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**Valorization of Pine Plant
(Biodiesel Synthesis)**

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وَفِي السَّمَاءِ رِزْقُكُمْ وَمَا تُوعَدُونَ ﴿٢٢﴾

Dedication

Benhelal Amani

I dedicate this modest work to my parents, my wonderful mother S. Abouismail and my dear father Benhelal Belkhir who have provided me with all the love and care of the world, and who have been supportive all the way in my endeavor to accomplish my Dreams. I want you to know that everything I do, I do it for you.

To my sister Mouna for her support and sacrifice for me

To my brothers Yahia and Mouhamed.

To my husband Sifeddine for all his support.

To my grandmother Arem and Fatimazohra and all my family

To my dear friends in particular my friends Safa ,Fatima, Sabrina, Oumelkhir and Ikhlas.



Chebboub Safa

The story ended and I lifted my hat farewell to the years that passed. I dedicate my graduation to my honorable parents, my mother, Mabrouka, and my father Mohammed Bachir, who supported me in my academic career. Thanks to them, I stand today in this beautiful and honorable position. Thanks to my brothers Hicham, Saifeddine, Rabie, Yasser, Ali and my Dear sisters Dounia and Hadil. My brother's wife, Nassima ben mouaffak, my nephew Moataz and my best friend Amani benhelal. Thank you to everyone who taught me a letter.

Thanks

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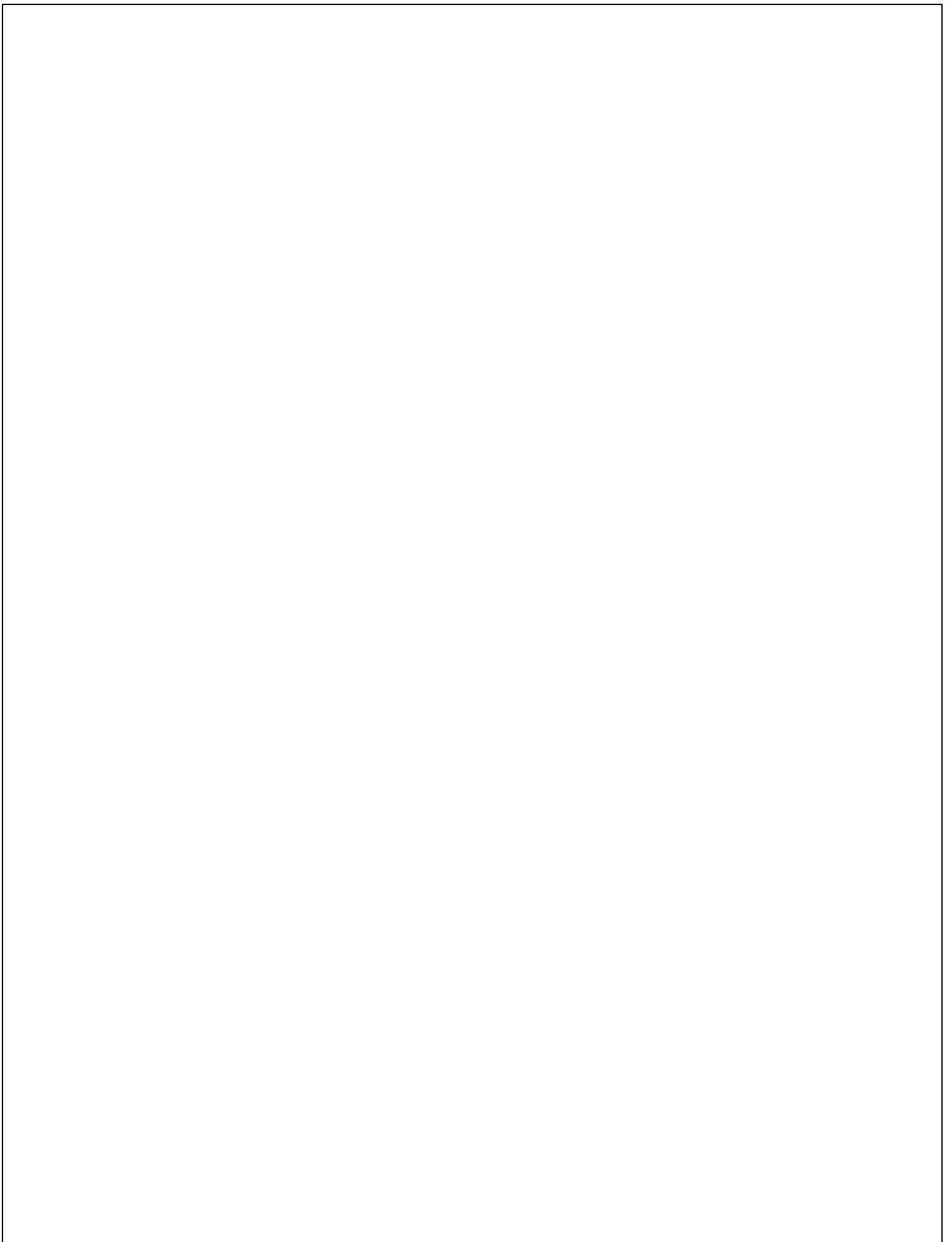
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General Introduction



General Introduction

The world is thinking about how to meet its energy needs in the future, with the decline in global oil reserves and the instability of oil prices. Production begins to gradually decline. Re-warming must be combated by reducing emissions harmful to the environment.

Greenhouse gases are a new stimulus in the search for new fuels. Alternatives that can reduce dependence on oil. Different types of biofuels. It can be produced from biomass, such as ethanol from sugar, starch or cellulose, biodiesel from vegetable oils.

Pyrolysis and synthesis gases from wood, agricultural waste and hydrogen. Microorganisms that also decompose water into hydrogen and oxygen. Methane produced by the anaerobic digestion of organic matter, in recent decades. Biodiesel production has received global attention [1].

Biodiesel is a renewable biofuel made from raw materials of animal and plant origin that is biodegradable and non-toxic (it does not contain sulfur and aromatic compounds) and produces fewer emissions compared to fossil fuels when burned. It is alkyl esters of fatty acids (Methyl Ester, Ethyl ester) [2].

Biodiesel fuel reduces greenhouse gas emissions in the atmosphere and does not take thousands of years to produce unlike fossil fuels. Biodiesel can also be used in many diesel vehicles without making major modifications to the engine. More than 40 countries are currently producing biodiesel, led by the United States, followed by Germany, then Argentina, then Brazil and Indonesia in fifth place. There is no Arab country in this list [3].

In recent years, biodiesel fuel has raised a lot of controversy, as the latter was produced in several previous studies that differed in the raw material, i.e. the source of triglyceride extraction. Its development led to the emergence of several generations.

The first generation is that the raw material is from crops directly from the fields such as grains, corns and rapeseeds [4].

In 2014, sweet almond oil and groundnut oil were used by **Giwa** and **Oniya** respectively, depending on transesterification and base catalysts (NaOH_KOH) and yields (sweet almond oil

85.9%) and (groundnut oil 86.8%) [5]. In 2016, coconut oil was used to produce biodiesel to obtain a yield of (49.8%) [6]. **Kareem et al** in 2017, also reached a yield of (95.3%) [7]. Whereas in the year 2018, **Ayodji et al** (soybean oil) and **Eboibi et al** (jatropha oil) were used, with yields of (97.1%, 45%) respectively [8]. In 2019, **Dagde** used avocado seed oil, where it reached a yield of 78% [9]. The promotion of the first generation of biodiesel caused problems in the interaction with human food-chains including balancing supply and demand, land use and water management. Do not compete with food production [10]. The second generation of biodiesel comes from lignocellulosic materials to municipal solid waste. It is the woody part of plants that does not compete with food production [5]. It was followed by the third generation derived from microalgae as a viable alternative energy source free from the major barriers associated with first generation and second generation biofuels [11].

Several methods have been relied upon in the manufacture of biodiesel, including direct blending, pyrolysis and micro-emulsion, and the most common method is transesterification [12].

In the esterification of different types of oils, the triglycerides react with the alcohol. Generally methanol or ethanol to produce esters and glycerol. To make this possible, a catalyst is added to the reaction. The overall process is usually a series of three consecutive steps, which are reversible reactions. In the first step, diglycerides are obtained from triglycerides, monoglycerides and diglycerides are produced and in the last step, monoglycerols are obtained. In all of these reactions esters are produced. The relationship between alcohol and oil is 1:3. However, an excess of alcohol is usually more favorable for improving the reaction to the desired product (1:3, 1:6, 1:9, 1:12) [13].

Among the catalysts that were used in previous studies (alkali catalyzed, acid catalyzed, enzymatic, supercritical) [14].

In this study, pine seed oil was chosen for the production of biodiesel, as pine is considered one of the trees rich in oils that can be extracted from several parts of needles - cones - seeds and twigs.

It is also taken into account the ease of extraction so that it does not need expensive technologies and methods. Pine has the property of survival and long life and resistance to environmental conditions. Pine trees are among the most famous species of plants in the world. It is a family

consisting of 250 species of woody plants that produce seeds. It is also one of the most widespread trees in the world and is found throughout the northern hemisphere.

It is known that the pine tree has extracts that contain essential oils and many chemical compounds (Terpenoids - tTerpenes ... etc.) [15]

The public aspires to reach 100% sulfur-free biodiesel fuel, so we decided to conduct this study, starting with the extraction of pine seed oil by two methods (hydrolic extraction and soxhlet extraction) and comparing them, then moving to the stage of esterification of the oil extracted from these seeds by Bio alcohols and bio catalyzed And the comparison between it and the usual alcohols ethanol and methanol and catalysts (NaOH-KOH) in terms of yield and physical and chemical properties.

In this research, we aim to value the pine plant in the field of energy and industry by extracting its oils from the seeds and converting them into biofuel 100% free of sulfur. We used pine seed oil because it is not widely used in the field of nutrition, which makes it suitable for use in the field of industry.

The first chapter: a bibliography that contains a study on pine nuts and vegetable oils, and finally a theoretical study on biofuels in general and biodiesel and bioethanol in particular.

The second chapter: an experimental study in which we explain the methods used to extract pine oil and study the physicochemical properties of the latter and finally biodiesel synthesis from pinus oil.

The third chapter: results and discussion, where we analyze and discuss the obtained results.

CHAPTER I

Theorecal study

I.1. Study of the plant

I.1.1. Origine and spread

Pine of Jerusalem, White pine (Provence), Aleppo Pine, Pino carrasco, Aleppo Kiefer, Sanaoubar halabi (Syrie, Liban). This Pin was first described by DUIIAMEL in 1755 as *Pinus Heirosolimitana*. MILLER later rewrote it in 1768 as *Pinus halepensis* Mill, and it was retained by all botanists [16].

Pinus halepensis species belonging to the *Pinaceae* family and is the most widely distributed pine in this region. Where it covers more than 25,000 km² (Maestre et al., 2003). The main Aleppo pine forests are found in Spain, France and North Africa (Raeda and Arianoutsou, 2000) especially in Algeria and Tunisia where they constitute a clump (Nahal, 1986) [17].

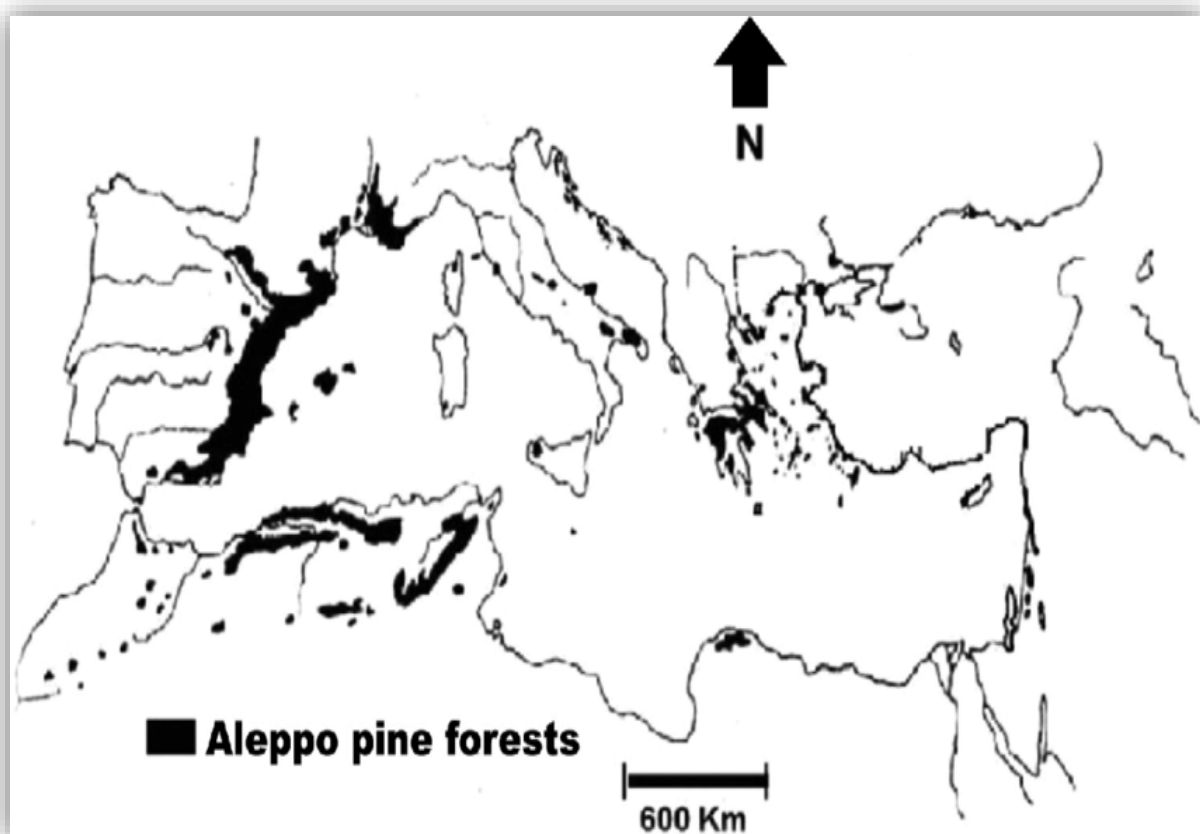


Figure I.1: Aleppo pine forests spread

I.1.2. The distribution of Aleppo pine in Algeria

Aleppo pine occupies 35% of Algeria's forest area and it covers 850,000 hectares [18].

It spreads mainly in the northern part of the country. It occupies vast areas in the Tebessa region, the Plateau of Constantinois and the Aures region. From Algiers (Forest of Medea), the west of the Sahara Atlas (SidibelAbbes, Saida, Tlemcen, Tiaret, Warsenis) (Monts de Ouleds Nails) [19].

I.1.3. taxonomic classification

The family Pinaceae (Pinaceae), is a family of gymnosperms, distributed throughout the world and mainly around the Mediterranean coasts. It is divided into three subgenera and the subgenera into sections [16].

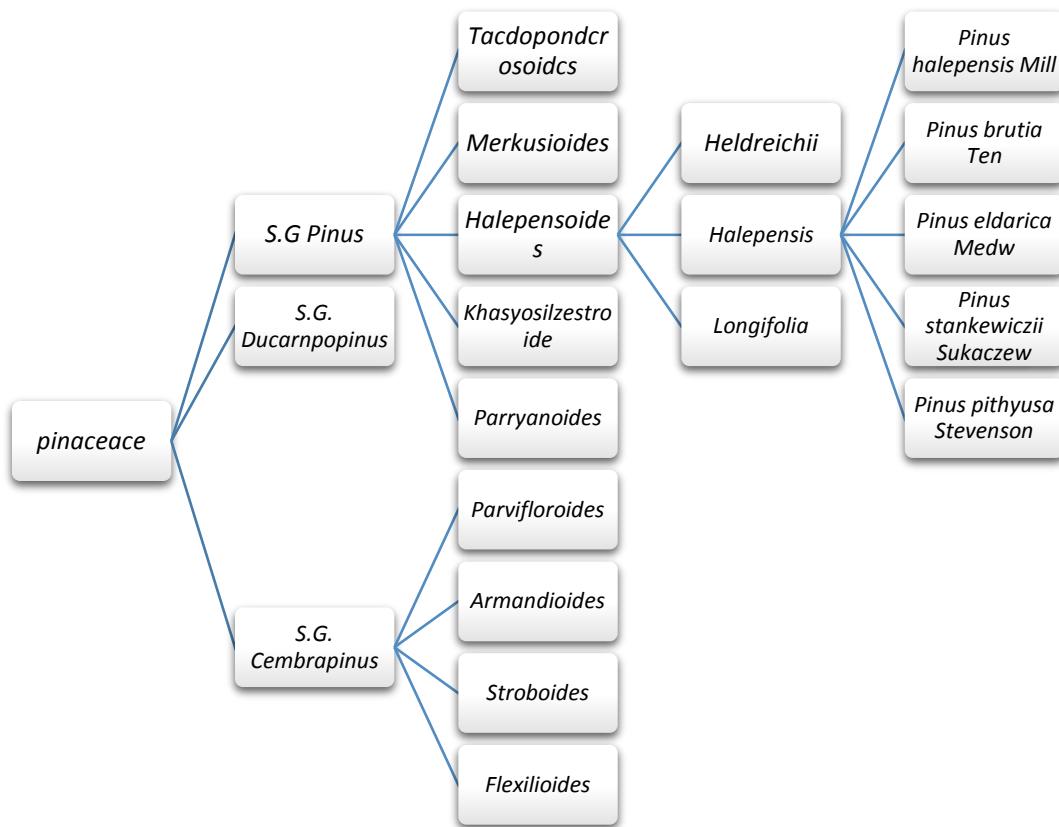


Figure I.2: Systematic position of *pinus halepensis Mill*

Table I.1: Classification of *Pinus Halepensis* Mill

Kingdom	Plantea
Phylum	Spermaphyte
Sous-phylum	Gymnosperme
Class	Coniférophyte
Ordre	Coniférale, Pinoidine, Pinale
Familly	Pinaceae (Abietaceae)
Sous-familly	<i>S.G Pinus</i>
Genus	<i>Halepensis</i>
Scientific name	<i>Pinus halepensis</i> Mill

I.1.4. Botanical description

Aleppo pine (*Pinus halepensis*) of the pine family. It is sometimes called “Jerusalem pine” or “white pine” [20]. It is a tree that grows spontaneously on the edge of the Mediterranean basin. The trunk is twisted and shaped like a parasol. Its gray bark cracks with age. Its needle-like leaves are slender, soft, smooth, 6–10 cm long [16], and the leaves are clustered in pairs at the ends of the branches and are initially yellowish green, which is accentuated with age. Its reproductive organs are male and female cones, which are separate but on the same tree. The female cones are 8–12 cm long and remain on the branch for several years. Its abundant seeds are about 5 mm long and have large, persistent wings that allow them to disperse quickly and over a wide area.

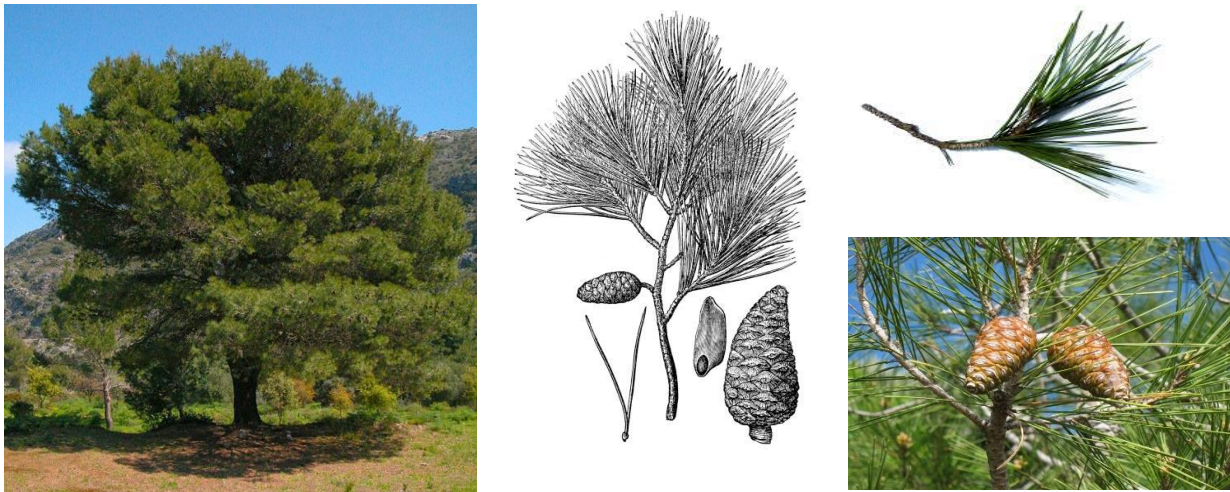


Figure I.3 :Photos of *Pinus Alepensis* Mill tree and their parts

I.1.5.Uses and applications

economic uses	Aleppo pine Pure gum contains 20-24% turpentine and 75-80% cellophane . it yields about 3 kg of resin per tree per year [19]. It is used for timber, furniture, and amber, wood and telegraph poles. [21].
Ecological uses	It is a forest species of primary importance , it is used in programs of reforestation of degraded soils in the Mediterranean basin, case observed in the south of Algeria « green belt » [22].
Edible and therapeutic use	Pinushalepensis has long known therapeutic virtues; its needles, buds and resin are used in traditional medicine as an antiseptic and antirhumatismal, antidiabetic [23]. A black or brown oily and viscous product known as tar is also extracted from wood and is intended to treat several skin conditions for both humans and domestic animals [21].
It contains several biological activities	P. halepensis extracts are rich in secondary metabolites such as terpenoids, essential oils, terpenes and phenolic compounds [24. 26]. Essential oils extracted from the leaves and cones of Aleppo pine have an anti-inflammatory activity and Antibacterial, antioxidant, antifungal and herbicide activities as well as a wound healing effect [27 .30].

I.2. Vegetable oils

I.2.1.what is vegetable oil

Vegetable oils are triglycerides usually derived from plants. Vegetable oils have been used by people for centuries room temperature vegetable oils are liquids made up of triglycerides [31].

Many parts of the plant can provide the oil, and the oil is extracted mainly from seeds (Corn, fruit, Peanuts, olive trees, canola, castor beans, soybeans, sunflowers.....)[32].

Vegetable oil is a substance that does not dissolve in inorganic solvents. The main ingredient is triglycerides, which is called an ester of fatty acids [33]. Structurally, triglycerides are a glycerol molecule is made up of three acid molecules monocarbons with hydrocarbon chains called fatty acids.

I.2.2. Chemical composition of vegetable oils

Vegetable fats are essentially composed of fatty acids represented by triglycerides. To these fatty acids are added other non-glyceride components, also called minor components or free fatty acids, and unsaponifiables

I.2.2.1. Lipids

There are two types of lipids:

❖ Simple lipids

They are essentially composed of triglycerides (accumulation of fatty acids and glycerol) [34]. Free fatty acids Hydrolysis of triacylglycerols [35] their derivatives It can also be obtained by the action of enzymes (lipases) on phospholipids. Also note the presence of diglycerides and monoglycerides in the oil.

❖ Complex lipids

These are lipids that in addition to carbon, hydrogen, and oxygen are either sulphur, phosphorus or oxygen. The containing phosphorus are called phospholipids.

These are large molecules unlike small free fatty acids.

I.2.2.2. Triglycerides

Triglycerides, which account for more than 95% by weight of crude fats and oils and more than 98% by weight of refined fats and oils, are a combination of one molecule of triol (glycerol) and three molecules of fatty acid. Each fatty acid molecule (R-COOH) has an acid functional group (-COOH). Triglycerides are produced in condensation reactions between one molecule of glycerol and three fatty acids.

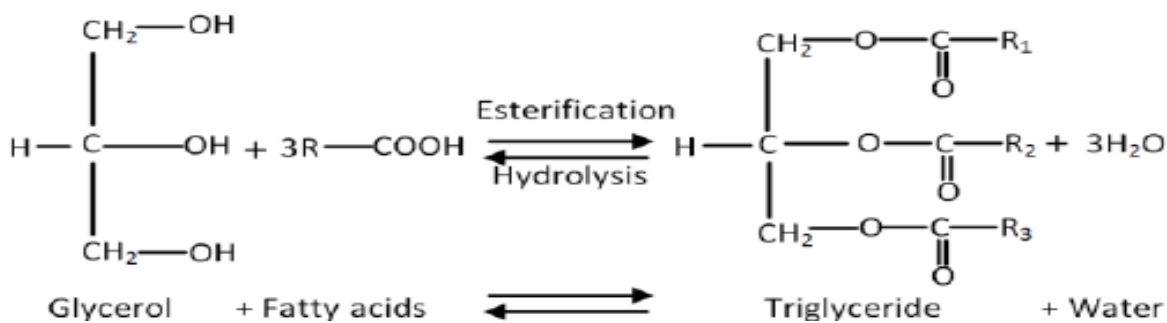


Figure I.4: Triglyceride formation reaction

I.2.3. Classification of fatty acids

Depending on the degree of carbon chain establishment

The number of double bonds determines her three groups of fatty acids.

S. Saturated fatty acids (SFAs)

In a saturated fatty acid each carbon atom has its 4 valences engaged in bonds with other atoms of 20 carbon or hydrogen (or oxygen for the carbon of the Carboxyl group)

b. Mono-unsaturated fatty acids (MFAs)

These are fatty acids in which two adjacent carbon atoms in the chain each have a free, unsaturated valence, which they pool so that two carbon atoms are joined together by a double bond. (palmitoleic acid (C16) and oleic acid (C18)).

c. Polyunsaturated fatty acids (PUFA)

It is the fatty acids at 18, 20, and 22 carbon atoms that present in their chains two or more double – bonds separated by a methylene group (CH₂).

(linoleic acid (18:2), linolenic acid (18:3) and arachidonic acid (20:4))

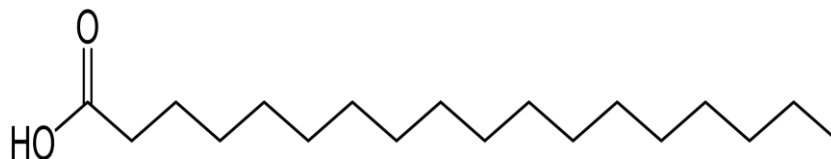


Figure I.5: Stearic fatty acid C₁₈H₃₆O₂

I.2.4. Oil extraction Techniques

Three main methods have been identified in oil extraction, mechanical extraction, solvent extraction and enzymatic extraction.

Mechanical press and solvent extraction are the most commonly used methods in vegetable oil extraction.

A/ Mechanical presses

This technique can use a manual piston press or an electric screw press. Are found that an electric screw press can extract 68-80% of that ram press only reached 60-65% This wider range indicates that seeds receive varying numbers of extractions by expeller. The oil extracted by mechanical presses needs further treatments like filtration and gum removing. Another problem associated with traditional mechanical presses is that their design is suitable for some particular seeds, and the oil yield is affected for other seeds [36..38]

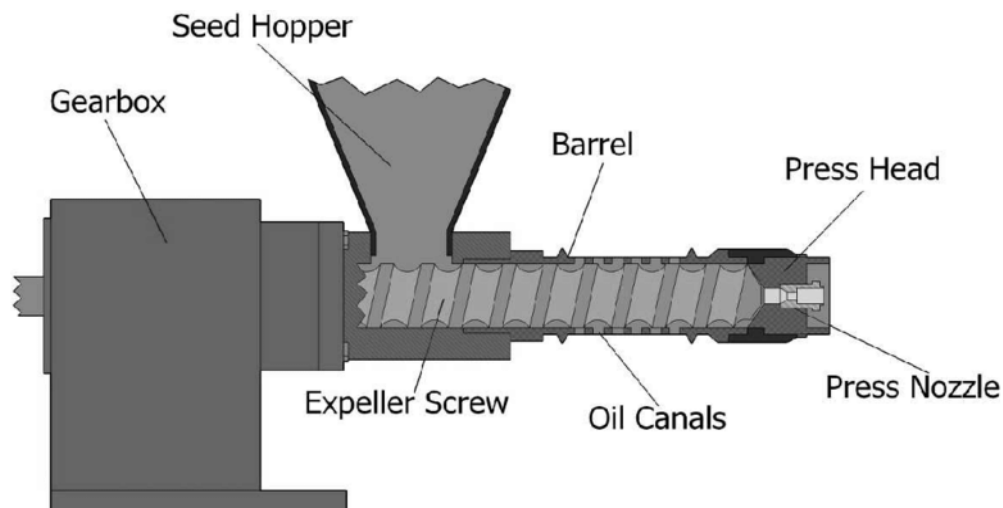


Figure I.6: Press Hydraulic Extrction

B/ Solvent extraction technique

Solvent extraction is the technique of removing one constituent from a solid by means of a liquid solvent. It is also called leaching. In this process, a chemical solvent such as n – hexane is used to saturate the crushed seed and pull out the oils. After completion of the extraction process the solvent is condensed and reclaimed [39]. There are many factors influencing the rate of extraction such as particle size, the type of liquid chosen, temperature and agitation of the solvent. The small particle size is preferable as it allows for a greater interfacial area between the solid and liquid. The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to circulate freely. Temperature also affects the extraction rate. The solubility of the material will increase with the increasing temperature. Agitation of the solvent also affects, it increases the eddy diffusion and therefore increases the transfer of material from the surface of the particles there are three methods that are used in this type as fellow [36.38].

- **Hot water extraction**

In this method water bath used for extraction of the oil. The crushed seeds are mixed with the solvent and taken in a beaker, which has incubated in the water bath at a fixed temperature for fixed period of time. Agitation provided externally for same period of time. After completion of the desired time interval, the beaker has allowed to stand at room temperature. The heavier crushed seeds settle down in the beaker and clear mixture of oil and hexane has separated by filtration process. The mixture of solvent and oil, taken in a round – bottomed flask has kept on the hot plate

/ heating mantle. The flask has fitted to the distillation apparatus. Because the solvent has a lower boiling point than the oil, it gets evaporated leaving behind oil in the flask. The solvent gets condensed back and has thus reclaimed. The advantage of this process is that, it has taken lesser time than soxhlet apparatus. The disadvantage of this process is that, it requires filtration and recovery of solvent lesser than the soxhlet apparatus [39].

- **Soxhlet extraction**

In comparison to water bath, improved oil yields were obtained using an ingenious device called a Soxhlet apparatus. This apparatus allows extraction of oil from the seed samples using the distillation extraction method. In the Soxhlet apparatus (also called extractor, or chamber), the sample soaks in hot solvent that is periodically siphoned off, distilled and returned to the sample. The process continues until the siphoned – off solvent becomes clear. The advantage of soxhlet apparatus over hot water extraction is that, there is no filtration necessary and oil yield is better than hot water extraction process. Hexane is the solvent most commonly used in the solvent extraction technique because of its relatively low cost and low toxicity. Other organic solvents such as benzene, alcohol, chloroform may also be used. Water as a solvent was evaluated to extract oil from soybean, but gave low yield and high potential of oil microbiological contamination [39].

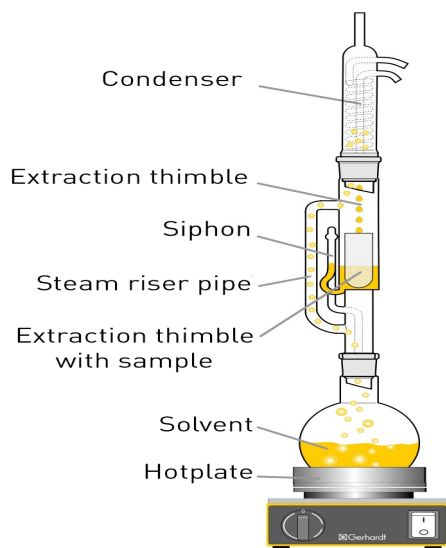


Figure I.7 : Soxhlet Extraction

C/ Ultrasonication technique

In this process an ultrasonic water bath has used. A flask or a test tube containing the crushed seeds and solvent has partially immersed in the bath. This has then subjected to ultrasonic vibrations. Ice may be added to prevent the apparatus from overheating. Colloid formation has an indication of extraction of oil from the seeds in the solvent. This method depends upon the surfactant solution. Operating temperature and degassing of the solution [39].

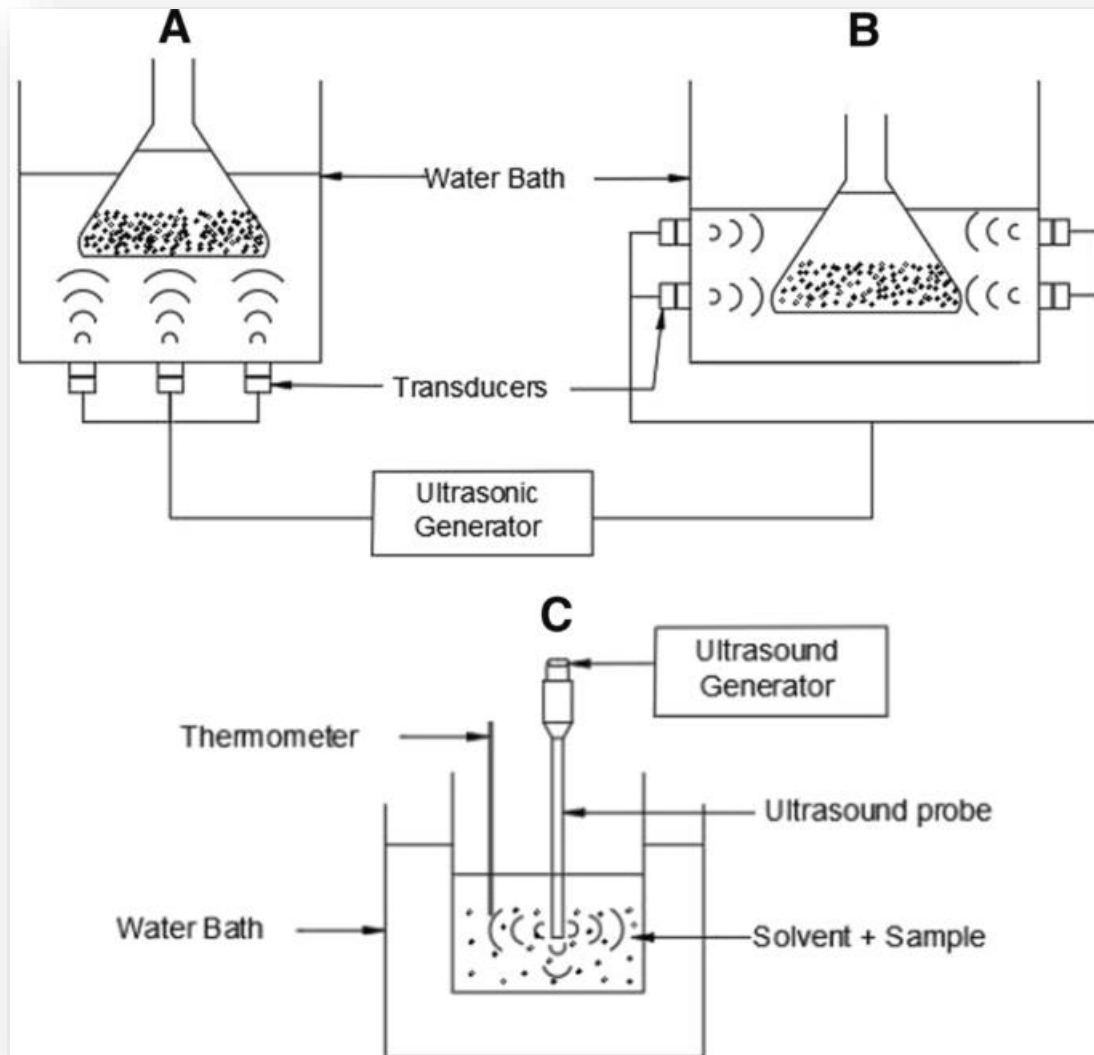


Figure I.8 : Application of Ultrasound and Ultrasound Assisted for Seed Oil Extraction

D/ Enzymatic oil extraction

Enzymatic oil extraction technique has emerged as a promising technique for extraction of oil. In this process suitable enzymes are used to extract oil from crushed seeds. Its main advantages are that it is environment friendly and does not produce volatile organic compounds. However, the long process time is the main disadvantage associated with this technique [37].

I.2.5. Physicochemical characteristics

Different physical and chemical parameters of oils were used to monitor the compositional quality of oils. These physicochemical parameters include iodine value (IV), saponification value (SV), viscosity, density and peroxide value (PV).

✚ Acid value

Acid number (AV) is an important indicator of vegetable oil quality. AV is expressed as the amount of KOH (in milligrams) required to neutralizing free fatty acids in 1.0 g of oil. However, free fatty acids (%FFA) are weight percent of a particular fatty acid, such as percent Oleic acid in oil. Therefore, acidity is a good indicator of oil Hydrolytic or enzymatic degradation. Acid number measurements are often used as a general indicator of oil condition and edibility. This is because with increasing acidity comes unpleasant tastes and odors. A low acid number in oil indicates that it is stable protects against rancidity over the long term, peroxide [40].

✚ Peroxide value

Peroxide value is used as a measure for the degree of rancidity reaction occurs during storage and this is the case used as an excellent standard for predicting quality, Oil stability [41]. High peroxide levels a high level of unsaturation may be the culprit. This causes oxidative rancidity [42]. With increasing storage time, temperature, light, etc and Exposure to atmospheric oxygen [43].

✚ Saponification Value

Saponification value is an indication of the size or nature of fatty acid chains esterified to glycerol. And gives a measure of the average length of the fatty acid chain that makes up a fat[44]. In combination with acid values, saponification values are useful in providing information as to the quantity, type of glycerides and mean weight of the acids in a given sample of oil. The lower value of saponification values suggests that the mean molecular weight of fatty acids is lower or that the number of ester bonds is less. This might imply that the fat molecules did not interact with each other [45].

✚ Iodine value (IV)

Iodine number” or “iodine index”) in chemistry is the mass of iodine in grams that is consumed by 100.0 of unsaturation contained in fatty acids. This unsaturation is in the form of double bonds which react grams of a chemical substance.

Amount with iodine compounds . (IV) measures the degree of unsaturation in a fat or vegetable oil. It determines the stability of oils to oxidation, and allows the overall unsaturation of the fat to be determined qualitatively [46].

✚ Refractive index (RI)

Refractive index plays an important role in many fields of physics, biology, and chemistry [47]. The refractive index of fats and oils is sensitive to composition. In fat, RI increases with increasing triglyceride fatty acid chain length, or with increasing unsaturation. This makes it an excellent spot test for fat compositional uniformity [48].

✚ Viscosity

Oils are mixtures of triglycerides (TGs) and their viscosity depends on the nature of the TGs present in the oil. The viscosity changed due to the different arrangement of the fatty acids on the glycerol backbone of the triglyceride molecule. The oil viscosity has a direct relationship with degree of unsaturation and chain length of the fatty acids in lipids. Its value increases with increasing degree of saturation [49] .Viscosity also depends on sheer stress and temperature.***

✚ Density

The density of a material or liquid is defined as its mass per unit volume.

✚ GC/MS analysis of oil

GC/MS has long been used for the selective analysis of non-polar compounds. The carboxylic fatty acids require prior hydrolysis from their glycerolipid sources and derivatization to a respective ester form for separation on capillary chromatographic columns. The detection of structural molecular ions generated from the MS source provides more sensitive and selective assay of varied arrays of fatty acids present in lipid samples. Fast quadrapole technology present in most modern mass spectrometers facilitate for selective ion monitoring with simultaneous full scan capabilities. This allows selective quantitation of molecular specific ion peaks while retaining a full mass spectrum of each peak for interpretation, confirmation or library searching.

I.3. Biofuels

I.3.1. Biofuels definition:

With world energy consumption predicted to increase by 54% from 2001 to 2025, primary attention has been directed toward the development of carbon-neutral energy and sustainable sources to meet future needs [8]. A biofuel is a type of fuel that derives its energy from biological carbon fixation and it is an attractive substitute to current petroleum-based fuels. Biofuels are fuels produced directly or indirectly from organic matter (biomass), including plant and animal waste. Biofuels can also be obtained from forests, agricultural products, municipal waste, and by-products and waste from agribusiness, the food industry.

There are two main types of biofuels produced today from plant-based feedstocks on a large scale. Liquid (butanol, biodiesel, and ethanol) or gaseous (methane, hydrogen).

Biofuels can be added directly to conventional fuels in variable amounts without special engine tuning. Also, it is not a complete replacement for oil. Beyond a certain threshold, their development competes with the need for food.



Figure I.9: Biofuels Generations

1. First-generation biofuels

First-generation biofuels are produced from food crops such as corn and wheat, sugar, starch, and vegetable oil. It makes up the majority of the biofuels used today.

Biologically produced fuels such as ethanol, propanol, and butanol are produced by the action of microorganisms and enzymes through the fermentation of sugars or starches, or cellulose. First-generation biofuel processes are useful but there is a threshold above which they cannot produce enough biofuel without threatening food supplies and biodiversity. Many first-generation biofuels are dependent on subsidies and are not cost-competitive with existing fossil fuels such as oil, and some produce only limited greenhouse gas emission savings. Considering emissions from production and transport, life cycle assessment from first generation biofuels frequently exceed those of traditional fossil fuels [50].herefore, there is a need to move away from relying on first-generation biofuels because their feedstock would otherwise be human food [51].

2. Second-generation biofuels

These biofuels can be manufactured from different types of biomass as it defines any source of organic carbon. This can be renewed rapidly as part of the carbon cycle. Second-generation biofuel technologies have been developed because first-generation biofuel manufacture has important limitations [52]. Second-generation biofuels can solve these problems and can supply a larger proportion of biofuel sustainably and affordably with greater environmental benefits. The goal of second-generation biofuel processes is to extend the amount of biofuel that can be produced sustainably by using biomass.

Specifically, biomass is the residual nonfood parts of current crops, such as stems, leaves, and husks, that are left behind once the food crop has been extracted.

Furthermore, other kinds of crops that are not used for food purposes, such as switch grass, wheat straw, cereals, etc. that bear little grain, can also be extracted [53].

3. Third generation biofuels

Third generation of biofuels which are derived from marine biomasses [51,52]. Third generation biofuels derived from microalgae are considered to be a viable alternative energy resource that is devoid of the major drawbacks associated with first and second generation biofuels. Microalgae are able to produce 15–300 times more oil for biodiesel production than traditional crops on an area basis. Furthermore compared with conventional crop plants which are usually harvested once or twice a year, microalgae have a very short harvesting cycle (\approx 1– 10 days depending on the process), allowing multiple or continuous harvests with significantly increased yields .

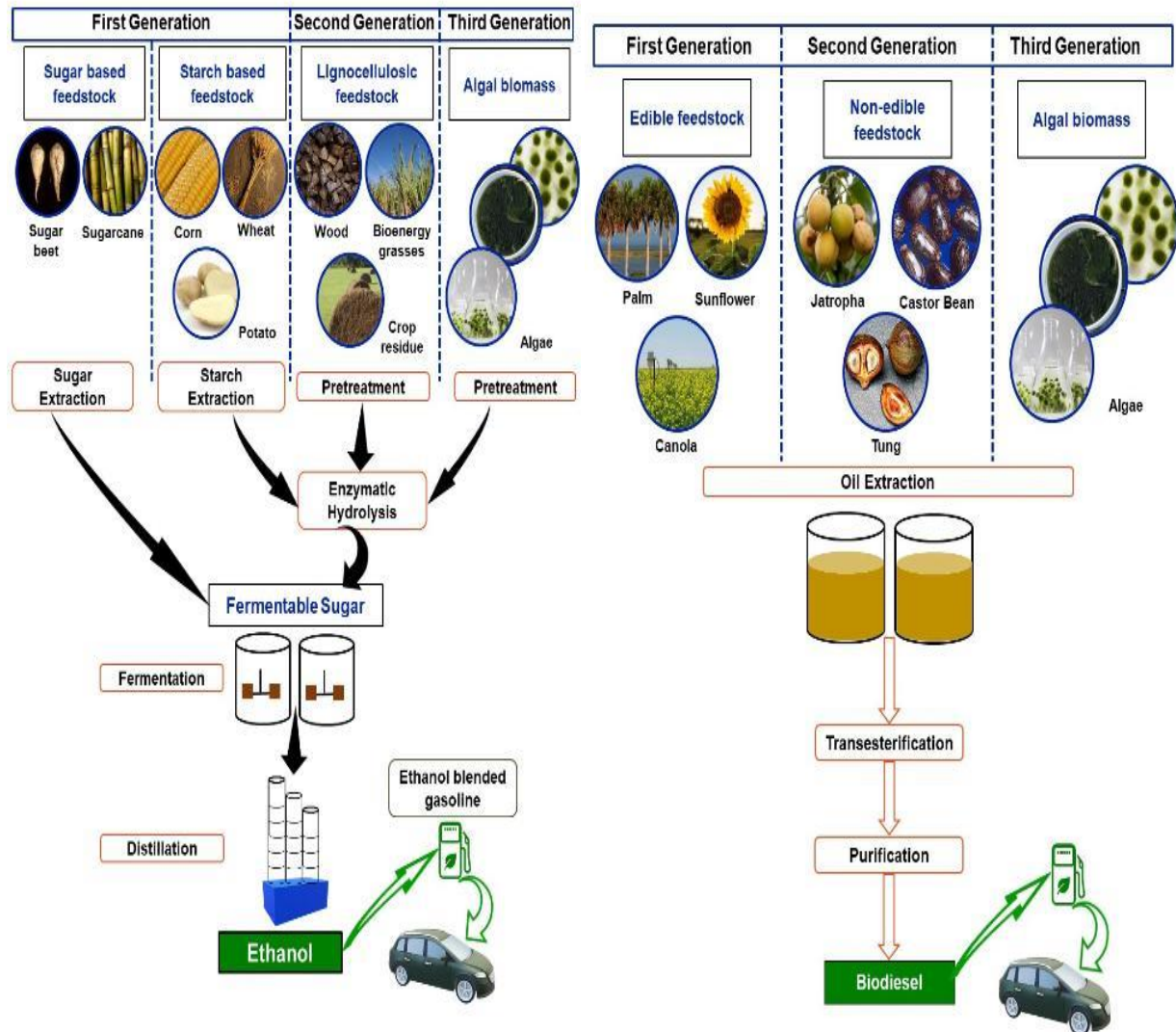


Figure I.10: Biodiesel and Bioethanol Across the Three Generations

I.3.2. Bioethanol

Bioethanol is created from biomass by fermenting sugary substances (including sugar, starch, and agricultural and municipal waste). Because it makes a way for mixed fuels in an engine, it is regarded as one of the most significant strategies to minimize both the consumption of crude oil and environmental pollution [60]. Given that it differs from gasoline in terms of its qualities, the created bioethanol can be utilized directly as a substitute for gasoline in engines [54].

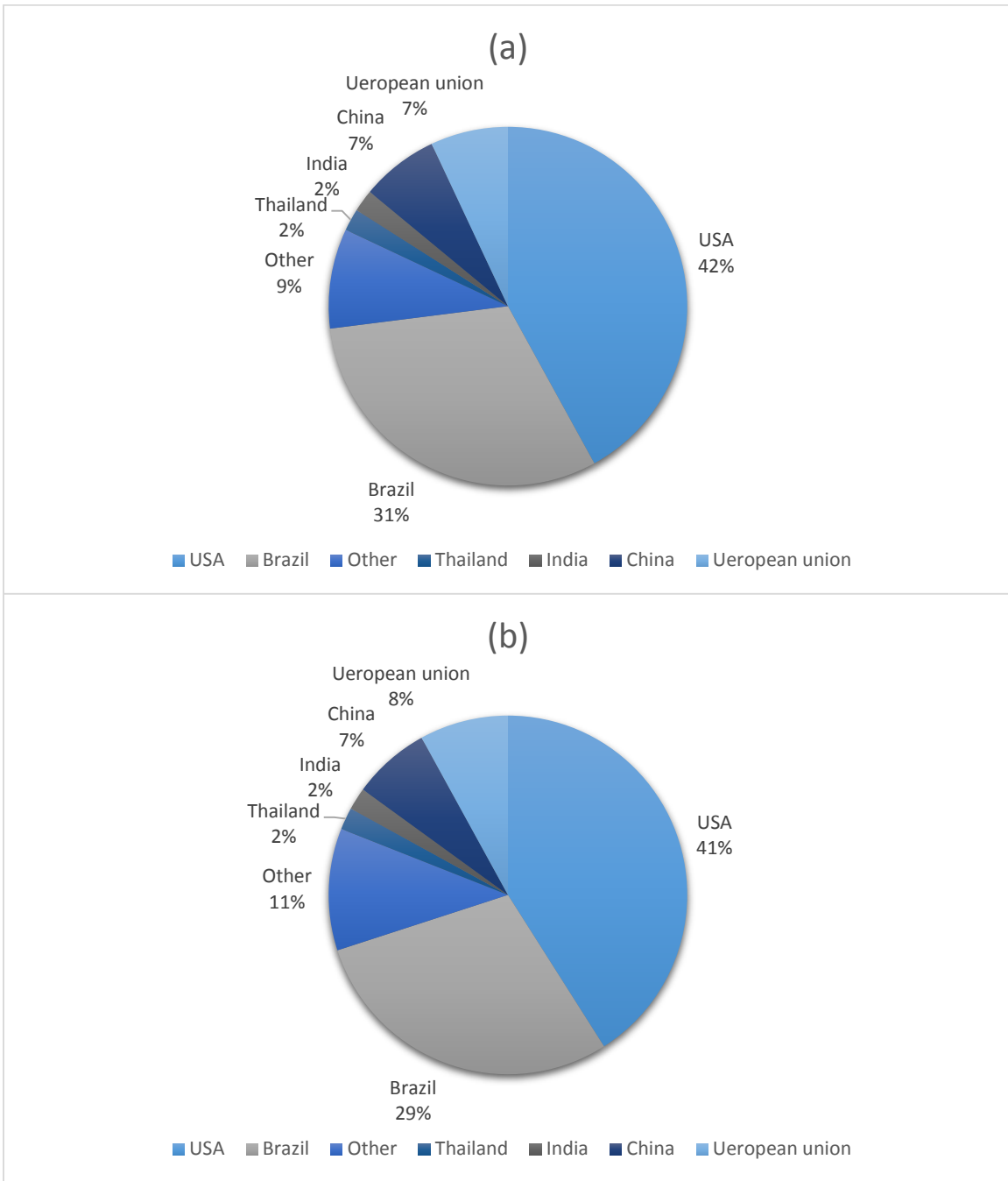


Figure I.11 : Predictions of the world bioethanol production (a) and consumption (b) [55]

I.3.3. Biodiesel

Biodiesel is product made from renewable organic materials, mainly replacing petroleum derivatives of fossil origin and therefore non-renewable [56].

Chemically, biodiesel consists of methyl (or ethyl) esters of fatty acids. Biodiesel is produced by a chemical process the esterification of fatty acids produced from vegetable oils [57].

Practically all diesel engines can run on biodiesel or blend of biodiesel with normal diesel [56] .

Property	Units	Diesel		Biodiesel (B100)	
		ASTM D975	EN 590	ASTM D6751	EN 14214
Density @ 15°C	kg/m ³		820–845		860–900
Kinematic Viscosity @ 40°C	mm ² /s	1.3–4.1	2–4.5	1.9–6.0	3.5–5.0
Cetane Number, Min.	–	40	51	47	51
Distillation temperature	% vol. recovered	90%: 282°C–338°C	85%: 350°C max	–	–
Ester content		5% vol. max	5% vol. max	–	96.5% min
Ash content, Max.	% wt	0.01	0.01	–	–
Sulfur Content, Max.	% mass	S500: 0.05% S5000: 0.50%	50 mg/kg 10 mg/kg	S15 15 ppm S500 0.05%	10.0 mg/kg
Flash Point	°C	60–80	Min. 55	100–170	Min. 120
Cloud Point	°C	–	Report	Location & season dependent	Location & season dependent
Cold Filter Plugging Point	°C	–	–	Location & season dependent	Location & season dependent
Lubricity, Max.	µm	520	–	460	–
Water and sediment, Max.	vol.%	0.05		0.05	
Water Content, Max.	mg/kg	–	200	–	500
Acid Value, Max.	mgKOH/g	–	–	0.5	0.50
Copper strip corrosion, Max	–	No. 3	Class 1	No. 3	Class 1
Carbon residue on 10% distillation residue, Max.	wt. %	0.15-0.35	0.3	0.05	–
Oxidation stability	–	–	25 g/m ³ max	Min. 3 h	Min 8 h
Iodine Value, Max.	g I ₂ /100g				120

Figure I.12: Difference Between the Characteristics of Diesel and Biodiesel

i. Transesterification

Transesterification is the process by which triglycerides (oils or fats) are broken down into methyl or ethyl esters, the renewable biodiesels, using alcohol, typically methanol or ethanol. This procedure can be carried out with or without an acid- or alkali-based catalyst. Transesterification is a series of three reversible processes (Equations (1)–(3)) that result in the formation of diglyceride, monoglyceride, and glycerine. For every alcohol molecule used in each reaction step, one ester molecule is produced. In order to create 3 moles of alkyl esters and 1 mole of glycerol as

a byproduct, the reaction requires 1 mole of triglyceride and 3 moles of alcohol, as given in Equation (4).

However, in practice, too much alcohol is added to complete the conversion and to boost the yields of alkyl ester (biodiesel) by altering the reaction equilibrium in favor of esters. Furthermore, the surplus alcohol enables the phase separation of glycerol and biodiesel [58].



Alcohols used in Biodiesel production

Methanol, ethanol and butanol are examples of short-chain alcohols that can be used in the synthesis of biodiesel. Because of their affordability and usefulness, methanol (CH₃OH) and ethanol (C₂H₅OH) are the most often utilized alcohols. Despite its high toxicity, methanol is frequently chosen to ethanol for the manufacture of biodiesel due to its easier technology requirements, ability to recover surplus alcohol at a low cost, and faster reaction rates. It must be kept in mind that for biodiesel to qualify as a totally renewable fuel, it must be made from animal and vegetable fats along with an alcohol derived from biomass, such as bioethanol, rather than being a petrochemical. Several nations, including Spain and Brazil, are conducting research to achieve this goal. This is what our study aims at.

Table I.2 :Vegetable oils used in biodiesel

	<i>References</i>	<i>Method</i>	<i>Yield</i>	<i>Catalyst/Temp. oC</i>
<i>RBD Plam Olein</i>	(Felix et al., 2020)	TE	62.5%	KOH 65 °C
<i>Palm Oil</i>	(Kareem et al., 2017)	TE	95.3%	Lipase 40 °C
<i>Palm Kernel Oil</i>	(Akhabue and Ogogo, 2018)	TE-Opt	94.6%	CaO 60 °C
<i>Coconut Oil</i>	(Musa et al., 2016)	TE	49.8%	NaOH 65 °C
<i>Avocado Seed Oil</i>	(Dagde, 2019)	TE	78%	KOH 65 °C
<i>Jatropha Oil</i>	(Eboibi et al., 2018)	TE	45%	NaOH 60 °C
<i>Soybean Oil</i>	(Avodeji et al., 2018)	TE	97.1%	NaOH 60 °C
<i>Groundnt Oil</i>	(Oniva and Bamgboye, 2014)	TE	86.8%	KOH 60 °C
<i>Sweet Almond Oil</i>	(Giwa and Ogunbona, 2014)	TE	85.9%	NaOH 60 °C

ii. Catalysis in transesterification reactions:

Chemical or biological catalysts are used for activation transesterification process. Chemical catalyst contains homogeneous active ingredients (alkaline or acid), heterogeneous active ingredients active ingredient (solid acid or solid alkali catalyst), heterogeneous Nanocatalysts and Supercritical Fluids (SCF). This catalysts are effective in helping complete the process. This reaction requires a lot of energy and time, cumbersome refining process to purify final product [60, 61]. Biocatalysts include immobilized ones Lipase is preferred.

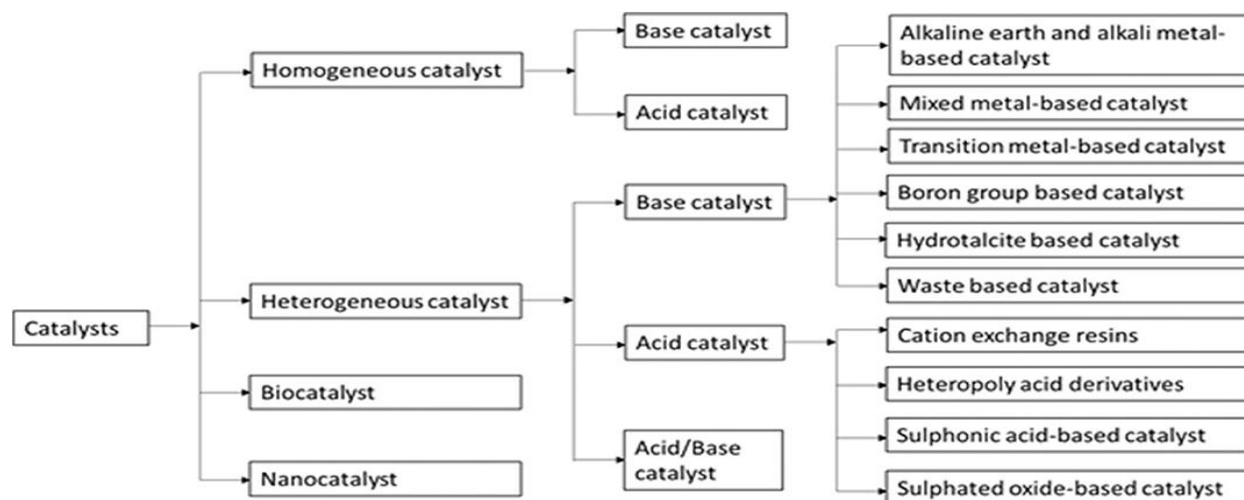


Figure I.13. Different Catalysts Used for Biodiesel Production.

1/ Homogeneous catalyst

Homogeneous catalysis is a **series** of reactions catalyzed by **chemicals** that **are** in the same phase as the reaction system. The homogeneous catalyst is the most popular catalyst for use in the production of biodiesel because it is easy to use and takes less time to complete the reaction. Catalysts that are both acidic and basic fall into this category. In order to dissolve homogeneous catalysts, the solvent is typically in the same phase as all of the reactants [62]

Base catalysts

Homogeneous base catalysts are alkaline liquids such as sodium hydroxide (NaOH), sodium methoxide (CH₃ONa), and potassium hydroxide (KOH).

NaOH dissolves quickly and is preferred over KOH in methanol. NaOH is considered in transesterification reactions due to its high purity and low cost. Which is also relatively low less quantity is required compared to KOH [63-64].

However, more alkali metal alkoxides are found it is more active than hydroxide [65]. Basic catalysts are highly active in transesterification reactions [66]. Metal hydroxides are often used as catalysts because of their low price, but they are generally less active than alkoxides. The rate of base-catalyzed reactions is reported to be 4,000 times faster than that of acid-catalyzed reactions [67].

A known drawback is that oils containing large amounts of FFAs cannot be completely converted to biodiesel, leaving large amounts as soap [68]. Alkaline catalysts can catalyze the reaction up to 5%, but additional amounts of catalyst are required to compensate for catalyst loss due to soap [69]. Most studies recommend that his FFA content for biodiesel production using homogeneous catalysts should be less than 2 wt%.

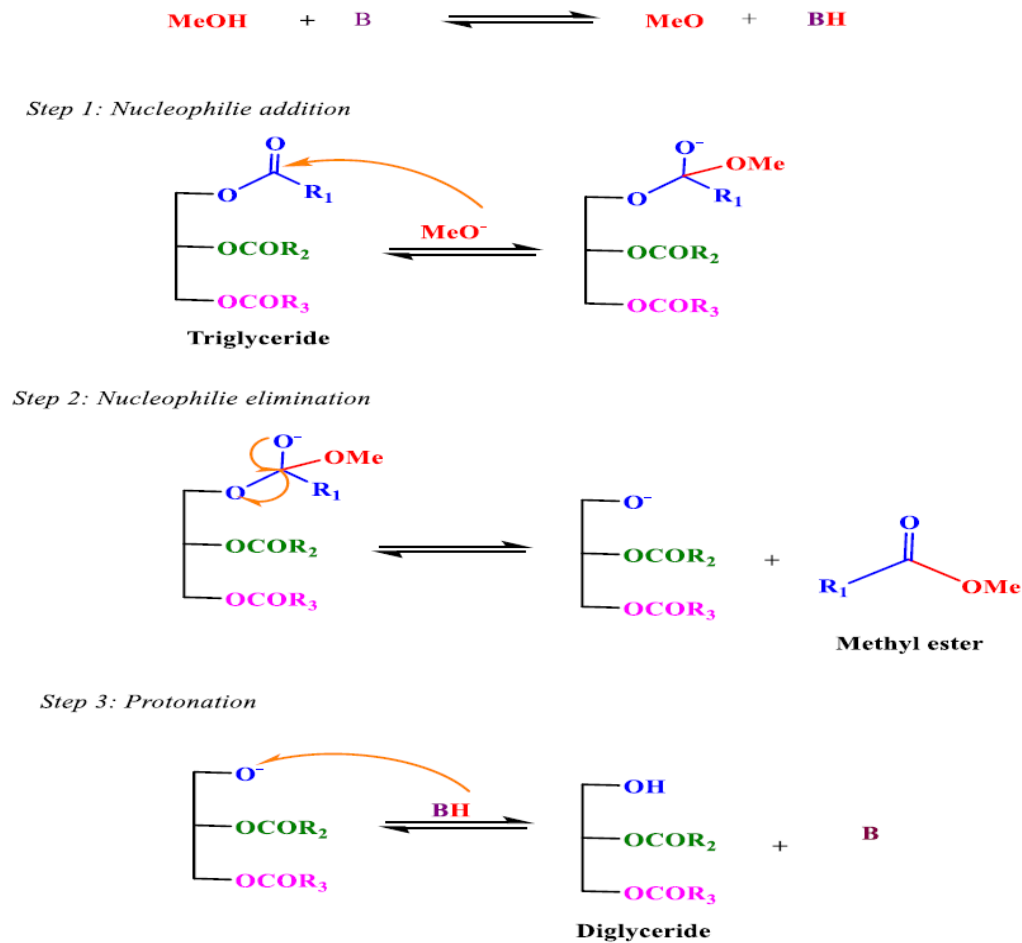


Figure I.14: Mechanism of Esterification Reaction in the Presence of a Base Catalyst

Acid Catalyst

In alkali-catalyzed transesterification, even if water-free vegetable oils and alcohol are used, a certain amount of water is formed by the CH_3O^- solution because of the interaction between NaOH and methanol. Water and FFA cause soap to develop by hydrolyzing the triglycerides, which lowers the output of biodiesel and lowers the product's quality [70,71,72]. If the oil contains more than 2% FFA, product recovery in an alkali-catalyzed transesterification reaction becomes challenging; in such a situation, a portion of the reaction may proceed via saponification, producing soap. The resulting soap prevents the separation of glycerine and biodiesel.

As a result, two-step transesterification with acid and alkali coming thereafter is advised the esterification process is catalyzed by Brønsted acids, preferably sulfonic acid, sulfuric acid as well as hydrochloric acids. These catalysts produce alkyl esters in very high yields. However, the reaction is slow compared to alkali-catalyzed reactions and the increased energy demand makes

this process economically problematic. Homogeneous acid catalysts are not affected by FFA content and can catalyze both esterification and transesterification reactions [73.74].

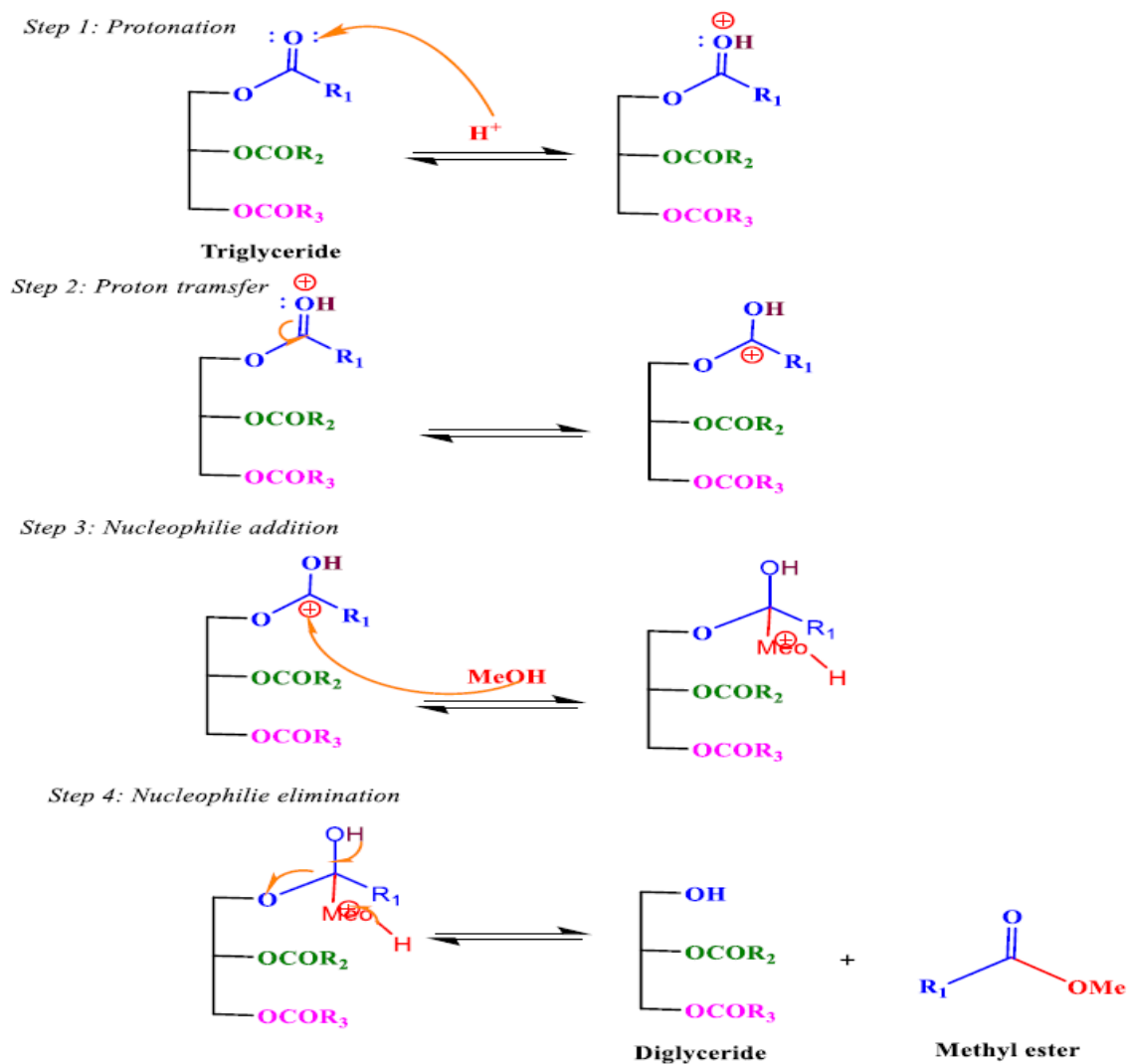


Figure I.15: Mechanism of Esterification Reaction in the Presence of an Acid Catalyst

2/ Heterogeneous catalysts

Heterogeneous catalysts are in a different phase or state than the reactants. These are a type of catalyst that periodically generate active sites with the reactants during the reaction. Key benefits include ease of separation and purification, improved transesterification processes by eliminating additional processing costs associated with homogeneous catalysis, and reduced pollutant formation. These catalysts withstand high FFA and moisture levels. Efficient and inexpensive heterogeneous catalysts can help minimize the overall cost of biodiesel production. Disadvantages

of this catalyst include higher temperatures and higher oil/alcohol ratios compared to homogeneous catalysts [75].

Base catalysis

Heterogeneous base catalysis is intended to overcome limitations such as saponification that hinder the separation of glycerol from the methyl ester layer associated with the use of homogeneous base catalysis. These catalysts exhibit excellent catalytic activity even under mild conditions. Many metal-based oxides, including alkali metal, alkaline earth metal, and transition metal oxides are used as catalysts in oil transesterification processes. The structure of metal oxides consists of positive metal ions (cations) with Lewis acid properties and negative oxygen ions (anions) with Bronsted base properties.

1/ Alkaline earth and alkali metal-based catalyst

CaO, MgO, SrO, BaO. The more oxides on the basic sites, the more effectively the reaction is promoted.

Among metal-based catalysts, CaO possesses many advantages such as long catalyst life, relatively high basic strength, high activity, low solubility in methanol, and requires only moderate reaction conditions, thus making it a bio- It is most studied as a catalytic material for diesel production [76].

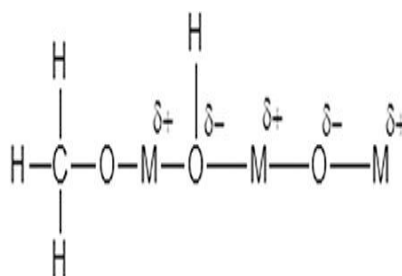


Figure I.16. Surface Structure of Metal Oxides (M represents the metal).

2/Mixed metal-based catalyst.

3/Transition metal-based catalyst.

4/Boron group-based catalyst.

5/Hydrotalcite-based catalyst.

6/Waste-based catalyst.

Acid Catalysts

Compared to homogeneous acid catalysts, heterogeneous acid catalysts are less corrosive, less toxic, and cause less environmental problems. Although these catalysts give promising results under moderate reaction conditions, they are very slow when compared to solid-based catalysts. Furthermore, the use of this type of catalyst requires high catalyst loadings, high temperatures and long reaction times [76].

1/ Cation-exchange resins.

2/ Heteropoly acid derivatives.

3/ Sulfonic acid-based catalysts.

4/ Sulfated oxide-based catalyst.

5/ Acid/Base Catalyst.

6/ Zirconia and its derivatives.

7/ Zeolite-based catalyst.

3/ Biocatalysts

Chemical catalysis is an energy-intensive method of producing biodiesel that also yields undesirable by-products such soaps and polymeric pigments that make it difficult to separate the product from glycerol and other acylglycerols. These barriers can be removed by using biocatalysts. Enzymes, usually referred to as biocatalysts, are obtained from living things that facilitate chemical reactions without changing their own chemical makeup. The two main types of enzymatic biocatalyst are:

- **extracellular lipases**
- **intracellular lipase**

The complexity of separation and purification processes and their accompanying cost are a downside of using extracellular enzymes as a catalyst. By utilizing microbial cells as whole-cell biocatalysts with a suitable biodiesel production, this can be decreased. Whole-cell biocatalysts have been identified in filamentous fungi. At the conclusion of the process, lipase utilized in whole-cell form cannot be recycled [75].

4/ Nanocatalysts:

Due to their high catalytic effectiveness, nanocatalysts have recently attracted a lot of attention for the generation of biodiesel. These catalysts are more active than traditional catalysts because of their large surface area. These catalysts also have a high surface-to-volume ratio, excellent saponification resistance, high stability, and good reusability. Many techniques can be used to create nanocatalysts [75].

Water and free fatty acids in esterification reaction

Water and free fatty acids are important variables in the transesterification process. The level of free fatty acid content in the oil prevented its transformation through the saponification reaction (soap production). This is why the oil's acidity should be less than 3%. In fact, parallel parasitic reactions are occurring there at the same time as this transformation. To create soap, fatty acids react with a catalyst (basic). With rises of temperature, the triglyceride molecules in water split into glycerol and fatty acid molecules. These latter ones will accelerate the saponification reaction. This will lower the yield of converting oil to ester.

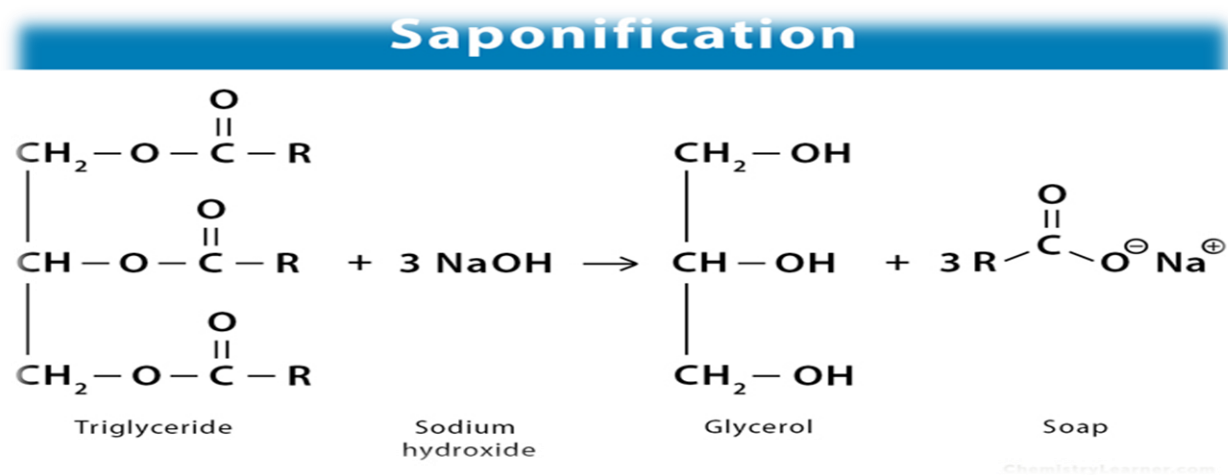
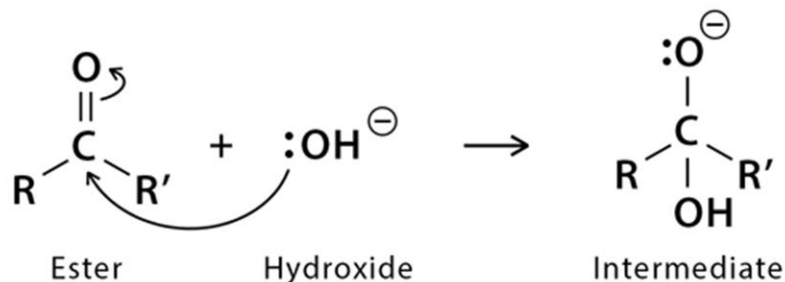


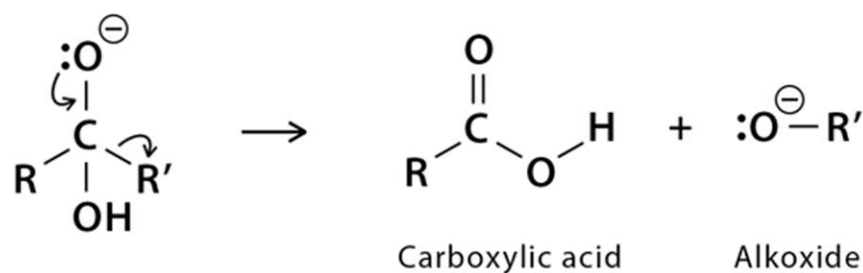
Figure I.17: General Reaction of Saponification by Using NaOH

Mechanism of Saponification

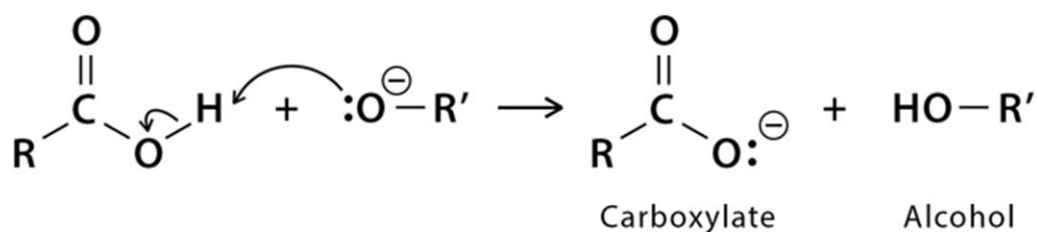
Step 1: Nucleophilic attack on the carbonyl carbon by the hydroxide



Step 2: Removal of the leaving group



Step 3: Deprotonation of the alcohol by the alkoxide



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Figure I.18: Mechanism of Saponification Reaction

This reaction is encouraged by acidic oil or the presence of water. In fact, the triglycerides easily hydrolyze in the presence of water, resulting in glycerol and free acids. One can easily obtain the soap of these acids using potassium or soda [77].

Physicochemical characteristics of biodiesel

Viscosity

The most significant characteristic of biodiesel is its viscosity, which has a significant impact on engine performance and pollutant emissions as well as on how well it burns. The consistency Low atomization caused by high levels decreases the biodiesel's air contact surface. Incomplete combustion in the engine is caused by weak atomization coupled with inadequate volatility. Because of this inefficient combustion, the engine's performance is reduced, and polluting emissions (such as soot, carbon monoxide, and unburned hydrocarbons) are increased. It will be simpler to pump the fuel and spray it into tiny droplets the more the viscosity is within the guidelines. The weight molecular weight of triglycerides is reduced to one-third that of a triglyceride during the transesterification process, and the viscosity is decreased by a factor of about eight .Biodiesel has a viscosity close to that of diesel fuels[1].

Calorific value

This number tells you whether a certain biodiesel can be used in a diesel engine. The calorific value rises as the carbon chain lengthens. Use lipids extracts from heterotrophic microalgae in methanol with H₂SO₄. Succeeded in producing biodiesel with a calorific value of 41MJ/kg, which is comparable to the calorific value of diesel (40–45MJ/kg) [1].

Cloud Point

The temperature at which crystallization starts is known as the cloud point causing a loss of clarity. One of the characteristics is the cloud point.

The pour point or filterability limit temperature (TLF) for biofuel is low. The growth of crystals at low temperatures (winter) might block the fuel filter and cut off the engine's power [1].

Point pour

The temperature at which a liquid ceases to flow is known as the pour point. It is assumed that fuel pumping is no longer practicable at this temperature. Compared to petroleum diesel, biodiesel has greater cloud and pour points [1].

The cetane number

Cetane number is one of the most cited indicators for defining quality the fuel exhibits the ability to self-ignite under the influence of temperature. Compressed inside the cylinder. Therefore, the cetane number is biodiesel ignition and combustion quality in diesel engines.

The zero point on the scale of this index is the value for methylnaphthalene, which shows a higher value as an anti-inflammatory drug, the latter has been replaced by heptamethylnonane.

A new standard, the value 100 is given by the highly combustible cetane.

Cetane number is generally a function of biodiesel composition. According to fatty acid distribution of the oil or fat from which it is made. The cetane number increases or decreases with the length of the hydrocarbon chain of the fatty acid along with the degree of unsaturation. Unsaponifiables content does not seem to have any effect cetane number of biodiesel [1].

A low cetane number can be caused by:

- Large ignition delay.
- Increased emissions of pollutants.
- The noise level increases. On the other hand, a too high exponent (>60) will reduce engine noise but degrade performance.

Thermodynamic efficiency of the engine.

Oxidation

Oxidation of biodiesel can occur when FAME comes in contact with oxygen. It is then converted to hydrogen peroxide, aldehydes, acids, and other oxygen-containing compounds. Deposits can form inside the engine. Oxidation of biodiesel degree of unsaturation. This problem can be overcome by adding antioxidants to biodiesel blends for long-term storage several months[1].

Lubricating power

The definition of diesel lubricity is viscosity, acidity, water and sulfur compounds .Even with additives, the measured friction is (units not declared) at a temperature of 25 °C, the energy of biodiesel (0.114 and 0.117) is lower than that of diesel (0.238 and 0.210) . Therefore, biodiesel blends with low sulfur content are advantageous. Use with conventional gasoline diesel is intended to improve lubricity. [1]

Density

The density of biodiesel is known to be primarily influenced by its ester concentration, methyl acids, and the remaining methanol component. A biodiesel's density has an impact engine performance-related. Biodiesel injection pumps are volumetric pumps, and the dose is determined by figuring out how much mass is being injected into how much volume. A fuel with a high density requires more gasoline to be injected, which raises consumption.

This feature is mostly determined by the kind of vegetable oil used, with some effect also coming from the production techniques utilized [1].

Advantages and disadvantages of Algeria

Advantages

- ❖ Green energy.
- ❖ Biofuels as renewable and sustainable energy source.
- ❖ Large quantities of biomass available around the world, it can be manufactured from a wide range of materials.
- ❖ Scalable and flexible energy source.
- ❖ Mature technology due to extensive research in the past.
- ❖ Diversification of raw materials.
- ❖ Relative safe technology.
- ❖ Low levels of greenhouse gas emissions (CO, THC...).
- ❖ Creating local jobs.
- ❖ Better lubricating properties.

Desadvantages

- ❖ Biofuels production can be quite inefficient.
- ❖ Large amounts of raw materials need to be used.
- ❖ Use of chemical fertilizers and pesticides in the production chain leads to significant greenhouse gas emissions.
- ❖ Require high initial investments.
- ❖ Increase of food prices in the world.
- ❖ High global hunger and starvation.
- ❖ High water demand in production.
- ❖ Production chain makes pollution.
- ❖ Biofuel production needs large areas of land.
- ❖ Biodiversity loss.

Chapter II

Methods and Materials

II.1. Introduction

In the previous chapter, we did a theoretical study about the Aleppo pine plant first, and vegetable oils second. During this research, we will use two methods to extract pine seeds oil (**Mechanical extraction and Solvent extraction**) and use it in the production of biodiesel, by choosing the Esterification process as a reaction method in the presence of a group of different alcohols (MeOH, EtOH and BIO-EtOH) and different catalysts then we will to compare them.

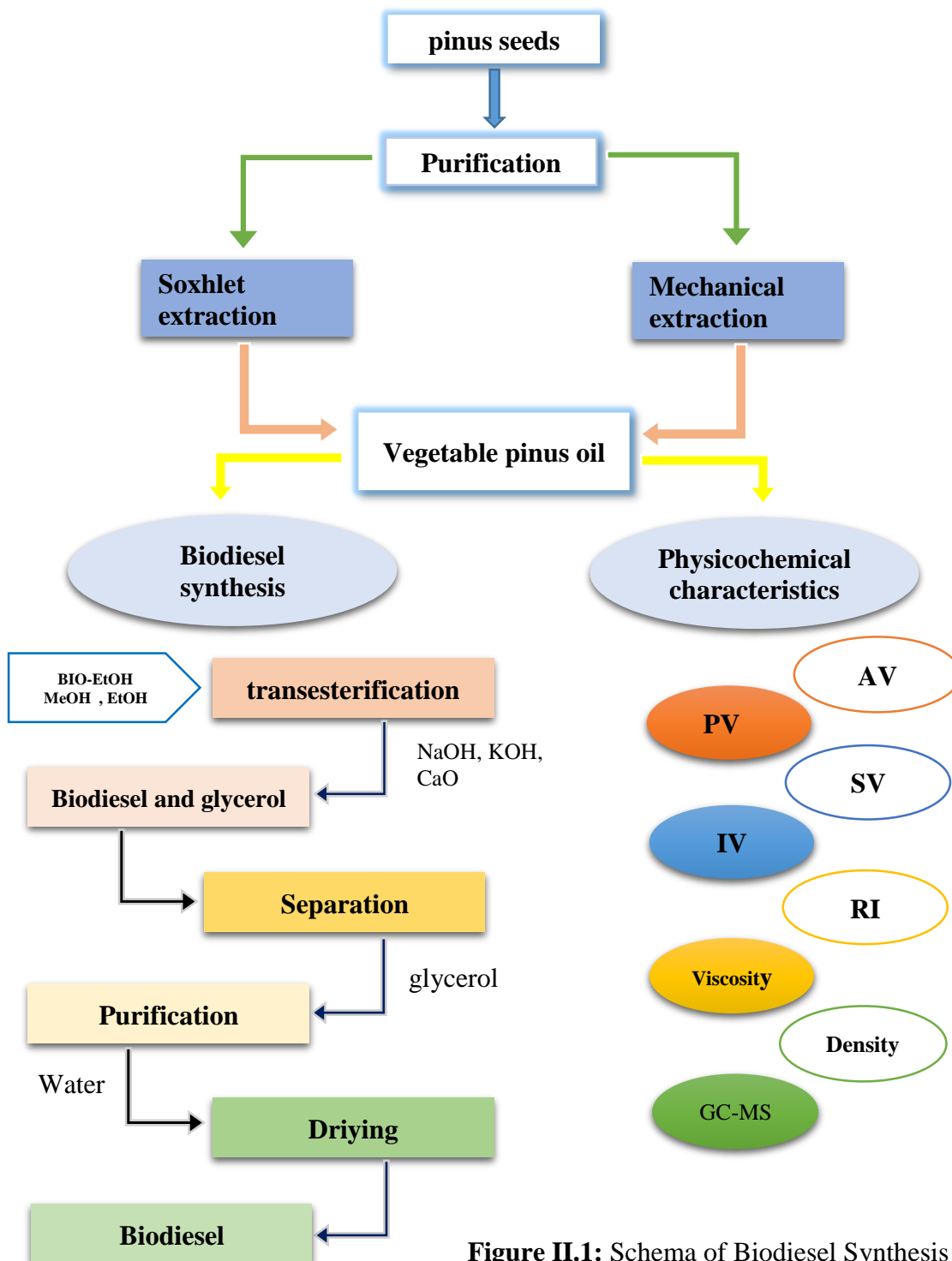


Figure II.1: Schema of Biodiesel Synthesis

II.2. Oil extraction

After sorting and purifying the sample two methods have been used to extract pinus seeds oil.

II.2.1. Mechanical extraction

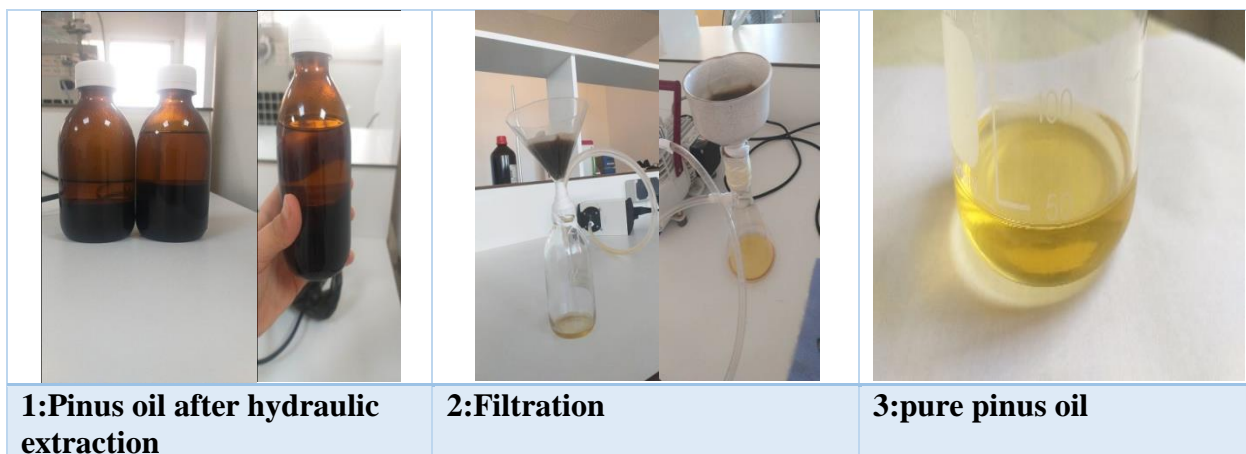
After sorting seeds from all impurities compressed pine seed oil was mechanically extracted in a hydraulic extractor on cold . This proses was done in center of Djanet ouargla for the extraction of natural oils. (Djanat Bio Cosmetique Espace de la nature).



Figure II.2: Oil Extraction Photos

Filtration

After hydraulic extraction, the oil is not pure and needs to be filtered, so the filtration protocol was used under vacuum.

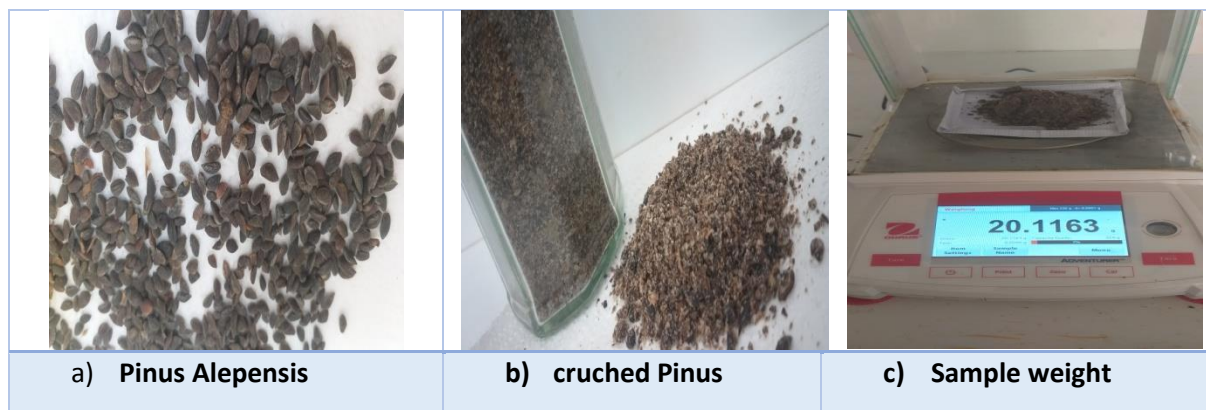


FigureII.3: Filtration of oil

II.2.2. Solvent extraction (Soxhlet extraction)

The oil was extracted from pinus seeds powder using a solvent extraction method with hexane as a solvent.

1. The seeds were crushed and placed in paper bags. The sample placed in a Pyrex glass Soxhlet extractor, attached with condenser and a Pyrex round bottomed flask (500 mL capacity).
2. Extraction was carried out using a water bath with n-hexane as extraction solvent.
3. 20 grams (20g) of pinus seed were weighed and covered by purified cotton.
4. Then 300 ml of n-hexane as solvent was added. The sample with the solvent was placed in the soxhlet extractor for the cycle was allowed to repeat many times for about 8 hours, Sample renewed 5 times.
5. After the oil extraction, the solvent was removed under vacuum in a rotary evaporator machine (Series fitted with an Aspirator and a Digital Water Bath) at 45°C. The solvent (hexane) and oil were separated using distillation at a temperature of slightly higher than the boiling temperature of hexane, which is recovered again for further extraction with fresh hexane.



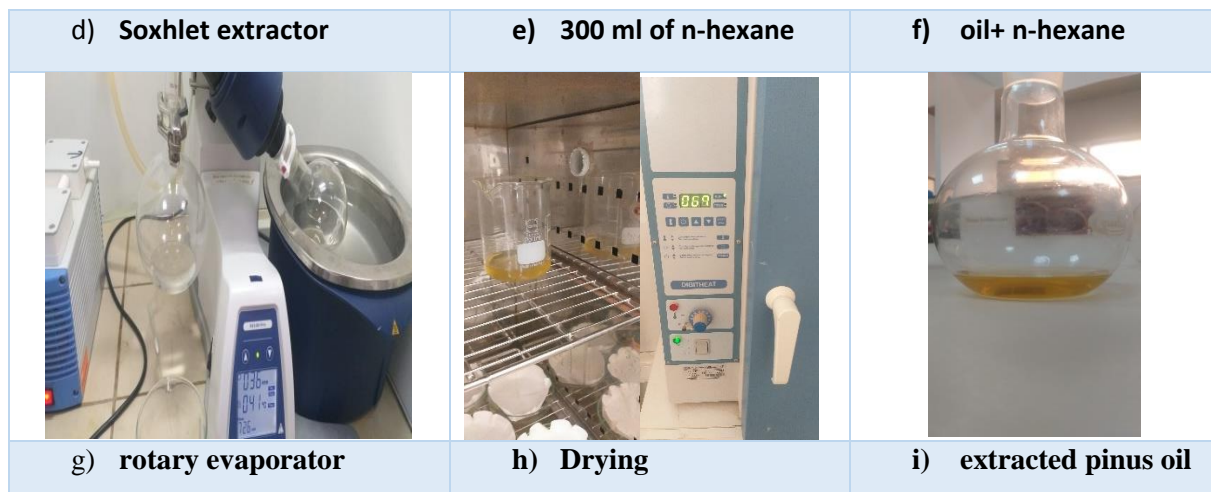


Figure II.4: Solvent Extraction Stages

Determination of percentage (%) yield

The percentage (%) yield was calculated using the equation (1)

$$\text{Percentage yield of oil \%} = \text{weight of oil(g)} \times 100 / \text{Total weight of seeds} \dots\dots\dots (1)$$

Table II.1: Results of the Extraction Yield

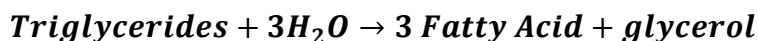
	Hydraulic extraction	Soxhlet extraction
Equation application	Yield%=933(g)/192.6291(g)	Yield%=33.2721(g)/100.9227(g)
Results	Yield%=20%	Yield%=32.96%

II.3.GCMSAnalysis

Peak#	R.Time	Area	Area%	Height	Peak Report TIC			Name	CAS#
					Height%	Similarity	Ret. Index		
1	12.102	3741845	0.15	1853739	0.70	95	Myristic acid, methyl ester	124-10-7	
2	13.582	1806438	0.07	745071	0.28	87	Pentadecanoic acid, methyl ester	7132-64-1	
3	14.839	3449390	0.14	1316295	0.50	93	Methyl hexadec-9-enoate	10030-74-7	
4	14.915	5533849	0.23	2232838	0.85	95	9-Hexadecenoic acid, methyl ester, (Z)-	1120-25-8	
5	15.321	193105111	7.93	37302643	14.18	90	Hexadecanoic acid, methyl ester	112-39-0	
6	16.536	10300147	0.42	3691676	1.40	90	Hexadecanoic acid, 14-methyl-, methyl ester	2490-49-5	
7	16.638	2875819	0.12	914739	0.35	91	(Z)-10-heptadecenoic acid methyl ester	0-00-0	
8	17.065	5201781	0.21	1741518	0.66	95	Heptadecanoic acid, methyl ester	1731-92-6	
9	18.224	137739728	5.66	24253797	9.22	92	Methyl 5,9,12-octadecatrienoate	0-00-0	
10	18.303	98759074	4.06	15424506	5.86	82	Methyl 5,9-octadecadienoate	0-00-0	
11	18.885	1069870107	43.93	40190095	15.28	88	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	112-63-0	
12	19.088	346783392	14.24	40841354	15.53	82	9-Octadecenoic acid, methyl ester, (E)-	1937-62-8	
13	19.477	175966887	7.23	31829215	12.10	95	Methyl stearate	112-61-8	
14	21.285	3311496	0.14	763290	0.29	84	Heneicosanoic acid, methyl ester	6064-90-0	
15	23.709	171061672	7.02	23653716	8.99	88	Methyl 5,11,14-icosatrienoate	0-00-0	
16	23.821	45248744	1.86	9433260	3.59	90	Methyl 5,13-docosadienoate	0-00-0	
17	24.394	43788288	1.80	6115980	2.33	90	cis-11,14-Eicosadienoic acid, methyl ester	0-00-0	
18	24.574	57966158	2.38	10647195	4.05	91	cis-13-Eicosenoic acid, methyl ester	69120-02-1	
19	25.440	47413213	1.95	8539470	3.25	89	Eicosanoic acid, methyl ester	1120-28-1	
20	33.671	11464474	0.47	1523295	0.58	89	Docosanoic acid, methyl ester	929-77-1	
		2435387613	100.00	263013692	100.00				

FigureII.5: Fatty Acids Composition From GC-MS Results

According to the results of GCMS analysis and to the triglycerides hydrolysis equation, we find:



$$M_{oil} = 3 \sum (M_{acid} * \alpha_i) + M_{gly} - 3M_{H_2O}$$

M_{oil} : Molar mass of oil

α_i : Percentage of fatty acid in the oil

M_{acid} : Molar mass of fatty acid

M_{gly} : Molar mass of glycerol molecule (136 g/mole)

M_{H_2O} : Molar mass of water (18 g/mole)

II.4. Physicochemical characteristics of pinus oil

II.4.1. Determination of Acid value

TableII.2: Products and Materials of Acid Value Determination

Products	Materials
<ul style="list-style-type: none">○ (0.5 g) pinus oil○ 50 ml of ethanol (96%)○ Phenolphthalein indicator○ Potassium hydroxide solution (0.1N)	<ul style="list-style-type: none">○ Analytical balance○ Stir bar○ Conical flask○ Stir motor○ Buret, ring stand

Procedure

- Oil sample (0.5 g) was weighed.
- Dissolved oil with 5 ml of ethanol in a conical flask.
- Added Two drops of phenolphthalein indicator and titrated to pink end point (which persisted for 15 minutes) with (0.1 N) potassium hydroxide solution (KOH). Acid value was calculated by (Equation 2)

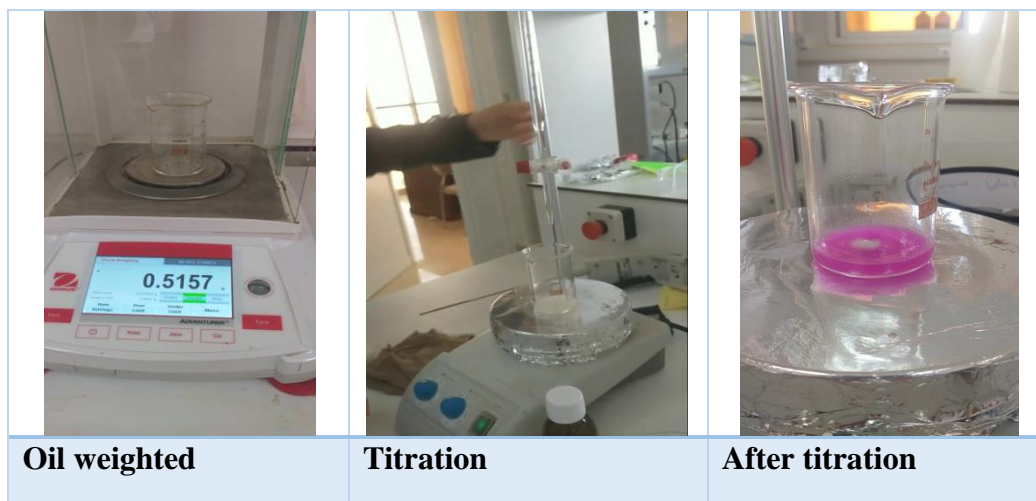
$$\text{Acid value} = \frac{56.1 * V_{KOH} * C_{KOH}}{m_{oil}} \dots\dots\dots (2)$$

56.1: equivalent weight of KOH.

V_{KOH} : is the volume in ml of standard volumetric KOH solution used. (0.1ml)

C_{KOH} : is the exact concentration in KOH solution used (0.1N).

M_{oil} : is the mass in grams of the oil. (0.5g)



FigureII.6: Titration of Acid Value Results

Determination of the Free Fatty Acids

Free fatty acid is weight percent of specific fatty acid for example (percent of oleic acid).
 Calculated by (Equation 2)

$$FFA\% = \frac{N_{c18:1} * V_{KOH} * C_{KOH} * 100}{m_{oil} * 1000} \dots\dots\dots (2)$$

$N_{c18:1}$: Normality of Oleic Acid.

V_{KOH} : is the volume in ml of standard volumetric KOH solution used (0.1ml).

C_{KOH} : is the exact concentration in KOH solution used (0.1N).

m_{oil} : is the mass in grams of the oil (0.5g).

II.4.2.Determination of Saponification value

TableII.3: Products and Materials of Saponification Value Determination

Products	Materials
<ul style="list-style-type: none"> ○ KOH ○ Ethanol ○ Distilled water ○ Phenolphthalein ○ HCl 	<ul style="list-style-type: none"> ○ Flask 250 ml ○ Reflux ○ Water Bath ○ Analytical balance ○ Stir bar ○ Stir motor ○ Buret, ring stand

Procedure

1. Prepared Ethanolic KOH solution (0.2 M).
2. Prepared Hydrolic Acid solution (1M).

$$N_1 V_1 = N_2 V_2 \quad V_1 = \frac{N_2 V_2}{N_1} \quad N_1 = \frac{1.49 \cdot 0.38 \cdot 1000}{36.5} \quad V_1 = \frac{0.5 \cdot 50}{15.51}$$

$$N_1 = 15.51$$

$$V_1 = 1.6ml$$

3. 0.4 of the oil was weighted with an Analytical balance in a Flask (250ml).
4. 20ml of Ethanolic KOH solution (0.2M) was added to the Flask.
5. The contents was heated under reflux in a water bath for 30 minutes.
6. After cooling the mixture, a few drops of phenolphthalein were added.
7. Titrated it with HCl solution (1M) to end point (The pink color disappeared).
8. A blank titration was also carried out omitting the oil under the same condition and saponification value was calculated using the equation (3).

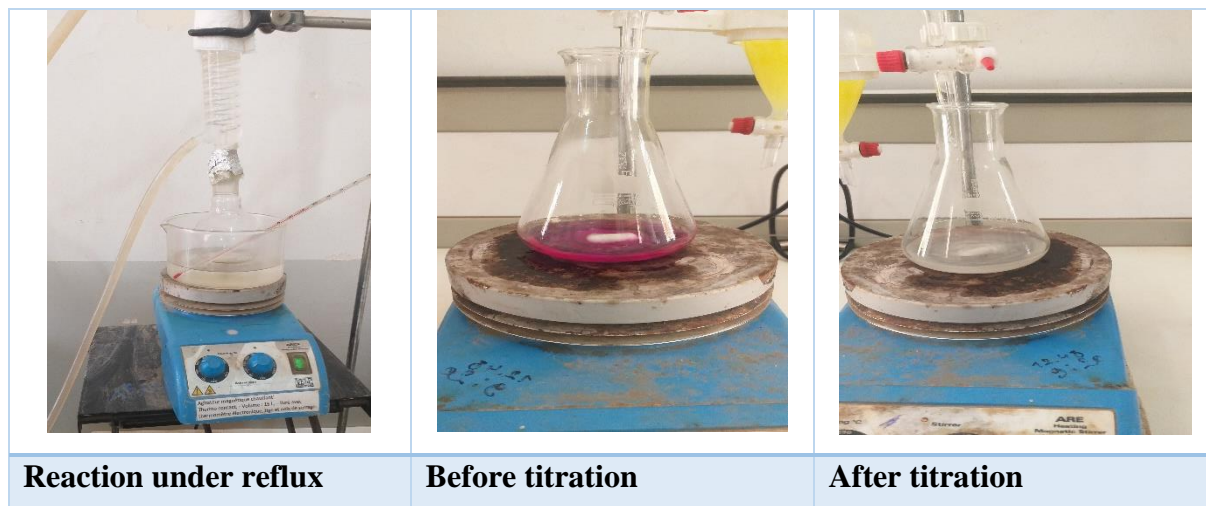
$$SV = \frac{56.1 \cdot C_{HCl} \cdot (V_0 - V_1)}{m_{oil}} \dots \dots \dots (3)$$

V₀: HCl volume used in Blank titre (4.3ml)

V_1 : HCl volume used in Real titer (12.4ml)

C_{HCl} : The exact concentration in HCl solution used (1M).

m_{oil} : is the mass in grams of the oil. (0.4g)



FigureII.7: Titration of Saponification Value Results

II.4.3. Determination of peroxide value

TableII.4: Products and Materials of Peroxide Value Determination

Products	Materials
<ul style="list-style-type: none"> ○ Chloroform ○ acetic acid ○ KI solution ○ Distilled water ○ sodium thiosulphate $Na_2S_2O_3$ ○ starch detector 	<ul style="list-style-type: none"> ○ flask ○ Analytical balance ○ Stir bar ○ Stir motor ○ Buret, ring stand

1. 2.5g of the oil sample was weighed in a flask.
2. 6ml of chloroform and 9ml of acetic acid was added to the oil.
3. 1ml of KI solution (KI solution prepared by 0.5g of KI with 1 ml of water).
4. The mixture was shaken for 1 minute and keep it in the dark for 5minutes.
5. 35.5 ml of water was added with drops of starch detector and titrated with 0.01M sodium thiosulphate $Na_2S_2O_3$.
6. Blank titration (Same process without oil).
7. Peroxide value was calculated using the equation (4)

$$PV = \frac{C_{Na_2S_2O_3} * (V_1 - V_0) * 1000}{m_{oil}} \dots \dots \dots (4)$$

$C_{Na_2S_2O_3}$: The concentration of sodium thiosulphate $Na_2S_2O_3$ solution used (0.01M).

V_0 : $Na_2S_2O_3$ Volume used in Blank titre (1.3ml).

V_1 : $Na_2S_2O_3$ Volume used in Real titre (1.9ml).

m_{oil} : is the mass in grams of the oil (2.5g).

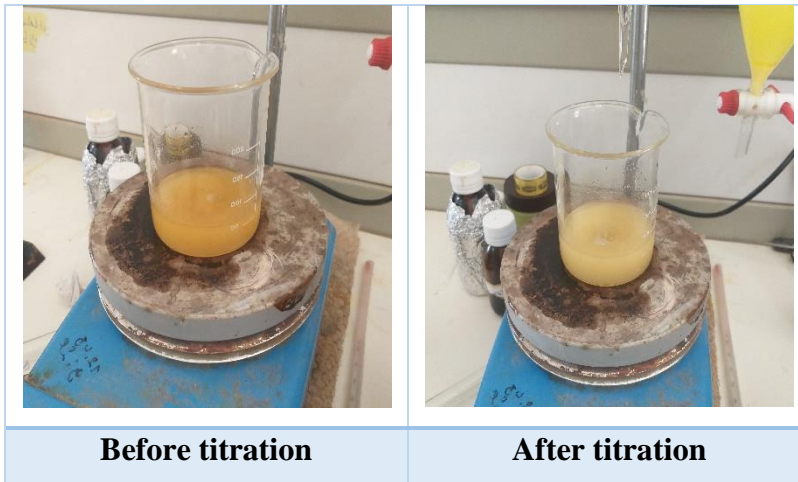


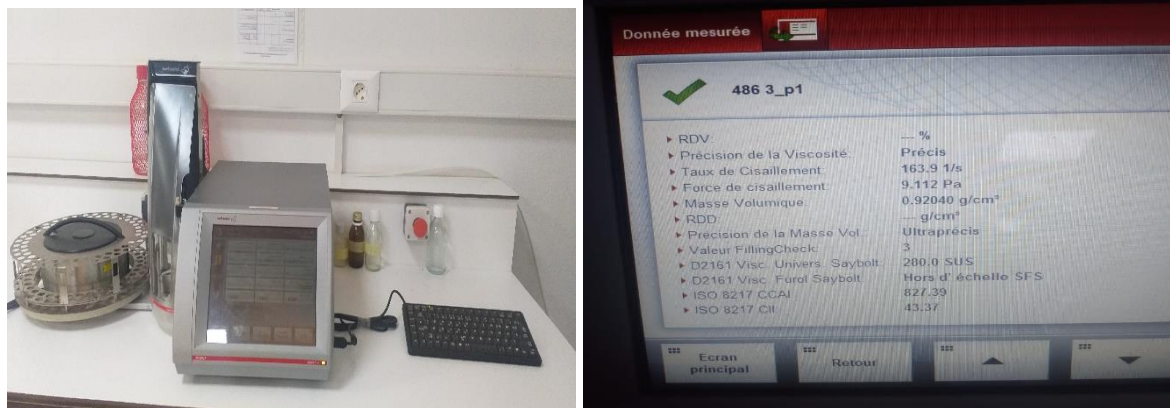
Figure II.8: Titration of Peroxide Value Results

II.4.4. Viscosity and Density

In our work the vibration viscometer (Anton Paar SVM3001) was the appliance used to determine the viscosity and density of pinus oil.

Procedure

Before using the viscometer, it is necessary to get rid of the suspended gasses in the oil using the sonic device then takes samples without moving them and places them in the viscometer, while adjusting the temperature to 25 C and operating the device. The results appear as follows:



FigureII.9: Viscometer (Anton Paar SVM3001)

II.4.5. Refractive index

To determine the refractive index of pinus oil, we used a refractometer (Bellingham+ Stanely RFM300-M Refractometer)



FigureII.10: Bellingham+ Stanely RFM300-M Refractometer

Procedure

Used cotton and ethanol to clean the device slide.

We open the moving prism and put drops of oil on the surface, then close the moving prism.

We adjust the light source to illuminate the visual field using the moving arm of the two prisms until lines appear Slender which determines the dividing line. Then we read the refractive index at the temperature of the laboratory.

II.5. Transesterification

In this work transesterification was carried out by two methods, volumetric and massie reports, to synthesize the biodiesel. Each time the esterification conditions were changed (type of catalyst, type of alcohol, time and Alcohol/oil ratio)

II.5.1. Massic report

According to the methods of Dr. BEN CHEIKH and Dr.SERROTI, we discussed the use of the following method by changing the interaction conditions each time.

Calculation of the amount of alcohol

According to Dr. BEN CHEIKH's results, the yield of biodiesel was higher at the ratio of 1:9

$$M_{oil} \rightarrow M_{alcohol}$$

$$m_{oil}(g) \rightarrow x_{alcohol}(g)$$

$$9x = m_{alcohol}(g)$$

Procedure

Reaction

1. We used the (Bio Ethanol /oil) and (ethanol/ oil) with 9:1 ratio molar and (1%NaOH and 2%CaO) as catalysts each time.
2. The catalyst dissolved with alcohol and then added the mixture in the reactor with the heated oil.
3. Introduce a thermometer from the neck of the flask, the reaction is left for two hours (55-60° C) for 6min, 800rpm.

Separation phase

1. Allow Glycerin and Biodiesel to separate into two phases for 24h in a Separator Funnel.
2. Pour the glycerin into a bottle and leave the esters in the Separator Funnel.
3. We carry out the Washing process to get rid of the alcohol and the Catalyst by adding 10 ml of water.

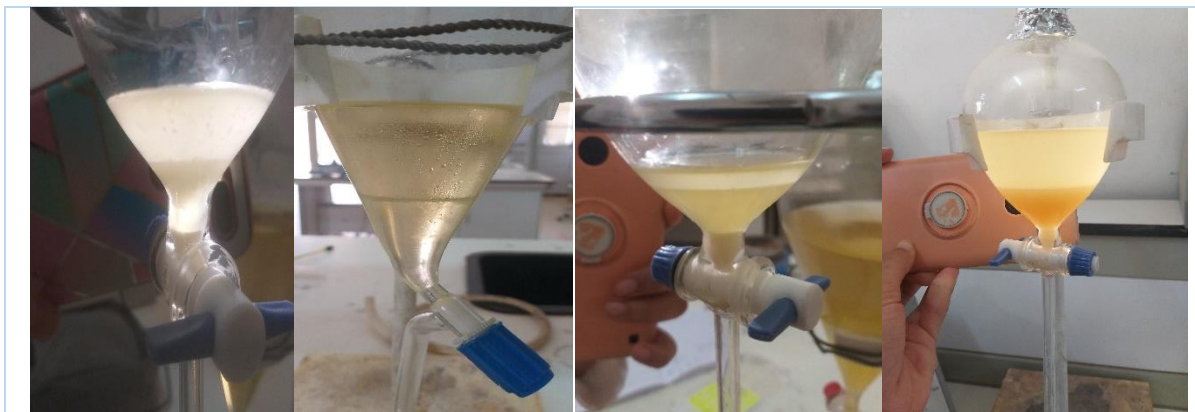
II.5.2.Volumetric report

According to the methods of Dr.FANDOUGOUMA:

A 20 g quantity of the oil was heated in a round-bottomed two-necked flask equipped with a reflux condenser and a thermometer. After 30 minutes of heating, a quantity of 0.1 g of potassium hydroxide KOH (used as catalyst) dissolved in 60 g of methanol, was added to the flask. The reaction took place for 90 minutes at the specified reaction temperature (55+5°C) under reflux while the mixture was simultaneously stirred at 600 rpm. At the end of the reaction, the synthesized FAMES were separated using a separatory funnel. The methyl esters layer was freed from excess methanol by the rotary evaporator.



FigureII.11: Reaction of Transesterification



FigureII.12: Separation Phase

Chapter III

Results and discussion

III.1.Oil extraction

Table III.1: Comparison between Soxhlet Extraction and Hydraulic Extraction Methods

	Soxhlet extraction	Hydraulic extraction
Yield	32.96%	20%
Time	100g → 24h	100g → 15min
Cost	More expensive	Lower cost
Wasted material	Less	More
Industrially	Unsuitable	Suitable
Laboratory	Suitable	Unsuitable
Risks	Solvents and heat risks	No risks
Purity	purier	Less pure

III.1.1. Yield of Pinus oil between Algeria and other regions

The seeds of Aleppo pine are a good source of oil (20% - 32.96%). After comparing with seeds grown in other regions, the oil content of seeds in our study was very close to Jordan pine(23.1%) and higher than Turkish pines (21.1%), but it is lower than Australia (34.1%) and France (35%), it was much lower than the oil yield obtained from Tunisian pine seeds (43.3% -38.12%). this change in oil yield may be due to the difference in the degree of seeds maturity, Cone age, and variation under environmental and ecological conditions.

III.2. GC-MS analysis (Fatty acid composition)

The fatty acid composition of oil extracted from Aleppo pine seeds is shown in Table (?). Linoleic Acid is the predominant fatty acid (43.93%), followed by Oleic Acid (14.24%), Palmitic Acid (7.93%), Stearic Acid (7.23%), Sciadonic Acid (7.02%), and linolenic Acid (5.66%). Unsaturated fatty acids account for 81.16% of total fatty acids, with Linoleic and Oleic acids comprising 71.67% of total unsaturated fatty acids. So pinus oil is an unsaturated oil, which indicates the quality of the oil. From what the table () shows:

Table III.2: The Chemical Composition of Pinus Oil by GC-MS

Molecular Name	Molecular Formula	Area%	Molecular Weight
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	0.15%	228.37 g/mol
Pentadecanoic Acid	C ₁₅ H ₃₀ O ₂	0.7%	242.40 g/mol
Palmitelaidic Acid	C ₁₆ H ₃₀ O ₂	0.14%	254.4082 g/mol
Palmitoleic acid	C ₁₆ H ₃₀ O ₂	0.23%	254.41 g/mol
Palmitic Acid	C ₁₆ H ₃₂ O ₂	7.93%	256.42 g/mol
14-methyl-hexadecanoic acid	C ₁₇ H ₃₄ O ₂	0.42%	270.5 g/mol
cis-10-Heptadecenoic acid	C ₁₇ H ₃₂ O ₂	0.12%	268.4 g/mol
Margaric acid	C ₁₇ H ₃₄ O ₂	0.21%	270.5 g/mol
Pinolenic Acid	C ₁₈ H ₃₀ O ₂	5.66%	278.4 g/mol
Taxoleic acid	C ₁₈ H ₃₂ O ₂	4.06%	280.4 g/mol
linoleic acid	C ₁₈ H ₃₂ O ₂	43.93%	280.4 g/mol
<u>Oleic Acid</u>	C ₁₈ H ₃₄ O ₂	14.24%	282.4614g/mol
stearic acid	C ₁₈ H ₃₆ O ₂	7.23%	284.5 g/mol
Henicosanoic acid	C ₂₁ H ₄₂ O ₂	0.14%	326.6 g/mol
Sciadonic Acid	C ₂₀ H ₃₄ O ₂	7.02%	306.5g/mol
Eicosadienoic Acid	C ₂₀ H ₃₆ O ₂	1.80%	308.5 g/mol
Paullinic acid	C ₂₀ H ₃₈ O ₂	2.38%	310.51g/mol
Arachidic acid	C ₂₀ H ₄₀ O ₂	1.59%	312.5 g/mol
Behenic acid	C ₂₂ H ₄₄ O ₂	0.47%	340.6 g/mol

III.3. Physicochemical characteristics

Table III.3: Physicochemical characteristics Results

Characteristic	Value
Acid value	1.122
FFA%	0.56492
Peroxide value	2.4
Saponification Value	1136.025
Refractive index	72.5
Viscosity dyn(25°C)	55.593
Viscosity cin(25°C)	60.401
Density(25°C)	0.92040

➤ **Acid value and FFA**

The acid and free fatty acid (FFA) values are used to indicate the level of rancidity and edibility of oils. The acid value for pinus oil was 1.122 and the FFA was 0.56492, which is the percentage by weight of a specified such as the percent of oleic acid in the oil. These high values could be attributed to decomposition, poor extraction techniques, use of damaged seeds, and incorrect or lengthy storage that can be accelerated by light and temperature. Nevertheless, the most common factor is not being refined, which leads to remain higher acidity (Rajko et al ., 2010)

➤ **Peroxide value**

The value of pine oil peroxide was 2.4. This value is used as an indicator of the quality and stability of fats and oils. It was also found that the peroxide value increased with storage time, temperature, and air handling of the oil sample.

➤ **Saponification value**

The saponification value of pine oil is **1136.025**. This value is greater than the expected range. A larger value indicates that the average molecular weight of the fatty acids is greater or that the number of ester bonds is greater. This may mean that the fat molecules do not interact with each other.

➤ **Refractive index**

The value of the refractive index of pine oil was (72.5), which is considered a relatively high value as it is likely that this sample contains high unsaturated fatty acids or long-chain triglycerides.

➤ **Viscosity and density**

(Dyn 55.593), (cin60.401)) at 25°C represents the value of the viscosity of the oil. It is directly related to the degree of unsaturation and the length of the fatty acid chain in the fat.

Its value increases with increasing degree of saturation (Fadl et al., 2015). The density of vegetable oils ranged between (0.5_0.935), where the density of pine oil was 0.92. At this value, the degree of purity of the oil can be predicted. While oil from pinus seeds has an average ratio in the triglyceride chain.

III.4. Transesterification

We repeated the experiment several times because we were unable to produce biodiesel fuel. In the first method, when we got to the stage of separating and washing the resulting esters, with water, a homogeneous mixture was created. In the second method, the result was that at the stage of evaporating excess methanol, all liquids evaporated.

The formation of a homogeneous mixture with water after the washing stage indicates that there are no esters (no reaction happened) or that the resulting biodiesel is of poor quality. The goal of evaporation after separation is to get rid of residual methanol (which has not gone into the reaction). Evaporation of all liquids means that there are no esters, meaning that no reaction has occurred.

Finally, we explain the results that the main problem is not in reaction conditions. Rather in pinus oil, which was found to be 100% non-vegetable oil and it contains essential oils and other components that caused the inability to produce biodiesel.



Figure III.1: Results of Washing and Evaporated

General Conclusion

General Conclusion

Biodiesel is an alternative clean-burning renewable fuel similar to conventional diesel. It is produced using animal fats, vegetable oils. Due to its biodegradable nature, it is used as a replacement for fossil diesel fuel. The aim of this study was to valorize the pine plant and convert its oil into 100% biofuel using inexpensive methods through the transesterification process using different catalysts (KOH, NaOH) and different alcohols (ethanol, methanol, bioethanol) but in the end we did not reach biodiesel and that was not for a Technically reasons, the main reason was that pinus oil contains essential oils (not 100% vegetable oil). So this study is considered the start of new scientific research in the field of biodiesel manufacturing, where it has been estimated ways to make pinus oil suitable for biodiesel synthesis by separating essential oils from vegetable oils. The latter is used in the synthesis of biodiesel fuel and essential oils, which have anti-inflammatory, antibacterial, antioxidant, antifungal and herbicide activity, in addition to the effect of wound healing. On the other hand, other parts of the pine tree can be used to obtain natural extracts that contain many compounds, including (Terpenoids, Terpenes, Phenolic compounds...etc.)

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Abstract

Several experiments were carried out to obtain biodiesel by cross-esterification of oils extracted from pine seeds by changing the conditions of the experiment each time. In this study, we analyzed the results of GCMS, as well as determining the physicochemical properties of pine oil. It was found that linoleic acid is the highest percentage (43.93%) and the percentage of fatty acids unsaturated (81.16%) and that the oil is not 100% vegetable oil.