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Biodiesel Production from Waste Cooking Oil

Catalyst Selection and Optimization

This Dissertation is submitted for the Fulfilment of the Master Degree in Catalysis in Petrochemical Engineering- (University of 20 August 1955 - Skikda)

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Dedication

I dedicate this dissertation end of study to the

people I love most in the world my parents my

idol in life my father Benbrahim Abdelhamid, and

to the best mom in the world Sakkour Salima

And my brothers and my family

And to all of my friends.

BenBRahim Aimen

Dedication

I would like to thank my mom and dad for their love and support throughout my entire life, without them I would not be the person who I am today. My older brothers and Sisters, equally brilliant and compassionate, have always been willing to lend advice and be suitable role models to follow. Finally, I would like to recognize the countless relationships I have established as a graduate student. I have cherished my time here and I'm pleased to have created so many memories.

"Do. Or do not. There is no try."

- Yoda (*The Empire Strikes Back)*

Chitour Aimen Abdellah

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BENRBAHIM aimen

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Abbreviations

VOME: Vegetable oil methyl ester.

GHG: Greenhouse gas.

PET: Polyesters.

WCO: Waste cocking oil.

SFA: Saturated fatty acids.

PUFA: Polyunsaturated fatty acids.

TAG: Triacyl glycerides.

WWTPs: Wastewater treatment plants.

FAME: Fatty acid methyl ester.

FFA: Free fatty acid.

ASTM: American Society for Testing and Materials.

ISO: International Organization for Standardization.

EN: European Norm.

FP: Flash point.

PP: Pour point.

BD: Biodiesel.

TE: Transesterification.

Glycerol: Glycerin.

MeOH: Methanol.

KOH: Potassium hydroxide.

NaOH: Sodium hydroxide.

ALUMINA: Aluminum oxide.

IR: Infrared Spectroscopy.

Abstract

In the last few years, from the climate change crisis to the Ukrainian–Russia conflict, the shortage of supply chains has led to severe energy shortages in many countries, all of which have opened up orientation and reliance on renewable energy sources, including biofuels. However, we need to improve its productivity and reduce its cost because these are the obstacles facing the biofuels industry. Therefore, we want to develop and improve the catalyst used because it has the greatest impact on productivity and cost.

By trying different potential catalysts, each one of theme was synthesized using a different method, such as a mixture of KOH and NaOH as a homogeneous catalyst to using aluminum oxide as catalyst and finally making a heterogeneous catalyst by impregnation of KOH and NaOH in alumina and comparing it with the most used catalyst to produce biodiesel which is, NaOH; the comparison was based on the yield production under the same conditions (temperature, reaction time, molar ratio, and mass ratio) and the same WCO to ensure that we obtained the most accurate result.

In this study, we found that the highest yield production (93.1 %) was achieved with NaOH/alumina, and the NaOH yield was 89.9%, then studied the effects that control biodiesel production for NaOH/alumina, such as temperature, reaction time, MeOH: WCO molar ratio, and catalyst mass ratio, then we manager to optimize it to 94.4%.

In conclusion, we optimized the biodiesel catalyst to produce a higher yield and, at the same time, reuse it multiple times because of the nature of the heterogeneous catalyst, which helps reduce the cost of the catalyst.

Key words: Biodiesel, Catalyst heterogeneous, yield, Alumina, Optimize, Cost.

résumé

Au cours des dernières années, de la crise des changements climatiques au conflit entre l'Ukraine et la Russie, la pénurie de chaînes d'approvisionnement a entraîné de graves pénuries d'énergie dans de nombreux pays, ce qui a ouvert la voie aux sources d'énergie renouvelable, y compris les biocarburants. Cependant, nous devons améliorer sa productivité et réduire ses coûts parce que ce sont les obstacles auxquels l'industrie des biocarburants est confrontée. Par conséquent, nous voulons développer et améliorer le catalyseur utilisé parce qu'il a le plus grand impact sur la productivité et les coûts.

En essayant différents catalyseurs potentiels, chacun des thèmes a été synthétisé en utilisant une méthode différente, comme un mélange de KOH et de NaOH comme catalyseur homogène à l'utilisation de l'oxyde d'aluminium comme catalyseur et, enfin, à la fabrication d'un catalyseur hétérogène par imprégnation de KOH et de NaOH dans l'alumine et à la comparaison avec le catalyseur le plus utilisé pour produire du biodiesel qui est, NaOH; la comparaison était fondée sur la production de rendement dans les mêmes conditions (température, temps de réaction, rapport molaire et rapport de masse) et le même OMD pour nous assurer d'obtenir le résultat le plus précis.

Dans cette étude, nous avons constaté que le rendement le plus élevé (93,1 %) a été atteint avec NaOH/alumine, et le rendement en NaOH était de 89,9 %, puis nous avons étudié les effets qui contrôlent la production de biodiesel pour NaOH/alumine, comme la température, le temps de réaction, le rapport molaire MeOH:WCO, et le ratio de masse du catalyseur, puis nous gérons pour l'optimiser à 94,4%.

En conclusion, nous avons optimisé le catalyseur de biodiesel pour produire un rendement plus élevé et, en même temps, le réutiliser plusieurs fois en raison de la nature du catalyseur hétérogène, ce qui aide à réduire le coût du biodiesel production

Mots clés : Biodiesel, Catalyseur hétérogène, Rendement, Alumine, Optimiser, Le coût

ملخص

في السنوات القليلة الماضية، من أزمة تغير المناخ إلى الصراع الأوكراني الروسي، ونقص سلاسل التوريد أدى إلى نقص حاد في الطاقة في العديد من البلدان، مما فتح التوجه والاعتماد على مصادر الطاقة المتجددة، بما في ذلك الوقود الحيوي. ومع ذلك، نحن بحاجة إلى تحسين إنتاجيتها وتقليل تكلفتها لأن هذه هي العقبات التي تواجه صناعة الوقود الحيوي. تطوير وتحسين المحفز المستخدم لأنه له أكبر تأثير على الإنتاجية والتكلفة.لذلك، نريد

من خلال تجربة محفزات محتملة مختلفة، تم تصنيع كل واحدة باستخدام طريقة مختلفة، مثل مزيج من هيدروكسيد البوتاسيوم وهيدروكسيد الصوديوم كعامل حفاز متجانس واستخدام أكسيد الألومنيوم كعامل حفاز وأخيراً صنع حفاز غير متجانس عن طريق تلقيح هيدروكسيد البوتاسيوم وهيدروكسيد الصوديوم في أكسيد الألومنيوم ومقارنته بالمحفز الأكثر استخداماً لإنتاج البوتاسيوم الحيوي ؛ استندت المقارنة إلى إنتاج الغلة في نفس الظروف (درجة الحرارة ووقت التفاعل الكتلة) ونفس زيت الطهي المستخدم لضمان حصولنا على النتيجة الأكثر دقة.ونسبة المولي ونسبة

في هذه الدراسة، وجدنا أن أعلى مردودية (93,1%) تم تحقيقه باستخدام هيدروكسيد الصودويم/أكسيد الألومنيوم، و ثم 89,9% مردودية هيدروكسيد الصودويم، ثم درسنا التأثيرات التي تتحكم في إنتاج الديزل الحيوي لهيدروكسيد الصودويم/الألومنيوم، مثل درجة الحرارة ووقت التفاعل ونسبة المولا إلى الكحول، من خلال هته الدراسة استطعنا تحسين المردودية الى(94,4%).

في الختام، قمنا بتحسين محفز الديزل الحيوي لإنتاج عائد أعلى، وفي الوقت نفسه، إعادة استخدامه عدة مرات بسبب طبيعة المحفز غير المتجانس، مما يساعد على تقليل تكلفة انتاج الوقود الحيوي.

الكلمات الرئيسية: الديزل الحيوي، المحفز غير المتجانس، المردودية، أكسيد الألومنيوم، التحسين، التكلفة

Introduction

The decrease in fossil energy resources and the awareness of the impact of greenhouse gas emissions on the environment have created the need to find alternative energy sources to traditional energy sources. Thus, for several years, we have seen the development of several renewable energy production channels, notably under the impetus of incentives from public authorities.[1]

Biodiesel is a renewable fuel produced for diesel engines from natural oils and fats. Biodiesel offers economic, environmental, fuel quality and energy security advantages over petroleum diesel [2].

Algeria has an unused plant potential that can be used to produce different oils whose consumables can be used for the production of biodiesel. To this end, the candidate plants are numerous such as castor, sunflower, cactus (prickly pear in particular), algae and marine microalgae [3].

Vegetable oil has been considered as a potential automotive fuel since at least 1912, when **Rudolf Diesel** (inventor of the eponymous engine) mentioned it in a patent application. Since the 1970s, more focused work has been done on modifying diesel engines to run on crude vegetable oil (CVO). This work has shown that the concept works well. However, a number of structural barriers to the success of this fuel on the market must be overcome if it is to play a role in the future fuel supply [4] Among the problems to be overcome is the high viscosity of the oils, and the process most commonly used to reduce the viscosity of the oils is transesterification, which leads to the formation of biodiesel.

Biodiesel is produced by the conversion of lipids (oils and fats) into fuel through transesterification. Transesterification is the chemical reaction in which a lipid reacts with an alcohol to generate three fatty acid esters (biodiesel) and one glycerol molecule. The reaction requires a homogeneous or heterogeneous catalyst to occur.

Homogeneous catalysis is efficient at low temperatures but it leads to soap formation and subsequent problems of product separation and in particular glycerin purification. These drawbacks can be overcome by using heterogeneous catalysis, which is already done on a commercial scale but at higher temperatures than the homogeneous process.

Given the growing importance of biodiesel, it was justified to study the production of this biofuel by transesterification of waste oils.

This thesis comprises three key chapters. Chapter 1 provides a comprehensive overview of biofuel, biodiesel, and vegetable oils, exploring their significance as renewable energy sources. It encompasses a thorough examination of their composition, production methods, and environmental benefits, establishing a foundation of general knowledge in this field. In Chapter 2, the focus shifts to the synthesis of biodiesel, with an emphasis on the implementation of different catalysts. In Chapter 2, the focus shifts to the synthesis of biodiesel, with an emphasis on the implementation of different catalysts. The chapter dive into the methodology employed for conducting experiments and explores the process of performing proper analysis for biodiesel production. It outlines the steps followed, such as the selection and preparation of reactants, the choice of catalysts, and the optimization of reaction conditions. Additionally, it describes the techniques utilized for monitoring and analyzing key parameters during the synthesis process, ensuring accurate and reliable results. In Chapter 3, the focus is on presenting the results obtained from the biodiesel synthesis experiments, specifically exploring the effects of molar ratio, mass ratio, temperature, and time on the yield. The chapter begins by providing a detailed analysis of the experimental data, including the variations in yield under different molar ratios, mass ratios, temperatures, and reaction times. It discusses the trends and patterns observed in the results, highlighting the impact of each parameter on the overall yield of biodiesel. Furthermore, the chapter examines any correlations or relationships between the variables studied and identifies the optimal conditions for achieving the highest yield. The results are presented in a clear and concise manner, supported by appropriate statistical analysis and graphical representations to enhance understanding and interpretation.

Chapter I

Background

1.1 Definition of biofuels:

Biofuels (or agrofuels) are fuels derived from the transformation of non-fossil organic materials from biomass. Can be considered as biofuel any organic material that can produce energy (e.g., wood, waste). [5]

There are two main biofuel production channels: first generation and second generation.

1.2 1st generation biofuels:

Depending on the production method used, they group together two main types of products. We have the biodiesel sector and the alcohol sector, the best known of which is ethanol.

1.2.1 The biodiesel industry

Biodiesel is a fuel that can be used pure and/or mixed in diesel fuel for diesel engines. It is made up of vegetable oil methyl esters (VOME), which themselves come from vegetable oils (coconut, palm, soya, etc.). Indeed, esters are hydrocarbons obtained by transesterification reaction between triglycerides and alcohols. In our case, the alcohol used is ethanol

Methyl esters thus have the formula **R-COOCH3**, where **R** is a group alkyl.

They are currently being developed and used as an alternative fuel. They are incorporated in the composition of gas oils up to 5% by volume because they have similar combustion characteristics to gas oils (viscosity, cetane number, etc.). The cetane number is one of the main indicators of diesel quality and characterizes the ignition delay of the fuel when it is injected into the combustion chamber.

1.2.2 The alcohol industry

Alcohols (mainly ethanol) are produced from sugar plants (beet, sugar cane) and cereals (wheat, corn, barley). They are used for the reformulation of commercial gasoline in varying proportions depending on the country. Alcohols, with the formula R- OH, have many interesting characteristics, including high octane ratings (the octane rating indicates the resistance of a fuel to knocking in a spark-ignition engine).

The prospects for the development of these first-generation biofuels are real, but their production sometimes raises serious questions in society because of the competition with the food needs of the population. Moreover, the quantities produced today are still limited and can only replace a small proportion of fossil fuels. The so-called second-generation production routes promise an increase in the production of these fuels, without competing with food uses, which will always remain a priority. [6]

1.3 2nd generation biofuels:

Second generation biofuels are obtained from biomass that does not compete with food use: cereal straw, miscanthus, wood and forest residues and dedicated crops. There are two possible production channels:

1.3.1 The biochemical industry:

It is the production of cellulosic ethanol by fermentation. This process is carried out in 3 main steps. Of the three major constituents of lignocellulosic biomass (cellulose, hemicelluloses and lignin) only cellulose can be transformed into ethanol today. A first step consists in extracting the cellulose and then transforming it into glucose by hydrolysis with the help of enzymes (enzymes produced in reactors from microorganisms are able to naturally degrade cellulose into glucose). The glucose is then fermented by yeast into ethanol. Finally, the ethanol is purified by distillation and dehydration.

1.3.2 The thermochemical sector:

One route is the production of synthetic diesel fuel BtL (Biomass to Liquid). For the thermochemical route, the biomass is first conditioned by pyrolysis or torrefaction. Then it is gasified at more than 1000°C in the presence of steam or oxygen. This produces the synthesis gas, which consists of carbon monoxide **(CO)** and hydrogen **(H_2)**. The next step is the Fischer- Tropsch synthesis, a catalytic chemical transformation of the synthesis gas into linear kerosenes which, hydrocracked and isomerized, will produce a synthesis gasoil.

1.4 3rd generation biofuels:

These are agrofuels from microalgae or Algae fuel. Microalgae can provide different types of renewable energy. These include methane produced by anaerobic digestion of algae, biodiesel derived from the oil of microalgae and the production of hydrogen by photobiology.

The idea of using microalgae as a fuel source is not new, but it is beginning to be considered seriously due to the escalating oil prices and global warming that is associated with fossil fuel consumption.

The cultivation of microalgae seems, from a theoretical point of view, 30 to 100 times more efficient than terrestrial oilseeds according to some authors. To obtain an optimal oil yield, the growth of microalgae must be carried out with a CO2 concentration of about 13%. This is possible at a very low cost by coupling with a CO2 source, for example a coal, natural gas or biogas power plant, or an alcohol fermentation unit, or a cement plant. Microalgae cultivation in open ponds is also being experimented with in algae farms in New Mexico and in the Negev desert. However, major challenges remain (price, fertilizer input, environmental impact, yield limitation of photosynthesis...). [7]

1.5 Biofuels Environmental and Economic Impacts:

1.5.1 Environmental Impacts:

A study indicates that biofuels have a positive impact on the environment in contrast to fossil fuels, whose combustion leads to the production of a high percentage (72%) of carbon dioxide and greenhouse gases CO2, NO2, SO2), unlike biofuel, which reduces emissions The greenhouse gases by (65%- 40%). Because the combustion of both types of fuel does not have the same effect as shown in the figure, where fossil fuels produce toxic carbon dioxide in the atmosphere, which leads to global warming, unlike biofuels, which burn better because it contains the oxygen atom is in a chemical formula, where the carbon emitted from it acts as a source of energy for plants (they use it in the photosynthesis process). As a result, biofuels are more environmentally friendly.

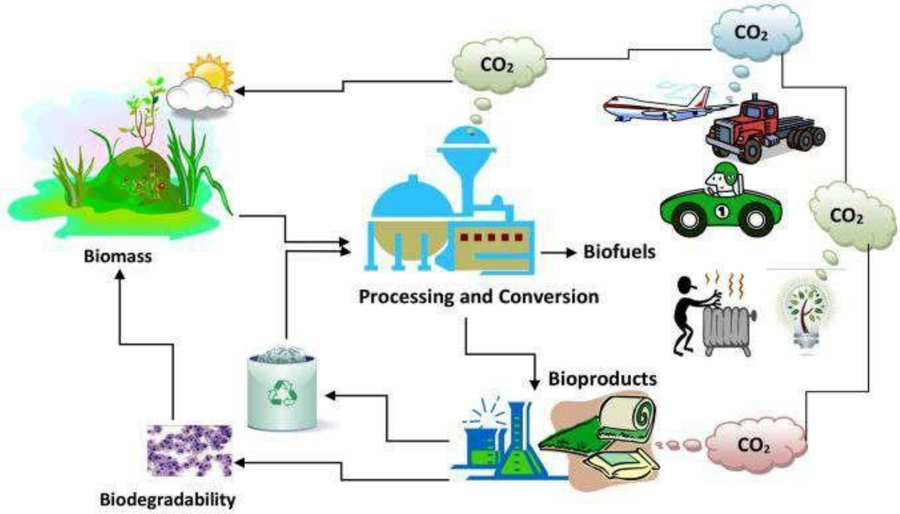

Figure 1:*Biomass life cycle for biofuels. [3]*

1.5.2 Economic Impacts:

- Job creation: Biofuel production and distribution create employment opportunities in farming, processing, transportation, and other related sectors.
- Diversification of rural economies: Biofuel’s production can provide an additional revenue stream for farmers and rural communities, reducing dependence on traditional agricultural markets.
- Price stability: Biofuel can help stabilize fuel prices by reducing dependence on volatile petroleum markets, as feedstocks for biodiesel can be domestically sourced.
- Energy security: Investing in Biofuels production strengthens national energy security by diversifying the energy mix and reducing dependence on foreign oil.
- Economic growth: Biofuel industry growth stimulates economic activity, attracting investments in research, development, and infrastructure. [7]

1.6 Biodiesel Situation in Algeria:

Some African countries are in greater need of access to clean and renewable sources of energy. Oil-producing nations like Algeria rely on this source of energy to meet their energy needs and optimize their economic and industrial interests. Other African countries rely on fossil fuels, firewood, and charcoal. This situation severely limits economic and social development. At the present time, the African biofuels industry appears to be one of the solutions to the continent's energy and economic problems.

Far from being synonymous with energy independence (production and consumption), biofuels would enable the development of African economies, currently stifled by the high demand for fossil fuels. What's more, the biofuels industry could create jobs and limit unemployment to a certain extent.

Our country's wealth in hydrocarbons and its membership in the Organization of the Petroleum Exporting Countries (OPEC) (over 90% of Algeria's exports come from oil and natural gas) have hampered any attempt to use and exploit renewable energies, despite the country's natural wealth in solar, wind, biomass, and geothermal energy.

Algeria is located in an area vulnerable to the adverse effects of climate change due to pollution and environmental imbalances. Today, the transport sector generates a quarter of the greenhouse gas emissions responsible for this climatic imbalance, which could account for a third of these emissions by 2030. What's more, energy consumption and demand for an exhaustible fossil fuel source will outstrip supply. Figure 2 shows the chronological comparison between demand and supply for diesel fuels in Algeria. [3]

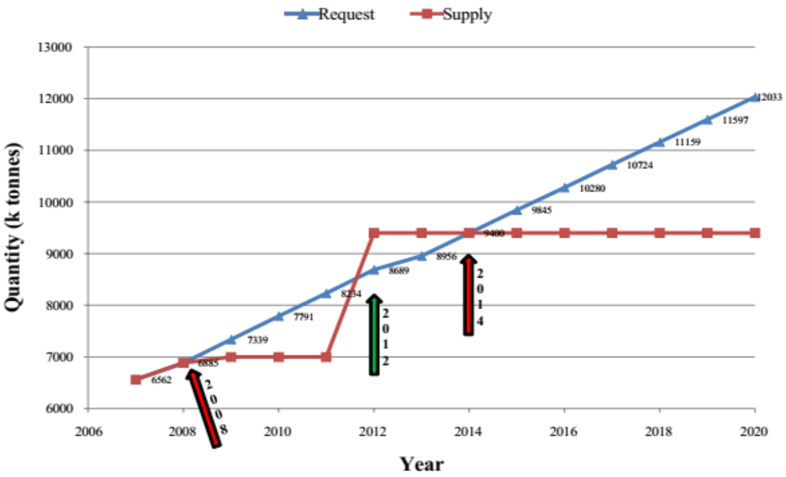

Figure 2:Diesel demand and supply trends in Algeria

1.6.1 An Estimation Cost for Biodiesel production:

Table 1:*An Estimation Cost for Biodiesel production.*

Item	Price
Methanol cost ($/liter biodiesel)	0.072
KOH cost ($/liter biodiesel)	0.02
Waste cooking oil cost ($/liter biodiesel)	0.333
Utilities cost ($/liter biodiesel)	0.036
Other chemicals costs ($/liter biodiesel)	0.027
Fixed cost (maintenance, salaries and insurance) ($/liter biodiesel)	0.027
Biodiesel production cost ($/liter)	0.515
Biodiesel production cost ($/gallon)	1.949
Current market price biodiesel ($/gallon)	3.77
Current market price Petro-diesel in USA ($/gallon)	2.561
Current market price Petro-diesel in Algeria ($/gallon)	0.810

1.7 Advantages and disadvantages of biofuels:

The main advantages and disadvantages of biofuels are summarized in the following table:

Table 2: The main advantages and disadvantages of biofuels [8]

THE BENEFITS	THE DISADVANTAGES
- Renewable. - Limit greenhouse gas (GHG) emissions and non-renewable energy consumption. - Emit less pollutants such as Sulphur (the cause of acid rain), soot and fine particles. - They allow to diversify the sources of energy production and to reduce the dependence on black gold and to develop domestic resources.	- The increase in demand for biofuels has resulted in higher world prices for grains and oilseeds - They are energy-intensive, expensive to grow, collect and process. - they create a formidable competition between energy crops and food crops. - The development of biofuels from energy crops can be a threat to ecosystems and sinks.

1.8 Biodiesel:

Biodiesel is the name that has been given to transesterified vegetable oils. It is a reaction between oil and alcohol, forming methyl or ethyl esters of vegetable oils (alternative fuel to diesel of fossil origin) and glycerol, known as glycerin, which is a product of great value, its valuation is crucial for the economic balance of the sector. [9]

Biodiesel can be produced from the oils of a very wide range of oil-producing plant species. However, for the first generation of biodiesel, only a few plant species are cost-effective for relatively small-scale use as fuel. On the other hand, it is possible to produce biodiesel from animal fat and waste oil, but the limited availability of these feedstocks compromises large-scale production.

The production of biodiesel from oleaginous agricultural products involves two processing phases:

- ✓ The first phase is identical to that required for human consumption, it consists of the

  extraction of oil by pressing (hot or cold) or by solvent extraction.
- ✓ The second phase, consists of the transformation of the oil into biodiesel by Transesterification; a chemical process that, with the help of an alcohol, allows to obtain ester compounds (main component of biodiesel).

The production of biodiesel from oilseeds generates two types of co-products.

On the one hand, we have oilseed cakes, the solid residue of grain crushing, which represents 50% to 75% of the grain mass. The economic value of these co-products depends on their protein content, which varies from one species to another. The income generated by the sale of co-products allows to amortize the cost of biodiesel, given the large quantity of oilcake generated. On the other hand, glycerol is a liquid that has several applications, notably for the manufacture of pharmaceutical and cosmetic products.

Obviously, the production of biodiesel is easier to develop than the production of ethanol, in the sense that ethanol production processes require more processing steps and more chemical inputs to reach the final product. For first generation biofuels, a technological breakthrough allowing a dramatic decrease in production costs no longer seems feasible as the techniques used are reaching maturity. [5]

1.9 The conversion of triglycerides into biodiesel:

Biodiesel is a fuel that has more or less the same characteristics as Petro diesel. Generally, vegetable oils are used such as coconut oil, soybean oil, rapeseed oil or palm oil. These oils are subjected to a chemical reaction: **transesterification**.

Transesterification is a catalytic chemical reaction between oil and an alcohol (methanol, ethanol, ...) whose product is a mixture of esters and glycerol (glycerin). The mixture of esters is biodiesel, it is mixed with diesel

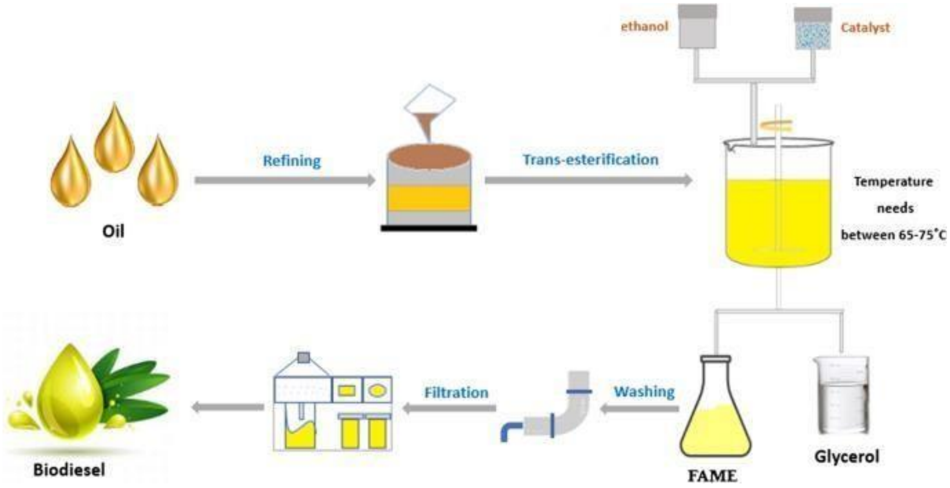

Figure 3 : *Biodiesel Production.*

Glycerol can be valorized; indeed, one of the possible valorizations is the synthesis of monoglycerides (or glycerol monoesters). The monoglycerides from glycerol can be added to biodiesel on the one hand; on the other hand, they have a particular interest in the synthesis of drugs, cosmetics, detergents, soaps, etc. [3]

1.10 General information on vegetable oils:

1.10.1 Definition:

Is a pure vegetable oil from rapeseed, mustard, sunflower, for example? In principle, most oils available in any supermarket can be used. straight vegetable oil (SVO) or pure plant oil (PPO) simply has optimal fuel performance for modified diesel engines. [4]

Vegetable oils are triglycerides, which are compounds consisting of glycerin (a trivalent alcohol) and three linked fatty acids. Glycerin is responsible for the viscosity.

At 40°C, vegetable oil is almost ten times thicker than diesel oil.[10]

1.10.2 The different sources of oil:

In principle, any source of fat can be used to prepare biodiesel. However, some sources are preferred over others depending on the country. Thus, in the United States, manufacturers use soybean oil. They are the largest producers of soybean oil before Brazil. The Brazilians, for their part, use different sources of oil because of the biodiversity of the country. For example, in the north of the country it is mainly palm oil and soybean oil

In the central-west, the main products are soybean, cotton, castor and sunflower oil. In France, producers mainly use rapeseed oil [7]

1.10.3 Chemical characteristics of vegetable oils:

All vegetable oils are composed, in varying proportions, of three types of fatty acids: saturated, monounsaturated and polyunsaturated. They are classified according to the predominant fatty acids. All vegetable oils are hydrophobic in nature. They must be formulated with appropriate surfactants in order to emulsify them in water for application. [11]

1.10.4 Usage:

Vegetable oils are obtained by grinding oil seeds. After their purification by various processes (decantation, filtration, etc.), these so-called "pure" vegetable oils can be used under certain conditions as fuel in diesel engines:

- In slightly modified diesel engines: 100% oil can be used, however, since pure oil is more viscous than diesel, the injection systems must be protected.
- In unmodified diesel engines: vegetable oils are converted into methyl esters, better known as diester (in France) or biodiesel. The latter can be used in any proportion in an unmodified diesel engine. It is simply a matter of ensuring that the pipes and seals are resistant to the properties of this fuel. This is the case for the vast majority of manufacturers and new car models. [12]

1.11 Chemical Changes occurring in oils and fats during frying:

Frying is a process of immersing food in hot oil with a contact among oil, air, and food at a high temperature of 150°C to 190°C. The simultaneous heat and mass transfer of oil, food, and air during deep-fat frying produces the desirable and unique quality of fried foods. The hydrolysis, oxidation, and polymerization of oil are common chemical reactions producing volatile or nonvolatile compounds. [11]

1.11.1 Hydrolysis of oil:

When food is fried in heated oil, the moisture forms steam, which evaporates with a bubbling action and gradually subsides as the foods are fried. Water, steam, and oxygen initiate the chemical reactions in the frying oil and food. Water, a weak nucleophile, attacks the ester linkage of triacylglycerols and produces di- and monoacylglycerols, glycerol, and free fatty acids.

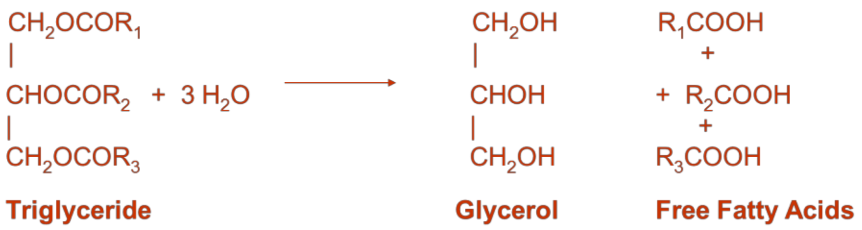

Figure 4 : Hydrolysis Reaction [11].

1.11.2 Oxidation of oil

Oxygen, which is present in fresh oil and is introduced into the frying oil at the oil surface and by addition of food, activates a series of reactions involving formation of free radicals, hydroperoxides, and conjugated dienoic acids. The chemical reactions that occur during the oxidation process contribute to the formation of both volatile and nonvolatile decomposition products. The chemical mechanism of thermal oxidation is principally the same as the autoxidation mechanism. The thermal oxidation rate is faster than the autoxidation, but specific and detailed scientific information and comparisons of oxidation rates between thermal oxidation and autoxidation are not available. The mechanism of thermal oxidation involves the initiation, propagation, and termination of the reaction.

1.11.3 Polymerization of oil

Polymerization occurs during frying, producing a wide variety of chemical reactions that result in the formation of compounds with high molecular weight and polarity. Polymers can form from free radicals or triglycerides by the Diels–Alder reaction. Cyclic fatty acids can form within one fatty acid; dimeric fatty acids can form between two fatty acids, either within or between triglycerides; and polymers with high molecular weight are obtained as these molecules continue to cross-link.

Type of Reaction	***Causative Agent***	***Resulting Compounds***
Oxidation	Oxygen	Oxidized monomeric triglycerides Dimeric and oligomeric triglycerides Volatile compounds (e.g., aldehydes, ketones, alcohols, esters, hydrocarbons, and aromatic compounds)
Thermal degradation	Temperature	Cyclic monomeric triglycerides Nonpolar dimeric and oligomeric triglycerides
Hydrolysis	Moisture	Fatty acids Monoglycerides

Table 3: Compounds Formed during Deep- Frying [11].

1.12 The transesterification reaction:

1.12.1 Background:

Transesterification of triglycerides is not a new process. It dates back to 1853 when Patrick and Duffy conducted this reaction many years before the first diesel engine was functional.

This reaction has been the subject of intensive research due to the various uses of these products including the synthesis of polyesters or PET in the polymer industry, the synthesis of intermediates for the pharmaceutical industry, the curing of resins in the paint industry and in the production of biodiesel as an alternative to diesel [7].

I.6.1. Definition:

Transesterification is the reaction of an alcohol and fatty esters to form esters of that alcohol and glycerin. The fatty esters are solid triglycerides at room temperature in the case of fats; and liquid at room temperature in the case of oils. The transesterification reaction can be written [13].

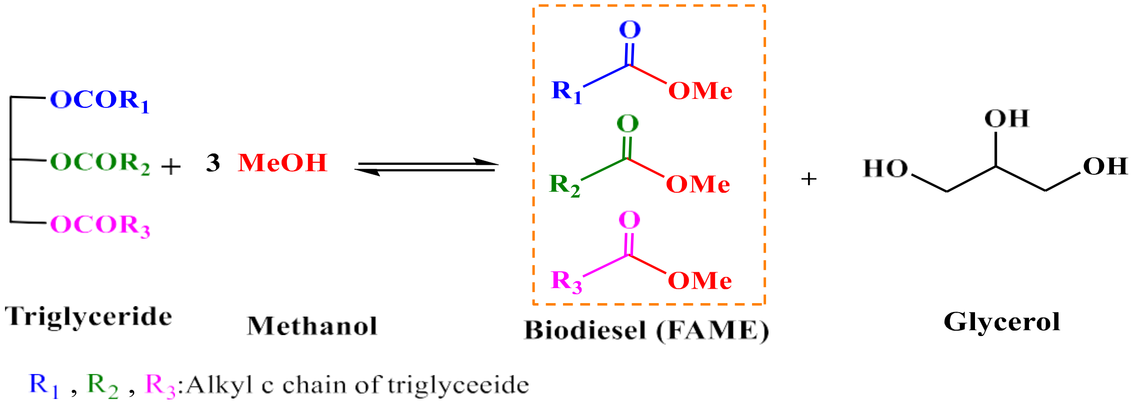

***Figure 5**:General equation for the transesterification reaction*

1.12.2 The Mechanism of the transesterification reaction:

The transesterification reaction takes place in three successive steps:

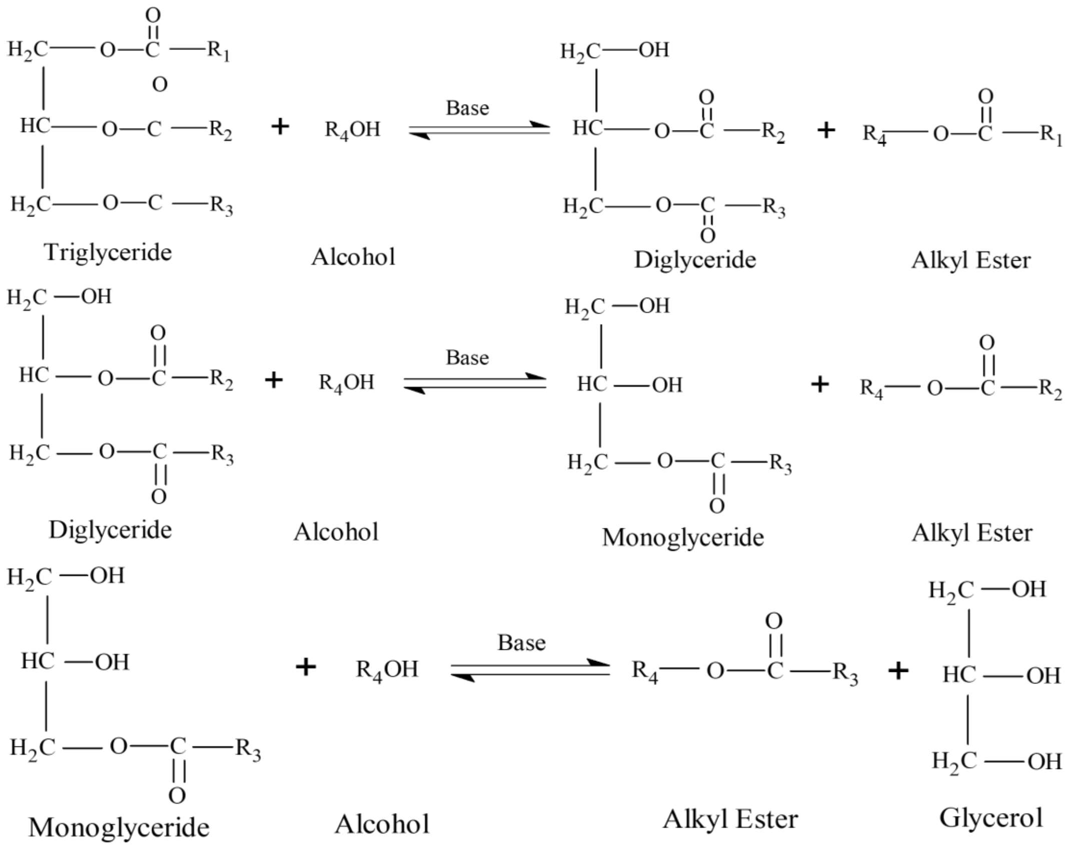

Figure 6: *Successive reactions of transesterification.* [7]

The transesterification reaction is chemically balanced. Steps (1) and (2) are fast because the primary ester functions are transesterified first, step (3) is slower. [7]

1.12.3 Mechanism of transesterification in case of basic catalysis:

The reaction mechanism of the Transesterification with the basic catalysts each of the previous transformations takes place in three steps, steps (1) and (2) fast because the ester functions are converted first, and step (3) is slower. As shown in the figure

$$MeOH + B \rightleftharpoons MeO + BH$$

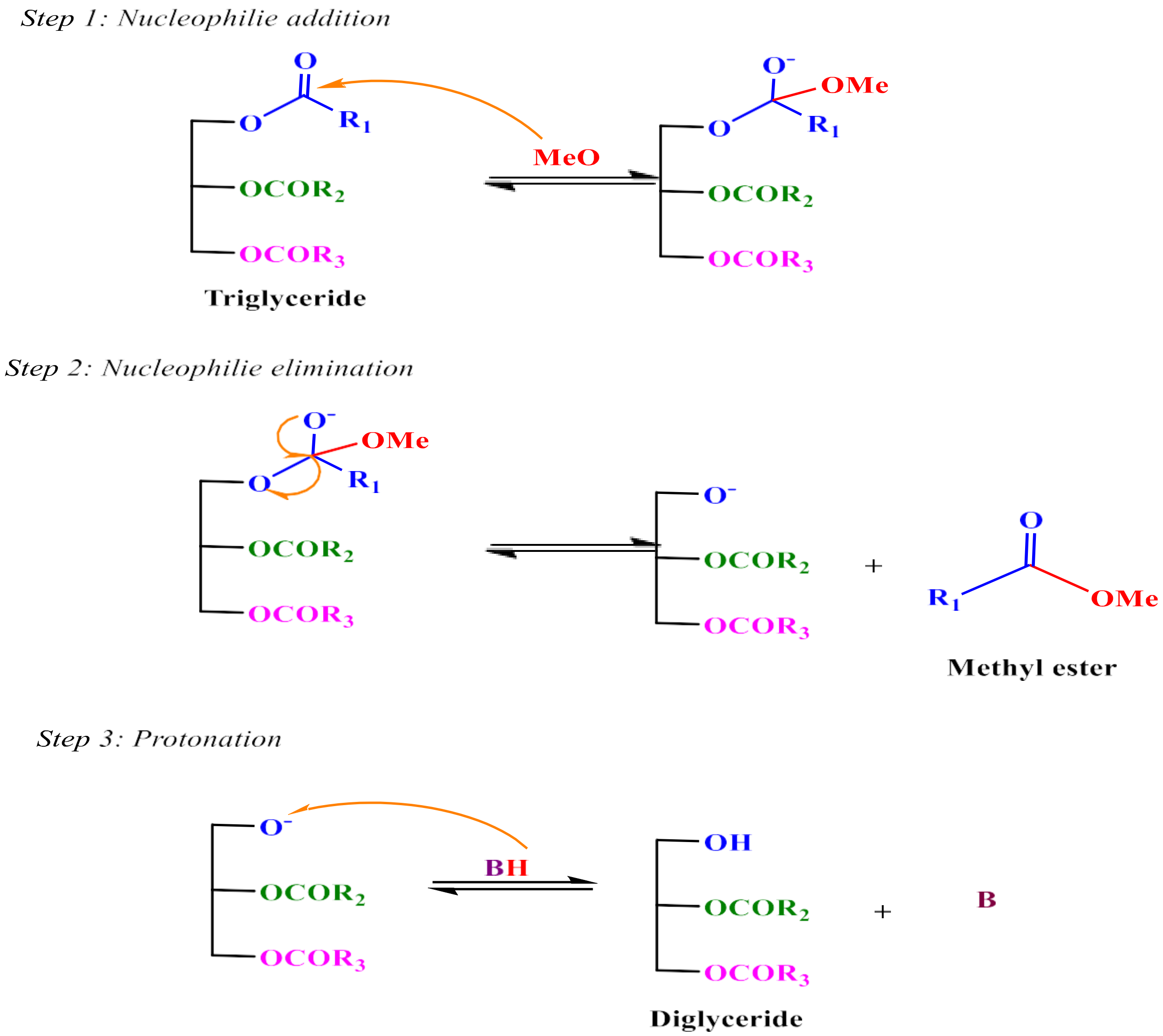

Figure 7: *Mechanism of the Transesterification reaction of triglycerides with methanol in the presence of a basic catalyst*

1.12.4 Acid catalyst mechanism

The reaction mechanism of the Transesterification with the acid catalysts each of the three transformations takes place in four steps.

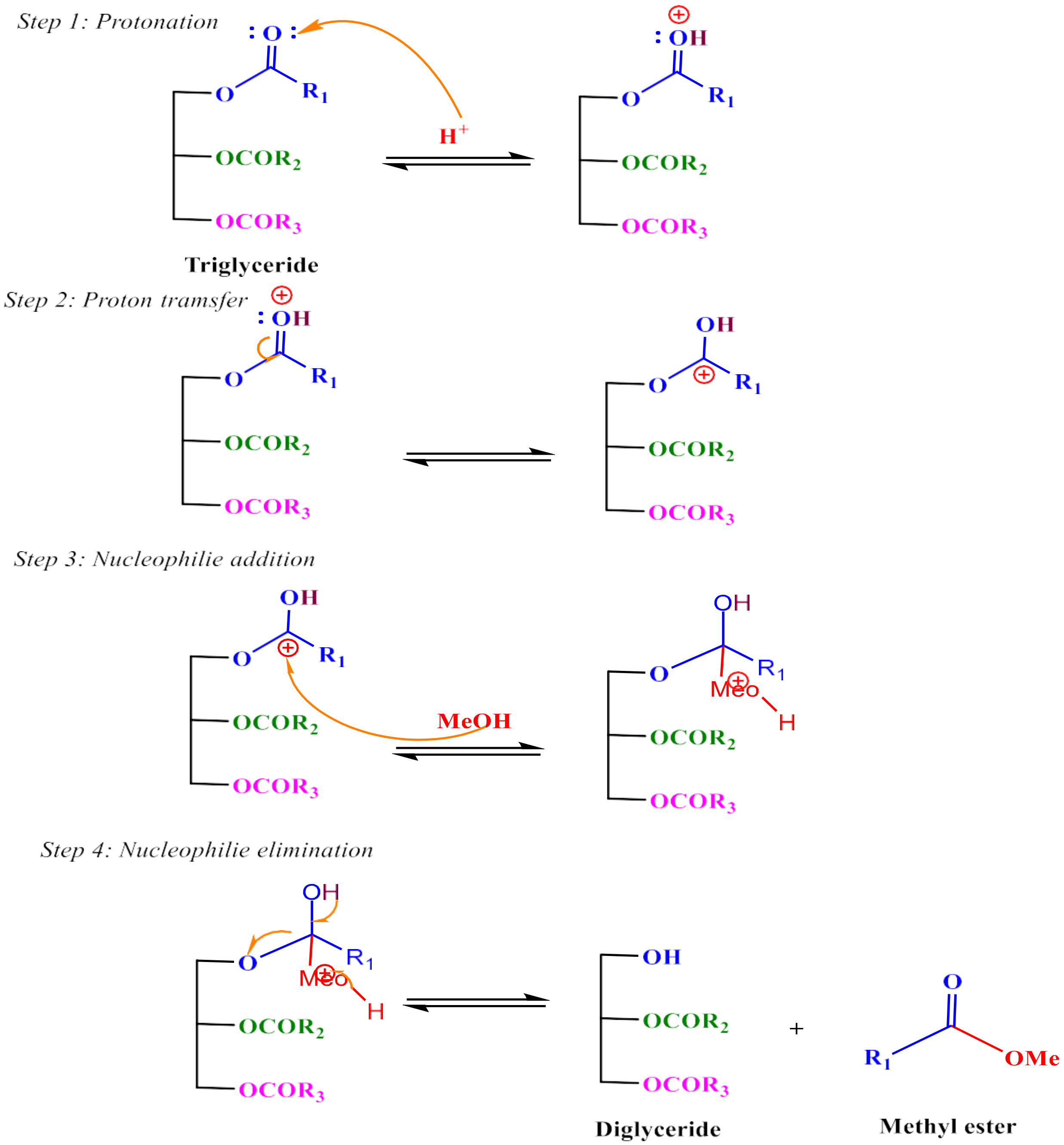

***Figure 8**: Mechanism of Transesterification reaction of triglycerides with methanol in the presence of an acid catalyst*

1.13 Purpose of the transesterification reaction:

The thermal decomposition of an oil which is an ester of glycerin, in the absence of oxygen leads to the formation of glycerol and a mixture of esters.

The objective of such a study is the use of the obtained esters as diesel fuel; the study leads at the same time to:

a) The total elimination of glycerin,
b) The decrease of the boiling point of the oil,
c) The decrease of the flash point of the oil,
d) The use of glycerin in the chemical industry,
e) The use of by-products in the soap and detergent industry. [15]

1.14 The parameters influencing the kinetics of this reaction:

1.14.1 alcohol/oil ratio:

The reaction is in both directions (transesterification and condensation); therefore, to shift the equilibrium in the direction of ester formation, an excess of one of the two reactants is required. The stoichiometry of the transesterification reaction shows that the number of moles of alcohol is three times that of triglycerides. So at least the number of moles of one of the reactants must be doubled. For various reasons the alcohol is taken in excess; the molar ratio alcohol/oil is at least 6. The literature shows that this ratio is very variable depending on the nature of the oil and the catalyst used.

1.14.2 The nature and quality of the oil:

Secondary (parasitic) reactions can take place if the oil contains water and free fatty acids. And as a result, the transesterification kinetics are affected.

1.14.3 Nature, quantity and type of catalyst:

Transesterification is often performed with a catalyst. The catalyst can be a chemical substance (homogeneous and heterogeneous catalysis) or an enzyme (enzymatic catalysis);

1.14.4 Temperature and pressure:

The literature shows that virtually all studies of catalyzed transesterification of vegetable oils are conducted under atmospheric pressure. As for the temperature it varies from 40 to 300 °C approximately; depending on the nature of the oil, the type of catalysis of the reaction and the catalyst [3]

1.15 Catalysis:

1.15.1 Definition

A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. Catalysts work by lowering the activation energy required for a reaction to occur, making it easier for reactant molecules to overcome the energy barrier and react with each other. Catalysts are widely used in industrial processes to increase reaction rates and efficiency, and they also play important roles in many biological processes. (**Romain RICHARD, 2011)**

1.15.2 Homogenous Catalysis:

Homogeneous catalysts are the latest catalysis route for the transesterification of triglycerides with alcohols. Currently, basic homogeneous catalysts are the most used in industrial transesterification processes for biodiesel production, mainly because of their efficiency at relatively moderate temperatures and their lower cost than heterogeneous and especially enzymatic catalysts. Homogeneous acid catalysts are used a little less because they can cause corrosion problems. [16]

The mechanism of the catalyzed transesterification reaction is therefore an essential parameter for understanding the reactivity of the catalysts. In homogeneous catalysis, these mechanisms have been described in a rather exhaustive way in the literature. They are classified with a set of three letters followed by a number. The first letter designates the type of mechanism (A: acidic, B: basic), the two following ones, the location of the break around the bridging oxygen of the ester function. If the break is on the alcohol side, the mechanism is AL. If the break occurs on the acid side, the mechanism is AC, as shown in the Figure [17]

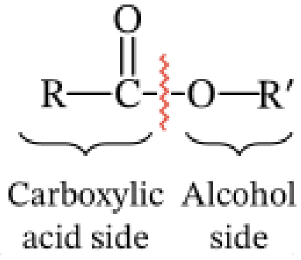

Figure 9: *Two possible types of bond breaks*

1.15.3 Heterogeneous catalysis:

Heterogeneous (solid) catalysts can also be used in the framework of transesterification reactions of vegetable oils. Their main interest is their easy separation from the reaction medium, by simple filtration, as well as their more or less long life depending on the catalyst. The possibility to reuse heterogeneous catalysts in several reaction cycles is a significant advantage for the production of biodiesel on an industrial scale:

The reduced catalyst consumption means lower production and processing costs. The resulting process would ultimately be safer, less expensive and more environmentally friendly. The heterogeneous catalysts tested so far can be acidic or basic.

Under optimal reaction conditions, these heterogeneous catalysts can lead to satisfactory yields of fatty acid esters (above 95%). However, in addition to their synthesis and implementation sometimes difficult, the major disadvantage of this type of catalyst is their cost which is, in general, higher than that of the homogeneous catalysts [16]

1.15.4 Enzymatic catalyst:

An enzymatic catalyst is a type of catalyst that is composed of biological molecules called enzymes. Enzymes are specialized proteins that catalyze biochemical reactions in living organisms by binding to specific molecules, called substrates, and facilitating their conversion into different molecules, called products.

Enzymatic catalysts are highly specific in their actions and can often distinguish between different substrates based on their molecular structure. They are involved in many important biochemical processes in the body, including digestion, metabolism, and energy production

They are also widely used in industry for a variety of applications, such as in food processing, pharmaceuticals, and biofuels production. They offer several advantages over traditional chemical catalysts, including higher selectivity, milder reaction conditions, and greater efficiency. [14]

1.15.5 Comparison between homogeneous and heterogeneous catalysis:

Table 4 : *Comparison between homogeneous and heterogeneous catalysis [18]*

Homogeneous:	Heterogeneous:
• often more active and selective • Difficulties in separating and recycling solvents and catalyst • Simpler reactors and more favorable heat exchange • Corrosion and material transport problems	• More stable but less active and less selective catalysts • Easier separation of reaction products and catalyst • More complex reactors with significant heat exchange problems • Reaction heat recoverable at a higher thermal level

Chapter II

Methodology and Synthesis

Biodiesel production from waste cooking oil (WCO) offers a sustainable and economically viable solution for reducing waste and promoting renewable energy sources. The efficiency and selectivity of the catalyst employed in the transesterification process play a crucial role in determining the overall performance of biodiesel production. This thesis aims to explore and compare the effectiveness of different catalysts specifically chosen for their potential to enhance the transesterification reaction and maximize biodiesel yield.

The primary focus of this research is the investigation of catalysts, rather than a comprehensive analysis of biodiesel production in general. By narrowing our scope to catalyst selection, we can evaluate the specific advantages and limitations of each catalyst and determine the most suitable option for large- scale biodiesel production from WCO.

The catalysts under investigation include sodium hydroxide (NaOH), alumina (Al2O3), a combination of NaOH and alumina, a combination of NaOH and potassium hydroxide (KOH), and a heterogeneous catalyst NaOH and KOH impregnated with alumina. These catalysts were selected based on their potential to enhance transesterification reaction kinetics, conversion rates, and biodiesel yield.

By comparing the performance of these catalysts, we aim to identify the most effective catalyst for biodiesel production from WCO. This research will provide valuable insights into catalyst selection and its impact on reaction efficiency, thereby contributing to the development of an efficient and sustainable biodiesel production process.

In the subsequent sections, we will describe the experimental methodology employed for catalyst preparation, the transesterification reaction setup, and the characterization techniques used to evaluate catalyst performance. The obtained results and their analysis will be discussed in chapter 3 to compare the different catalysts and draw conclusions regarding their efficacy for biodiesel production from WCO.

2.1 The Waste Cooking Oil (WCO) as a Feedstock for Biodiesel

2.1.1 Cooking Oil Types

2.1.1.1 Sunflower Oil:

Sunflower oil is one of the most important vegetable oils employed for deep-frying. It has been used in the cooking of food such as French fries and frozen prefried foods at home, in fast-food restaurants, and in the industry [19]

Sunflower oil is made with 11 percent saturated fatty acids, 20 percent monounsaturated fatty acids and 69 percent polyunsaturated fatty acids [20]

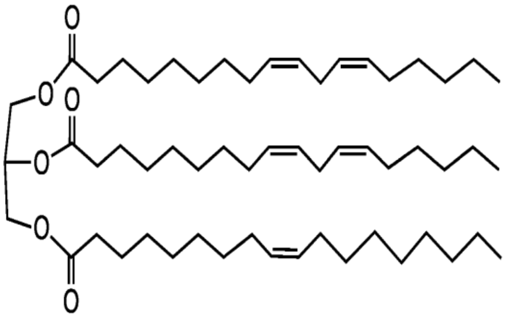

Figure 10: *sunflower oil chemical structure.*

2.1.1.2 Corn Oil:

Corn oil is highly effective food oil for lowering serum cholesterol. Because of its low content of SFAs which raises cholesterol and its high content of PUFAs which lowers cholesterol, consumption of corn oil can replace SFAs with PUFAs, and the combination is more effective in lowering cholesterol than simple reduction of SFA [21]

Corn oil is produced from the germ of the corn kernel which is obtained by degerminating corn in the hominy, starch and glucose industries. The germ represents approximately 10% of the dry kernel and contains about 50% of oil. [22]

2.1.1.3 Palm Oil:

Palm oil is obtained from the reddish pulp (mesocarp) of the fruits, mainly those of the African palm.

Palm oil is a typical multipurpose vegetable oil; it is used in food products (cooking oils, margarine and other spreads, crisps, baked food, food additives, confectionary, dairy and dairy replacements, prepared foods, snacks), in food for livestock and household pets (as fat supplement), and in several non-food productions (biodiesel, oleochemicals, cosmetics and textiles). The wide range of applications for mesocarp oil is due to its fatty acid (FA) composition. Palm oil has approximately equal amounts of saturated (SFA) and unsaturated fatty acids (UFA) [23]

2.1.1.4 Olive Oil:

Olive oil is one of the most reputative traditional foods in the world. Indeed, the cultivation of olives to produce olive oil has deep roots in the history of the Mediterranean region.[24]

The composition of olive oil is primarily triacylglycerols (~99%) and secondarily free fatty acids, mono- and diacylglycerols, and an array of lipids such as hydrocarbons, sterols, aliphatic alcohols, tocopherols, and pigments. A plethora of phenolic and volatile compounds are also present. Some of these compounds contribute to the unique character of the oil [25]

2.1.1.5 Canola Oil:

Canola oil is the only known vegetable oil with a Sulphur atom in some fatty acid structures that are responsible for the Sulphur flavor in the oil.

Canola oil has unique characteristics such as fatty acid composition and levels of tocopherols, phytosterols, and polyphenols. Canola oil contains about 12% α-linolenic acid (omega-3) and about 65% oleic acids. Also, it contains a low amount of saturated fatty acids (< 7%) compared to other common vegetable oils.[26]

2.1.2 Cooking oil characteristics

2.1.2.1 Lipid composition:

The chemical composition of a fat partly dictates its physical and functional properties. The chemical nature of lipids is dependent on fatty acid structure and distribution on the glycerol backbone. Fatty acids vary in chain length and in the number, position, and configuration of double bonds. TAGs composed of saturated fatty acids have high-melting points and are generally solid at ambient temperature, whereas TAGs consisting of unsaturated (monoene, polyene) fatty acids are usually liquid at room temperature [27].

In frying, oil is heated in air and in the presence of light at temperatures of 160-200 °C for relatively long periods of time. For economic reasons, the same oil/fat is used many times or continuously.

The conditions used for frying cause major physical and chemical changes in the oil, which differs from oil to oil, depending on their composition. Some common physical changes observed in vegetable oil after frying are (i) an increase in the viscosity, (ii) an increase in the specific heat, (iii) a change in the surface tension, (iv) a change in color, and (v)an increase in the tendency of fat to foam [28].

2.1.3 Cooking oil production worldwide:

This statistic shows the global consumption of vegetable oils from 2013/14 to 2019/20. In 2018/19, sunflower seed oil consumption amounted to 18.07 million metric tons worldwide. Global vegetable oil production amounted to around 203 million metric tons in 2018/2019 [29]

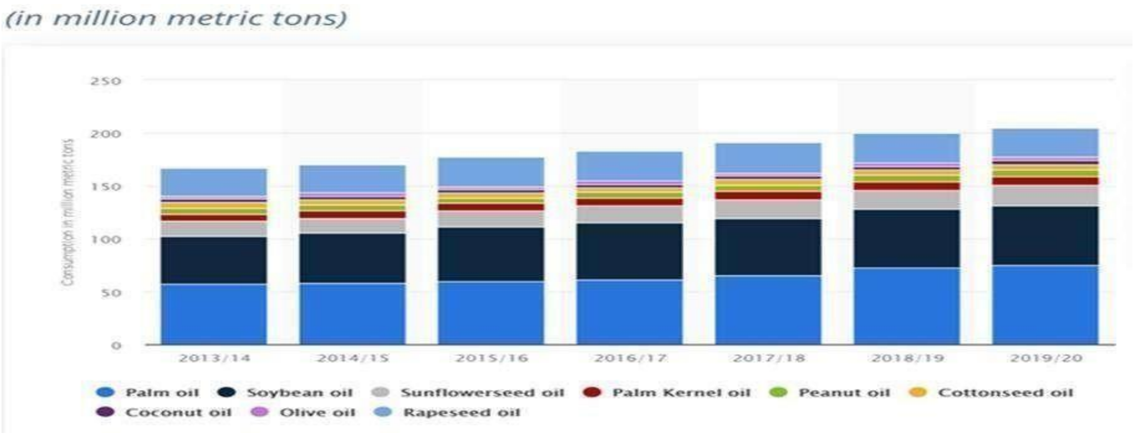

***Figure 11:** Consumption of vegetable oils worldwide from 2013/14 to 2019/2020, by oil type [29]*

2.1.4 Cooking oil used in Algeria

2.1.4.1 Sunflower oil:

Algeria exported 112 tons of sunflower oil in 2018. Through 2018 alone, the demand for the processed category has seen significant growth, changing by 100% over the previous year 2017. Between 2015 and 2018, sunflower oil exports grew by 100 per cent, earning Algeria $0.12m for the year 2018. The sunflower oil exports are categorized as:

Crude sunflower-seed or safflower oil the yearly growth in the volume of Algeria sunflower oil between 2015 and 2018 was 100% compared to the period between 2017 and 2018. Algeria's share of the world's total sunflower oil exports in 2018 was less than 1% [30].

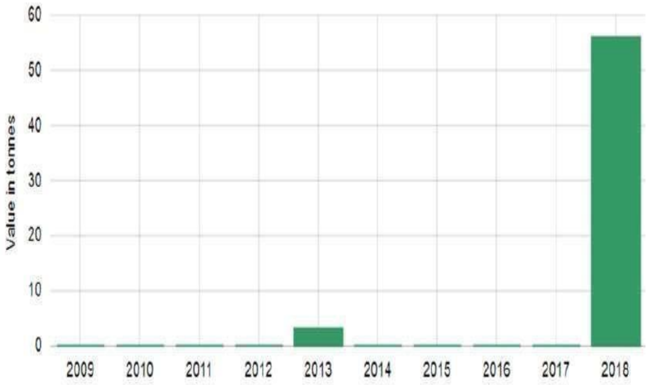

Figure 12: *value of sunflower oil in tunes – Algeria [30]*

2.1.4.2 Olive oil:

Algeria is one of the biggest producers of olive oil in the world (9TH PLACE). In 2006, the area covered by olive trees was 263,352 HA with a production of 196,258 TONS (17.8 L of oil /quintal of olives). According to International Olive Oil Council (I.O.C.) data, the Algerian production of olive oil, in 2007, WAS 215,000 TONS, while the Italian production was 490,000 TONS and the European community production was 2,030,800 TONS of oil. The olericultures concentrated mainly in the center of the country, the “KABYLIE” with 58.4% of the total oliviculture area. [31]

2.1.4.3 Waste cooking oil:

Waste cooking oil, which is much less expensive than pure vegetable oil, is a promising alternative to vegetable oil for biodiesel production.

The quantity of waste cooking oil generated per year by any country is huge. The disposal of waste cooking oil is problematic, because disposal methods may contaminate environmental water. Many developed countries have set policies that penalize the disposal of waste oil through the water drainage The production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically [32]

2.1.5 The Impact of Used Cooking Oil

2.1.5.1 Environmental Impact:

- Air Pollution

Used frying oils have minimal impact on the air, unless they are mixed with household waste and incinerated in open air, leading to the emission of pollutants into the atmosphere.

- Soil Contamination

When disposed of in the environment, used cooking oil affects the chemical composition of the soil, resulting in reduced long-term fertility

- Water Pollution

Used cooking oil poses the following risks to water bodies:

- ➢ Oil, being less dense than water, floats on the surface, creating an impermeable layer that hinders oxygen penetration, suffocating aquatic flora and fauna.
- ➢ Oil adheres to the gills and skin of fish, disrupting their normal functioning
- ➢ Discharging used oils into sewage systems and wastewater treatment plants (WWTPs) is not a viable solution. It leads to several issues:

Oil mixing with chemicals like fabric softeners or detergents forms a gelatinous layer that clogs drain, resulting in flooding, unpleasant odors, and the potential for pests such as cockroaches or rodents in kitchens.

It hampers the proper functioning of WWTPs, which employ aerobic bacterial treatment, leading to oxygen depletion. [33]

2.1.5.2 Economic Impact:

The impacts of used cooking oils extend beyond the environment and have economic repercussions Some examples include: [34]

- Investment is required to repair blocked or ruptured canals.
- The de-oiling process in WWTPs consumes energy.
- The decontamination of oil-affected soil or rivers incurs substantial costs

2.2 Biodiesel Production

The biodiesel production has been widely used in many countries, However, the production of biodiesel by waste cooking oil has several levels, The reaction between the reacts (waist cooking oil, alcohol and catalysts), when the reaction is done, two phases will appear, Biodiesel and glycerin, which lead us to the next level, the separation level, but that is not the final results, the biodiesel still needs to be washed by water and dried.

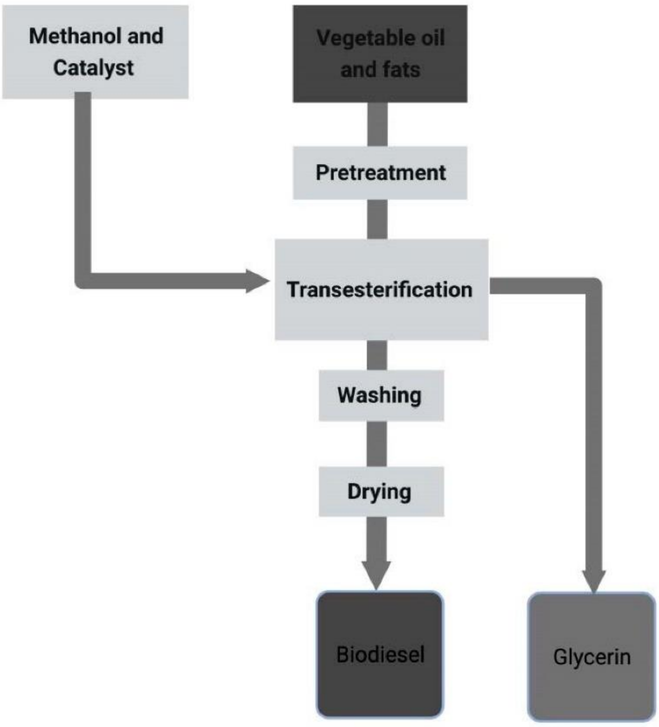

Figure 13: *Biodiesel production process.[35]*

2.2.1 Biodiesel production Levels

2.2.1.1 Transesterification

For the production of biodiesel, Waste Cooking Oil oil reacts with ethanol or methanol in the presence of a catalyst. From this, methyl or ethyl esters are obtained, which are the components of biodiesel. Along with the esters, glycerol is also produced. That reaction is called transesterification. Stoichiometrically, when the reaction takes place, for every mole of triglycerides reacting, three moles of alcohol are used. However, a higher molar ratio of alcohol is usually used for maximum ester production.[36]

2.2.1.2 Separation

Once the transesterification reaction is completed, two major products exist: esters (biodiesel) and glycerol. The glycerol phase is much denser than the biodiesel phase and settles at the bottom of the reaction vessel, allowing it to be separated from the biodiesel phase. Phase separation can be observed within 10 min and can be completed within several hours of settling. The reaction mixture is allowed to settle in the reaction vessel in order to allow the initial separation of biodiesel and glycerol, or the mixture is pumped into a settling vessel. In some cases, a centrifuge may be used to separate the two phases.[37]

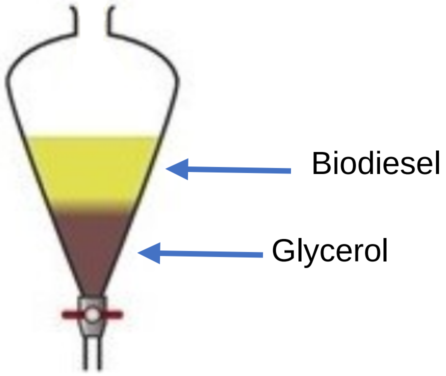

Figure 14: *Biodiesel Separation process.[35]*

2.2.1.3 Biodiesel Washing

Water washing is generally carried out to remove soap, catalyst, methanol and other contaminants from FAME.[38]

Crude methyl ester was purified by washing gently with warm water. Washing was carried out at pH 4.5 in order to neutralize the residual catalyst and soap. Excess amount of water may be present in the washed methyl esters. According to the ASTM standard of biodiesel, this amount of water must be lowered to a maximum of 0.05% (v/v).[39]

2.2.1.4 Drying

Biodiesel were then dried at a temperature of 100-110 degrees Celsius until the air bubbles disappear.[40]

2.2.2 Main factors affecting the production

2.2.2.1 Molar ratio of methanol to oil

The methanol/oil molar ratio is one of the most important variables affecting the ester yield. The stoichiometric ratio for transesterification is 3:1 (methanol/oil). Since this is an equilibrium reaction, an excess of methanol will increase the oil conversion by shifting this equilibrium to producing FAME. An acid catalyzed reaction usually needs much more alcohol than an alkali catalyzed one.[41]

2.2.2.2 Reaction time

Freedman has observed the increase in fatty acid esters conversion when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast.[42]

2.2.2.3 Reaction Temperature

Reaction temperature is another important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. Usually, the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 50°c to 70°c depends upon the oils used.[42]

2.2.2.4 Effect of catalyst concentrations

A catalyst functions to accelerate the reaction rates. For transesterification reaction, an increasing amount of heterogeneous catalyst caused the slurry (mixture of catalyst to reactant) too viscous giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring. On the other hand, when the catalyst loading amount was not enough, maximum production yield could not be reached. To avoid this kind of problem, an optimum amount of catalyst concentration had to be investigated.[43]

2.2.2.5 Effect of Mixing Intensity

To achieve perfect contact between the reagent and oil during transesterification, they were mixed together. It has been observed that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of reaction. As phase separation ceases, mixing on the kinetics of the transesterification process forms the basis for process scale up and design.[43]

2.2.2.6 Effects of water and free fatty acids

Water and FFA in oils and fats can pose a great problem during transesterification. When water is present, especially at elevated temperatures, it can hydrolyze the triglycerides to diglycerides and form an FFA. However, the presence of water at average temperatures leads to formation of excessive soap formation. When an alkali catalyst such as sodium or potassium hydroxides is present, the FFA will react to form saponified product.[44]

2.3 Raw Materials and Chemicals

Table 5 : *Raw Materials and Chemicals*

Chemical Products	**Materials**
Sodium hydroxide (NaOH)	Heating Magnetic Stirrers
Potassium hydroxide (KOH)	Separation Funnel
Alumina (AL2O3)	Erlenmeyer Flask
Methanol (CH3OH)	Round Bottom Flask
Waste Cooking Oil	Becher
	Funnel
	Measuring Cylinder
	Drying Oven
	Muffle Furnace

2.4 Preparation of the Reagents

Noting that the NaOH catalyst preparation was carried out in the Skikda RA1K refinery laboratory, under the supervision of trained chemists. This ensured a solid foundation and a better understanding of chemical handling and safety protocols. The other experiments were conducted at the laboratory of the University of 20 August 1955, Skikda.

2.4.1 Pre-treatment of the cooking oil

Collection of WCO: The first step in the pre-treatment process is to collect Waste Cooking Oil from various sources such as restaurants, households, or food processing industries

Initial filtration: Once the WCO is collected, it is necessary to remove larger particles and solid impurities before further processing. This can be achieved by passing the oil through a filter paper or a mesh filter to trap any solid particles present in the oil.

Figure14:*WCO Filtration*

Water Removing: After initial filtration, the WCO is subjected to heat treatment to remove any residual water content. Water in the oil can lead to the formation of unwanted byproducts during subsequent processing steps. The WCO is heated up to 100°C and maintained at this temperature for approximately three hours. This heating process helps to evaporate any water present in the oil and ensures its complete removal.

2.4.2 Homogeneous catalysts

2.4.2.1 Sodium Hydroxide (NaOH)

Sodium hydroxide, an alkali-based catalyst, is a highly effective and commonly used catalyst for biodiesel production due to its ability to accelerate the transesterification reaction, break ester bonds, and aid in the separation process. NaOH is readily available, cost-effective. Alternative catalysts like potassium hydroxide and acid catalysts are also utilized based on specific needs.

To begin, we determined the amount of NaOH catalyst needed, which was 1.5% of the weight of the oil sample. We then measured the required amount of methanol in a measuring cylinder, maintaining a molar ratio of 1:7 between oil and methanol.

Next, we prepared the catalyst mixture by combining NaOH with methanol in a Becher. We stirred the mixture for 10 minutes at a speed of 500 rpm to ensure a homogeneous solution. This step was important for activating the NaOH and creating an optimal environment for the transesterification process.

***Figure 15**: The Catalyst Methanol Mix*

In parallel, we prepared the WCO by heating it in an Erlenmeyer flask. To control the temperature, we attached a thermometer and used a heating magnetic stirrer (we later switched to a three-neck round-bottom flask equipped with a thermometer and a reflux condenser. The new setup provided improved control over the reaction temperature and allowed for better refluxing of the reactants. The condenser reflux setup facilitated the recycling of volatile components, minimizing their loss during the heating process.). The oil was heated to a range of 55-60°C, as this temperature range promotes efficient reaction kinetics.

Once the WCO reached the desired temperature, we introduced the catalyst mixture into the flask. We carefully poured the NaOH and methanol mixture into the heated WCO while maintaining a stirring speed of 500 rpm. The reaction was allowed to proceed for 2 hours within the same temperature range (55-60°C). This duration ensured sufficient time for the transesterification and esterification reactions to occur, resulting in the formation of biodiesel.

Figure 16: *Reflux Condenser Setup*

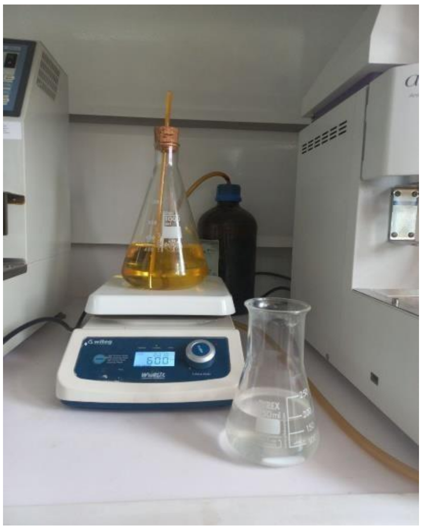

Figure 17*: Erlenmeyer Setup*

After the completion of the reaction, we allowed the mixture to cool off to room temperature. This step was necessary to ensure safe handling and subsequent separation of the biodiesel from the byproducts. Once cooled, we transferred the mixture to a separation funnel and left overnight to facilitate the separation of the mixture.

2.4.2.2 Sodium Hydroxide (NaOH) + Potassium hydroxide (KOH)

By taking advantage of the individual characteristics of NaOH and KOH, we aimed to improve the conversion of triglycerides and fatty acids into biodiesel. This alternative approach by combining NaOH with KOH. aim was to enhance the efficiency and the yield of the biodiesel production process from waste cooking oil (WCO).

Similar to the previous experiment, we measured the catalysts required based on a 1.5% weight ratio to the oil sample and 1:7 molar ration Methanol/WCO. However, this time, we used a 1:1 mass ratio of NaOH to KOH. This combination was chosen to leverage the unique properties of both catalysts and potentially improve the overall reaction.

2.4.3 Heterogeneous catalysts

We transitioned to a heterogeneous catalyst system for several reasons. Firstly, the heterogeneous catalyst offered improved recyclability compared to the previous catalyst system. This change was motivated by our desire to create a more sustainable and cost-effective process. Additionally, the use of a heterogeneous catalyst simplified the separation process, making it easier to recover and reuse the catalyst material. This change also had the potential to enhance the purity of the biodiesel product, ensuring a higher quality end product. Moreover, the introduction of a heterogeneous catalyst presented an opportunity for higher biodiesel yield, addressing the limitations we encountered in previous experiments. In summary, the decision to switch to a heterogeneous catalyst aimed to optimize conversion efficiency and increase the overall yield of biodiesel.

2.4.3.1 Aluminum oxide (Al_2O_3)

In our quest to improve the biodiesel production process, we initially utilized alumina (Al2O3) as a heterogeneous catalyst. We followed the same measurements and procedures as before

Alumina, also known as aluminum oxide (Al2O3), is a widely used catalyst in various chemical processes, including the production of biodiesel. Its unique structure and catalytic properties make it an excellent choice for biodiesel production.

a) Structure of Alumina:

Alumina is a ceramic material composed of aluminum cations (Al3+) and oxygen anions (O2-). It can exist in several crystallographic forms, but the most common ones are alpha-alumina (α-Al2O3) and gamma-alumina (γ-Al2O3). The structure of alumina is characterized by its high surface area, porosity, and acidic properties, which play a crucial role in its catalytic activity.

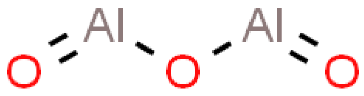

Figure 18:*Structure of Aluminum oxide*

b) Catalytic Properties of Alumina

- ✓ High surface area: Alumina has a large surface area due to its porous structure, providing more active sites for catalysis. This increases the contact between reactants and the catalyst, promoting more efficient chemical reactions.

- ✓ Acidic properties: Alumina exhibits Brønsted and Lewis acidity, meaning it can donate protons (H+) and accept electron pairs, respectively. These acidic sites play a crucial role in the esterification and transesterification reactions involved in biodiesel production. In the transesterification process, the acidic sites facilitate the reaction between triglycerides (present in vegetable oils or animal fats) and alcohol (e.g., Methanol or ethanol) to form biodiesel (fatty acid methyl or ethyl esters) and glycerol.

- ✓ Thermal stability: Alumina possesses excellent thermal stability, ensuring its effectiveness even at high temperatures commonly encountered in catalytic reactions.

- ✓ Resistance to poisoning: Alumina is less prone to poisoning or deactivation by impurities or contaminants present in the feedstock, making it a robust catalyst for biodiesel production. [3]

c) Alumina as a catalyst for Biodiesel

Alumina, as a catalyst for biodiesel production, offers several advantages:

- ✓ Low cost: Alumina is relatively inexpensive compared to other catalysts, making it an economically viable choice for large-scale biodiesel production.

- ✓ Readily available: Alumina is abundantly available in nature and can be easily synthesized, ensuring a stable and continuous supply for industrial applications.

- ✓ Efficient catalysis: The high surface area and acidic properties of alumina enhance the catalytic efficiency and facilitate the transesterification reaction, resulting in higher biodiesel yields.

- ✓ Tolerance to impurities: Biodiesel feedstocks, such as vegetable oils and animal fats, can contain impurities like water, free fatty acids, and other contaminants. Alumina's resistance to poisoning ensures stable performance even when the feedstock quality varies. [3]

2.4.3.2 Aluminum oxide Impregnated with NaOH- and KOH-

After facing challenges with the initial alumina catalyst, we further investigated potential catalyst options and developed the concept of using NaOH- and KOH-impregnated alumina as heterogeneous catalysts for biodiesel production from WCO. The decision to explore these catalyst systems was driven by several factors:

- Enhanced catalytic activity: Both NaOH and KOH are known for their strong catalytic activity in transesterification reactions. By impregnating NaOH and KOH onto the alumina support, we aimed to leverage their reactivity and improve the catalytic performance of the system. This approach offered the potential for higher conversion rates and increased biodiesel yield.

- Alumina stability and support: Alumina, chosen as the catalyst support, possesses excellent thermal and chemical stability. It can withstand the reaction conditions, maintaining its structural integrity and prolonging the catalyst's lifespan. Alumina also offers a large surface area for the impregnation of NaOH and KOH, ensuring efficient catalyst dispersion and interaction with the reactants.

- Optimization through experimentation: The idea of using NaOH- and KOH-impregnated alumina as catalysts was derived through a systematic approach of experimentation and evaluation. We conducted preliminary tests and observed promising results, indicating the potential of these catalyst systems to overcome the limitations encountered with the previous catalysts.

By combining the reactivity of NaOH and KOH with the stability of alumina, we aimed to develop highly effective catalysts for biodiesel production. The concept of NaOH- and KOH- impregnated alumina emerged as a result of careful consideration, experimental exploration, and the desire to optimize the reaction conditions for improved conversion and higher biodiesel yield.

The preparation of the catalysts involved three main steps: impregnation,
drying, and calcination.

In the impregnation step, we loaded 30 ml of a 50% aqueous solution of sodium hydroxide and 35% aqueous solution of potassium hydroxide onto 20 g of alumina separately. To prepare the 50% sodium hydroxide and the 35% potassium hydroxide solution, we carefully measured and mixed the appropriate amount of solid NaOH and KOH with distilled water. The impregnation process for both catalysts was conducted at 250 rpm for 3 hours at a temperature of 25°C. Subsequently, the temperature was gradually increased to 70°C until a slurry consistency was observed. The resulting slurries were then transferred to separate rotary evaporators and heated at 90°C for 1 hour to remove excess solvent.

Figure 19: *The impregnation process*

***Figure 20**: Excess solvent removal with The Rotary Evaporator*

Following impregnation, each catalyst was subjected to the drying process. The catalysts were placed in separate atmospheric dryers and kept at ambient temperature for 12 hours. This extended drying period allowed for complete removal of any remaining moisture and solvent, ensuring the stability of the catalysts.

The final step in the preparation was the calcination of each catalyst. The catalysts were placed in separate muffle furnaces and heated at 773 K (500°C) for 3 hours in the presence of air. Calcination is a critical step as it helps to activate the catalysts and remove any residual organic matter, resulting in catalysts with improved stability and catalytic activity.

Figure 21: Muffle Furnace or Muffle oven

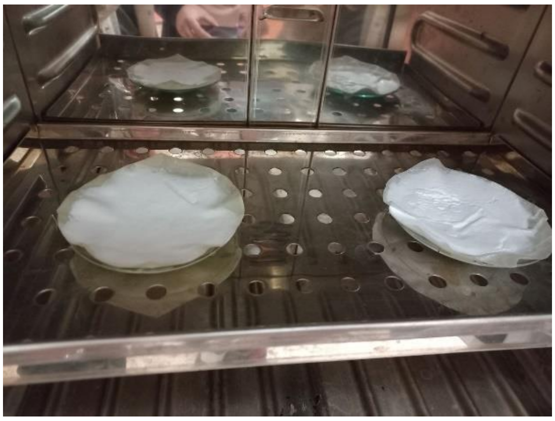

Figure 22: The Catalysts after Calcination

After successfully preparing the Both catalysts through the impregnation, drying, and calcination process, The NaOH/Alumina Catalyst show promising results. The catalyst exhibited excellent stability and catalytic activity, prompting us to further focus our study on its application in the transesterification process. To investigate the effect of catalyst concentration and molar ratio on the yield of biodiesel, we conducted experiments using different catalyst loadings ranging from 1%, 1.5%, 3% to 5% (by weight of waste cooking oil) and various molar ratios of oil to methanol, including 1:5, 1:7, 1:9, and 1:12. By systematically studying these parameters, we aimed to gain insights into the optimal conditions for achieving high biodiesel yields in the transesterification reaction.

2.5 WCO Characterization:

2.5.1 Density

Density is the mass per unit volume of any liquid at given temperature. Specific gravity is the ratio of the density of a liquid to the density of water. This property is important because it influences the efficiency of atomization of the fuel and also very relevant in the determination of the cetane index of an oil sample [45]. The density of the oil sample at 15 °C was determined following the ASTM standard D98.

2.5.2 Viscosity

The viscosity of WCO plays a significant role in the transesterification process. Higher viscosity can hinder the reaction kinetics and the mixing of reactants, leading to slower reaction rates and potential difficulties in achieving complete conversion of triglycerides. Moreover, higher viscosity can affect the separation and purification of biodiesel from the reaction mixture. [45]

2.5.3 Acid value

Acid value (or "acid number" or "acidity") is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. The acid number is used to quantify the amount of acid present, for example in a sample of biodiesel. It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1 g of sample. The oil samples were analyzed in order to ascertain their acidity index necessary to carry out the transesterification reaction. The acidity index of the raw oils was analyzed following a well-established experimental titration procedure according to ISO 1242:1999

2.5.3.1 Procedure

In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. Each titration was repeated four times and the standard deviation calculated. The value is defined as equation:

$$Y = \frac{\mathrm{C x\ V\ x\ 56.1}}{\mathrm{m}}$$

Where Y is the acid value, V is the consumed volume of KOH (ml), C is the concentration of KOH (mol/l), and the m is the mass of the tested sample (g) and 56.1 is the molecular weight of KOH. It can also be calculated as 1.99 x FFA %.

2.5.4 Saponification value

Saponification value represents the number of milligrams of potassium hydroxide or sodium hydroxide required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/tri-ester is in the 3 fatty acids, it allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat and the chain lengths are relatively small, given the following relation:

The calculated molar mass is not applicable to fats and oils containing high amounts of unsaponifiable material with free fatty acids less than 0.1 %.

2.5.4.1 Procedure

Measurement of saponification value was performed according to the official test methods. A sample of fatty acid is first saponified by adding 0.5 mol/L potassium hydroxide ethanol, and then the excessive potassium hydroxide is titrated with 0.5 mol/L hydrochloric acid until the endpoint is reached.

$$\text{Number of moles} = \frac{\text{mass of oil}}{relative\ atomic\ mass}$$

Where, V, is the volume, in milliliters, of specification hydrochloric acid solution required for the blank; V, is the volume, in milliliters, of specification hydrochloric acid solution required for the fat; c is the concentration of the specification hydrochloric acid solution, in moles per liter; m is the mass, in grams of sample taken.

The calculated molar mass is not applicable to fats and oils containing high amounts of unsaponifiable material with free fatty acids less than 0.1 %.

Where, V, is the volume, in milliliters, of specification hydrochloric acid solution required for the blank; V, is the volume, in milliliters, of specification hydrochloric acid solution required for the fat; c is the concentration of the specification hydrochloric acid solution, in moles per liter; m is the mass, in grams of sample taken.

The calculated molar mass is not applicable to fats and oils containing high amounts of unsaponifiable material with free fatty acids less than 0.1 %.

$$Saponification\ value = \frac{(\mathrm{V1} - \mathrm{V2})\ \mathrm{x}\ 56.1\ \mathrm{x}\ \mathrm{c}}{\mathrm{m}}$$

2.5.5 Water Content

During the transesterification reaction, the presence of water causes the loss of yield of methyl ester due to the formation of soaps. In the biodiesel product, water can promote biological growth and hydrolytic reactions which are linked with automotive filter blockage. The water content in the waste cooking and the vegetable oils was measured using a Thermo Orion AF7LC Coulometric Karl following EN ISO 12937 norm. The same method was used in the determination of the water content of the biodiesel obtained from the reactions.

2.6 Biodiesel Characterization

2.6.1 Density

Density is the ratio of the density of a liquid to that of water under a fixed pressure and temperature waves. The measurement temperature for oil and fuels is 15°C according to international standards. The density of fuel has an important effect on engine performance, such as certain engine properties such as cetane number, viscosity, and calorific value which are strongly related to density. A fuel having a high density leads to a greater mass of injected fuel, as a consequence of an increase in fuel consumption. Ester density depends on molar mass, free fatty acid content, water content, and temperature [14,15]. The density value is determined using an apparatus of Densimeter (Anton Paar 3001.)

Méthode: Density
Echantillon: bio
3:33:51 PM
Administrator
Masse Volumique 0.87876 g/cm³
Température cellule 19.98 °C
0.87878
Condition Densité Valide
28.73
Masse volumique API 15 °C 0.8822 g/cm³

Figure 23: Anton Paar SVM 3001

The Anton Paar SVM 3001 is a precision instrument designed to measure the density of liquids accurately

2.6.1.1 Instrument Setup

- Connect the SVM 3001 to a power source and switch it on.
- Allow the instrument to warm up for the specified duration as mentioned in the manufacturer's instructions.
- Ensure that the instrument is properly calibrated before starting any measurements. Follow the calibration procedure provided by the manufacturer.

2.6.1.2 Measurement Procedure

- Open the software interface or control panel of the SVM 3001.
- Select the appropriate measurement mode for density.
- Fill the sample chamber or measurement cell with the prepared sample, ensuring that it is completely filled without any overflow or air gaps.
- Close the sample chamber or measurement cell securely to prevent any leakage.
- Initiate the measurement process using the designated button or command on the software interface.
- Allow the instrument to stabilize and record the density value displayed on the screen.[46]

2.6.2 Viscosity

Viscosity is a principal parameter when any flow measurements of fluids, such as liquids, semi-solids, gases and even solids are made. Viscosity measurements are made in conjunction with product quality and efficiency. Anyone involved with flow characterization, in research or development, quality control or fluid transfer, at one time or another gets involved with some type of viscosity measurement. The viscosity of a lubricating oil can be considered as its most important physical property. It must be monitored and controlled carefully because of its impact on the oil and the oil’s impact on equipment life and reliability. Basically, the viscosity can be defined as the property of a liquid characterizing its internal friction or resistively to flow.

***Figure 24**: Tamson TV2000 for Viscosity measurements*

2.6.2.1 Measurement Procedure

- ASTM D445 requires the oil sample to be injected in a capillary viscometer tube, which is then immersed in a heating bath at the prescribed test temperature.
- The time taken for an oil to flow from one capillary section to another is used to determine its kinematic viscosity.
- We measure the viscosity of an oil according to a time and a tube constant.
- The time is measured between two points marked on the tube.
- Then the viscosity is obtained by applying the following calculation: $v = C \times t$ with v as the kinematic viscosity in cSt or mmÇ/s, C the constant of the tube and t the efflux time in seconds to flow between the two points. Several types of viscometer tubes can be used.[46]

2.6.3 Determination of flash point

The flash point (FP) is the lowest temperature at which volatiles are produced at a rate that allows them to be ignited when in contact with a heat source: flame or spark. If the heat source is removed, the ignition will stop, but not to support combustion. In other words, it is an indication of the presence of volatile and flammable materials in the fuel. A high flash point indicates that the material is less likely to ignite during storage or handling or transport. The flash point is determined using the Normalab Pensky Martens apparatus.

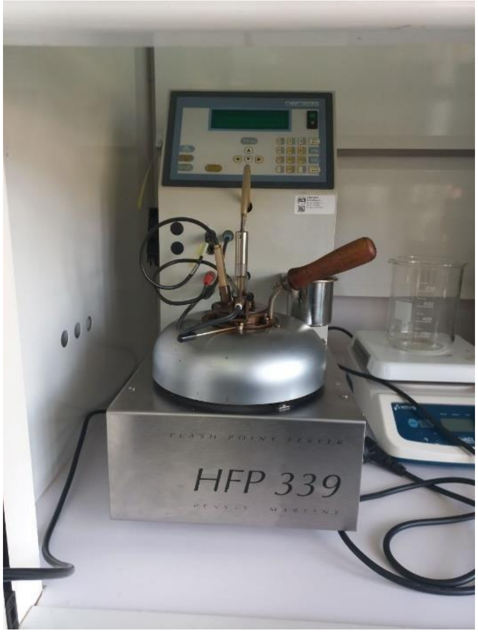

Figure 25: *Normalab Pensky Martens Closed-Cup Apparatus*

2.6.3.1 Instrument Setup

- Connect the PMC automated tester to a power source and switch it on.
- Allow the instrument to warm up for the specified duration, as recommended by the manufacturer.
- Ensure that the instrument is properly calibrated before starting any measurements. Follow the calibration procedure provided by the manufacturer.

2.6.3.2 Sample Preparation

- Prepare the sample according to the specifications outlined in the test method being followed (ASTM D93).
- Ensure that the sample container is clean and free from contaminants.

2.6.3.3 Measurement Procedure

- Open the software interface or control panel of the PMC automated tester.
- Select the desired test method (ASTM D93)
- setting up the test cup, placing the sample, and ensuring the apparatus is properly configured.
- Initiate the measurement process using the designated button or command on the software interface.

The instrument will automatically perform the test, heating the sample and detecting the flash point.[46]

2.6.4 Determination of pour point

The pour point (PP) of liquid fuel is the lowest temperature at which the fuel loses its flow characteristics. PP is also an important parameter in cold flow operation because the fuel can only be used above the pour point value. In general, biodiesel has higher CP and PP than conventional diesel. ASTM D 97 specifies the procedure for estimating the PP of biodiesel fuel, with the lowest PP of 18°C and the highest value of 15.5°C.

Apparatus and Materials

- Cloud point test apparatus: This typically consists of a sample cell or tube with a cooling bath or refrigeration system.
- Thermometer: Use a suitable thermometer capable of measuring temperatures within the test range.
- Sample container: Clean and dry containers to hold the test sample.
- Cooling medium: Use an appropriate cooling medium, such as a mixture of alcohol and dry ice or a refrigeration system, capable of reaching the desired test temperature.
- Timer or stopwatch: To accurately measure the test duration.

2.6.4.1 Test Procedure

- Fill the sample cell or tube with the prepared sample, ensuring there are no air bubbles.
- Place the sample cell or tube into the cooling bath or refrigeration system.
- Gradually lower the temperature at a specified rate, typically around 1°C per minute.
- Observe the sample closely during the cooling process.
- Record the temperature at which the first appearance of a haze or cloudiness is detected within the sample. This is the cloud point.

2.6.5 Distillation

The distillation process is an integral part of biodiesel characterization, serving two main purposes: separating biodiesel from impurities and obtaining valuable information about its physical properties. Distillation allows us to determine the boiling point range of biodiesel, which is a necessity parameter for assessing its quality and compliance with industry standards.

To perform the distillation, we employ a standard distillation setup, consisting of a distillation flask, a condenser, and a receiver. The biodiesel sample is placed in the distillation flask and heated gradually. As the temperature rises, the components of the biodiesel begin to vaporize. The vapor passes through the condenser, where it condenses back into a liquid state and collects in the receiver. .[46]

Figure 26: Distillation Setup

2.7 Summary

Our thesis centers around the production of biodiesel from waste cooking oil, with a specific focus on exploring different catalysts and optimizing the overall process.

The First experiment was conducted under the supervision of the Skikda RA1K refinery laboratory. Subsequent experiments were carried out at the laboratory of the University of 20 August 1955, Skikda, where we had access to the necessary resources for analysis and evaluation.

The initial catalysts used were sodium hydroxide (NaOH) and a combination of NaOH and potassium hydroxide (KOH). However, the results obtained from these catalysts did not meet our expectations. In response, we decided to shift towards a heterogeneous catalyst, our investigation began with alumina (Al2O3), followed by the utilization of NaOH-KOH- impregnated alumina for further experimentation.

The preparation of the catalyst involved several steps, including impregnation, drying, and calcination. Impregnation was carried out by applying a 50% aqueous solution of sodium hydroxide and 35% aqueous solution of potassium hydroxide onto 20 g of alumina separately; followed by thorough drying to eliminate any remaining moisture and solvent. Calcination was then performed to activate the catalyst and remove any organic residues.

To assess the impact of catalyst concentration and molar ratio on biodiesel yield, we conducted experiments using varying weight percentages of the catalyst and different oil-to-methanol ratios.

Our approach encompassed a comprehensive exploration of catalysts and process optimization, with the primary goal of achieving high biodiesel yields from waste cooking oil. Throughout the entire process, we prioritized safety, accuracy, and the aim to obtain insightful findings and contributing valuable information to the field.

Chapter III

Results and Discussion

3.1 Results of WCO characterization

Impurities and contaminants, water content, and FFA content are good indicators of the quality of WCO used in biodiesel production, and the results are summarized in this table:

Table 6 : *WCO quality check by characterized and compared with ASTM Norm*

Property	Value	ASTM Norm D6751
Density (g/ml)	0.91	0.904-0.928
Viscosity at 40˚C(Mm²/s)	67.882	35.3-132.15
Water and sediment percentage (%)	0.8	0.32-1.134
Acid Value (Mg KOH/g WCO)	3.27	0.824-3.89
saponification	171.12	170-200

The results of the waste cooking oil characterization are presented in Table, along with the recommended reference value to produce biodiesel by transesterification. The density showed values close to those reported in previous characterization; viscosity obtained was significantly lower compared to others, the humidity presented values were similar to those reported in previous studies, the high acid value indicates a high content of free fatty acids, and the WCO is not in optimal conditions for human consumption, but is a good condition for producing biodiesel.

3.2 Comparing the yield production of all the catalyst

To ensure that the comparison is fair, all reactions were performed under the same conditions such as T = 2h temperature 70 °C, wt% of the catalyst/WCO, and the same molar ratio of MeOH:WCO, and the results are summarized in this table.

Table 7*: Results of all yields produced by different catalysts.*

Catalysts	NaOH	NaOH/KOH	Aluminum oxide	NaOH/Aluminum oxide	KOH/Aluminum oxide
Yield %	89.8%	83.1%	-	93.1%	86.3%

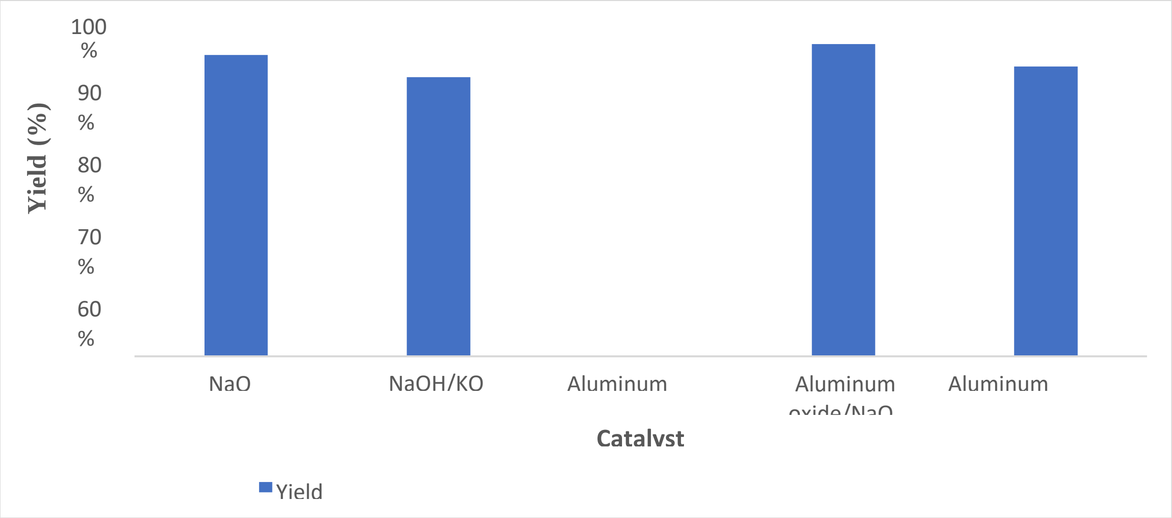

Figure 27: *The yield of each catalyst*

We noticed that yield production was at its highest when we used NaOH/aluminum oxide with 93% yield, followed by NaOH; the NaOH/KOH catalyst produced the lowest yield at 83.1%, and aluminum oxide did not produce any yield at all.

The reason why that aluminum oxide/NaOH did better than the others is that aluminum oxide enhanced NaOH activity in the reaction of transesterification, also it offers a great porosity and large surface area ensuring efficient NaOH dispersion and interaction with the reactants, in the case of aluminum oxide alone did not give as yield cause the reaction did not complete however it did have the selectivity to start the reaction of transesterification.

After comparing the catalysts, it is clear that NaOH/aluminum oxide is the superior catalyst in terms of biodiesel production; therefore, we studied the impact of different conditions that affect the transesterification reaction to optimize the production. We used 29 different reactions to study the effects of temperature, molar ratio of alcohol:WCO, wt% of the catalyst used, time of the reaction, let`s look at the results in the next phase.

3.3 Assessment of Process Parameters

3.3.1 Effect of the reaction time

The time in the transesterification reaction is an important factor that help you know when to stop the reaction and when its complete and maximum yield production, to ensure that its optimal for our catalyst we tested difference reaction times 1h,2h and 3h at temperature of 70 °C, with MeOH: WCO molar ratio of 7:1, the results are summarized in this table:

Table 8: *impact of the time of the reaction on the yield*

Catalyst wt% from WCO weight **Reaction time**	**1.5**	**3**
1	87%	80%
2	93.1%	87%
3	90%	76%

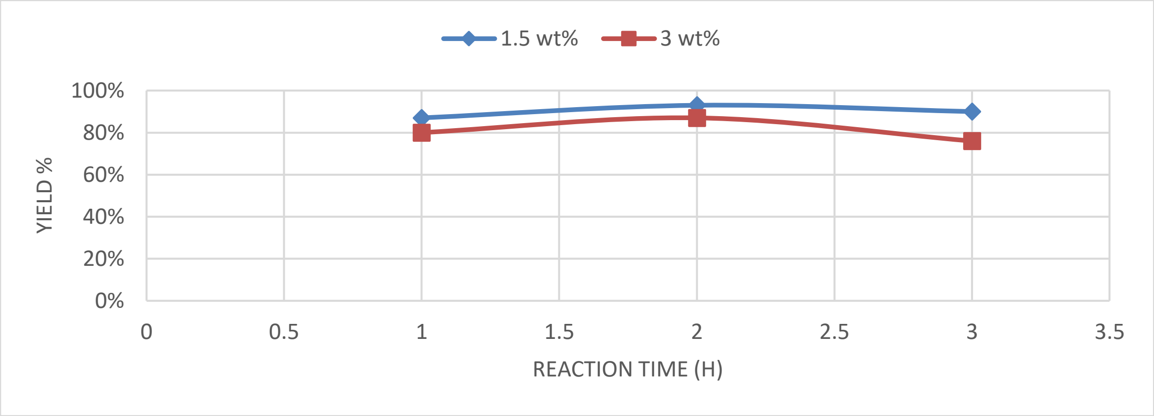

Figure 28: *Biodiesel yield as a function of Reaction Time 1h, 2h and 3h, MeOH: WCO Molar Ratio 7:1, and reaction temperature at 70 °C, and the wt% of the catalyst was 1.5% and 3% of the WCO*

By observing the results of the six tests with two different catalyst wt% 1.5 and 3 from the table and the figure, we noticed that at 2h the bd production was at its peak, there that 2h was the optimum time for the TG reacti

3.3.2 Effect of temperature

To make the transesterification reaction, the temperature of the WCO needs to be between 6 0 °C and 80 °C, and the difference between the catalyst and other so we put 10 reactions at different temperatures (60 °C, 65 °C, 70 °C, 75 °C, and 80 °C, MeOH: WCO molar ratio 7:1, Catalyst/WCO Mass 1.5% and 3%, reaction Time 2h, The results are summarized in this table:

Table 9: *Temperature effect on biodiesel yield.*

Catalyst/WCO mass ratio (%) **Temperature (°C)**	**1.5**	**3**
60	93.6%	86.8%
65	94.4%	88%
70	93.1%	87%
75	92.6%	87%
80	91.3%	85%

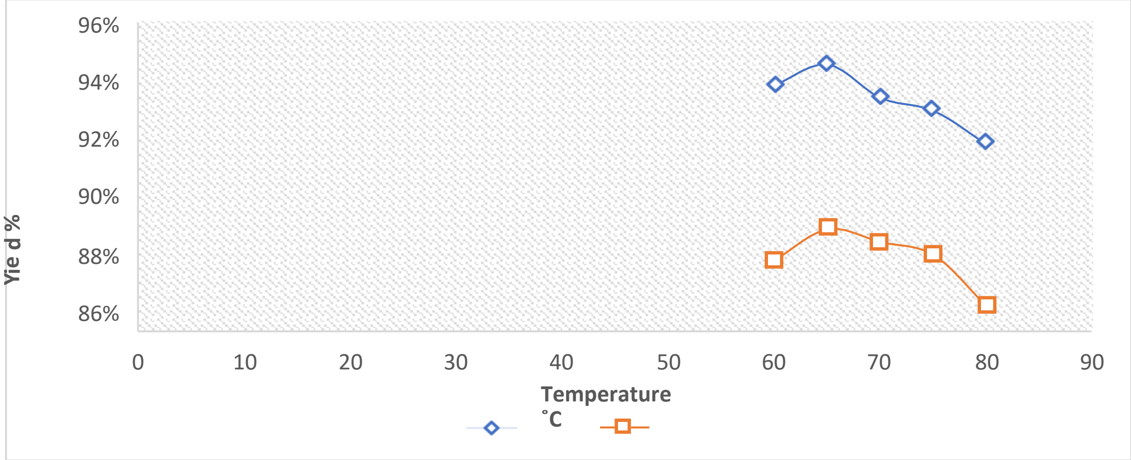

Figure 29: *Yield production of biodiesel as function of temperature, reaction time 2h, MeOH: WCO molar ratio 7:1, catalyst/WCO mass percentage 1.5% and 3%.*

By observing the table and figure, we notice that plays a significant role in the production of yield in both tests of the catalyst wt% (1.5% and 3%), and the optimum temperature for the transesterification reaction is 65 °C.

3.3.3 Effect of the catalyst/WCO mass ratio

In the transesterification reaction, the weight of the catalyst used compared to the wight of WCO is very important and has a big impact on the finish product so we tested different weight 1 wt%,1.5wt%, 3 wt% and 5 wt% For the reaction and we used 44 g of WCO (50 ml), the most yield was obtained with 1.5% that make it the optimum value of catalyst, The results are summarized in this table:

Table 10 : *Catalyst/WCO mass ratio effect on biodiesel yield.*

MeOH: WCO Molar ratio **mass ratio Catalyst /WCO**	**5**	**7**	**9**	**12**
1	58.2%	86%	64.8%	56.7%
1.5	78.6%	94.4%	87.6%	78.3%
3	75%	88%	77.3%	74.6%
5	72.5%	80.9%	78.3%	73.1%

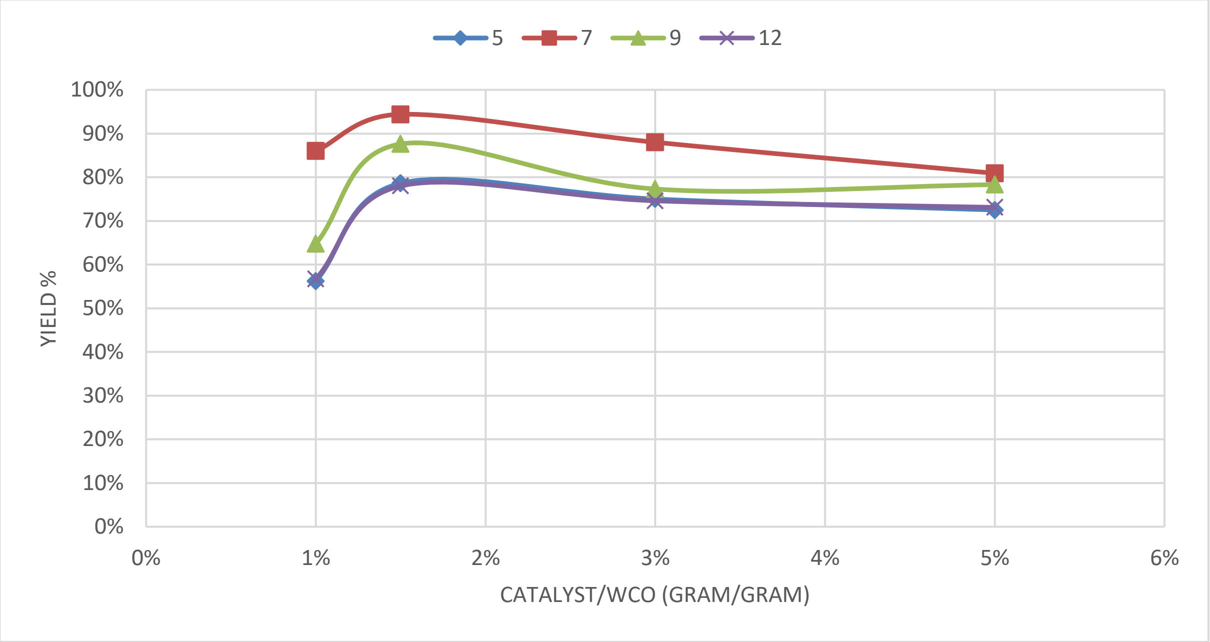

Figure 30: Yield produced of biodiesel as function of Catalyst/WCO mass ratio, Temperature 65 ˚C. reaction time 2h. molar ratio Methanol/WCO 5:1, 7:1, 9:1 and 12:1.

After the observation of table and the figure, we notice that the highest yield produced is 94%, so the most efficient wt% of the catalyst by far is 1.5%.

3.3.4 Effect of the Molar ratio Methanol/WCO

The transesterification method involves the reaction of TG with an alcohol and a catalyst to form FAME and crude glycerol. Stoichiometrically, 1 mole of TG and 3 moles of alcohol are required for a complete transesterification reaction. In practice, this ratio must be greater than the stoichiometric ratio to attain maximum ester yield. As this process is reversible, surplus alcohol is employed to transfer the balance to the synthesis of esters (product) [8]. The impact of various MeOH: WCO molar ratios i5:1, 7:1, 9:1, and 12:1) on the transesterification reaction in 44 g of WCO (50 ml) at a preset temperature of 65 °C and catalyst content of 1.5 wt%. The results are summarized in this table:

Table 11: *Molar ratio impact on yield production*

catalyst /WCO mass ratio **Molar ratio MeOH:WCO**	**1%**	**1.5%**	**3%**	**5%**
5	56.2%	78.6%	75%	72.5%
7	86%	94.4%	88%	80.9%
9	64.8%	87.6%	77.3%	78.3%
12	56.7%	78%	74.6%	73.1%

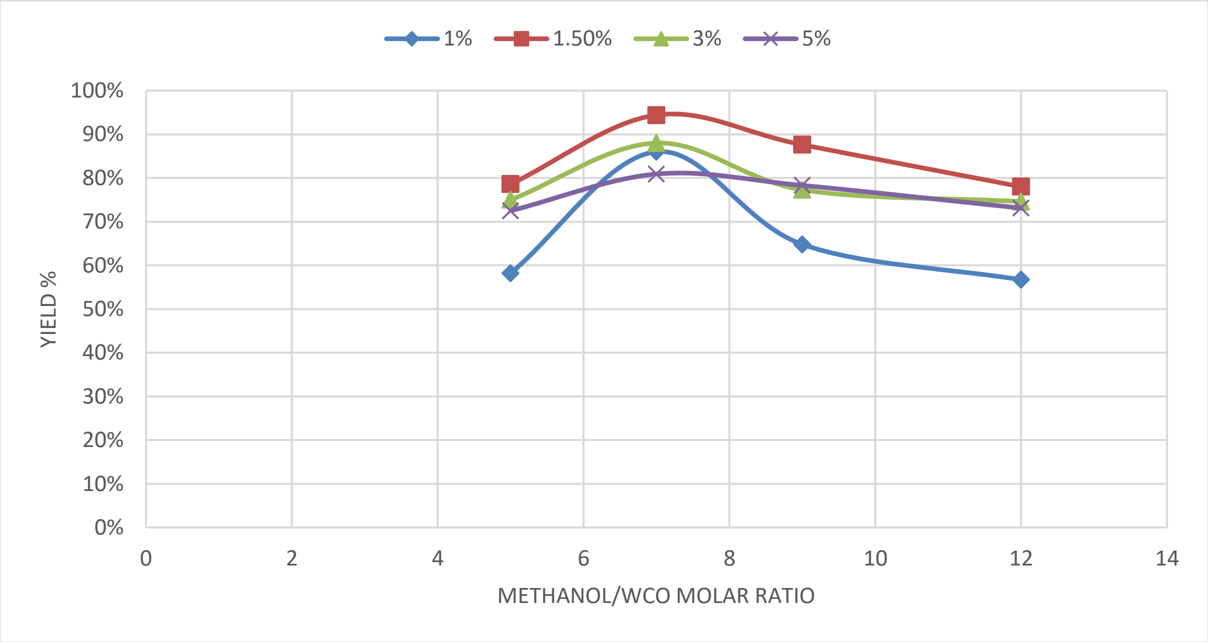

Figure 31: *yield produced of biodiesel as function of Methanol/WCO molar ratio, Temperature 65 ˚C, reaction Time 2h, Catalyst to WCO mass percentage 1%,1.5%,3% and 5%.*

From the table and figure, we notice that the highest yield produced from different molar ratios is 94%, so we conclude that the optimum yield is 7:1.

3.4 Characterization of biodiesel:

The characterization of biodiesel involves evaluating various parameters that determine its quality, performance, and suitability for use in diesel engines, The results are summarized in Table 12.

***Table 12**: Results of characterization of the obtained biodiesel.*

Property	Value	ASTM Norms D6751	Reference
Density	0.9	0.860-0.9	[47]
Viscosity	7.1	1.9-6	[47]
Flash point (˚C)	225	Min 120	[47]
Pour point (˚C)	-4	Min -2	[47]
Water content %	0.044	Max 0.05	[47]
Temp recovered ˚C	354	Max 360	[47]
Boiling point ˚C	338	315-350	[47]

The results of waste cooking oil characterization are presented in table as well as the recommended reference value from ASTM, the density and viscosity shows value close to the reported one that mean that the engine that will use our biodiesel will have no problems injecting precise amount of fuel to provide a proper combustion, the flash point a bit higher than norms which means that it will be easy to manage the storage and transportation without any risk, the pour point is in the lower end that`s make it easy to storage and makes it that biodiesel will conserve it`s properties to be used in cold weather, all the value that we obtained after analyzing our biodiesel are in the rage of the norms that has been set by the ASTM.

Conclusion

In this study, we synthesized different catalysts that are homogenous and heterogeneous for the transesterification reaction to optimize the catalyst that is usually used NaOH, tasting various catalysts, such as a mix of 50% NaOH/KOH, an aluminum oxide catalyst, a heterogeneous catalyst using wet impregnation of NaOH in Alumina Oxide, and calcinate impregnation of KOH in aluminum oxide, followed by calcination under the same conditions in terms of montage and the parameters (temperature, time, wt% of catalyst, and molar ratio of alcohol:WCO).

To abstract the full potential of our catalysts, we studied the variables that affect the quality and yield of biodiesel, such as the molar ratio of MeOH/WCO, the catalyst mass used for the reaction, the temperature, and the time of the reaction, and the conclusion was as follows:

For the effect of the molar ratio of alcohol/WCO:

- The maximum yield was 94% at a 7:1 molar ratio; anything less will not be enough to make the reaction complete and the more alcohol you add, then a 7:1 molar ratio will reduce the yield.

For the effect of the catalyst mass:

- The maximum yield produced was 94%, and we used catalyst/WCO wt% 1.5; the higher the wt% of the catalyst we use the lower the yield; if we use less, it will not be sufficient to push the reaction to the maximum potential.

For the effect of temperature:

- Although the temperature of the reaction doesn`t seem too important is did play a big role in the reaction and yield production it helps finish the reaction faster the best result was 65˚C.

For the effect of the time:

- The best results for maximum yield production we set the reaction for 2h anything more than that did make the quality of biodiesel go down and any less then that will not push the reaction to the maximum.

Based on the results of this study, we can conclude that NaOH/aluminum oxide is the most optimum among all the ones we tested, as it achieved all the marks this project aimed to achieve higher yield production and less catalyst quantity required, without mentioning the potential to recycle and use the catalyst repeatedly; our country is fertile ground to enter the biodiesel race and compete in it and make clean and affordable energy in our country and a valuable product to sell to the world.

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Annex

Analysis of WCO of Other Studies

Table Physical and chemical properties of waste cooking oil collected.

Properties	Waste Cooking Oil Values		
	1	2	3
Acid value (mg KOH/gm)	28.5	1.86	35.4
Saponification value	175.87	181.25	234.7
Viscosity (mm^2/s)	46.97	42.01	–
Density (kg/m^3)	908	–	916
Free fatty acid (%)	14.25	–	18
Flash point (ºC)	223	234	–
Moisture content (%)		0.1	0.136

Analysis on biodiesel

Figure. Kinematic viscosity of biodiesel in Sample 1, Sample 2 and Sample 3 at 30 °C.

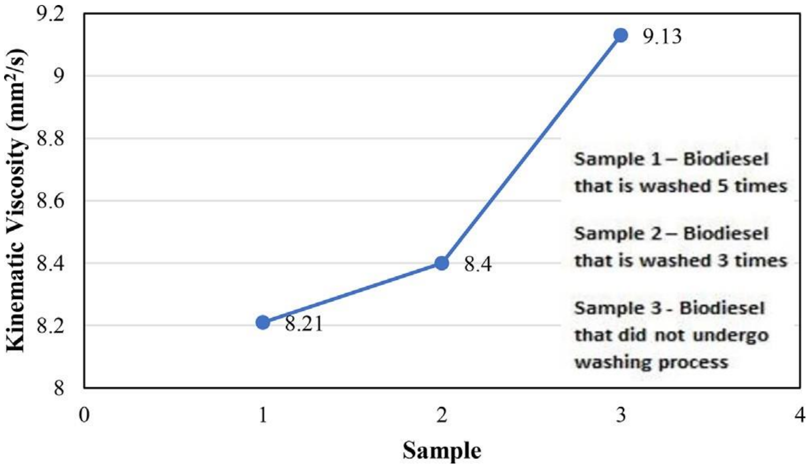

Table. Density of biodiesel in each sample.

Sample	**1**	**2**	**3**
Density (g/cm^3)	**0.834**	**0.862**	**0.918**

Annex

Different catalysts Yield:

Table. catalyst use for biodiesel production from waste cooking oil with percentage of yield.

Catalyst	Yield (%)
NaOH	89.8
H2SO4	82.4
KOH	91.2
CaO	91
CaO/Al2O3	30.91

Impact of the conditions of the transesterification reaction:

impact of WCO/Alcohol molar ratio:

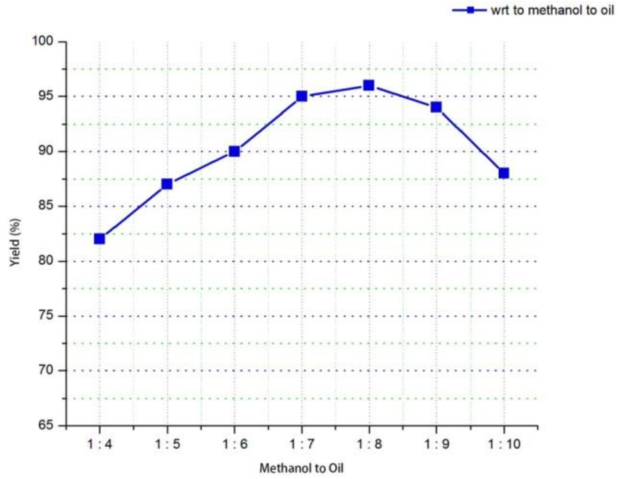

Figure. The effect of WCO to methanol ratio range from 1:4 to 1:10 on biodiesel yield (%).

Impact of temperature:

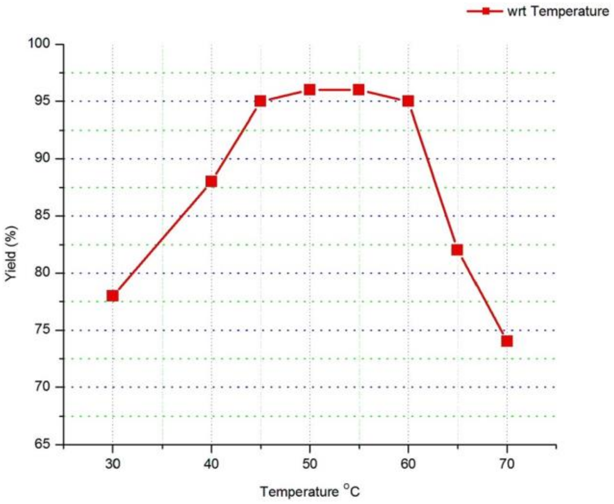

Figure. The effect of reaction temperature on biodiesel yield (%).

Impact of Time:

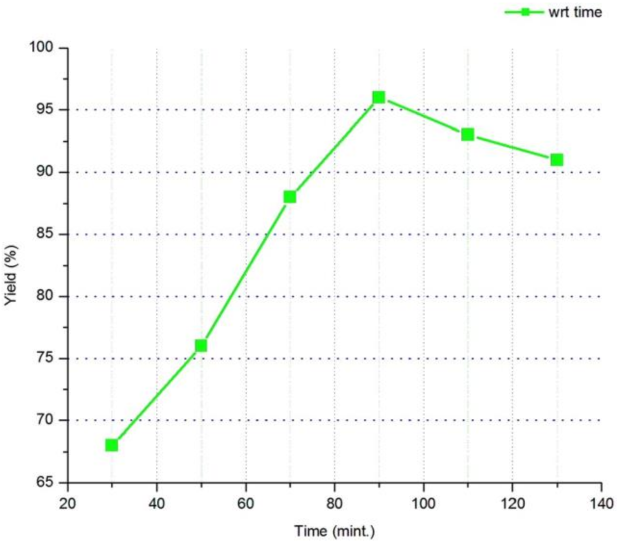

Figure. The effect of reaction time (minute) on biodiesel yield (%).