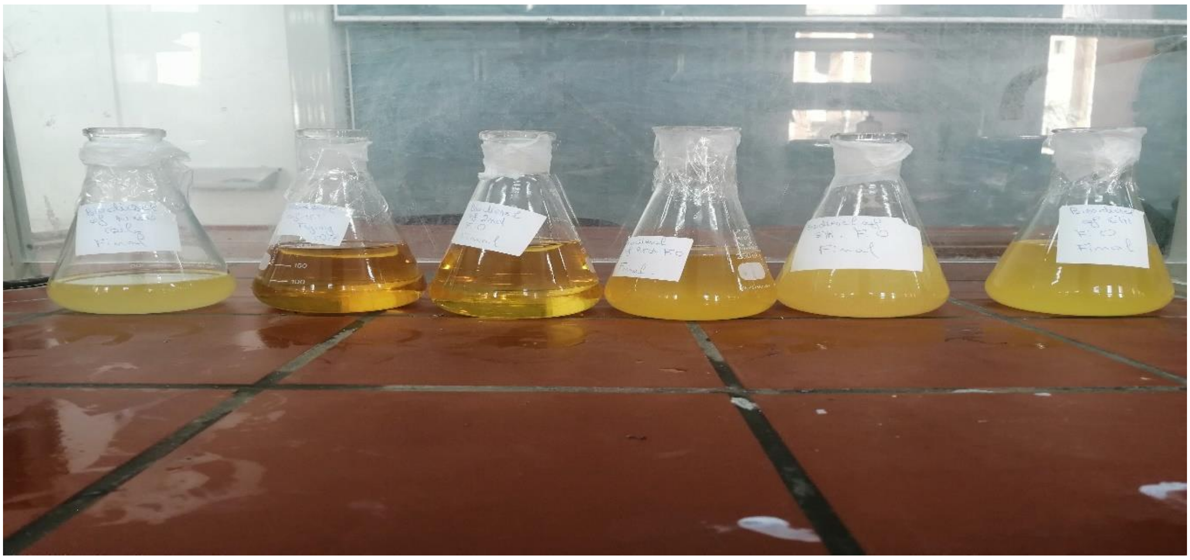


Figure III.14: Different types of biodiesel oils after end process.

III.4.5. Characteristics of Biodiesel

As we have seen in the beginning of this chapter, about determining some characteristics of oils by indexes such as acid index, refractometer, viscosity measurement and relative density. We will do same determining for biodiesel. Figure (**III.15**) shows experimental example of biodiesel 5th frying type before titration and after titration.

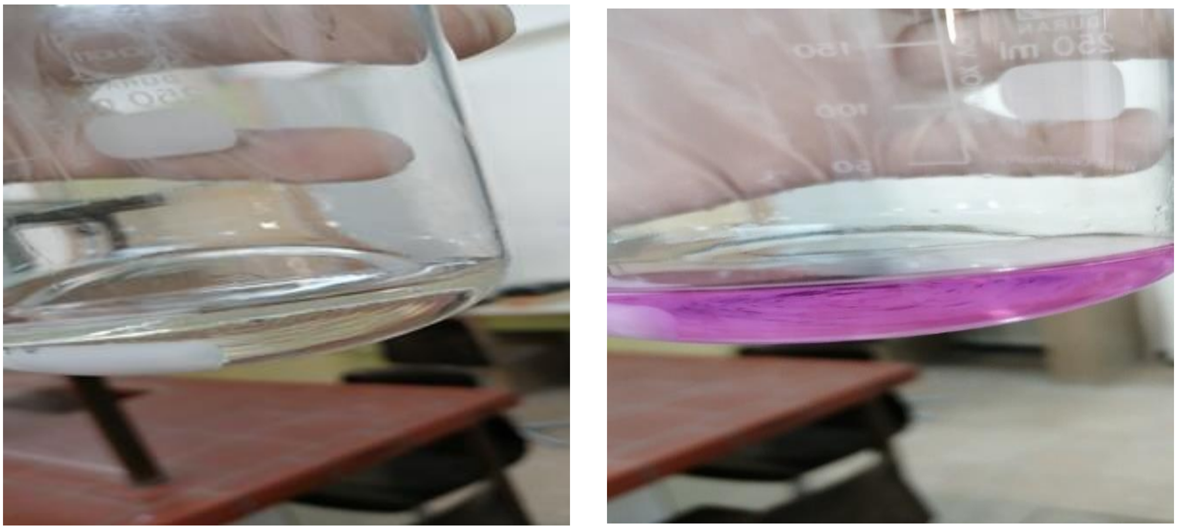


Figure III.15: Experimental example of Biodiesel 5th frying type

before titration and after titration

III.4.6. Tests for Biodiesels

III.4.6.1. Miscibility test

To check the miscibility between our biodiesel and fuel oil, we will follow the following protocol; in a 25ml graduated cylinder, we are going to pour 10ml of our previously synthesized biodiesel as well as 10ml of fuel oil. After agitation and decantation, there will be three possible cases:

- ✓ **Case n°1:** If two distinct phases are visible and have the same volume, then the two liquids are immiscible.
- ✓ **Case n°2:** If two distinct phases are visible but their volumes are different, this indicates that the two liquids are partially miscible with each other. We can then define a certain solubility.
- ✓ **Case n°3:** If only one homogeneous phase is visible, then the two liquids are miscible. For these proportions, if they are miscible whatever the proportions. We can say that they are miscible in all proportions **[93]**.

III.4.6.2. Flammability test

During the combustion process, the gases produced react with the oxygen in the air. The reaction produces sufficient heat to form a flame, which passes through the mixture consisting of gases emanating from the product and air. When the gas above the liquid ignites, the heat produced is generally sufficient to evaporate enough additional gas to maintain the flame and we will be saying that it is inflamed liquid. In fact, it is the gas which burns and which is continually renewed by the liquid **[94]**.

Chapter IV

Discussion of Results

IV.1. Introduction and study of oils

IV.1.1. Different types of marketed oils in Algeria

Actually, there is different brands of vegetable oils alimentary on the Algerian market as shown in Table (**IV.1**). They are fabricated locally or imported. They can be pure for example: soybean oil, sunflower oil and palm oil or mixed. These are intended for seasoning, cooking and frying. Oils based on soybeans and sunflowers are the most widespread on the national market. It should be noted that the most important vegetable oils refining units are Cevital, Afia, Labelle, Cogral and prolipos. Therefore, we have a Table (**IV.2**) percentage fatty acid composition of Elio oil **[91]**.

Table IV.1: Different types of marketed oils in Algeria

Operators	Brand	Composition
Cevital	Elio	80% soybeans, 20% sunflower
	Fleurial	100 % sunflower
Afia	Afia	95% soybeans, 5% corn
	Huilor	100 % soybeans
Labelle	Bonal	100 % soybeans
Prolipos	Lynor	90% soybeans, 10% palm
Cogral	Safia	100 % soybeans

Table IV.2: Percentage fatty acid composition of Elio oil.

C(16:0): Palmitic acid, C(18:1): Oleic acid, C(16:1): Palmitoleic acid, C(18:2): Linoleic acid, C(18:0): Stearic acid, C(18:3): Linolenic acid

C(16:0)	C(16:1)	C(18:0)	C(18:1)	C(18:2)	C(18:3)
10.64%	traces	4.20%	23.97%	54.43%	6.76%

IV.1.2. Characterization of new oil from brand Elio by IR-FT Spectroscopy

The bands observable in the 3000 to 2800cm^{-1} region are attributable to the vibrations of elongation of (C–H) bond in CH_2 and CH_3 groups. An intense band at 2930cm^{-1} is attributable to the symmetrical elongation vibration of the CH_2 group. In the low frequency region, only the CH_2 group deformation vibration is observable with bands at 1463cm^{-1} and 1384cm^{-1} are due to shear strain vibrations outside the plane. A band around 720cm^{-1} is due to the "cis" stretching vibration of the group (C=C–H).

The most intense band of the spectrum is observable around 1747cm^{-1}. This band is attributable to the stretching vibration of the group (C=O) which is characteristic of the esters. The low frequency region often contains low intensity bands. The only clearly observable band is at 1162cm^{-1}. This band is attributable to the stretching vibration of the (C–O) group of the esters as shown in Figure (**IV.1**) [95].

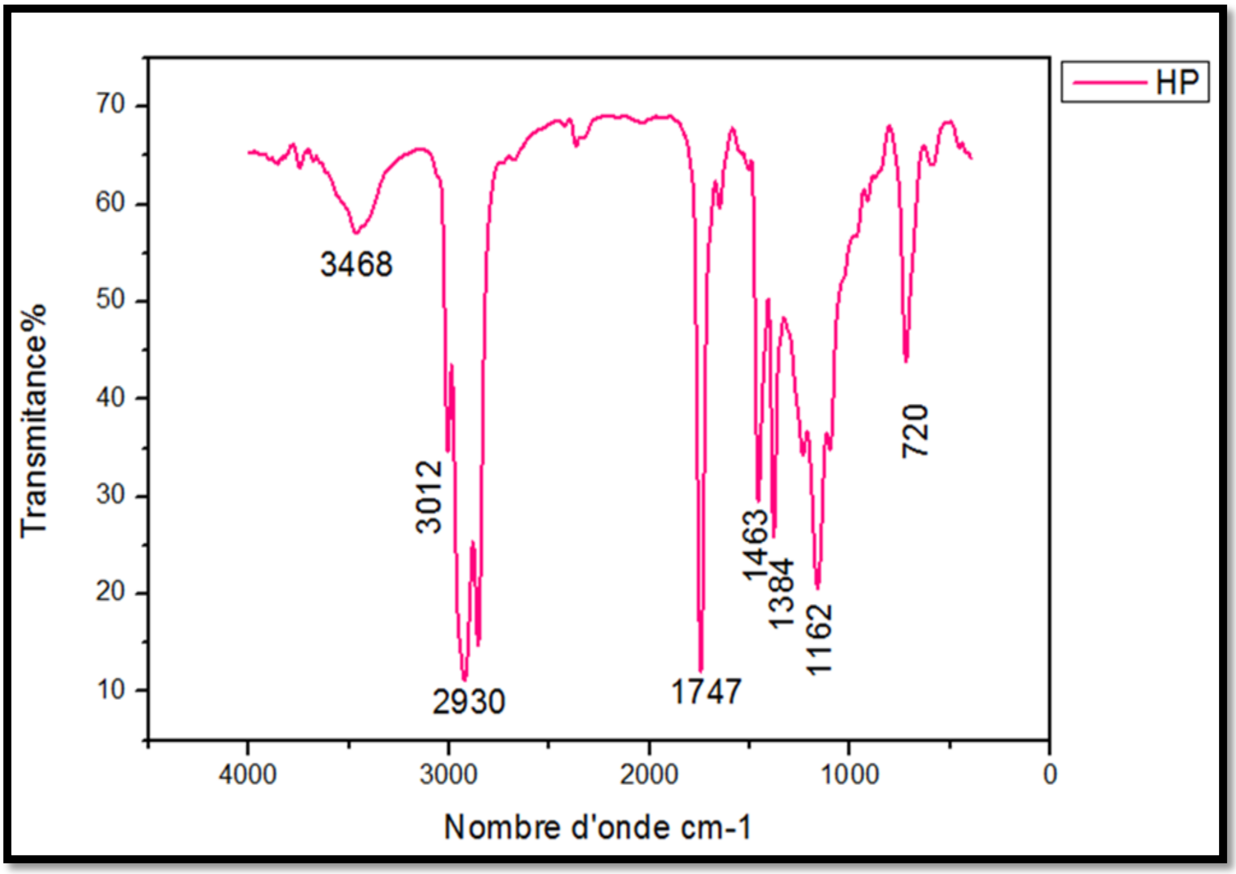


Figure IV.1: Spectrum of FT-IR for new oil with brand Elio

IV.2. Physico-chemical study of oils and frying oils

IV.2.1. Results from frying oil process

As we studied in the second chapter about the physical chemical properties of oils and their types. That oil is a hydrocarbon liquid substance that is greasy to the touch and is formed by natural resources or the breakdown of fats. Also, we saw that it comes in many forms as diverse as crude oil and vegetable oil which serve very different purposes. It means could be come from vegetable oils like palm tree, olive tree, soybeans and sunflowers, and for non-edible such as Jatropha and karanja trees. Frying oils are the oils that have been used as raw material in the cooking processes of restaurants, canteen and chip shops and food industries. Oils rich in monounsaturated fatty acids, such as olive oil and peanut oil, are more stable and can be reused several times after being heated. Frying oils defined as a process of drying and cooking of food by immersing food in oil at a high temperature, usually 165 to 190°C. Through the beginning of experiments. We fried the oil six times. Each type of frying has frying conditions such as temperature and time taken to fry. Therefore, we designed the Table (**IV.3**) to show in summary the frying conditions.

Table IV.3: Conditions for Frying oil process

Frying Oil Type	Temperature (°C)	Time Taken (mn,s)
1st Frying	150°C - 165°C	12mn, 39s
2nd Frying	165°C - 170°C	9mn, 43s
3rd Frying	160°C – 165°C	10mn, 12s
4th Frying	170°C – 175°C	10mn, 25s
5th Frying	170C° - 180°C	11mn, 17s
6th Frying	175°C - 180°C	12mn, 34s

IV.2.2. Physico-chemical characterization by indexes for new oil and frying oils

So after taking all the samples from frying oil. Subjecting them to several experiments so that we can be determine the physico-chemical characteristics of oils and types of frying oils. Subsequently. The possible results are illustrated in next following Table (**IV.4**).

Table IV.4: Physico-chemical characterization for new oil and frying oils

	New Oil	1st frying	2nd frying	3rd frying	4th frying	5th frying	6th frying
Acid index (A %)	0,476	0,594	0,701	1,093	1,458	1,935	2,440
Density	0,928	0,912	0,910	0,902	0,893	0,868	0,625
Viscosity [m/s] .10^{-3}	1,379	1,167	1,140	1,077	1,054	1,041	0,996
Refraction index	1,4725	1,4730	1,4735	1,4745	1,4745	1,4745	1,4750

Through the results obtained in the above Table (**IV.4**). We notice that the acid index, which expresses the level of free fatty acids, increases during heating going from 0.476% of new oil to 2.440% of sixth frying oil. This variation is very significant and indicates that a large majority of the oil is transformed into free fatty acids and as shown in Figure (**IV.2**).

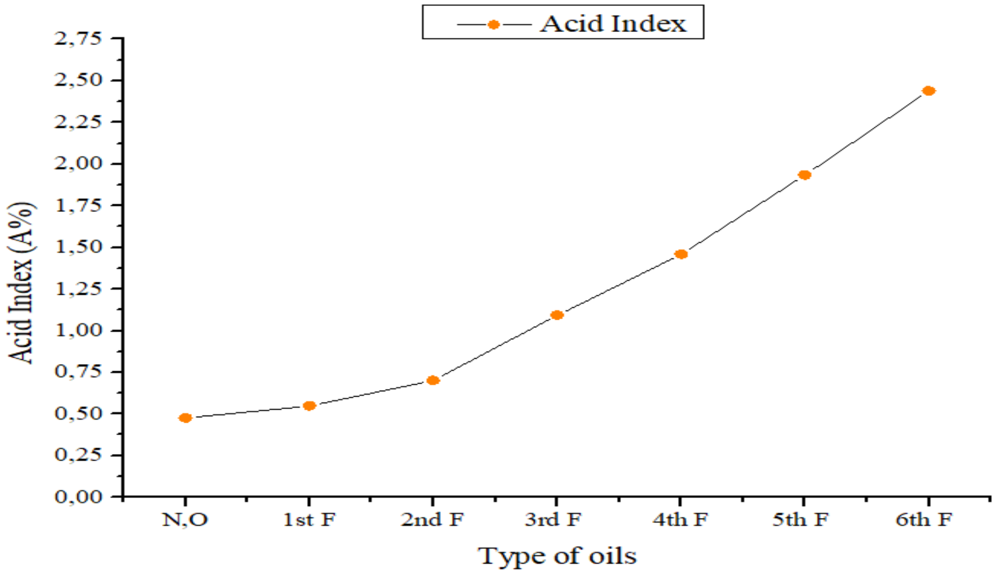


Figure IV.2: The graph curve represents Acid index changes with different type of oils

We also observe that the density that it is almost stable during heating or we can say that It changes with very slight changes from 0.928 of new oil to 0.868 of fifth frying oil. Notice that in sixth frying oil, its density is about 0.625 means it is different from other that due to conditions of frying process with temperature and time taken to fry according to Table (**IV.3**). The density changes are shown in Figure (**IV.3**).

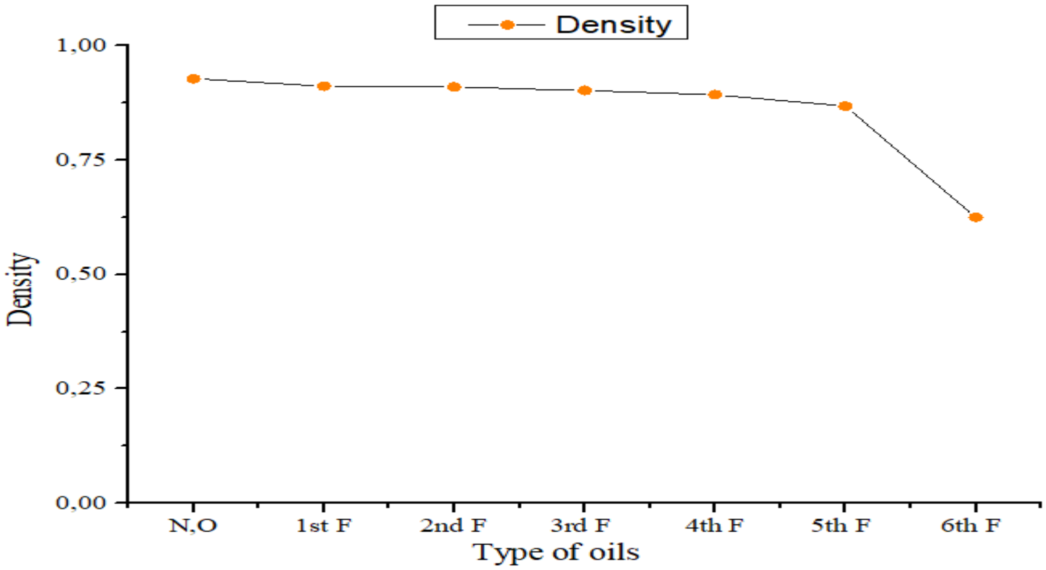


Figure IV.3: The graph curve represents density changes with different type of oils

The same goes for viscosity in term of speed except that there is a big decrease for oil heated between [150°C-180°C] in 9mn - 12mn for each type of frying oil. From [1,379*10^{-3}m/s] of new oil to [0,996*10^{-3}m/s] of 6^{th} frying oil. It means high viscosity with fact most of oil contains of triglycerides, where they break and produce free fatty acids as large molecular weight compounds become short and in large amount in frying oil, which causes the thickness of the molecules. These variations are shown in Figure (**IV.4**).

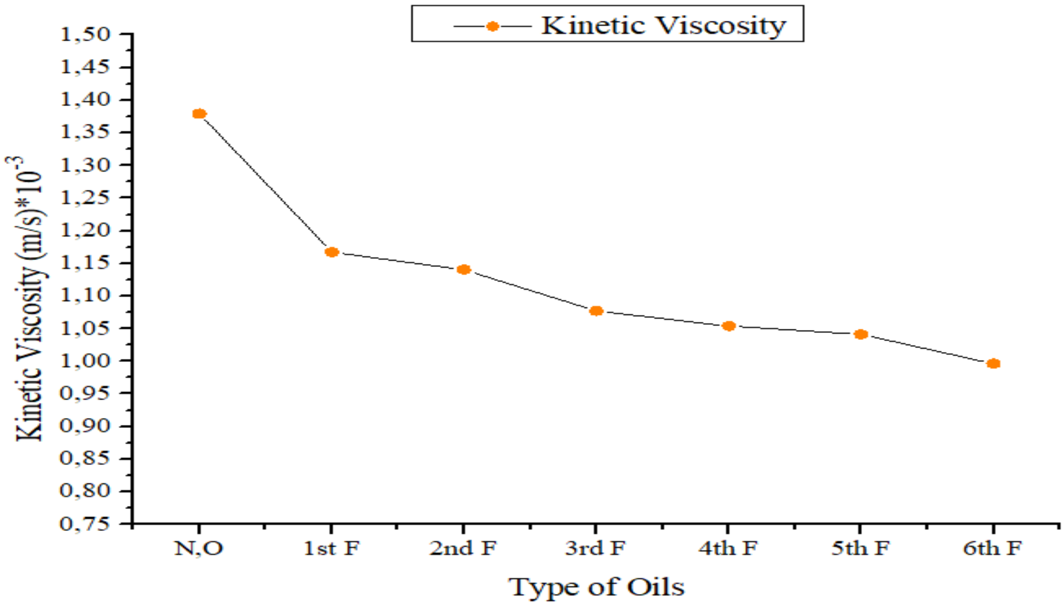


Figure IV.4: The graph curve represents viscosity in term of speed changes with different type of oils

Refraction index of oils according to table show that is a little bit stable from 1.4725 of new oil to 1.4750 of sixth frying oil. Its varies depending to their impurity due to the oxidation of fatty acids either in terms of short carbon chain or in terms of conversion of acid groups into other functions such as aldehydes, ketones and even peroxides. This variation also shown in Figure (**IV.5**).

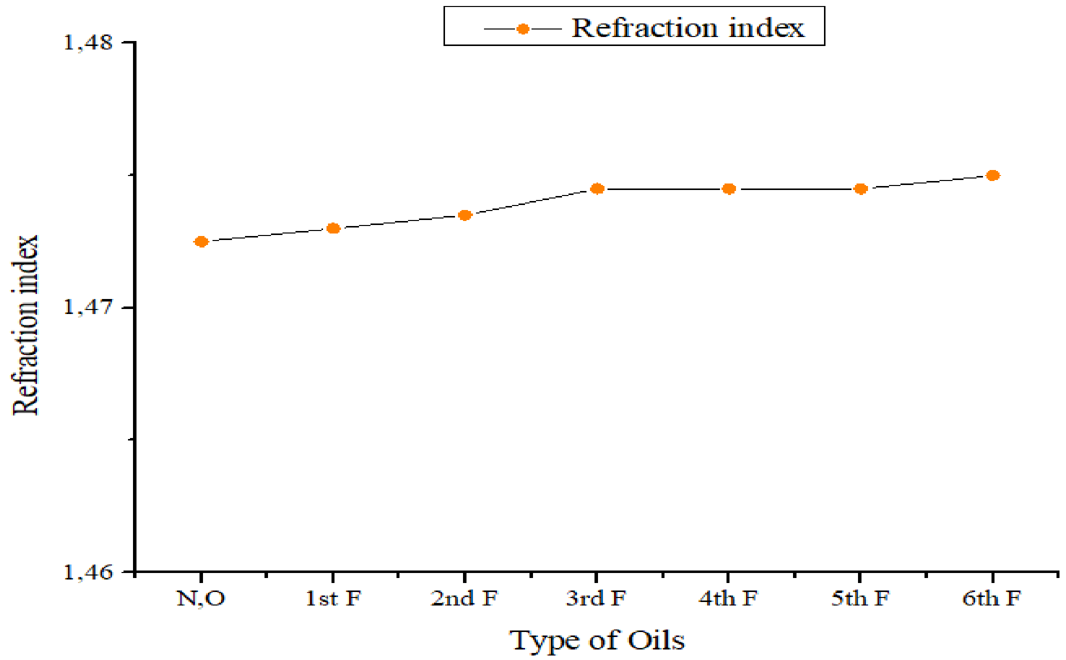


Figure IV.5: The graph curve represents refraction index changes with different type of oils

IV.2.3. Comparison with recent analyses of physical chemical characteristics for oils and frying oils

Wanodya Asri Kawentara and Arief Budimanb published that waste cooking oil is a promising alternative for producing biodiesel because it is a cheaper raw material that also avoids the cost of waste product disposal and treatment. But, these used frying oils have different properties from those of refined and crude vegetable oils. The presence of heat and water accelerates the hydrolysis of triglycerides and increases the content of free fatty acids (FFA) in the oil. Second-used cooking oil used in the research was obtained from street sellers in Yogyakarta City, Indonesia. Prior using the oil for biodiesel production, it was filtered and precipitated. The characteristic of second-used cooking oil is summarized in Table (**IV.5**) [96].

Table IV.5: The Characteristics of second used cooking oils.

Type of Analyses	Value
Density (g/ml)	0.900
Free Fatty Acid (FFA%)	0.820
Saponification Value (mg KOH/g oil)	192.142

Aylin Beycar Kafadar et al proved that the presence of heat and water accelerates the hydrolysis of triglycerides and increases the content of free fatty acids (FFA) in the oil. The FFA and water content have significant effects on the transesterification reaction negatively. They also interfere with the separation of fatty acid esters and glycerol. Especially, the viscosity of the oil increases considerably **[97]**. Mohammed Abdul Raqeeb and Bhargavi reported that vegetable oil contains saturated hydrocarbons (triglycerides) which consist of glycerol and esters of fatty acids. Used vegetable oil is a product from hotels, fast food restaurants and shops selling fritter and product of an operating vegetable oil refinery. For serving better quality food, they usually throw this waste cooking without any treatment. In fact, using waste vegetable oil reduces the need for biodiesel-producing crops and the competition with food. The typical chemical and physical characteristics of WCO are shown in Table (**IV.6**) .The usual values for Properties like density, kinematic viscosity and acid value shown in the table. They found that properties of WCO can change depending on the frying conditions, such as temperature and cooking time. The cooking process causes the vegetable oil, Triglyceride to break down to form Diglycerides, Monoglycerides, and free fatty acids (FFAs). Therefore, it causes a growth of the Free Fatty Acids (FFAs) in the WCO. Moreover, because of oxidation and polymerization reactions, there is an increase in the viscosity and the saponification number of the WCO when compared with the original oil **[98]**.

Table IV.6: the Main Properties of WCO

Property	Value
Density (g/cm^3)	0.91 – 0.924
Kinematic Viscosity at 40°C (mm^2/s)	36.4 – 42
Saponification Value (mg KOH/g)	188.2 – 207
Acid Value (mg KOH/g)	1.32 – 3.6

IV.3. Physico-chemical study of biodiesel

IV.3.1. Biodiesel, Transesterification and its challenges

Indeed, traditional diesel is a mixture of hydrocarbon chains of different lengths, generally from 10 to 18 carbon atoms per chain. Cetane (or n-hexadecane) is a predominant diesel oil; its molecular formula with $C_{16}H_{34}$. Biodiesel is chemically similar to petroleum diesel, but it made up of fatty acid methyl esters (FAME) rather than hydrocarbon chains. Esters are composed of an organic acid, in this case a fatty acid, and an alcohol, which it is methanol. Biodiesel generally produced from triacylglycerols from animal fats or vegetable oils. Triacylglycerols have three fatty acid molecules attached to one molecule of glycerol (an alcohol). The transesterification reaction converts the triacylglycerol esters to fatty acid methyl esters. All you need for a transesterification reaction is an alcohol and a chemical catalyst. Methanol is the most used alcohol, and KOH base is the most used catalyst **[69]**.

However, all of this information we need to consider of parameters and influents conditions to transesterification reaction with accreditation to recent Table (**IV.3**) of conditions for frying oil process with temperature and time taken to fly. Temperature in the transesterification process is important parameter that influences the reaction and the yield of biodiesel. Increasing of temperature decreases the oil viscosity and the biodiesel yield decreases. If the temperature is above the boiling point of the alcohol used, a leak could occur due to alcohol vaporization **[99]**.

In the transesterification process, different researchers have reported different reaction times. However, the reaction may be slow at the start of the experiment because of dispersion between the oil and the alcohol, which is enhanced by agitation. Generally, biodiesel yield increases with reaction time. However, excess reaction time probably leads to a reduction in the conversion yield because of temperature condition, which ultimately causes more fatty acids to form soaps, leading to loss of esters **[99]**.

IV.3.2. Physico-chemical characterization by indexes for types of biodiesel

After frying process and after completely finished from transesterification reactions, by mixing new oil and frying types with a large amount of alcohol and catalyst KOH. We get types of biodiesel and subjecting them to several experiments so that we can be determine the physico-chemical characteristics of these types. In the last. We got a Table (**IV.7**) that it is showing these characteristics that were recorded in recent experiments.

Table IV.7: Physico-chemical characterization by indexes for Biodiesel.

	BIO.D N.O	BIO.D 1^{ST} F	BIO.D 2^{ND} F	BIO.D 3^{RD} F	BIO.D 4^{TH} F	BIO.D 5^{TH} F	BIO.D 6^{TH} F
Acid index (A %)	0,168	0,196	0,252	0,280	0,241	0,196	0,140
Density	0,838	0,853	0,879	0,926	0,930	0,935	0,942
Viscosity [m/s] .10^{-3}	7.382	8.655	10.458	11.409	11.952	12.550	13.944
Refraction index	1,4555	1,4560	1,4545	1,4545	1,4545	1,4545	1,4550

From Table (**IV.7**) above, we can see that acid index increases from 0,168% with biodiesel of new oil to 0,252% with biodiesel of 3rd oil and decreases to 0,140% with biodiesel of 6th frying oil.

The increasing part due to that still majority of oil in biodiesel transformed into free fatty acid with consideration of temperature for frying process was stable (150C°-165C°) and also in transesterification process with (45C°- 55C°) in types of 1st,2nd and 3rd frying oil.

However, decreasing part proves that free fatty acids in types of 4th, 5th and 6th frying oil transformed to esters biodiesels through transesterification process. All these variations are shown in following Figure (**IV.6**).

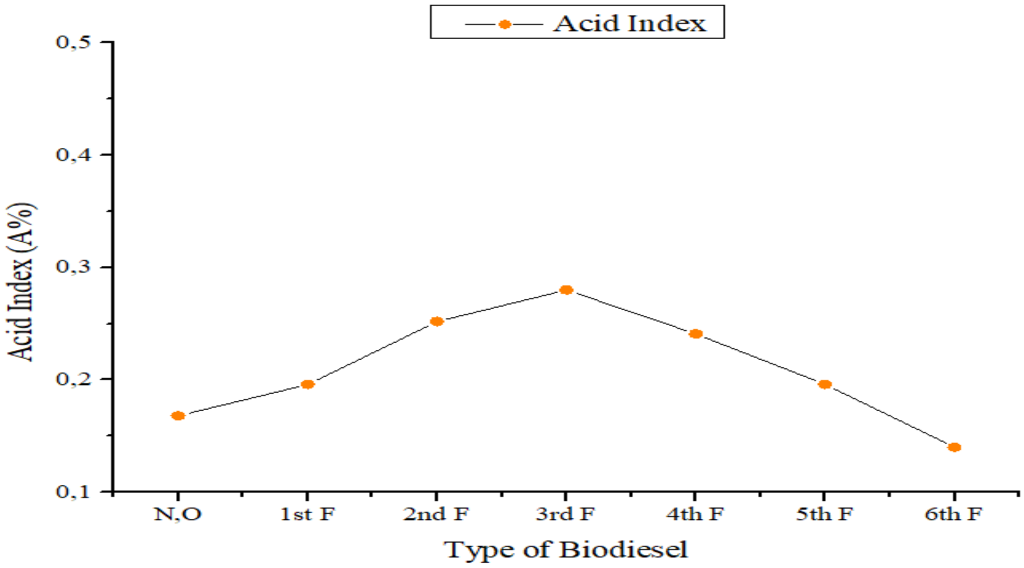


Figure IV.6: The graph curve represents acid index changes with different type of biodiesel.

For density, we notice that it is increasing from 0,838 with biodiesel of new oil to 0,942 with biodiesel of 6th frying oil. Because that density is an important characteristic, mainly for biodiesel, because it conditions the dimensioning and the technological particularities of the feed members (pumps, injectors). If biodiesel has a higher density, it will be necessary to inject a slightly higher mass of fuel and therefore the density of all types of biodiesel that we have, they increase from the new oil to 6th frying oil. These variations are illustrated in next Figure (**IV.7**).

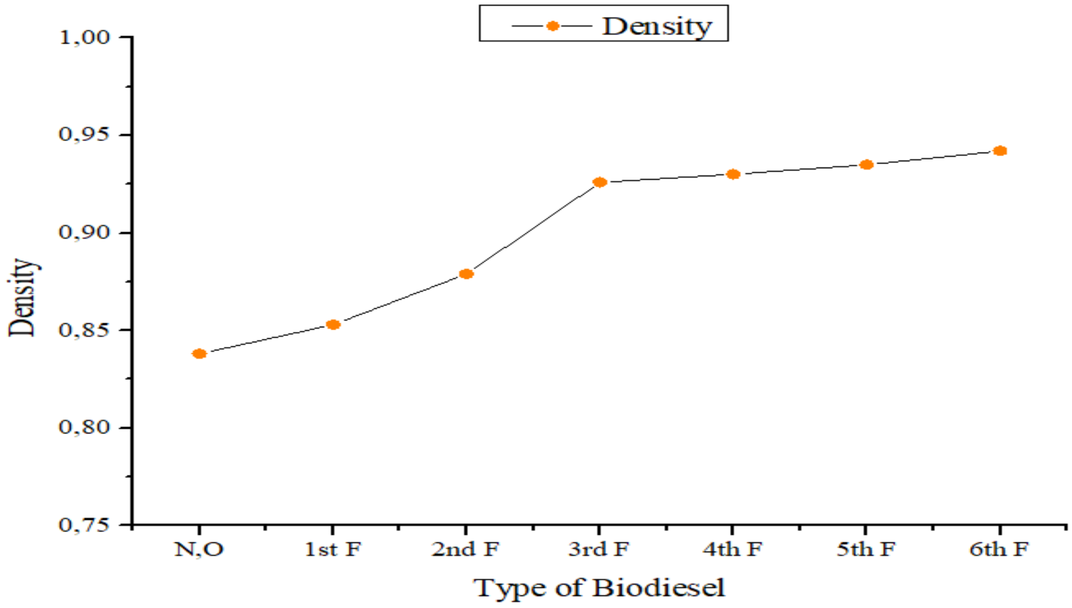


Figure IV.7: The graph curve represents density changes with different type of biodiesel.

Viscosity is the most important of biodiesel since it affects the operation of fuel injection equipment. It well known that vegetable oils are lowest viscosity in term of speed meaning is highly viscous as we seen in recent Figure (**IV.4**) of viscosity in term of speed changes with different type of oils. As purpose of transesterification reaction for reducing high viscosity of oils. As we see in recent Table (**IV.7**), that viscosity in term of speed increase from 7,382*10^{-3} m/s with biodiesel of new oil to 13,944*10^{-3} m/s, due to reducing of high viscosity. Less viscous means less difficulty for motor engine to injection and higher the volatility characteristics of biodiesels to be better replacement for fuels or gasoline. These changes are also illustrated in following Figure (**IV.8**).

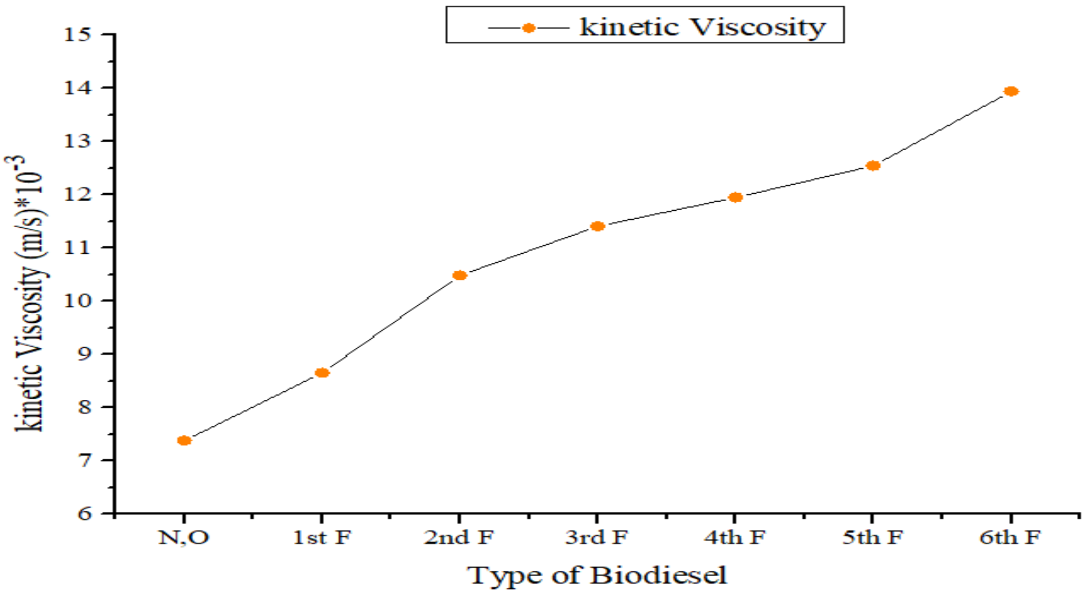


Figure IV.8: The graph curve represents viscosity in term of speed changes with different type of biodiesel

Refraction index of oils according to Table (**IV.7**) shows that is a little bit stable from 1.4555 of new oil to 1.4550 of sixth frying oil. Also due to their impurity of oxidation in biodiesel even though it is less than in oils and frying types. The following Figure (**IV.9**) show variation of refractive index in biodiesels.

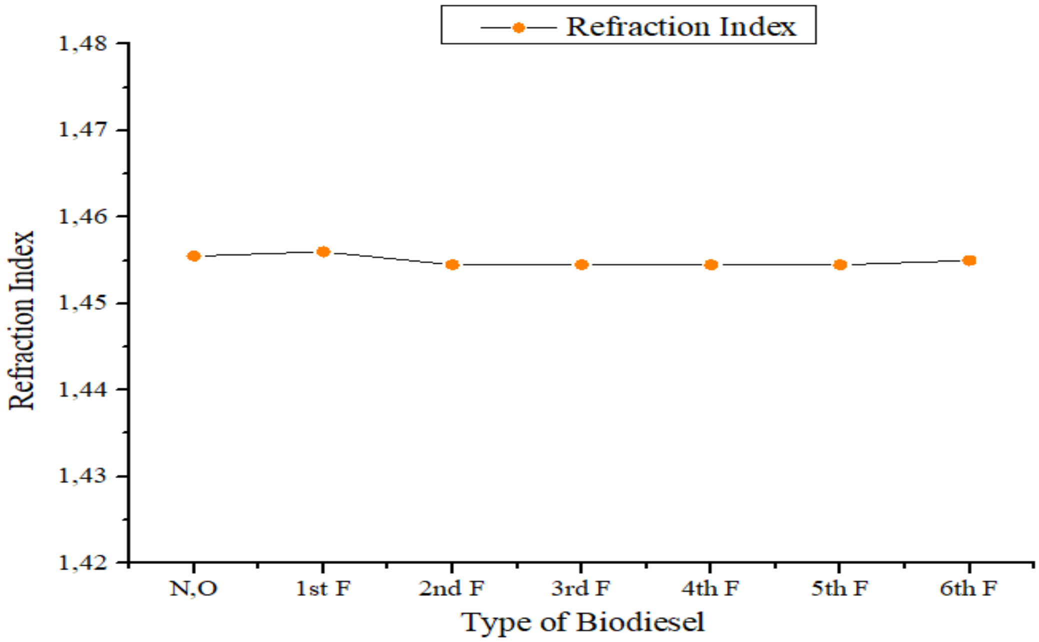


Figure IV.9: The graph curve represents refraction index changes with different type of biodiesel

IV.3.3. Comparison with recent analyses of physical chemical characteristics for Biodiesel

Jun Cong Ge et al reported that density and viscosity of biodiesel fuel are important factors in engine operation. Density will directly affect the mixing of biodiesel and diesel, and excessively high density will lead to stratification of mixed oils. Also, they reported that Viscosity is an important factor that directly affects the combustion performance and exhaust characteristics of an engine. High viscosity deteriorates the atomization efficiency, extends ignition time, reduces injection pressure, and hinders full combustion of the fuel. They have studied a variety of biodiesel blended fuels (diesel blended with sunflower, cottonseed, soybean, corn oils, and waste palm oil) and have also discovered that the viscosities of the 20% blend fuels are very close to that of pure diesel fuel **[100]**.

Ypatia Zannikou et al, they studied four types of ethyl esters in terms of their physicochemical properties. Then to study whether their quality parameters where indeed within the European standard EN. The results of analysis are given in Table (**IV.8**). It is observed that three out of four types of ethyl esters do satisfy the European norm of viscosity. The ester which was different from the other three was the used frying ethyl ester, which appeared to be above the highest limit (5cSt) of the European specification. On the other hand, each every type of ethyl ester had a density within the range of 860 – 900 kg/m3 **[101]**.

Table IV.8: Properties of Fatty acid ethyl esters

Property	**Sunflower oil**	**Rapeseed oil**	**Olive oil**	**Frying oil**	**EN 14214 Limits**
Density (Kg/m3)	882.7	881.2	881.5	888.5	860-900
Kinematic **viscosity ($mm^2.s^{-1}$)**	4.63	4.84	4	5.81	3.50 – 5.0
Acid Value (mgKOH/g)	0.15	0.35	0.19	0.46	0.5 max

Sivaramakrishnan and Ravikumar in their report for determination of cetane number of biodiesel and it is influences of physical properties. They emphasized the importance of relative density and viscosity measurement for biodiesels factory and engine operation. So, they reported that Relative Density is an important property of biofuel. Density is the mass per unit volume of any liquid at a given temperature. Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. They found the temperature of transesterification reaction is increased viscosity of biodiesels decreases and it is therefore able to flow more readily. The lower the viscosity of biodiesels, the easier it is to pump, atomize, and achieve finer droplets. Particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. Table is shown properties of vegetable oil methyl ester [102].

IV.4. Comparison between types of oils and types of biodiesels

IV.4.1. Acid index

Figure (**IV.10**) clearly shows that the acid index is increasing for oils but with almost stable for biodiesels, which gives the impression that biodiesel is different from that of the oil used. Because oils after frying process, they contains of triglycerides that broke to free fatty acids in larger amount. However, through transesterification reaction, theses free fatty acids mixing with methanol converts to esters (biodiesels) and amount of free fatty acids is gradually decreasing.

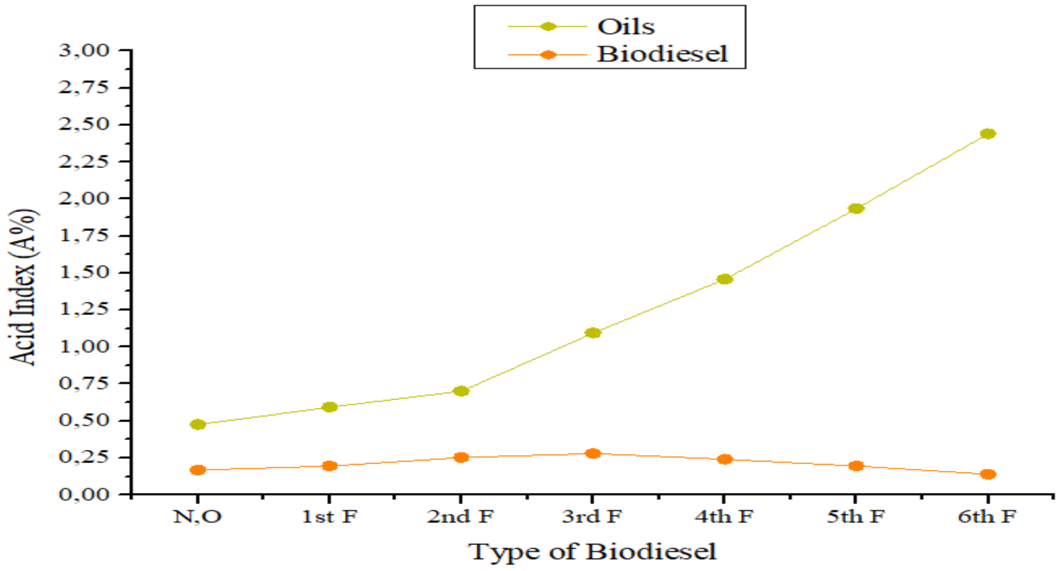


Figure IV.10: Evolution of the acid index of oils and biodiesels

IV.4.2. Density index

According to the figure (**IV.11**), the density values of frying oils are higher than those types of biodiesel derived there from type of new oils to type of 3rd frying oil. However, with from 4th frying type to 6th frying type, we see the density values of biodiesel are higher than oils. Due to that density is an important parameter for fuel atomization and distribution, if the biodiesel has a higher density, it will be necessary to inject a slightly higher fuel mass.

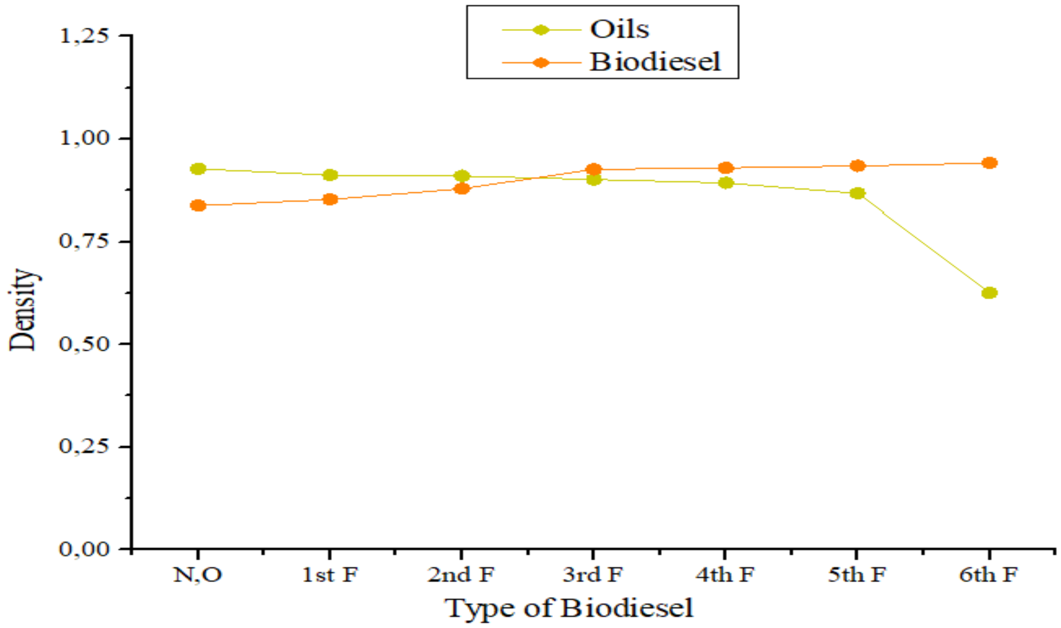


Figure IV.11: Evolution of the density index of oils and biodiesels

IV.4.3. Viscosity index

Figure (**IV.12**) clearly shows that the viscosities in term of speed of oils are stable with increasing of temperature, but with increasing for biodiesels. Due to purpose of transesterification reaction for reducing high viscosity of oils. The higher the viscosity of a liquid, the lower its susceptibility to flow. The lower the viscosity, the greater the fluidity of this liquid which it is suitable as characteristics of fuels. As we told in recent results that less viscous means less difficulty for motor engine to injection, and higher the volatility characteristics of biodiesels to be better replacement for fuels or gasoline.

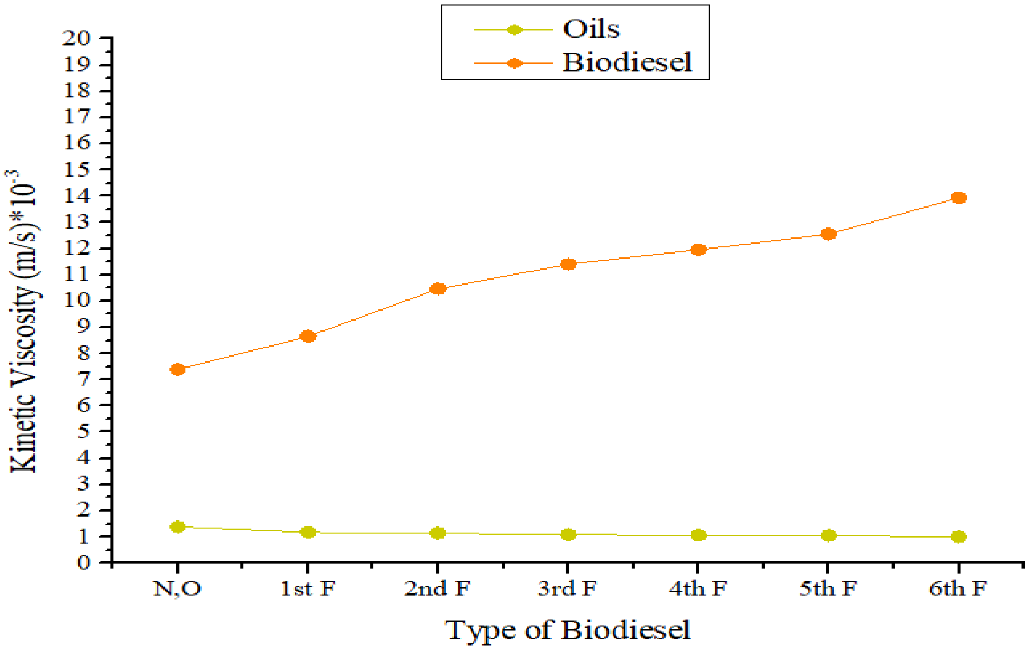


Figure IV.12: Evolution of viscosity in term of speed of oils and biodiesels

IV.04.04. Refraction index

We see in next Figure (**IV.13**), that refraction values both of oils and of biodiesels, they are in slight increase with augmentation of time for each type frying oils. However, it should be noted that refractive values of biodiesel are less than values for oils and types of frying oils. It means that biodiesels after transesterification process and derived from types of frying oils. It became little bit darker in color then its original oils.

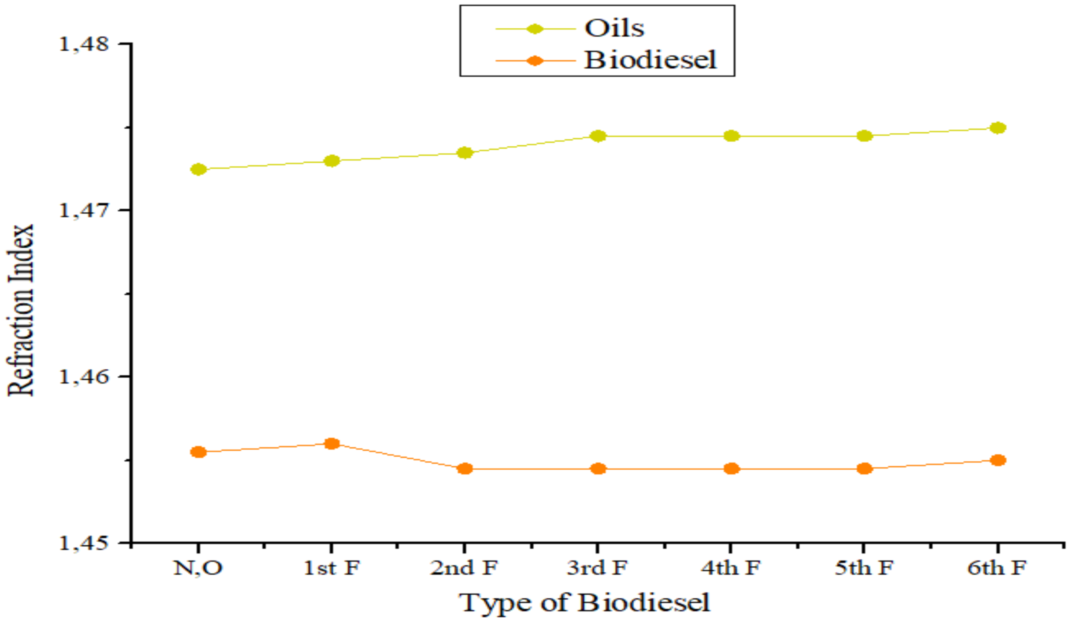


Figure IV.13: Evolution of the refraction index of oils and biodiesels

IV.5. Opinions and researches about biodiesel in Algeria

Algeria is located in an area vulnerable to the harmful effects of climate change due to pollution and environmental imbalances. Today, aware of the growing interest in renewable energies and their challenges, Algeria has integrated the development of this type of energy into its energy policy. The adoption of a legal framework favorable to the development of these energies, the construction of important infrastructures in this field and the planning of projects are the perfect illustration of this despite the development of bioenergy still on an experimental scale in the laboratories of research. Regarding energy crops, raw materials for the production of biofuels, in the case of Algeria, it is not possible to have recourse to edible sources for this task. It would then be better to turn to second-generation biofuels produced from non-food sources, cellulose and waste **[103]**.

Researcher at the Bio Energy and Environment Laboratory at the Center for the Development of Renewable Energies, Dr. Majda Amina Aziza confirmed in an interview to a site called “Liberte Algerie” that Algeria is taking a keen interest in these alternative fuels. She said: ‘‘currently, sugar cane, corn, wheat, barley and beet molasses are used in the production of bioethanol (blended with gasoline). In contrast, soy, sunflower and palm oil are used in the production of vegetable oils, fuels and biodiesel”. She also expressed her opinions on production of biofuels in Algeria; she said: “Algeria is a country located in an area classified as arid and semi-arid, and therefore very vulnerable to the harmful effects of climate change, even if it is not one of the polluting countries. The use of biofuels can represent an interesting alternative and a way of helping to reduce the greenhouse effect. There is however no question of using food products such as wheat or corn to produce them, the alternative of waste and crops not intended for food proves interesting”. She add: “On the other hand, it is necessary to assess the economic and environmental impacts of a production of biofuels which depend closely on the raw material used, the process, the co-products generated in parallel and the actual use of the biofuel” **[104]**.

Radia Selaimia et al worked on the synthesis of biodiesel from vegetable oil, to prove that biofuels intended to replace the fuel from petroleum, also they are sustainable alternative to fossil fuels because they are renewable and less toxic to the environment. Offering a renewable energy source meeting the energy issues of the day as the mastery of greenhouse gas emissions and preservation of non-renewable fossil resources. They published that used vegetable oils contain solids and free fatty acids due to oil breakdown during the frying process. The synthesis of biodiesel by transesterification of vegetable oils was carried out in their study. The transesterification reaction refines the oil since most of the phospholipids and free fatty acids will be eliminated. Free fatty acid disappears completely with basic catalysts. They collected waste vegetable oils from fried food companies. Transesterification reaction was performed in a stirred tank reactor at 60°C using a solution of 1.2% KOH and 30% methanol. Equivalent to 8.6:1 (molar ratio), after 40min of vigorous stirring. Reaction then stopped, settled to decant to remove the alcohol and catalyst residues from biodiesel and the ester phase was washed with the aid of distilled water. They found out that after frying process and transesterification reaction proved that kinematic viscosity is decreasing with increasing of temperature. That its purpose to reduce higher viscosity and to be better replacement for gasoline fuels in injection system as shown in Table (**IV.9**) [105].

Table IV.9: Different of characteristics between Olive oil, Diesel fuels and blends of biodiesel with gasoline (Bx)

Property	Olive-pomace oil	Diesel fuel	B_{20}	B_{30}
Density (15C°) Kg/m	904	827.1	840.1	843.6
Kinematic-Viscosity mm^2/s	45.27 at 4°C	5.12 at 20C°	4.81 at 20C°	5.61 at 20C°
Cetane Number	-	50.95	52.02	51.68

A.Boulal et al, with the experimental of reaction mixture of 100ml of a used edible oil and 50ml of alcohol is introduced in the presence of 1% of the NaOH catalyst subjected to continuous stirring for 1h at a temperature of 40°C. It is direct influence of the temperature on the viscosity of the oil transferred to the biodiesel formed was reduced with increasing of temperature. He concluded that concern of losing fossil fuel sources has been resolved by the search for an alternative that can meet our future needs such as a biofuel. It is biodiesel that can replace diesel at a certain percentage [106].

M. Khelafi et al, with Date Seeds (DS) and transesterification of sunflower oil was carried out in a round bottom flask equipped with a water cooled reflux condenser using methanol and calcined DS as catalyst, the system was heated by oil bath under given conditions: temperature (45–95°C), time (0.5–2h), methanol/oil molar ratio (3/1–21/1). They found that reaction temperature is an important factor in the transesterification reaction. As the temperature rose from 45 to 65°C, the biodiesel yield increased. However, when the temperature was beyond 65°C, the biodiesel yield decreased. The physical properties of produced biodiesel are tabulated in Table (**IV.10**). The measured kinematic viscosity at 40°C was slightly below the upper limit of 6.0mm^2/s. The measured density at 15°C was slightly above the lower limit of 860 kg/m^3 **[107]**.

Table IV.10: Physical properties of produced biodiesel

Property	Value	EN Standard	ASTM Standard
Density at 15°C (Kg.m^{-3})	880	860 – 900	-
Kinematic Viscosity at 40°C (mm^2.s^{-1})	4.41	3.5 – 5.0	1.9 – 6.0

General Conclusion

General Conclusion

Biofuels are the best alternative to industrial fuels, as it plays a large role in the economy of the developed countries, as it is particularly dependent on it in recent times. These fuels are mainly derived from biomass, biowaste, Plants and cereals. But the focus is on sugar rich sources and oils to produce either bioethanol or biodiesel. It has many positives like high biodegradability, reduction in greenhouse gas emissions and is obtained from renewable source like vegetable oils, animal fat.

The study showed that biodiesel is a renewable alternative to diesel fuel with almost similar physical properties. Biodiesel is synthesized by transesterification, which is the most used technique for the synthesis of biodiesel. It is a chemical reaction that involves substituting alcohol for one ester and replacing it with another. This process is widely used to reduce the viscosity of triglycerides. This what our objective of transesterification reaction for reducing high viscosity of vegetables oils. As we been said before that less viscous means less difficulty for motor engine to injection and higher the volatility characteristics of biodiesels to be better replacement for fuels or gasoline. It proves with results that biodiesel is very similar of its characterization as density relative and viscosity measurement with characterizations of gasoline fuels. All that just could be work from different resources of types oils as vegetables oils (for example; sunflower oils, olive oils, soybeans, palm oils and others….) and through transesterification reaction with amount of alcohol and catalyst to produce the amount of biodiesels oils to be replacement for fuels.

So, the vegetable oils used as raw materials can be obtained from different oil crops that may be grown in a wide variety of environments. Biofuels represent an ecologically friendly source of energy that is replaceable, unlike petroleum based fuels which are not. This is why developed countries decided and made researches laws to grow these plants intensively and also to reduce dependence on Arabic oils and make their own power of producing oils. The Algerian government should consider this solution, which could change the state of the bad economy, improve the Algerian community's livelihood, provide self-sustaining food security and reduce foreign imports.

Annexes

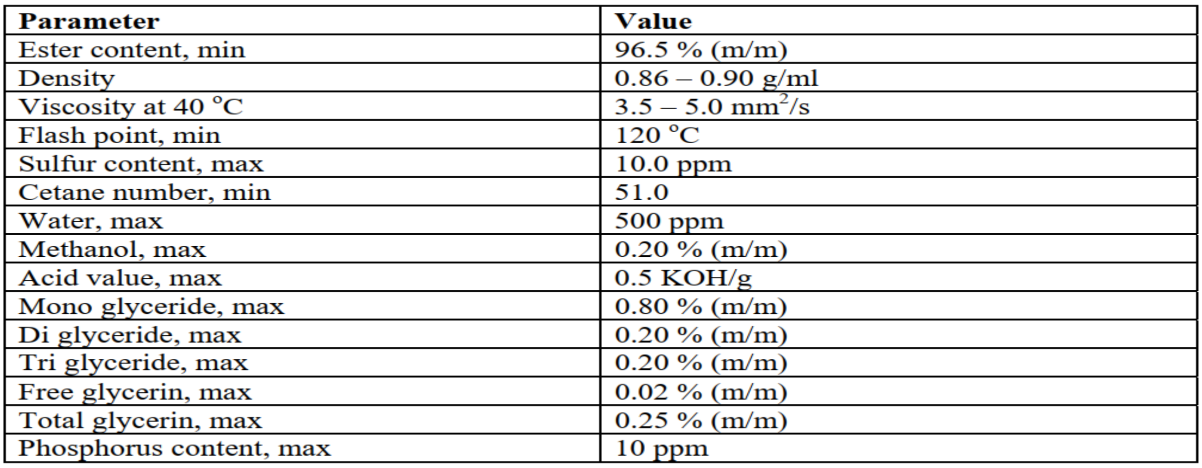
Annexe.1: Generally applicable requirements and test methods of biodiesel after EN.14214.

Property	Unit	Minimum	Maximum	Test Method
Ester Content	% (m/m)	96.5	-	prEN 14103
Density at 15 °C	kg/m^3	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40 °C	mm2	3.5	5.0	EN ISO 310
Flash Point	°C	Above 101	-	ISO / CD 3679
Sulfur Content	mg/Kg	-	10	-
Carbon Residue (10 % Bottoms)	% (m/m)	-	0.3	EN ISO 10370
Cetane Number	-	51.0	-	EN ISO 5165
Acid Value	mg KOH/g	-	0.5	pr EN 14104
Iodine Value	-	-	120	pr EN 14111
Linolenic acid methyl ester	% (m/m)	-	12	pr EN 14103
Polyunsaturated (≥ 4 double bonds) methyl esters	% (m/m)	-	1	-
Methanol Content	% (m/m)	-	0.2	pr EN 14110
Monoglyceride Content	% (m/m)	-	0.8	pr EN 14105
Diglyceride Content	% (m/m)	-	0.2	pr EN 14105
Triglyceride Content	% (m/m)	-	0.2	pr EN 14105
Free Gylcerol	% (m/m)	-	0.02	pr EN 14105 pr EN 14106
Total Gylcerol	% (m/m)	-	0.25	pr EN 14105

Annexe.2: Examples of parameters in the Indian Biodiesel specification standard IS.15607.

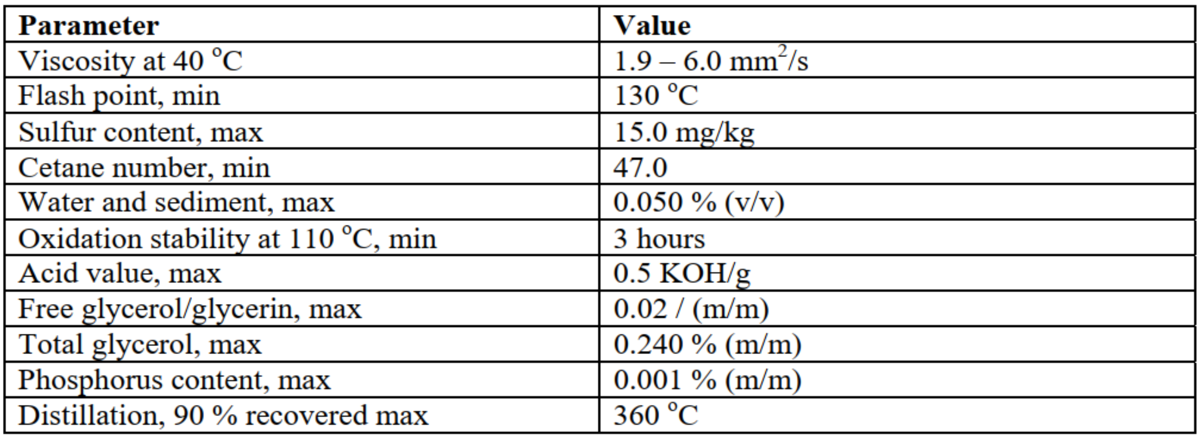
Parameter	Value
Ester content, min	96.5 % (m/m)
Density at 15 °C, max	860 – 900 kg/m^3
Viscosity at 40 °C	2.5 – 6.0 mm^2/s
Flash point, min	120 °C
Sulfur content, max	50.0 mg/kg
Cetane number, min	51.0
Water, max	500 mg/kg
Methanol, max	0.20% (m/m)
Ethanol, max	0.2 % (m/m)
Acid value, max	0.5 KOH/g
Free glycerol, max	0.02 % (m/m)
Total glycerol, max	0.25 % (m/m)
Phosphorus content, max	10 mg/kg

Annexe.3: Examples of parameters in the Japanese specifications standard on FAME for blending purposes. JIS K 2390.



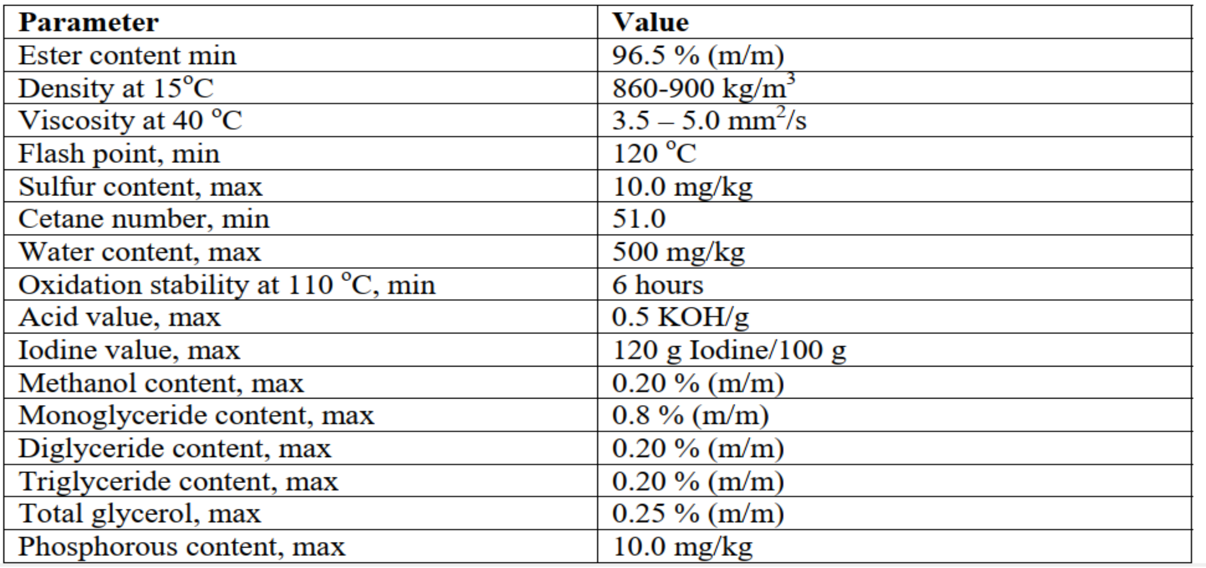
Parameter	Value
Ester content, min	96.5 % (m/m)
Density	0.86 – 0.90 g/ml
Viscosity at 40 °C	3.5 – 5.0 mm^2/s
Flash point, min	120 °C
Sulfur content, max	10.0 ppm
Cetane number, min	51.0
Water, max	500 ppm
Methanol, max	0.20 % (m/m)
Acid value, max	0.5 KOH/g
Mono glyceride, max	0.80 % (m/m)
Di glyceride, max	0.20 % (m/m)
Tri glyceride, max	0.20 % (m/m)
Free glycerin, max	0.02 % (m/m)
Total glycerin, max	0.25 % (m/m)
Phosphorus content, max	10 ppm

Annexe.4: Examples of parameters in ASTM standard D6751 for biodiesel fuel blend stock (B100) for middle distillate fuel.



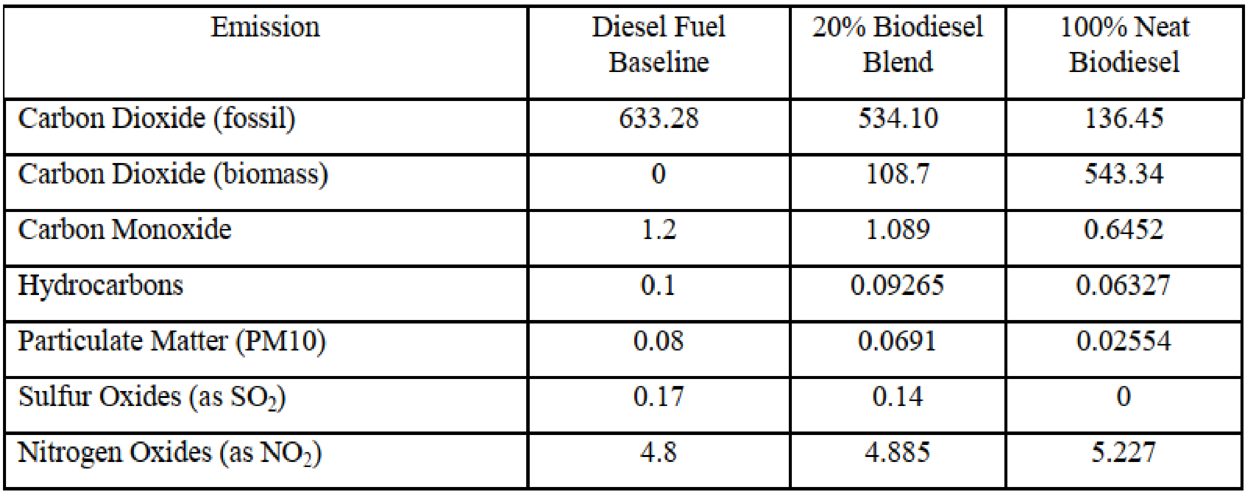
Parameter	Value
Viscosity at 40 °C	1.9 – 6.0 mm^2/s
Flash point, min	130 °C
Sulfur content, max	15.0 mg/kg
Cetane number, min	47.0
Water and sediment, max	0.050 % (v/v)
Oxidation stability at 110 °C, min	3 hours
Acid value, max	0.5 KOH/g
Free glycerol/glycerin, max	0.02 / (m/m)
Total glycerol, max	0.240 % (m/m)
Phosphorus content, max	0.001 % (m/m)
Distillation, 90 % recovered max	360 °C

Annex.5: Examples of parameters in CEN standard EN 14214 – Automotive fuels – FAME for diesel engines – Requirements and Test methods.



Parameter	Value
Ester content min	96.5 % (m/m)
Density at 15°C	860-900 kg/m^3
Viscosity at 40 °C	3.5 – 5.0 mm^2/s
Flash point, min	120 °C
Sulfur content, max	10.0 mg/kg
Cetane number, min	51.0
Water content, max	500 mg/kg
Oxidation stability at 110 °C, min	6 hours
Acid value, max	0.5 KOH/g
Iodine value, max	120 g Iodine/100 g
Methanol content, max	0.20 % (m/m)
Monoglyceride content, max	0.8 % (m/m)
Diglyceride content, max	0.20 % (m/m)
Triglyceride content, max	0.20 % (m/m)
Total glycerol, max	0.25 % (m/m)
Phosphorous content, max	10.0 mg/kg

Annexe.6: Effect of Biodiesel on Tailpipe Emission.



Emission	Diesel Fuel Baseline	20% Biodiesel Blend	100% Neat Biodiesel
Carbon Dioxide (fossil)	633.28	534.10	136.45
Carbon Dioxide (biomass)	0	108.7	543.34
Carbon Monoxide	1.2	1.089	0.6452
Hydrocarbons	0.1	0.09265	0.06327
Particulate Matter (PM10)	0.08	0.0691	0.02554
Sulfur Oxides (as SO_2)	0.17	0.14	0
Nitrogen Oxides (as NO_2)	4.8	4.885	5.227

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Abstract

A biofuel is a hydrocarbon that is made by a living organism that we humans can use to power something. They can be used for any purposes, but the main use for which they have to be brought is in the transportation sector. Biofuels are fuels that are derived from plant material such as soy oil or animal fats. Biodiesel is a liquid biofuel obtained by chemical processes from vegetable oils or animal fats and an alcohol that can be used in diesel engines. In this study, we focused on synthesis of biodiesel by transesterification process with mixing elio oil and each type of six types frying oils with amount of methanol and catalyst KOH. Elio oil contains with 20% of sunflower and 80% of Soybeans. The aim of this study is to reduce high viscosity of Elio oil by transesterification reaction and also showing major characterizations between biodiesel and gasoline according to ASTM and EN standards.

- **Key words:** Biofuels, Biodiesels, oils, vegetables oils, fatty acids, frying oils, gasoline, Transesterification.

Résumé:

Un biocarburant est un hydrocarbure fabriqué par un organisme vivant que nous humains, pouvons utiliser pour alimenter quelque chose. Ils peuvent être utilisés à toutes fins, mais l'utilisation principale pour laquelle ils doivent être apportés est dans le secteur des transports. Les biocarburants sont des carburants dérivés de matières végétales telles que l'huile de soja ou les graisses animales. Le biodiesel est un biocarburant liquide obtenu par des procédés chimiques à partir d'huiles végétales ou de graisses animales et d'un alcool qui peut être utilisé dans les moteurs diesel. Dans cette étude, nous concentré sur la synthèse du biodiesel par processus de transestérification avec le mélange d'huile Elio et de chaque type de six types d'huiles de friture avec une quantité de méthanol et de catalyseur KOH. L'huile Elio contient avec 20% de tournesol et 80% de soja. Le but de cette étude est réduire la viscosité élevée de l'huile Elio par une réaction de transestérification et montrant également les majeures caractérisations entre le biodiesel et d'essence selon les normes ASTM et EN.

- **Mots Clés:** biocarburants, biodiésels, huiles, huiles végétales, acides gras, huiles de friture, essence, transestérification.

الملخص:

الوقود الحيوي هو هيدروكربون مصنوع بواسطة كائن حي دقيق يمكننا نحن البشر استخدامه لتشغيل شيء ما. يمكن استعمال هذه الوقود لعدة الأغراض في حياتنا اليومية، لكن سبب الرئيسي هو القطاع النقل. الوقود الحيوية هي الوقود مشتقة من مواد نباتية مثل الدهون او الشحوم الحيوانية. الديزل الحيوي هو وقود حيوي سائل يتم الحصول عليه عن طريق العمليات الكيميائية من الزيوت النباتية أو الدهون الحيوانية والكحول الذي يمكن استخدامه في محركات الديزل. في هذه الدراسة، نحن ركزنا على توليف وقود الديزل الحيوي عن طريق عملية الأسترة مع خلط زيت إليو وكل نوع من ستة أنواع من زيوت القلي مع كمية من الميثانول والمحفز هيدروكسيد الصوديوم. يحتوي زيت إيليو على 20٪ من عباد الشمس و80٪ من فول الصويا. الهدف من هذه الدراسة هو تقليل اللزوجة العالية للزيت إيليو من خلال تفاعل الأسترة وكذلك إظهار الخصائص الرئيسية بين الديزل الحيوي والبنزين بالنسبة للمعايير الاتحاد الأوربي والجمعية الأمريكية للاختبار والمواد.

الكلمات المفتاحية: الوقود الحيوي، الديزل الحيوي، الزيوت، الزيوت النباتية، الأحماض الدهنية، الزيت المقلي، الوقود، الأسترة.