KASDI-MERBAH Ouargla university

Applied science faculty
Departement of Process Engineering

Thesis

Dissertation

ACADEMIC MASTER

Domain: Sciences and Technology.
Field: Process Engineering.

Speciality: Environmental Process Engineering.

Presented by: Khoudrane Lamia.

Thème :

Optimization and Modelling of Biodiesel production from waste cooking oil using design of Experiment

Publically defended:

Before the jury:

Mr.	MAA	President	UKM Ouargla.
Mr.	Pr	Examinater	UKM Ouargla.
Mr.	MCA	Repporter	UKM Ouargla.

Year : 2019/2020

Didiccas:

To my beloved parents who had afforded everything i need during my studies.

To my dear friends Dounia , Oumaima , Hnanae , whovere was always there for help, and those who I spent all my university days with.

To every single person had been always beside me and encouraged me.

Acknowledgment:

I would like to thank the following people, without whom I would not have been able to complete this research, and without whom I would not have made it through my master degree:

Thank you to my patient and supportive supervisor, Dr Lessouad Ridha for providing guidance and feedback throughout this project. Furthermore for his support, encouragement and patience.

I would like to thank Process engineering department and Kasdi Merbah university in general.

A special thank to my friend Hammani dounia who I had spent almost all university days with, and to all my friends who had supported me through all my studies, never forgetting my colleges Zoubir Haizia, Benchikh Nouria and Bensedik Asma for their support and help.

Most importantly, I must express my very profound gratitude to my parents my great father Azzedine and my beloved mother Amel for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

Finally, I thank God for everthying.

Abstract

In this study, modeling and optimization of biodiesel production from waste cooking oil (WCO) were successfully carried out using RSM and CCD to assess the effect of operating parameters on response. Transestrification reaction was used to produce biodiesel, Using methanol alcohol and KOH catalysts, Two factors (Reaction temperature and oil to alcohol molar ratio) and one response (biodiesel production yield) were selected and evaluated using ANOVA. At the optimum conditions Temperature of 62.72°C, and oil: alcohol ratio of 4.3, a high biodiesel production efficiency was reached (96.2%) with 99.64%, 99.41% and 0.926 of coefficient of determination R2, R2adj and desirability, respectively. The results indicated an appropriate agreement between predicted and experimental data.
Key words: Experimental design, RSM, WCO, optimization, modeling, Transesterification, biodiesel.

Résumée

Dans le cadre de cette étude, la modélisation et l'optimisation de la production de biodiesel à partir d'huiles de cuisson usées (WCO) ont été effectuées avec succès à l'aide de RSM et de CCD pour évaluer l'effet des paramètres de fonctionnement sur la réponse. La réaction de transestrification a été utilisée pour produire du biodiesel, avec l'utilisation d'alcool méthanol et de catalyseurs KOH, deux facteurs (température de réaction et rapport molaire huile-alcool) et une réponse (rendement de production de biodiesel) ont été sélectionnés et évalués à l'aide d'ANOVA. Dans des conditions optimales, une température de 62,72 °C et un rapport huile-alcool de 4,3, un rendement élevé de la production de biodiesel a été atteint (96,2 %) avec 99,64, 99,41 et 0,926 du coefficient de détermination R2, R2adj et de la désirabilité, respectivement. Les résultats indiquaient un accord approprié entre les données prévues et expérimentales.
Mots clés: Plan d'expérience, RSM, WCO (déchets d'huile de cuisson), Optimisation, Modélisation, La Transestérification, biodiesel.

ملخص

في هاته الدراسة تمت معالجة و محاكات صناعة الوقود الحيوي من بقايا زيت القلي بنجاح باستخدام RSM وCCD لتقييم تأثير الشروط العملية على الاستجابة , استعملت عملية الاسترة لإنتاج الديزل الحيوي باستخدام كحول الميثانول اجابة ANOVA. (والمحفز هيدروكسيد البوتاسيوم , عاملين (درجة حرارة التفاعل و نسبة الكحول و الزيت المولية واحدة (المردود انتاج الوقود الحيوي) تم اختيارهم و تقييمهم بواسطة

في الشروط التجريبية المثلى كانت درجة الحرارة 62.7 ° و نسبة الزيت و الكحول المولية 4.3 حيث بلغت اعلى كفاءة لإنتاج الوقود الحيوي 96.2% مع 99.64 و 99.41 و 0.926 لكل من R^2, R^2 adj, Desirability. بالترتيب

و قد اظهرت النتائج توافق مناسب بين البيانات المتنبئ بها و البيانات التجريبية.

الكلمات الدالة: تصميم التجارب, استجابة السطح, بقايا زيت القلي, التحسين , النمذجة , الاسترة , الوقود الحيوي.

Tables lists

Part1 :Bibliographic study

I.1	Physical and chemical properties of No. 2 diesel Fuel…….……..	06
I.2	Biodiesel characterization…..……...…….....	10
I.3	Biodiesel usage among 2008- 2020. ……..……...……	13
I.4	Nomenclature and Chemical Structure of Fatty Acids Commonly Found in Vegetable oil.....	14
II.1	international biodiesel standard…….....	28

Part 2: Method, results and Discussion

I.1	Factors……..	42
I.2	The Experimental matrix	43
I.3	Predicted and experimental results for biodiesel production……...	44
I.4	Analysis of variance results……..	44
I.5	Model summary……	46
I.6	Numerical optimization criteria for maximum biodiesel production……...	52
I.7	Results comparison……	52
II.1	Material and products used……...	55

Figures list

Part1 : Bibliographic study

I.1 Biodiesel production in billion litres……..... 12
I.2 Vegetable oil chemical structure……... 14
I.3 Sunflower oil chemical structure……..... 15
I.4 Sunflower oil……15
I.5 Corn oil……...15
I.6 Palm oil……..16
I.7 Olive oil……..16
I.8 Canola oil……..…17
I.9 Consumption of vegetable oils worldwide from 2013/1.4 to 2019/2020……. 18
I.10 value of sunflower oil in tunes – Algeria…….. 18
II.1 The tranesterification Reaction…….. 22
II.2 Transesterification Mechanism…….. 23
II.3 The performance of different alcohols in the transesterification…….. 24
II.4 Biodiesel production process…… 25
III.1 Generation of a central composite design…….. 36

Part2: Method, results and discussion.

I.1 Pareto chart of the standardized effects……..46
I.2 Normal plot of the standardized effects…… 47
I.3 normal probability plot…….. 47
I.4 Residuals versus fits……... 48
I.5 Histogram of residual……. 48
I.6 Residual versus order…… 49
I.7 Main effects plot for yield…… 49
I.8 Interaction plot for yield…… 50
I.9 surface plot of yield vs. molar ratio, Temperature. ……...… 50
I.10 Contour plot of yield vs. molar ratio, Temperature. ……..… 51
I.11 optimal conditions……..……51
II.1 Transestrefication reaction…….……55
II.2 Biodiesel separation……...… 57

List of abbreviations

ASTM: American Society for Testing and Materials.

ANOVA: Analysis of variance.

BBD: Box bankhen design.

CCD: Central composite design.

CCFD: Central composite faced design.

DOE: design of experiment.

EN: European standards.

FGB: Fourth generation biofuel.

FA: fatty acids.

FFA: Free fatty acids.

FFD: Full factorial design.

GM: Generally modified.

ISO: International Organization for Standardization.

LOF: Lack of Fit.

Min: minute.

PAHs: Polycyclic Aromatic Hydrocarbons.

PUFAs: Polyunsaturated fatty acids.

PRESS: Predicted Residual Error Sum of Squares.

RSM: Response Surface Methodology.

SFAs: saturated fatty acids

.**TAGs:** TriAcylGlyceride.

WCO: waste cooking oil.

N°	Title	Page
	Dedicas……..	I
	Acknowledgment……..	II
	Abstract……..	III
	Tables listes……...	IV
	Figures List ……...	V
	List of abbreviations……..	VI
	General introduction……..	1
	Part1: Bibliographic study	
	Chapter I: Generalities	
I.1	Diesel……	05
I.1.1	Diesel characterisations……	05
I.1.2	Diesel advanatages and disanvantages……..	06
I.2	Biodiesel……	07
	Introduction……...	07
I.2.1	Biodiesel definition……...	07
I.2.2	Biodiesel types……..	07
I.2.2.1	According to the source……	07
I.2.2.2	Biodiesel generations……...	08
I.2.3	Biodiesel characterizations……	10
I.2.4	Advantages & disadvantages of biodiesel……	10
I.2.5	Comparison between diesel and biodiesel……	11
I.2.6	Biodiesel production……	11
I.2.6.1	Biodiesel production worldwide……	11
I.2.6.2	Causes and consequences of producing biodiesel……	12
I.2.6.3	The use of biodiesel among 2008-2020……..……	13
I.3	vegetable oils (cooking oils)……..……	13
I.3.1	vegetable oil definition……..	13
I.3.2	Cooking oil types……..	14
I.3.2.1	Sunflower oil……	14
I.3.2.2	Corn oil……..……	15
I.3.2.3	Palm oil……..	15
I.3.2.4	Olive oil……	16
I.3.2.5	Conola oil……..	16
I.4	Cooking oil characteristics……	17
I.4.1	Lipid composition	17
I.4.2	Cooking oil production worldwide……	17
I.4.3	Cooking oil used in Algeria……..	18
I.4.4	Waste cooking oil……..	19
I.5	Design of experiments (DOE)……..	19
I.5.2	Response of surface methodology……	19
I.5.2.1	Central composite design (CCD)	19
I.5.2.2	Box Behnken design (BBD)……..……	20
	Conclusion)……	20
	Chapter II : Biodiesel production	
	Introduction)……..	22
II.1	Biodiesel production Methods)……	22
II.1.1	Transesterification)……	22
II.2.2	Vegetable oil transestrification)……	22
II.2.3	Mechanism of Tranesterifcation)…….	23
II.3	tranestrification catalysts)…….	23
II.4	Alcohols used in the transestrification)……	24
II.5	Biodiesel production)……	24
II.5.1	Biodiesel production Levels)……	25
II.6	Main factors affecting the production)……..	26

II.7	Biodiesel characteristics)…….	27
II.8	International biodiesel standard specifications)……..	28
II.9	Calculation of biodiesel yield...)……...……	29
	Conclusion)……	29
	Chapter III: Design of experiments.	
	Introduction……	31
III.1	Design of Experiments……..	31
III.1.1	Definition	31
III.1.2	Design of Experiments Advantages……..	31
III.1.3	Design of Experiments process……	32
III.1.4	Terminology……..	32
III.1.5	DOE Software ……	33
III.1.6	Selection of DOE……...	33
III.1.7	Analysing the Results ……..	33
III.1.8	Design of experiments types	33
III.1.9	Modelling and optimization	34
III.2	Response surface methodology (RSM) ……	34
III.2.1	Definition	34
III .2.2	Response surface methodology Designs	35
III.2.3	Mathematical modelling ……..	36
III.3	Analyses of variances (ANOVA)……..	37
III.4	Graphical analysis ……	38
	Conclusion……	39
	Part 2 : Method , Results and discussion	
	Chapter I : Optimization and modelling of biodiesel production yield	
	Introduction……..……..	42
I.1	Materials and Methods ……..……..	42
I.2	Results and Discussion …….	43
I.2.1	Fitting of Process Models and Statistical Analysis……...……	43
I.2.2	Biodiesel Production and Analysis of Variance (ANOVA)……..	43
I.2.3	statistical analysis of results ……	46
I.2.4	Graphical analyses…….	49
I.2.5	Optimization …….	51
I.3	Results Comparison ……..……	52
	Conclusion ……	53
	Chapter II: Biodiesel production from waste cooking oil	
	Introduction ……..	55
II.1	Method	55
II.2	Materials and equipment ……..	55
II.3	Experimental Procedure ……..	56
	Conclusion ……	57
	General conclusion ……..…	59

General introduction

GENERAL INTRODUCTION

For more than a century, burning fossil fuels has generated most of the energy required to propel our cars, power our businesses, and keep the lights on in our homes. Even today, oil, coal, and gas provide for about 80 % of our energy needs. In addition, we are paying the price. Using fossil fuels for energy has exacted an enormous toll on humanity and the environment from air and water pollution to global warming [1].

When we burn oil, coal, and gas, we do not just meet our energy needs; we drive the current global warming crisis as well. Fossil fuels produce large quantities of carbon dioxide when burned. Carbon emissions trap heat in the atmosphere and lead to climate change [1].

More than 11billion tons of oil in fossil fuels are consumed every year. Crude oil reserves are vanishing at a rate of 4 billion tons a year. Several studies have projected that the crude oil reserves will be exhausted between 2050 and 2075 [2].

About 17 million tons of waste cooking oils are produced in the World annually and this production has an increasing trend. The biggest environmental problem is its improper disposal, since it has as a consequence clogging of the drainage systems, harm to the wildlife and much more other [107].

Developed and developing countries are encouraging research on the production of alternate fuels. Biodiesel is a fatty acid methyl ester, produced by the transesterification of vegetable oils or animal fats with an alcohol. Biodiesel emits fewer pollutants and is nontoxic. The ignition properties of biodiesel are similar to mineral diesel, and hence biodiesel is blended with other oils in all concentrations. A greater use of diesel fuels and a dependence on petroleum imports, in combination with high petroleum prices, environmental concerns, and government incentives, boosts the growth of the biofuel industry [2].

Biodiesel is not less effective than regular diesel, Moreover it is clean, priceless, renewable, biodegradable Fuel, It can be produced from different renewable resources such as cooking oil, But Before offering biodiesel to the costumers it is hard to convince Them To use biodiesel instead of diesel, Therefore we intended to optimize biodiesel quality and yield by using DOE.

Design of Experiments is used to determine which factors or variables and interactions are significant in contributing to the effect being measured, and those variables and interactions that are insignificant and do not contribute to either a particular product property or processing condition. Using DOE saves both time and money by providing a usable understanding of the properties and process [3].

The aim of this study is to produce un alternative clean fuel from waste cooking oil and the optimization and modelling of biodiesel production yield, RSM and CCD were applied to assess the effect of two factors (Temperature and oil to alcohol molar ratio) on one response (biodiesel production yield).

This thesis is divided into two parts as the following:

The first part contains three-chapter cover bibliography review including the biodiesel production from waste cooking oil process and optimization using design of experiments.

The second part contains two chapters concerning the analysis methods and the protocol adopted for biodiesel production from waste cooking oil.

Part 1: Bibliographic studies

***CHAPTER I**: Optimization and modelling biodiesel Production yield.*

I.1 Diesel

Diesel fuel oil is essentially the same as furnace fuel oil Diesel fuel, also called diesel oil, combustible liquid used as fuel for diesel engines, ordinarily obtained from fractions of crude oil that are less volatile than the fractions used in gasoline [4].

Petroleum diesel, also called petro-diesel, or fossil diesel is produced when crude oil undergoes fractional distillation between the temperatures of 2000°C and 3500°C at atmospheric pressure, to produce a mixture of carbon chains that contains between 8 and 21 carbon atoms per molecule. Petroleum diesel is a fuel that is used to operate diesel engine-internal combustion engine. Most commonly, it refers to a specific liquid fuel obtained by the fractional distillation of petroleum, often called petro-diesel [5].

I.1.1 Diesel characterisations

- **Fuel stability [[6**

This qualitative test is performed in order to determine if additional mixing, additives or heating (in case low temperatures produce gel formation) are necessary. The samples were tested at 25°C (ambient temperature), +30°C (representative temperature of summer), +8°C (representative temperature of not critical winter) and 18°C (representative temperature of critical winter). Each sample was checked once a week during a 5 weeks period, we estimate that this is enough time to get to know its behaviour in long periods of storage.

- **Density [6]**

Density was measured according to EN ISO 12185. Following this standard, density should be tested at the temperature reference of 15 or 20°C.

- **Viscosity [6]**

Kinematic viscosity was measured according to ISO 3104 which defines this property as the resistance to flow of a fluid under gravity at 40°C. The testing device used was a Walter Herzog GmbH MP-480, which measures kinematic viscosity within the limits of precision given in the standard**.**

- **Cloud point and pour point [6]**

Cloud point was measured according to ISO 3015. Following this standard, to determine cloud point a 45 ml sample was cooled at specified rate and examined periodically**.**

Pour point was measured according to ISO 3016. To determine pour point a 45 ml sample initially at 45°C is cooled at specified rate and examined in intervals of 3 C for flow characteristics.

- **Flash point [6]**

Flash point was measured according to ISO 2719. The testing device used was a Walter Herzog MP-329, which automatically determines empirical flash point of flammable liquids according to standardized test procedures.

➢ **Diesel properties :**

Table I.1: Physical and chemical properties of No. 2 diesel fuel. [7]

Property	Diesel fuel
Chemical formula	$C_{13.77}H_{23.44}$
C/H ratio	6.90
6.90	
Density at 15°C (g/cm3)	860
Viscosity at 40°C (cst)	3.0
Molecular weight (Kg/Kmol)	190
Surface tension factor (N/m)	0.028
Calorific value (MJ/Kg)	42.5
Flash point °C	76
Cetane number	48

I.1.2 Diesel advantages and disadvantages

- **Advantages [8]**

  - ➢ Least flammable, therefore least dangerous.
  - ➢ Easily available.
  - ➢ Longer lifespan of the engine compared to natural gas (dry combustion).
  - ➢ Relatively cheap, cheaper than gasoline in Europe.
  - ➢ Possibility to place a bigger external tank, home delivery is possible.

- **Disadvantages [8]**

  - ➢ Short shelf life: 18-24 months.
  - ➢ Big storage tanks = increased installation costs.

- Possibly unavailable during power failure.
- Not suited for shorter periods.
- Watch out for moisture.
- Heavy.
- It takes a couple of seconds before the chamber where combustion takes place is warmed up enough (preheating).

I.2 Biodiesel

❖ Introduction

The world now days has watched the increase of petroleum Use and energy's demand Due to the growth of human population and industrialization, This has resulted The increase of petroleum and diesel prices, With the rapid decrease in fossil fuel reserves and the rising concerns about global warming and other related social-economic issues, The alternative energy became more attractive and the world has turned the eyes into biodiesel fuel which is priceless, renewable, biodegradable and has less emissions .

I.2.1 Biodiesel definition

Biodiesel is an animal or vegetable oil based diesel fuel that burns without the emission of much soot, carbon dioxide and particulate matter. It consists of long chain mono-alkyl esters and is produced by transesterifying vegetable oil or animal fat. In this process, the animal or vegetable oil is converted into biodiesel when one mole of triglyceride reacts with three (3) moles of alcohol to produce a mole of glycerol and three moles of mono-alkyl esters. Biodiesel like petro-diesel is made of hydrocarbon chains that do not contain sulphur, or aromatics compounds in its composition. It is an alternative fuel that is obtained from renewable resources that burns in diesel engines with less environmental pollutants [4].

I.2.2 Biodiesel types

I.2.2.1 According to the source

❖ Edible plant oils

Vegetable oil is the basis of first-generation biodiesel that can be used as replacement of conventional fossil-based [9].

Biodiesel has been predominantly (more than 95 %) produced from edible vegetable oils (biodiesel first generation) all over the world, which are easily available on large scale from the

agricultural industry [10].

❖ **Non-edible plant oils**

The main commodity sources for biodiesel production from the non-edible oils can be obtained from plant species, such as Jatropha or Ratanjyote or seemaikattamankku (Jatropha curcas), Nagchampa rubber seed tree, neem, silk cotton tree, babassu tree, Euphorbia tirucalli, microalgae, etc. They are easily available in many parts of the world and are very cheap compared to edible oils in India [11].

❖ **Waste cooking oils**

Biodiesel is a product of a chemical reaction involving vegetable oil, alcohol and a catalyst. The feedstock mainly used for transesterification is edible vegetable oil. But this puts a strain on developing countries using this oil for cooking purposes. The solution to this problem would be to use used vegetable oil for production of biodiesel. Used vegetable oil is a by-product from hotels, restaurants and shops selling fritters. These shops usually throw away the used oil as using it the next day decreases the quality of the fritters .By using used vegetable oil for biodiesel production handles the problem for waste management. A single shop can provide about 150 ml to 200 ml of impure used vegetable oil in a day [12].

❖ **Microalgae**

There is a type of microalgae that can accumulate high lipid content and reserve it in the cell body to provide energy when carbon is not available in the medium. For biodiesel production, it is desired that the microalgae used have great lipid production capacity and that the lipid accumulated in the microalgae have similar composition as vegetable oil and animal fats that are currently used in commercial biodiesel production [13].

❖ **Animal fats**

Animal fats are primarily derived as by-products from meat animal processing facilities and by the rendering process. The main animal fats include tallow from processing cattle, lard and choice white grease from swine processing, and poultry fat from the processing of chicken, turkey, or other birds. The fats/oils generated by fish processing plant and leather industry fleshing wastes have also been found to be viable biodiesel feed stocks [14].

I.2.2.2 Biodiesel generations

I.2.2.2.1 First Generation Biofuels

The first-generation biofuels refer to such fuels that have been produced directly from food crops, for example, biofuels derived from biomass-containing starch, sugar, and vegetable

oil and fats [10].

The structure of biofuel remains identical between different generations of biofuel. The most common feed stocks used for the production of first-generation biofuel are wheat, corn, and sugarcane. First-generation biodiesel can be produced from vegetable oils, soy, palm oil, sunflower oil, and so on through transesterification. Biodiesel is a liquid with similar composition as of fossil diesel but without sulphur and it consists of fatty acid methyl esters (FAMEs). Biodiesel consists mostly of methyl or ethyl esters of fatty acids derived from plants and animals fats [10].

I.2.2.2.2 Second generation

Several kinds of second-generation feed stocks can be utilized to produce biodiesel such as energy crops, agricultural remains, and wood residual wastage. The most common energy crops for this purpose are Jatropha, Aleurites moluccana, salmon oil, Rubber tree Madhuca longifolia, tobacco seed, sea mango, and jojoba oil. In addition, waste from cooking oils, non-edible oil crops, restaurant grease, beef tallow, animal fats, and pork lard can also be utilized as biodiesel feed stocks. Animal fats are preferable over first generation feed stocks due to properties such as higher-octane numbers, non-corrosiveness, lack of waste and sustainability. However, the main drawback of this generation of feed stocks is the lack of active technologies for the commercial exploitation of waste generated by biodiesel production [15].

I.2.2.2.3. Third generation

The most accepted definition for third-generation biofuels is fuels that would be produced from algal biomass, which has a very distinctive growth yield as compared with classical lignocellulosic biomass. Production of biofuels from algae usually relies on the lipid content of the microorganisms. Usually, species such as Chlorella are targeted because of their high lipid content (around 60 to 70%) and their high productivity 7.4 g/L/d for Chlorella protothecoides. There are many challenges associated with algal biomass, some geographical and some technical [16].

I.2.2.2.4. Fourth generation

Fourth generation biofuel (FGB) uses genetically modified (GM) algae to enhance biofuel production. Although GM algae biofuel is a well-known alternative to fossil fuels, the potential environmental and health-related risks are still of great concern. An evaluation of these concerns and accordingly devising appropriate mitigation strategies to deal with them are important to a successful commercialized production of FGB. While extensive research has been carried out on genetic modification and other technologies that aim to increase the productivity of algae strains, only a handful of them deal with the legislative limitations

imposed on exploiting and processing GM algae [17].

I.2.3 Biodiesel characterizations

Table I.2: biodiesel characterization [18].

Property	Astm D6751 limits	UNE-UN 14214 limits
Acid value	≤0.5 mg KOH/g	≤0.5 mg KOH/g
Carbon residue	≤0.005 wt % (on 100 sample)	≤0.3 wt% (on 10% distillation residue)
Cetane number	≤47	≤51
Cloud point	According to the climate zone °C	-
Density at 15 °C	-	860-900 $kg.m^{-3}$
Kinematic Viscosity	1.9-6 $mm^2\ s^{-1}$	3.5-5 $mm^2\ s^{-1}$
Distillation temperature	≤360°C	-
Flash point	≥93°C	≥101°C
Free glycerol	≤0.02 wt %	≤0.02%
Total glycerol	≤0.240wt %	≤0.25 wt%
Methanol content	0.2 wt%	≤0.2 wt %
Methyl ester	-	≥96.5 wt%
Water and sediment	≤0.05%	≤500 mg kg^{-1}

I.2.4 Advantages & disadvantages of biodiesel

- **Advantages [19]**

  - Biodiesel is a renewable energy source as opposed to oil, the reserves of which are finite as the reserves of other fossil fuels.

  - Biodiesel can decompose easily under natural conditions, and over 90% pure biodiesel can be degrading in a few weeks.

  - Compared with common diesel and petrol, biodiesel has higher combustible value that makes it relatively safe to be stored and transport.

  - Biodiesel contains much less sulphur which not only provides lower share of toxic substances in the exhaust but also enables to provide the lubrication of movable parts

during the work of the engine. The decrease of other harmful compounds like PAHs and NO_x occurs due to a big percentage of oxygen and more complete combustion of fuel. And pure or blend biodiesel also could suppress the net production of carbon dioxide.

- **Disadvantages [19]**

  - High viscosity and surface stress would lead to bigger drops which may cause problems with the system of fuel injection.
  - Vegetable oil contains much more unsaturated compounds than diesel, so biodiesel from it is much easier subjected to oxidation. This parameter correlates with the iodine number.
  - More expensive due to the raw material. Nowadays, the raw material of biodiesel usually soybean oil in US and peanuts oil in EU.

I.2.5 Comparison between diesel and biodiesel

Biodiesel is one alternative fuel that is becoming increasingly popular for use in diesel engines. Biodiesel is biodegradable, considerably less toxic to aquatic organisms (in the event of spills) than petroleum diesel, has a high flash point, and is considered sustainable because it can be generated from renewable sources [20].

According to the National Biodiesel Board, over 500 fleets in the United States are using the plant-based fuel.17 A 2009 study performed by the U.S. Department of Agriculture determined that soy-based biodiesel yields 4.5 units of fuel product energy for every unit of fossil fuel energy required to produce it. By comparison, petroleum diesel yields 0.83 units of fuel product energy per unit of fossil fuel energy consumed. Furthermore, the use of soybean-based 100% biodiesel in an urban bus reduced net carbon dioxide emissions by 78%. Hill and colleagues determined that soy-based biodiesel provides 93% more energy than the fossil fuel energy invested in its production and reduces greenhouse gases by 41% compared with diesel. However, many argue that land-use changes may reduce some of the benefits of biodiesel [20].

I.2.6 Biodiesel production

I.2.6.1 Biodiesel production worldwide

The United States and Brazil were among the largest biodiesel producers in the world, totaling some 6.9 and 5.4 billion liters, respectively, in 2018. The United States is projected to reach production levels of over 1 billion gallons of biodiesel by 2025. After the implementation of the Energy Policy Act of 2005 which provided tax incentives for certain types of energy,

biodiesel production in the U.S. began to increase. The Volumetric Ethanol Excise Tax Credit is currently one of the main sources of financial support for biofuels in the United States. In 2010, the U.S. exported about 85 million gallons of their biodiesel products. Comparatively, Argentina accounted for over half of the world's total exports. The United States has one of the highest bioenergy capacities in the world, totaling 13,151 megawatts in 2017 [21].

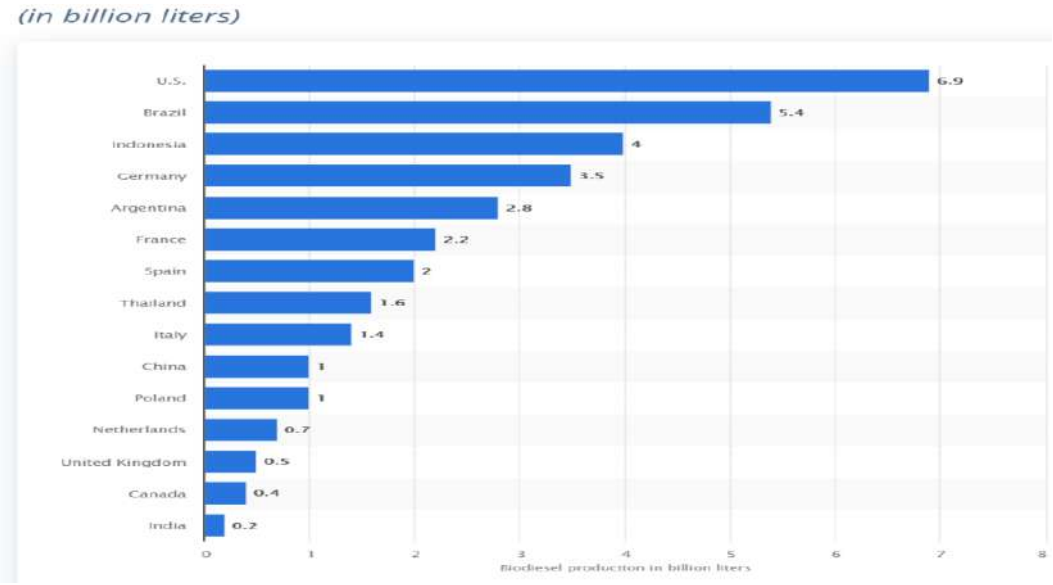

Figure I.1: Biodiesel production in billion liters [21].

I.2.6.2 Causes and consequences of producing biodiesel

- **Causes**

The continuous growth of global energy demands and the consequent environmental pollution over the last decades have turned into serious concern shared by policy-makers as well as the general public. On the other hand, the conventional resources of energy, such as oil, natural gas, and coal are non-renewable and fear of their depletion in the next century has also been the subject of intense debate, coal might be an exception though. In response to these challenges and to ensure harmonious coexistence of human and environment while sustainable economic growth and development are also achieved, the production and use of renewable energy carriers such as biofuels have been growing in many parts of the world [22].

- **Consequences**

Until recently, many policy-makers assumed that the replacement of fossil fuels with fuels generated from biomass would have significant and positive climate-change effects by generating lower levels of the greenhouse gases that contribute to global warming. Bioenergy crops can reduce or offset greenhouse gas emissions by directly removing carbon dioxide from the air as they grow and storing it in crop biomass and soil. In addition to biofuels, many of

these crops generate co-products such as protein for animal feed, thus saving on energy that would have been used to make feed by other means [23].

I.2.6.3 The use of biodiesel among 2008-2020

Table (I.3) bellow shows the use of biodiesel in 23 European country in 2008 -2020.

Table I.3: Biodiesel usage among 2008-2020 [24].

Country	Increase of biodiesel usage 2008 to 2020 (Ktoe)
UK	1764
Spain	2380
Germany	1963
Italy	972
France	916
Greece	136
Czech republic	396
Irland	304
Netherlands	252
Sweden	123
Romania	228
Portugal	313
Finland	280
Bulgaria	150
Luxemburg	150
Slovenia	154
Denmark	130
Austria	79

I.3 Vegetable oils (cooking oils)

I.3.1 Vegetable oil definition

Vegetable oils are liquids extracted from seeds and fruits of plants and consist of mixtures of organic compounds that contain, depending on their origin, approximately 98% of triglycerides and small amounts of monoglycerides and diglycerides, in addition to free fatty acids (long-chain carboxylic acids), phospholipids, carotenes, tocopherols, water, and other

impurities. Even after the refining process, small amounts of free fatty acids and water are present in the vegetable oils. Triglycerides are also found in animal fats. A triglyceride is a highly hydrophobic substance synthesized from the combination of 1 mole of glycerol with 3 moles of long-chain carboxylic acids, where the three hydroxyl groups present in the structure of the glycerol bind to the carboxylic radicals of the fatty acids, which, in turn, do not necessarily have chains with the same number of carbon atoms [25].

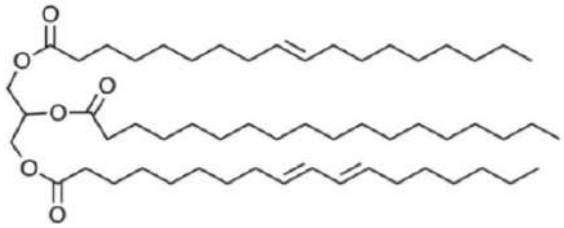

Figure I.2: Schematic representation of the structure of an unsaturated triglyceride [25].

Table I.4 represents the nomenclature and the chemical structure of some fatty acids found in vegetable oils and their systematic names. The left portion originates from glycerol; the right portion originates, from top to bottom, from oleic, palmitic, and linoleic acids.

Table I.4: Nomenclature and Chemical Structure of Fatty Acids Commonly Found in Vegetable Oils [25].

Common name	Sytematic name	Structure	Molecular formula
Lauric	**Dodecanoic**		**12:0**
Myristic	**Tetradecanoic**		**14:0**
Palmatic	**Hexadecanoic**		**16:0**
Stearic	**Octadecanoic**		**18:0**
Oleic	**9z- Octadecenoic**		**18:1**
Ricinoleic	**12-Hydroxy-9z-Octadecenoic**		**18:2**
Linoleic	**9z,12z Octadecarienoic**		**18:3**
Linoleic	**Eicasanoic**		**20:0**
Erucic	**13z Docosenoic**		**22:1**

I.3.2 Cooking oil types

I.3.2.1 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 [26].

Sunflower oil is made with 11 percent saturated fatty acids, 20 percent monounsaturated fatty acidsand 69 percent polyunsaturated fatty acids [27].

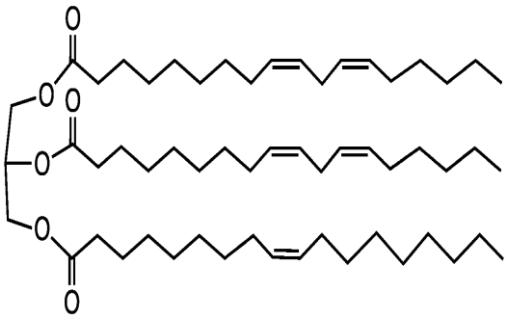

Figure I.3: sunflower oil chemical structure**.**

Figure I.4: sunflower oil.

I.3.2.2 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 [28].

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 [29].

Figure I.5: Corn oil.

I.3.2.3 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) [30].

Figure I.6: palm oil.

I.3.2.4 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 [31].

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 [32].

Figure I.7: olive oil.

I.3.2.5 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 flavour 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. [33]

Figure I.8: Canola oil.

I.4 Cooking oil characteristics

I.4.1 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 [34].

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 [35].

I.4.2 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 [36].

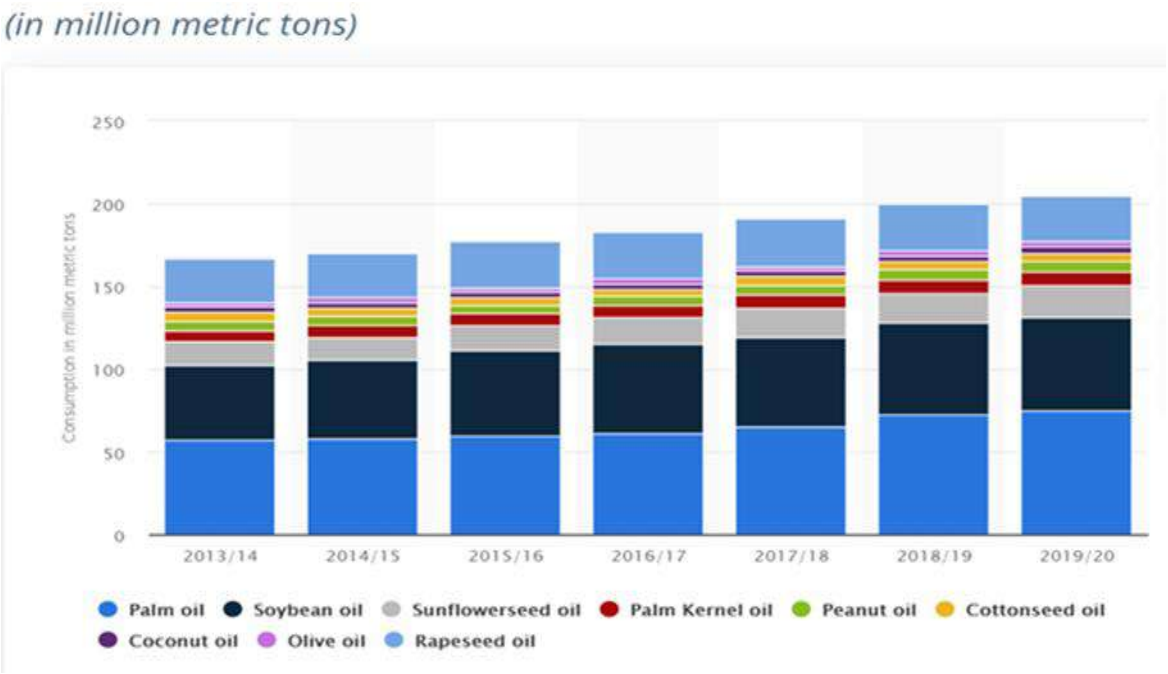

Figure I.9: Consumption of vegetable oils worldwide from 2013/14 to 2019/2020, by oil type [36].

I.4.3 Cooking oil used in Algeria

I.4.3.1 Sunflower oil

Algeria exported 112 tonnes 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 (HS code 151211) 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% [37].

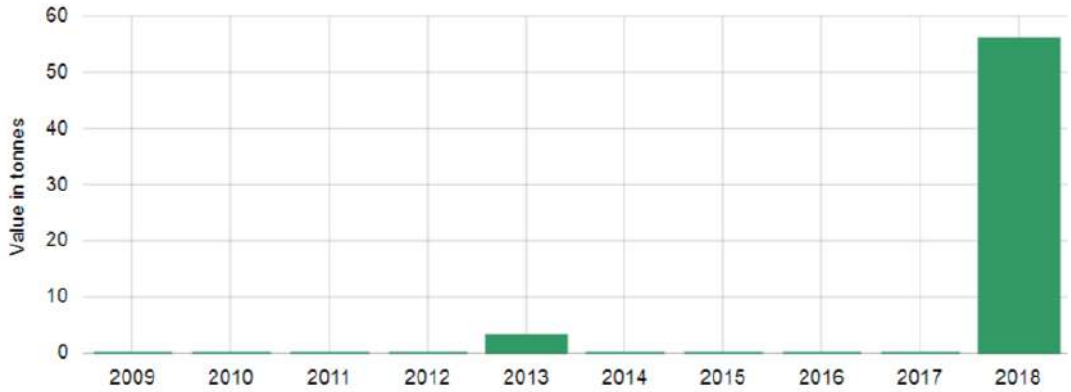

Figure I.10: value of sunflower oil in tunes – Algeria [37].

I.4.3.2 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 oliviculture is concentrated mainly in the centre of the country, the "KABYLIE" with 58.4% of the total oliviculture area (153,708 HA) [38].

I.4.4 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.10 The production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically [39].

I.5 Design of experiments (DOE)

I.5.1 Definition

The design of experiment (DOE) is very widely employed in various science domains because of its benefits, such as, minimizing the number of experiments that are required to be accomplished, whereby, the laboratory works are considerably reduced [40], Experimental design and optimization are tools that are used to systematically examine different types of problems that arise within [41]. DOE is a statistical formal methodology allowing an experimentalist to establish statistical correlation between a set of input variables with a chosen outcome of the system/process under study under certain uncertainties, called uncontrolled inputs [42].

I.5.2 Response of surface methodology

I.5.2.1 Central composite design (CCD)

The CCD optimization process involves three main steps:

(i) Conducting designed experiments.

(ii) Proposing the statistical model using regression analysis technique,

(iii) Predicting the experiment response variables and consequently checking the model using a confirmation test [43].

The CCD model has a more or less a linear relationship with Mach number, nozzle pressure ratio and area ratio whereas, a nonlinear relationship with L/D ratio [44].

I.5.2.2 Box Behnken design (BBD)

Box-Behnken designs (BBD) are a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. For three factors its graphical representation can be seen in two forms:

1 - A cube that consists of the central point and the middle points of the edges.

2- A figure of three interlocking 2*2 factorial designs and a central point.

❖ Conclusion:

Fossil fuels and diesel emissions are making huge negative impacts on our environment, However biodiesel is an attractive alternative that could decrease air pollution and gas emissions in the air, Moreover, biodiesel production from waste cooking oil will not just save the air from high pollution but also saves the water treatment stations by decreasing the oil thrown in the aquatic sewages.

Cooking oil is widely used and produced in the whole world, Thus biodiesel production would be costless, While catalysts and alcohols can be easily found, All what we must focus on is the yield and the quality of the production, which can be achieved using design of experiments.

***CHAPTER II**: Biodiesel production.*

❖ Introduction

The biodiesel production from waist cooking oils has been extensively studied in recent years. And many researchers have shown several ways to produce biodiesel, However, The transesterification has been considered as one of the best methods, concerning its low cost and popularity in the chemical laboratory.

In the transesterification we can use different catalysts and different alcohols as well, but ethanol and methanol are widely used alluding to their low cost and physical properties.

II.1 Biodiesel production Methods

- ✓ Blending.
- ✓ Microemulsions.
- ✓ Pyrolysis.
- ✓ Transesterification.

II.1.1 Transesterification

Transesterification is regarded as one of the best techniques to convert oil into biodiesel, as it has the most promising solution to the high viscosity problem among other approaches due to its low cost and simplicity. Furthermore, this technique has been identified as a widely available technique for industrialized biodiesel production due to its high conversion efficiency and low cost [45].

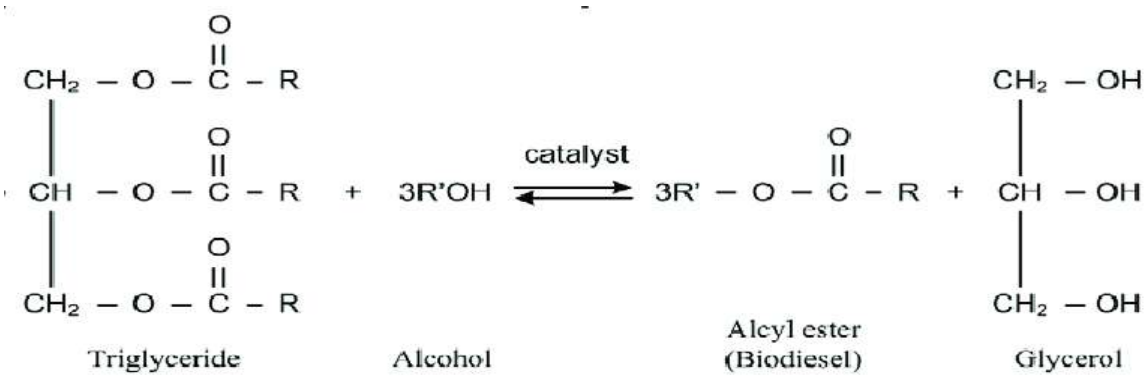

Figure II.1: The tranesterification Reaction [46].

II.2.2 Vegetable oil transestrification

Chemically vegetable oils are triglyceride molecules with structural differences in their glycerol bound alkyl moiety. Transesterification of these triglyceride molecules with short-

chain alcohols in the presence of suitable catalyst results in fatty acid methyl esters and glycerol [45].

II.2.3 Mechanism of Tranesterifcation

The mechanism for the transesterification is a series of consecutive reversible reactions, where a triglyceride is converted stepwise to diglyceride, monoglyceride and, finally, glycerol. In each one of the steps a mole of ester is liberated. They are reversible reactions even though the equilibrium tends toward the products, that is, glycerol and the free fatty esters [47].

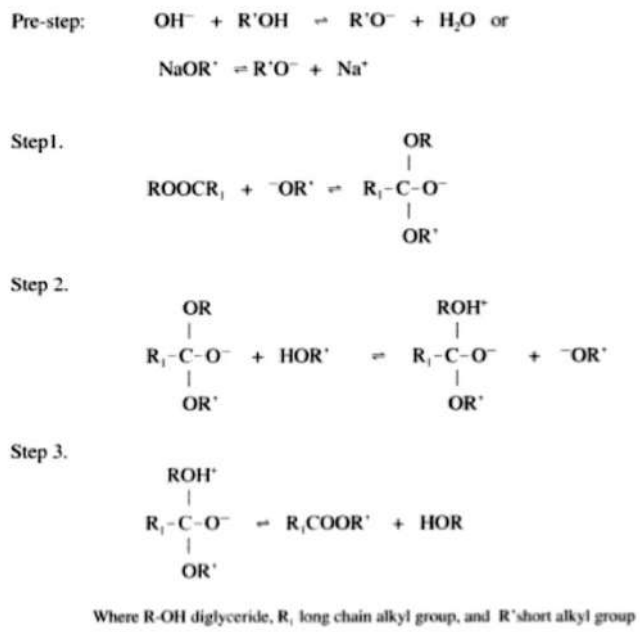

Figure II.2: Transesterification Mechanism [48].

II.3 Tranestrification catalysts

II.3.1 Acid catalysts

Transesterification has been carried out traditionally and most frequently by the use of acid catalysts such as sulfuric, sulfonic, phosphoric, and hydrochloric acids. This method is employable in various cases unless acid sensitive components are involved [45].

II.3.2 Base Catalysts

Base-catalyzed reaction is another conventional, popular transesterification. This reaction had been known since 1880s but it was not until 1920 and 1921 that systematic studies appeared in a comprehensive manner [45].

There are various alkali-based catalysts have been utilized as homogeneous and heterogeneous transesterification. Base catalyzed transesterification is substantially less time consuming with respect to acid catalyzed transesterification and it is regularly used technique for commercial purpose [49].

I.3.3 Amine catalysts:

Amine Catalysts Strongly basic amines have found extensive use as transesterification catalysts recently. Taber discovered the effectiveness of 4-(dimethyl amino) pyridine (DMAP), which was employed for /3-keto esters. 39 This class of compounds acts somewhat differently from others in transesterification [45].

II.4 Alcohols used in the transestrification

Methanol, ethanol, propanol, butanol and amyl alcohol have been used in biodiesel production. However, high prices and complex and expensive alcoholysis conditions make all but methanol and ethanol unsuitable for practical use [50].

In general, both methanol and ethanol can be obtained from plant materials. Since methanol is cheaper, it is the most commonly employed alcohol [50].

The Figure II.3 shows How The transesterification reaction Can be effected by different Type of alcohols:

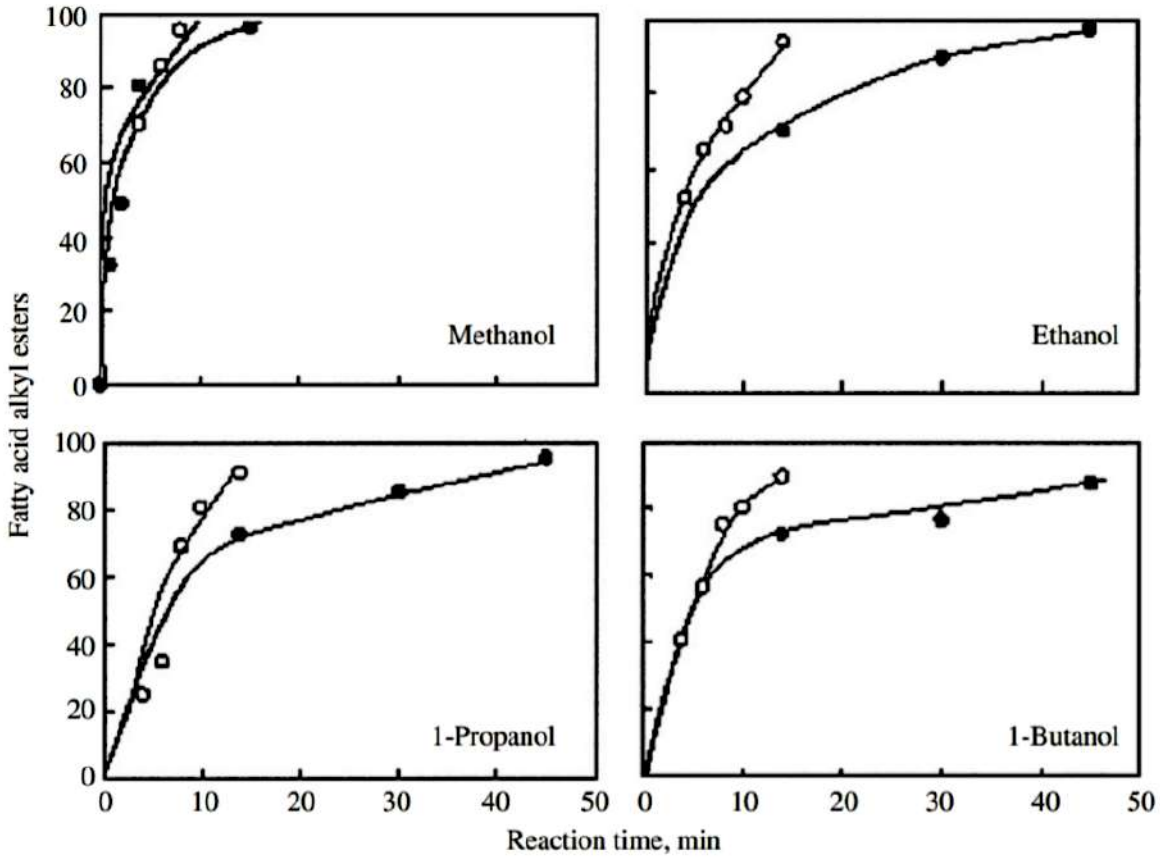

Figure II.3: The performance of different alcohols in the transesterification [51].

II.5 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 glycerine, 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.

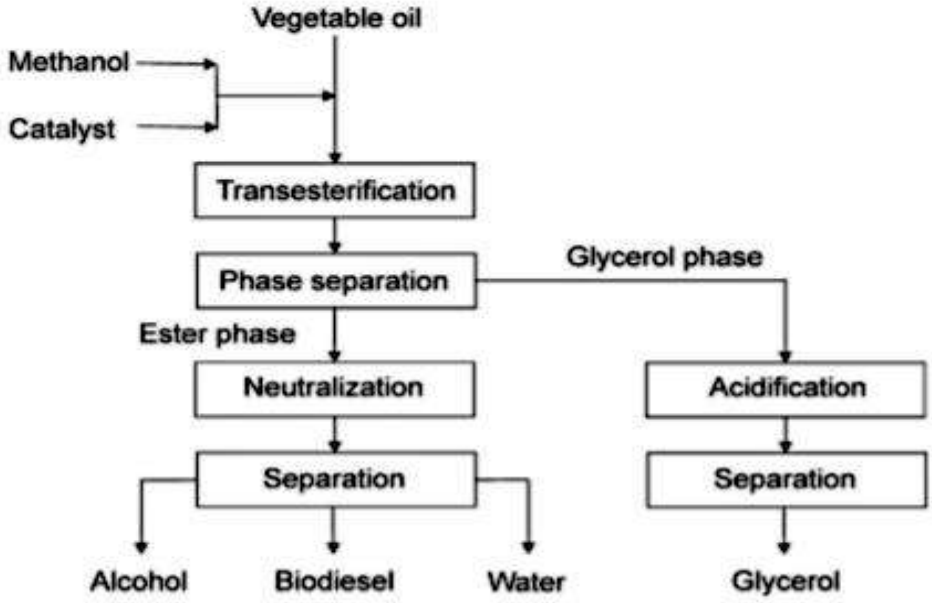

Figure II.4: Biodiesel production process [52].

II.5.1 Biodiesel production Levels

II.5.1.1 Transestrification

For the production of biodiesel, a vegetable 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 [48].

II.5.1.2 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 [53].

II.5.1.3 Biodiesel Washing

Water washing is generally carried out to remove soap, catalyst, methanol and other contaminants from FAME [54].

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) [55].

II.5.1.4 Drying

Biodiesel were then dried at a temperature of 100-110 degrees Celsius until the air bubbles disappear [56].

II.6 Main factors affecting the production

II.6.1 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 [19].

II.6.2 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. However the maximum ester conversion was achieved within < 90 min [57].

II.6.3 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 60°c depends upon the oils or fats used [57].

II.6.4 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 [58].

II.6.5 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 .The mixture is stirred At about 650 to 700 rpm for one hour .It was found that phase separation occurs after 3-4 minutes stirring but maximum ester yield was reached after 30 minutes of stirring [58].

II.6.6 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 [59].

II.7 Biodiesel characteristics

II.7.1 Viscosity of Biodiesel

Fuel viscosity is the main property that plays an important role in the combustion of fuel. The direct injection in the open combustion chamber through the nozzle and pattern of fuel spray decides the ease of combustion and thermal efficiency of the engine. Too low viscosity can lead to excessive internal pump leakage whereas system pressure reaches an unacceptable level and will affect injection during the spray atomization. The effect of viscosity is critical at low speed or light load conditions [47].

II.7.2 Flash point

The main purpose of the flash point specification is to ensure that the manufactured FAME has been sufficiently purified by removal of excess methanol. Even small amounts of residual methanol in FAME will cause a significantly depressed flash point [60].

II.7.3 Cloud point

The cloud point is defined as the temperature at which crystallization of the heavier fatty acid esters starts as the fluid is cooled. As the solid phase develops in the liquid bulk, the solution becomes cloudy. With a further decrease in the temperature, the crystal particles grow rapidly and agglomerate, reducing the capacity of the liquid to flow through porous media by plugging the filters, and eventually gel the fluid, preventing it from flowing altogether [61].

II.7.4 Cetane index

The cetane index is a basic property, and defined as a measurement of the ignition performance of a fuel. This parameter is influenced by structural features of fatty acid alkyl esters, such as chain length, degree of unsaturation and branching of the chain. It should be emphasized that the higher the cetane index, the better will be the combustion. Residual methanol in biodiesel is responsible for a decrease in the cetane index [61].

II.7.5 Pour point

The pour point is defined as the temperature at which the fuel can no longer be poured due to gel formation. The observation of the samples starts at a temperature that is at least 9° C above the expected pour point [62].

II.8 International biodiesel standard specifications

The table (II.1) below shows the biodiesel properties standards that help us to produce a Good biodiesel Following the international standards:

Table II.1: international biodiesel standards [63].

Properties	Units	ASTM method	EN14214
Ester content	% (m/m)	-	96.5
Flash point	°C	130 min	>101
Water and sediment	vol%	0.050 max	0.05
Kinematic viscosity, 40C	mm^2/s	1.9-60	3.5-5
Copper strip corrosion	Rating	No.3 max	Class1
Cetane	-	47 min	≥51
Cloud point	°C	Report	-
Acid number	Mg KOH/gm	0.50 max	0.50 max
Phosphorus content	mass%	0.001 max	0.001 max.
Total glycerine	%(m/m)	0.240 max	0.25 max.
Methanol content	%(m/m)		0.20max.
Sodium/potassium	ppm	5 max. combined	5 max.

II.9 Calculation of biodiesel yield

Biodiesel yield is calculated as the following equation (II.1):

$$\eta = \quad ; \qquad \text{(II.1)}$$

The theoretical amount of produced biodiesel for a 100 % yield is calculated taking into account that 3 mol biodiesel are produced from 1 mole oil. The real amount of produced biodiesel is calculated knowing the volume, density and molar weight of biodiesel [64].

The density calculated by equation (2) [64]:

$$\rho = \frac{m}{v} \; ; \qquad \text{(II.2)}$$

Volume yield is calculated as the following equation (3) [65]:

$$\text{Volume yield\%} = \frac{Volume\ of\ product}{volume\ of\ oil\ fed} \text{ X } 100 \; ; \qquad \text{(II.3)}$$

❖ Conclusion:

Biodiesel is an attractive alternative to diesel fuel, it can be made from waste cooking oil By transesterification reaction that needs alcohol and catalysts, methanol and ethanol alcohol are widely used in the transesterification, while the catalysts used could be an acid, base, or amine catalyst.

Many factors could affect the transestrification reaction such as oil:alcohol molar ratio , reaction temperature and time, thus, it can influence the production yield or quality .

Biodiesel follows international standards that should be considered after analysing it, therefore we can assume that our production enjoys High qualities.

In the next chapter we will be talking about design of experiments that would help us in biodiesel production.

***CHAPTER III**: Design of experiments*

Introduction

In the 21 century we are blessed with the huge help that technology offers us, however we cannot deny the help of programs in different processes, Such as Design of experiments (DOE).

Design of experiments minimizes bias in the comparison which helps in reducing error, Also DOE could help us to find better yield of production in a short time with law costs. We can use DOE in different processes and experiments, and biodiesel production is one of them, However DOE could enhance biodiesel quality and the yield of production.

III.1 Design of Experiments

III.1.1 Definition: DOE is a systematic approach to understanding how process and product parameters affect response variables such as process ability, physical properties, or product performance. It is a tool similar to any other tool, device, or procedure that makes the job easier. Unlike quality, mechanical, or process tools, DOE is a mathematical tool used to define the importance of specific processing and/or product variables, and how to control them to optimize the system performance while maximizing properties. DOE uses statistical methodology to analyze data and predict product property performance under all possible conditions within the limits selected for the experimental design. In addition to understanding how a particular variable affects product performance, interactions between different process and product variables are identified DOE is a technique or procedure to generate the required information with the minimum amount of experimentation, using the following **[66]:**

- Experimental limits
- Specific experimental conditions
- Mathematical analysis to predict the response at any point within the experimental limits.

III.1.2 Design of Experiments Advantages

- ✓ To generate knowledge in the experimental domain of interest.
- ✓ To reliably estimate the experimental variability (pure error).
- ✓ To guarantee the adequacy between the proposed model and the experimental data (to make it easy to detect the lack of fit).
- ✓ To predict the observed response, as exactly and precisely as possible, in points within the experimental domain where no experiments were done.

- ✓ To propose sequential strategies to carry out the experimentation with different alternatives according to the results obtained.
- ✓ To maintain a high efficiency with respect to economical cost, time, and any other practical limitations.
- ✓ To make the decision making possible under uncertainty conditions, reducing the ambiguity **[67]**.

III.1.3 Design of Experiments process

The process involved in conducting a successful design of experiments can be broken down into five steps [68]:

- Define the problem.
- Plan the experiment.
- Run the experiment.
- Analyse the data by using statistical methods.
- Report the results.

III.1.4 Terminology

Experimental design and analysis has a standardized terminology that is, unfortunately, different from that used in survey sampling [69].

- **Factor:** one of the variables under the control of the experimenter that is varied over different experimental units. If a variable is kept constant over all experimental units, then it is not a factor because we cannot discern its influence on the respondent from that used in survey sampling.
- **Levels:** values of the factor used in the experiment.
- **Response variable:** what outcome is being measured?
- **Treatment:** the combination of factor levels applied to an experimental unit. If an experiment has a single factor, then each treatment would correspond to one of the levels. If an experiment had two or more factors, then the combination of levels from each factor applied to an experimental unit would be the treatment. For example, with two factors having 2 and 3 levels respectively, there are 6 possible treatment combinations.

- **Experimental unit:** the unit to which the treatment is applied.

III.1.5 DOE Software

DOE can be quickly designed and analyzed with the help of suitable statistical software. For this purpose, there are some commercial and freeware statistical packages. The well-known commercial packages include: Minitab, Statistica, SPSS, SAS, Design-Expert, Statgraphics, Prisma, etc. The well-known freeware packages are: R and Action for Microsoft Excel **[70].**

III.1.6 Selection of DOE

Selection of a suitable design out of existing alternatives depends upon the availability of resources and the degree of control for probable validity to make decisions over errors as a part of desired hypothesis A design with minimal runs allows verification of curvature in a 2-level screening design and avails reserved resources to rerun process so as to evade unfavorable consequences **[68].**

III.1.7 Analyzing the Results

Analyzing the results of experiments is linked to the initial design choice. If the experiments are well-prepared, the results are easy to interpret, and they are also rich in information. Thanks to computers and software, the construction of experimental designs and the necessary analysis calculations have become simple. These tools also support graphical representations that illustrate the results spectacularly and increase understanding of the phenomenon **[71].**

III.1.8 Design of experiments types

III.1.8.1 Full factorial Design

In a Full factorial design (FFD), the effect of all the factors and their interactions on the outcome (s) is investigated. A common experimental design is one, where all input factors are set at two levels each. These levels are termed high and low or + 1 and − 1, respectively. A design with all possible high/low groupings of all the input factors is termed as a full factorial design in two levels. If there are k factors, each at 2 levels, a full factorial design will be of 2^k runs as mentioned earlier. When the number of factors is more than five, a full factorial design requires a large number of experimental runs and is not effective [72].

III.1.8.2 Fractional factorial design

Fractional factorial designs are designs that include the most important combinations of the variables. The significance of effects found by using these designs is expressed using statistical methods. Most designs that will be shown later are fractional factorial designs. This is necessary in order to avoid exponential explosion. Quite often, the experiment design problem is defined as finding the minimum number of experiments for the purpose [73].

III.1.9 Modelling and optimization

The virtues of using machine learning and evolutionary algorithms to model and optimize data rich environments thus seem promising because they are automatic, involving little human intervention and expertise. We believe and are exploring how they can be made adaptive to improve parameter estimates with increasing data, as well as seamlessly detecting system (and therefore model) changes, thus being capable of recursively updating and optimizing a modified or new model [74].

III.2 Response surface methodology (RSM)

III.2.1 Definition: Response surface methodology (RSM) is a tool that was introduced in the early 1950s by Box and Wilson (1951). RSM is a collection of mathematical and statistical techniques that is useful for the approximation and optimization of stochastic models. The objective function associated with such models is subject to random noise and is referred to as noisy or stochastic objective function. It also has important applications in the design, development, and formulation of new products, as well as in the improvement of existing product designs [75].

- the RSM procedure is carried out as follows [76]:

1- A series of experiments are performing for adequate and reliable measurement of the response of interest.

2- A mathematical model of the second-order response surface with the best fit is developed.

3- The optimal set of experimental parameters producing the optimum response value is determined.

4- The direct and interactive effects of the process parameters are represented through two and three dimensional plots.

The successful use of RSM is critically dependent upon the experimenter's ability to develop a suitable approximation for function. Usually, a low-order polynomial in some relatively small region of the independent variable space is appropriate. In many cases, either a first-order or a second order model is used. In general, the first-order model is [77]:

$$\beta_0 + \beta_1 x_1 + \beta_2 x_2 \quad \textbf{(III.1} \quad \textbf{(;}$$

the second-order model is:

$$\beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x^2 + \sum_{i \prec} \sum_{j=0}^{k} x_j x_i \textbf{;} \qquad \textbf{(III.2)}$$

III .2.2 Response surface methodology Designs

III.2.2.1 Central Composite Design (CCD)

Technological processes in the case of small number of preformed experiments compared with “one variable at a time” approach.

Response surface methodology comprised of several methods to design the experimental procedures and one of them is Central Composite Design (CCD). Optimization carried out with CCD can allow screening of a broad range of parameters as well as the role of each factor. In addition, CCD is also able to evaluate a single variable or the cumulative effect of the variables to the response. Although this ability is shared with the other types of experimental design such as full factorial and partial factorial method, it differs in a way that the experimental runs are reduced. For instance, with just four independent variables, full factorial method will suggest at least 81 experimental runs plus replication Otherwise when using CCD method, only 31 experimental points (16 factorial points, 8 axial points and 7 center points) are needed. Before any variables can be carried into experimental phase, the variables must be coded according to (III.3):

$$X_I = (X_i - \overline{X}_i) \ / \Delta X_i \ ; \qquad \text{(III.3)}$$

Where xi is the coded level; Xi is the natural level for the independent variable; $\overline{Xi}$ is the mean for the natural level of the independent variables; and ΔXi is the step change value [78].

CCD can be described as 2^n factorial design with additional central and axial points, allowing calculating parameters of a second-order model. It involves 2^n factorial points, 2^n axial points and one central point. Usually axial and/or central points are replicated. Axial points are placed at the distance α from the design center, thus CCD uses five levels of parameters: $+\alpha$, +1, 0, -1, $-\alpha$. The value of α is usually chosen to make design either orthogonal or rotatable **[79].**

III.2.2.1.1 Central composite faced design (CCFD)

In this design the star points are at the centre of each face of the factorial space, so α = ± 1 and only three levels are used. Complementing an existing factorial or resolution V design with appropriate star points can also produce this design. CCF designs provide relatively high quality predictions over the entire design range, but poor precision for estimating pure quadratic coefficients. They do not require using points outside the original factor range [73].

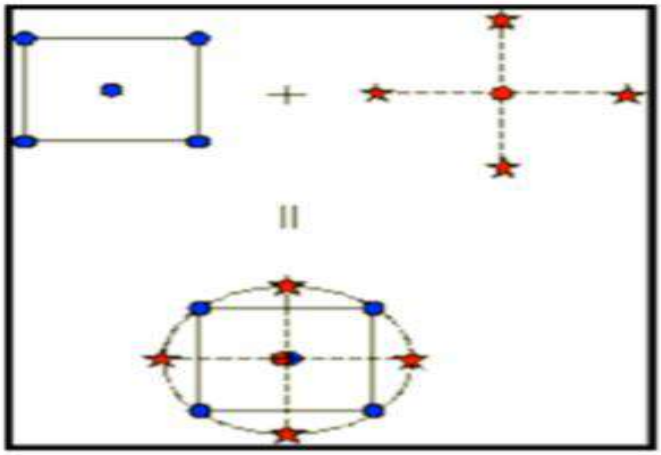

Figure III.1: Generation of a central composite design [80].

III.2.2.2 Box behnken Design (BBD)

Box–Behnken design (BBD) is an independent, rotatable quadratic design with no embedded factorial or fractional factorial points where the variable combinations are at the midpoints of the edges of the variable space and at the center [81].

These designs typically require more runs than CCDs in the same number of variables. To construct a Box-Behnken design in k factors, first identify an incomplete block design with k treatments divided into blocks of size b (Balanced incomplete block designs are often used, in which each of the k treatments is applied to the same number of experimental units, and each of the $\binom{n}{k}$ pairs of treatments are applied to the same number of pairs of experimental units in a common block.), Each of the k treatments corresponds to one of the k factors [82].

III.2.3 Mathematical modelling

The field of response surface methodology consists of the experimental strategy for exploring the space of the process or independent variables, empirical statistical modelling to develop an appropriate approximating relationship between the yield and the process variables, and optimization methods for finding the values of the process variables that produce desirable values of the response. In this report we will concentrate on the second strategy: statistical modelling to develop an appropriate approximating model between the response y and independent variables $x_1, x_2, \ldots, x_k$ [77].

In general, the relationship is:

$$Y = f(x_1, x_2 \ldots\ldots x_k) + \xi ; \qquad \text{(III.4)}$$

III.3 Analysis of variances (ANOVA)

III.3.1 Definition: Analysis of variance (ANOVA) is a statistical tool used to detect differences between experimental group means. ANOVA is warranted in experimental designs with one dependent variable that is a continuous parametric numerical outcome measure, and multiple experimental groups within one or more independent (categorical) variables. In ANOVA terminology, independent variables are called factors, and groups within each factor are referred to as levels. The array of terms that are part and parcel of ANOVA can be intimidating to the uninitiated, such as: partitioning of variance, main effects, interactions, factors, sum of squares, mean squares, F scores, family wise alpha, etc.. [83].

III.3.2 P-value: The p-value is calculated from the F null sampling distribution with matching degrees of freedom. But only if we believe that the assumptions of the model are (approximately) correct should we believe that the p-value was calculated from the correct sampling distribution, and it is then valid [84].

III.3.3 The coefficient of multiple determination R^2: R^2 is defined as the ratio of the explained variation to the total variation and is a measure of a degree of fit [85]. R^2 is a measure of the amount of reduction in the variability of y obtained by using the regressed variables k x_1, x_2,..., x_k in the model [77]. A very low R^2 indicate that the selected model for the experimental design does not accurately predicted the experimental data and hence the experimental data needs to be checked for conformance to the assumption of ANOVA [86].

The coefficient of multiple determination R^2 is defined as (III.5) [77]:

$$R^2 = 1 - \frac{SSe}{SSt}\ ; \qquad \text{(III.5)}$$

III.3.4 R^2 adjusted: The adjusted R^2 gives "the fraction of the variation explained by changes in the factor" when one is analyzing data collected using EIMSE- optimal box-behnken or central composite design, one expect adjusted R squared value in excess of 0.50 or 50% . Otherwise there is a concern that some or all of the responses are not trust worthy and/ or that the most important factors are unknown and uncontrolled during the testing [87].

III.3.5 F-value: Fisher F-test value explains the distribution of the actual data around the fitted model [95]. The F-value compares the mean square with the residual mean square [89].

III.3.6 The prediction error sum of squares (PRESS)

$$\mathbf{PRESS} = \sum_{i=1}^{n} \left(\frac{e}{1 - h_{ii}} \right)^2 \ ; \qquad \text{(III.6)}$$

From Equation (5) it is easy to see that the PRESS residual is just the ordinary residual weighted according to the diagonal elements of the hat matrix h_{ii}. Generally, a large difference between the ordinary residual and the PRESS residual will indicate a point where the model fits the data well, but a model built without that point predicts poorly [77].

III.3.7 R predicted: R prediction has already been proposed and is calculated from the prediction of the residual error sum of square (PRESS) [90].

III.3.8 Lack of fit (LOF): The test for lack-of-fit compares the variation around the model with pure variation within replicated observations. This test measured the adequacy of the different models based on response surface analysis [91].

III.4 Graphical analysis

III.4.1 Pareto chart: Screening designs are often used in the first step to DoE in order to select the most important input factors and discard the insignificant ones. Pareto charts are useful tools to achieve this purpose, because they allow to put the input factors (and their interactions) in order of importance [92].

The Pareto plot allows one to detect the factor and interaction effects that are most important to the process or design optimization study one has to deal with. It displays the absolute values of the effects, and draws a reference line on the chart. Any effect that extends past this reference line is potentially important [93].

III.4.2 Normal plot: The normal probability plot indicates whether the “residuals” follow a normal distribution, in which case the points will follow a straight line. Expect some moderate scatter even with normal data. Look only for definite patterns like an "S-shaped" curve, which indicates that a transformation of the response may provide a better analysis [86].

III.4.3 Histogram of the residuals: to detect multiple peaks, outliers, and nonnormality. The histogram should be approximately symmetric and bell-shaped [94].

III.4.4 Residuals versus the fitted values: to detect nonconstant variance, missing higher-order terms, and outliers. The residuals should be scattered randomly around zero [94].

III.4.5 Residuals versus order: to detect time-dependence of residuals. The residuals should exhibit no clear pattern [94].

III.4.6 Response optimizer plot: A response optimizer plot is useful in determining the operating conditions that will results in a desirable response [95].

III.4.7 Surface plot: The 3D response surface plot is a graphical representation of the regression equation. It is plotted to understand the interaction of the variables and locate the optimal level of each variable for maximal response [96].

Response surface plots such as contour and surface plots are useful for establishing desirable response values and operating conditions. In a contour plot, the response surface is

viewed as a two-dimensional plane where all points that have the same response are connected to produce contour lines of constant responses. A surface plot generally displays a three-dimensional view that may provide a clearer picture of the response [93].

III.4.8 Contour plot: A contour plot is a 2D plot of a three-dimensional surface where the corresponding surface intersects planes with constant elevation. It means that there is just one z value for every x and y pair on the contour plot [97]. Contour plot gives better understanding about the influence of variable and their interactions on the response as compared to the 3D surface plot [96].

❖ *Conclusion:*

Design of experiment is an important tool that is widely used in different section of science and productions, by using Response surface methodology, we can reach the best response of our production, and using DOE is a costless way to get a production with the qualities we want in a short period of time, Such as biodiesel production.

In the next chapter we will be using design of experiments in order to get a better biodiesel yield.

Part2 *: Method, Results and discussion*

***CHAPTER I**: Optimization and modelling biodiesel Production yield.*

❖ Introduction

Biodiesel production has been one of the most important productions worldwide, Due to its properties that make it an attractive alternative to diesel fuel.

But also we need to enhance both yield and quality of the biodiesel production, thus , Using design of experiment plays a huge rule helping us to reach a better yield, In fact, A strong model is important to gain both time and costs. In this chapter we will be using Minitab program, and CCD design and get a better yield and better results.

I.1 Materials and Methods

The aim of this study is the modelling of biodiesel production, The data was processed using statistical software (Minitab 19), applying response surface methodology 'RSM' to determine the optimum condition for biodiesel production.

The parameters were obtained from "Multivariable Analysis and Optimization of Biodiesel Production from Waste Cooking Oil 2018, by Mohammad Ali Zahed, Zahra Zakeralhosseini, Leila Mohajeri, Gholamreza Nabi Bidhendi and Saba Mesgari, Iran" where Temperature and Oil:Alcohol ratio were taken as factors and biodiesel production yield as a response.

TableI.1: Factor level.

Factor	Lower value	Higher value
Temperature	50° C	70 °C
Oil: Alcohol ratio	3	5

The Central composite Face-Centered Design (CCFD) carried out in the work offered a useful data linear, interactions and quadratic effects [98], The CCFD consisted of 14 experiments including 4 factorial experiments, 4 axial experiments, and 6 replicates of center point, The factor levels taken were 50°C -70°C of temperature and 3-5 oil: Alcohol molar ratio, as shown in table I.1.

The general model form shown in equation I.1 used in this study eq (I.1):

$$\beta_0 + \sum_{I=1}^{n} + \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} \overset{2}{x_i} + \sum_{i \neq j=1}^{n} \beta_{ij} x_i x_j + \varepsilon \quad ; \qquad (I.1)$$

Y= the Independent variable.

β_0: the model intercept.

β_i: the regression coefficient of the ith factor.

β_{ii}: the quadratic regression coefficient of the ith factor.

β_{ij}: is the ith and jth-factor interaction.

I.2 Results and Discussion

I.2.1 Fitting of Process Models and Statistical Analysis

The CCF employed is based on un-coded levels of the independent variables, the developed equation of the biodiesel production yield corresponds with this experiment is given by the by the equation (I.2):

$$\mathbf{Y}_{\mathbf{Biodiesel}} = -214.24 + 9.296\ T + 8.67\ M_{ratio} - 0.08094\ T*T - 2.494\ M_{ratio}*M_{ratio} + 0.2025\ T*M_{ratio}\ ; \quad (I.2)$$

- **Y biodiesel** = The biodiesel production yield.
- **T**= Temperature.
- **M.ratio** = oil: Alcohol molar ratio.

I.2.2 Biodiesel Production and Analysis of Variance (ANOVA)

The experimental matrix generated by Minitab software using by Central Composite Face Design was designed is shown in table I.2:

Table I.2: Expremetal matrix.

EXP	Point type	Temperature	Oil: Alcohol M.Ratio
1	+1	50	3
2	+1	70	3
3	+1	50	5
4	+1	70	5
5	-1	50	4
6	-1	70	4
7	-1	60	3
8	-1	60	5
9	0	60	4
10	0	60	4
11	0	60	4
12	0	60	4
13	0	60	4
14	0	60	4

The predicted and experimental results for biodiesel production are presented in Table I.3.

Table I.3: Predicted and experimental results for biodiesel production.

Number	Experimental	Predicted	Residual
1	82.1	82.1868	-0.08676
2	86.0	86.0034	-0.00343
3	79.6	79.8701	-0.27010
4	91.6	91.7868	-0.18676
5	83.8	83.4431	0.35686
6	91.5	91.3098	0.19020
7	92.2	92.1098	0.09020
8	94.3	93.8431	0.45686
9	95.1	95.3912	-0.29118
10	95.3	95.3912	0.40882
11	95.3	95.3912	-1.09118
12	95.3	95.3912	-0.49118
13	96.4	95.3912	1.00882
14	95.3	95.3912	-0.09118

In order to determine the effect of the individual terms and their interaction on the biodiesel production yield, moreover the importance and fitness of the quadratic regression model, the analysis of variances 'ANOVA' was carried out Statistical results are shown in table I.4.

Table I.4: Analysis of variance results.

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	5	417.365	99.64%	417.365	83.473	441.54	0.000
Linear	2	97.333	23.24%	97.333	48.667	257.43	0.000
T	1	92.827	22.16%	92.827	92.827	491.02	0.000
Mratio	1	4.507	1.08%	4.507	4.507	23.84	0.001
Square	2	303.629	72.49%	303.629	151.814	803.04	0.000
T*T	1	286.004	68.28%	185.625	185.625	981.88	0.000
Mratio*Mratio	1	17.625	4.21%	17.625	17.625	93.23	0.000
2-Way	1	16.402	3.92%	16.402	16.402	86.76	0.000

Interaction							
T*Mratio	1	16.402	3.92%	16.402	16.402	86.76	0.000
Error	8	1.512	0.36%	1.512	0.189		
Lack-of-Fit	4	0.679	0.16%	0.679	0.170	0.81	0.576
Pure Error	4	0.833	0.20%	0.833	0.208		
Total	13	418.877	100.00%				
Source	**DF**	**Seq SS**	**Contribution**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	5	417.365	99.64%	417.365	83.473	441.54	0.000
Linear	2	97.333	23.24%	97.333	48.667	257.43	0.000
T	1	92.827	22.16%	92.827	92.827	491.02	0.000
Mratio	1	4.507	1.08%	4.507	4.507	23.84	0.001
Square	2	303.629	72.49%	303.629	151.814	803.04	0.000
T*T	1	286.004	68.28%	185.625	185.625	981.88	0.000
Mratio*Mratio	1	17.625	4.21%	17.625	17.625	93.23	0.000
2-Way Interaction	1	16.402	3.92%	16.402	16.402	86.76	0.000
T*Mratio	1	16.402	3.92%	16.402	16.402	86.76	0.000
Error	8	1.512	0.36%	1.512	0.189		
Lack-of-Fit	4	0.679	0.16%	0.679	0.170	0.81	0.576
Pure Error	4	0.833	0.20%	0.833	0.208		
Total	13	418.877	100.00%				

The P-values are the results of hypotheses testing for every individual coefficient. P-value or probability value is a statistical method for evaluating the significance of the parameters, The P-values less than 0.05 were assumed to be significant [99].

According to the results shown in the table 3 the quadratic regression model has a p-value less than 0.0001, the test result shows that the temperature, molar ratio and their interaction Temperature*Temperature, molar ratio*molar ratio, molar ratio*Temperature have an important effect on the biodiesel production yield. The model is statistically significant at the 95% confidence level.

The ANOVA analysis also shows the Lack-of-Fit (LOF) value, which can be used to investigate the model sufficiency. LOF value of 0.81 > 0.05 implies that the Lack-of-Fit is not significant relative to the pure error. The model F- value of 441.54 implies that the model is

statistically significant.

The quality of the quadratic polynomial model fit was expressed by the coefficient of determination (R2), which is a key output of regression analyses. According to jogleka and May [100], for a good fit of a model, the correlation coefficient should be at a minimum of 0.80. High R2 value illustrates good agreement between the calculated and observed results within the range of experiment [100]. Noticing table I.5, R^2, R^2 (adj) and R^2pred values 99.46%, 99.41% and 98.89%, respectively, while R2 was 98.89%, which indicate a good predictability of the model.

PRESS value was 4.64 which refers to dependent response variable of the whole data scenario [108].

Table I.5: model summary.

S	R^2	R^2(adj)	PRESS	R^2(pred)	AICc	BIC
0.434799	99.64%	99.41%	4.64618	98.89%	41.24	27.05

I.2.3 statistical analysis of results

Pareto chart has a really clear reading and organizing to the absolute values of the standardized effects from the largest effect to the smallest effect, However all the bars that cross the reference line reference are significant, the bars that didn't cross the they are insignificant.

According to Fig I.1 all of the effects crossed the reference red line, which indicates that all the effects are significant, furthermore AA, A have a strong effect, while B has less effect but yet unnegligeable.

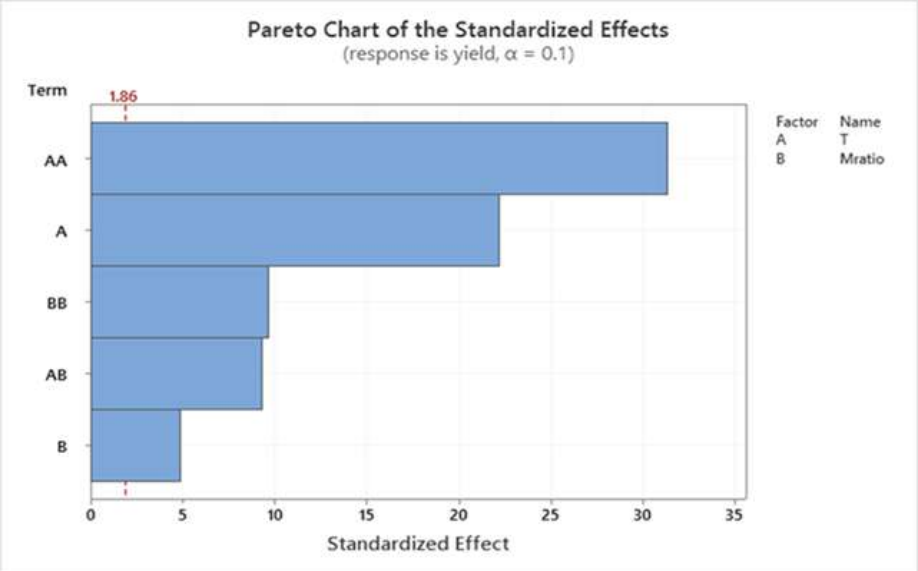

Figure I.1: Pareto chart of the standardized effects.

Each point on the normal plot represents a factor considered in the experimental design [102] points distributed along the straight line without any response transfer appears as a normal distribution curve of residuals [103]. Normal plot of the standardized effects shown in Figure I.2 all the factors are statistically significant.

The points A, B, AB have a positive effects, the increase of the Temperature (A) and Oil:Alcohol molar ratio (B) and the interaction AB leads to the increase of the biodiesel production yield, In fact, Temperature*Temperature (AA) and molar ratio*Molar ratio (BB) have a negative effects.

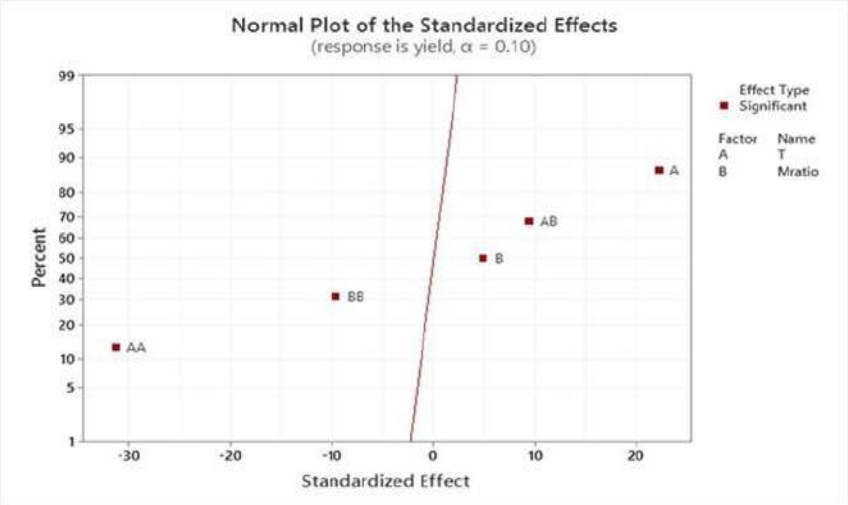

Figure I.2: Normal plot of the standardized effects.

The normal probability plot of the residuals was used to verify the assumption that the residuals are normally distributed. In the Normal probability plot shown in Figure I.3 the residuals are approximately follow a straight line, which indicates that the model prediction is accurate.

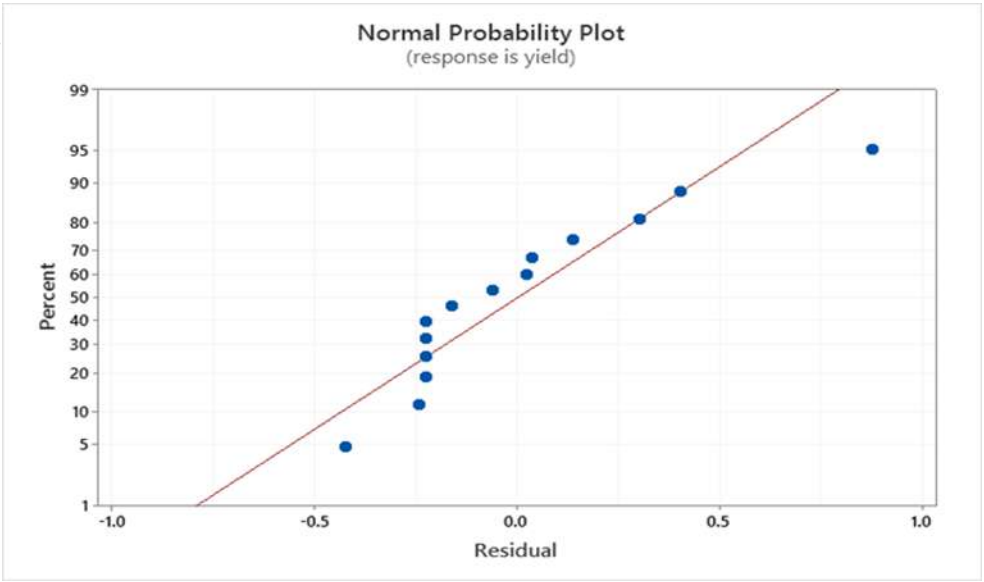

Figure I.3: normal probability plot.

A residual plot shows the deviation of predicted values from observed values. The residual values (vertical axis) are the differences between the experimental values and the fitted values and they are used to evaluate the adequacy of the model [102]. The residuals versus fits plot shows that the residuals are randomly distributed and have constant variance.

According to the figure I.4, the plot falls randomly around the centre line, which indicates that the residuals are independent.

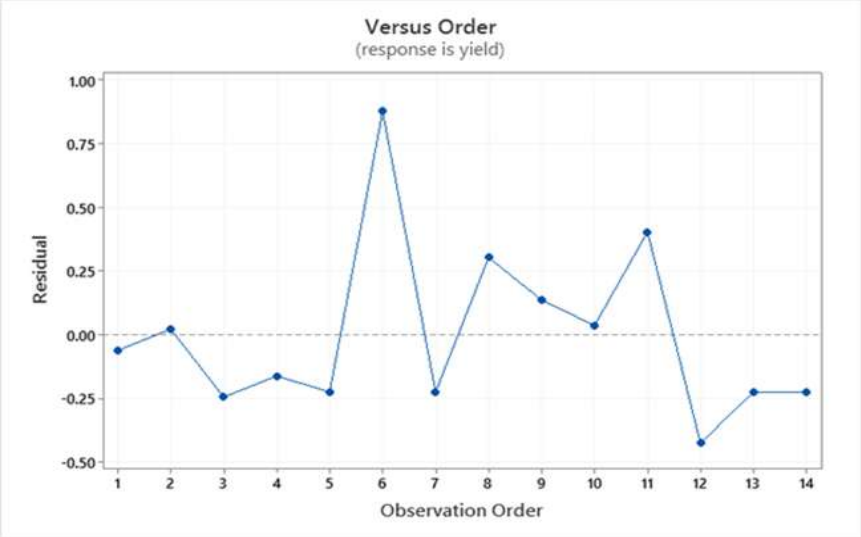

Figure I.4: Versus fit of residual.

The histogram plot shown in figure I.5 is used to determine whether the data are skewed or include outliers [104].

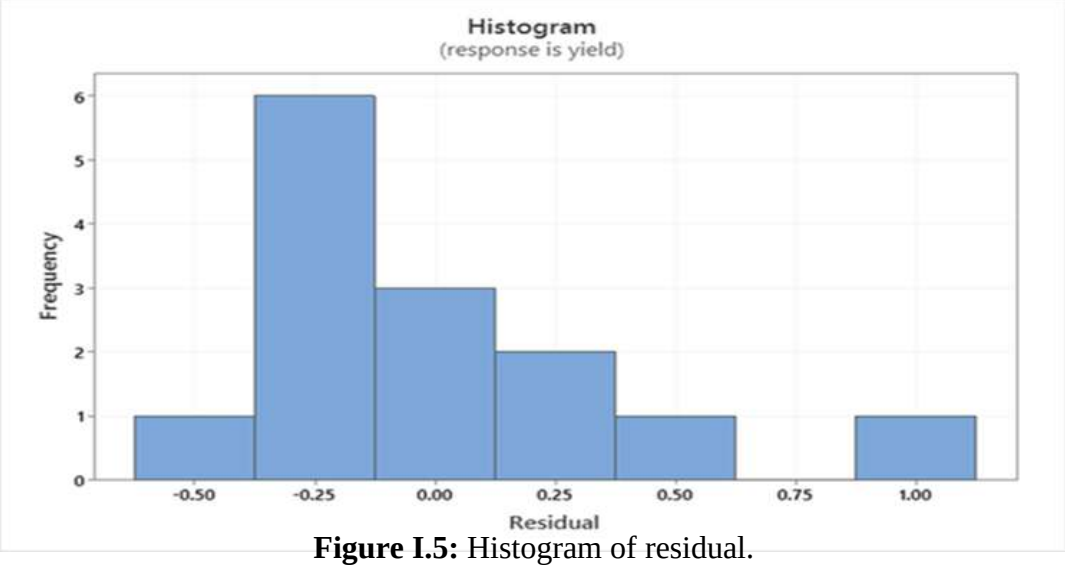

Figure I.5: Histogram of residual.

The figure I.6 shows the versus order, this is a plot of all residuals in the order that data was

collected and can be used to find non-random error. a positive correlation is indicated by a clustering of residuals with the same sign, a negative correlation is indicated by a rapid change in the signs of consecutive residuals [105].

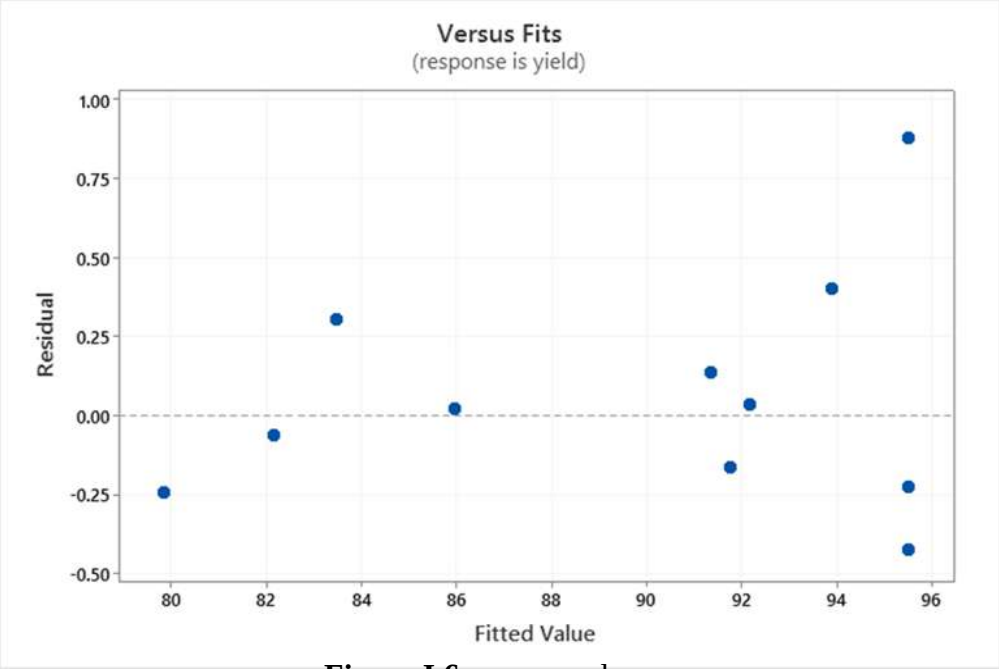

Figure I.6: versus order.

I.2.4 Graphical analyses

- **Factorial plot :**

- **Main effect plot**: According to figure I.7 Main effect plot shows that the best yield can be achieved when the temperature reaches 62 °C, and 4.3 of Alcohol to oil molar ratio.

- **Interaction plot:** In figure I.8 Interaction plot shows the best value of the interaction that helps for a better yield.

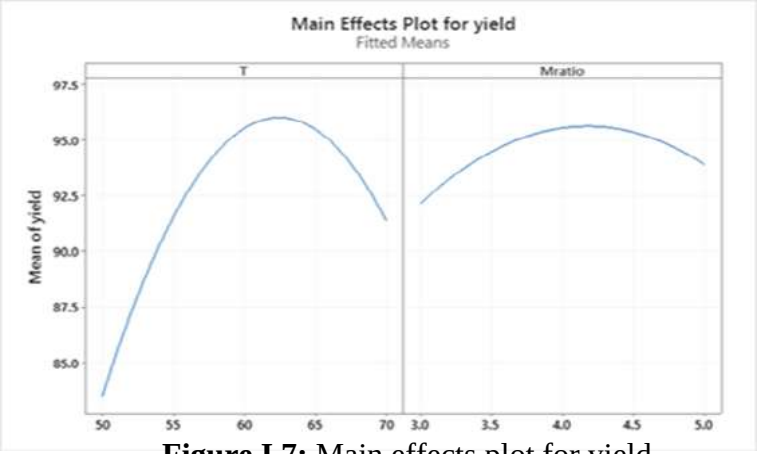

Figure I.7: Main effects plot for yield.

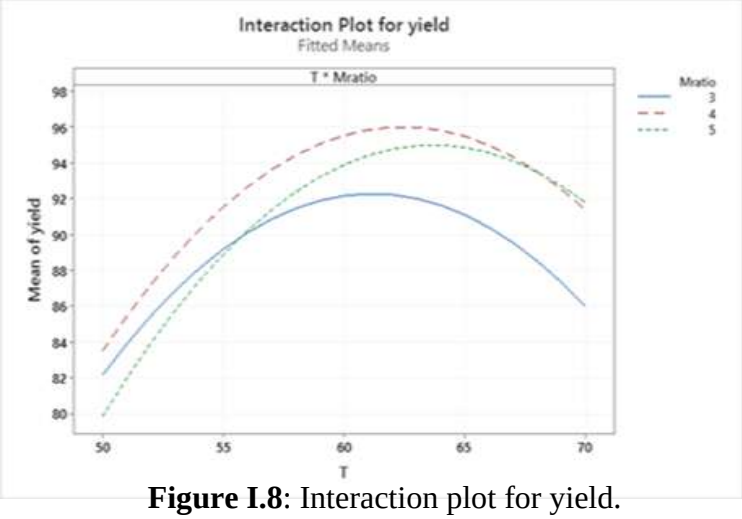

Figure I.8: Interaction plot for yield.

Surface plot shown in Figure I.10 shows the response surface plot of the biodiesel yield for the combined parameters temperature and molar ratio. The yield of biodiesel increased with an increment in the amount of the temperature near its medium value and then decreased sharply, however at the medium value of the molar ratio, the yield showed the same behaviour with noticeable decreasing at the level of higher and lower value. The results indicate that to get a higher biodiesel production yield, a medium value is preferred for both temperature and molar ratio, with 62°C of temperature and 4.3 of molar ratio.

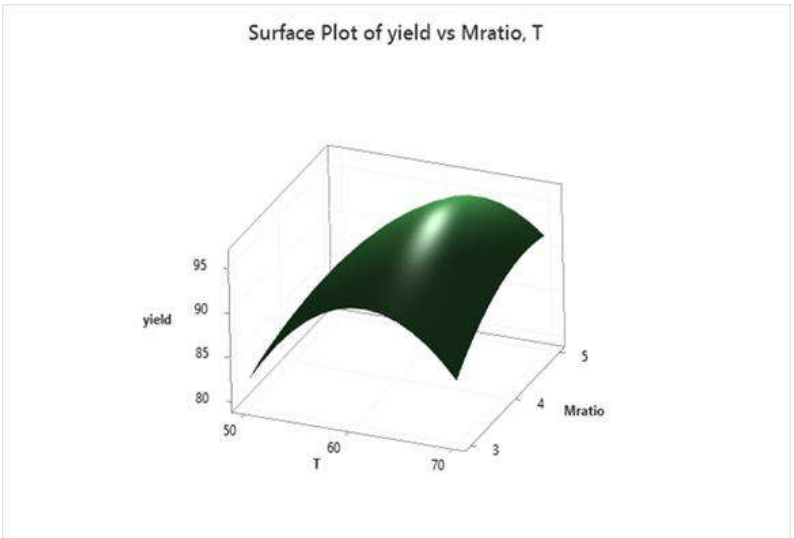

Figure I.9: Surface plot of yield vs molar ratio, Temperature.

The figure I.10 shows the contour plot vs molar ratio, temperature, The contour areas help to explain how the biodiesel yield varies with a change in the experimental conditions, and identifies the optimum operating conditions and related response values. The darkest area of the contour plot refers to ≥95% of the yield, that is correspondent to 60, 61,62, 63, 64,65 °C of

temperature, and 4.0, 4.3, 4.6, 5 of molar ratio.

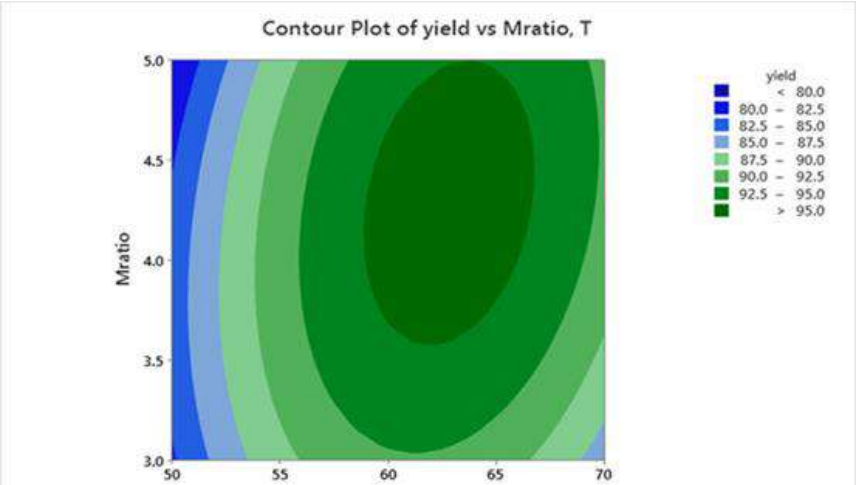

Figure I.10: contour plot of yield vs molar ratio, Temperature.

I.2.5 Optimization:

In this stage optimization of Biodiesel yield was done by using response optimizer part of Minitab 19 software, by running the optimization program, maximum Biodiesel production Yield obtained was 96.2%. The desirability function of biodiesel production yield is shown in figure I.11, The objective is to maximize the yield of biodiesel production, the predicted values are 62.72°C of temperature and 4.29 of oil to Alcohol molar ratio.

The desirability function (D) can take values from 0 to 1. Weight lower than 1 give more importance to the goal whereas weights than 1 give more importance to the goal [106]. The desirability of biodiesel yield d=0.926 was achieved as presented in Table I.6.

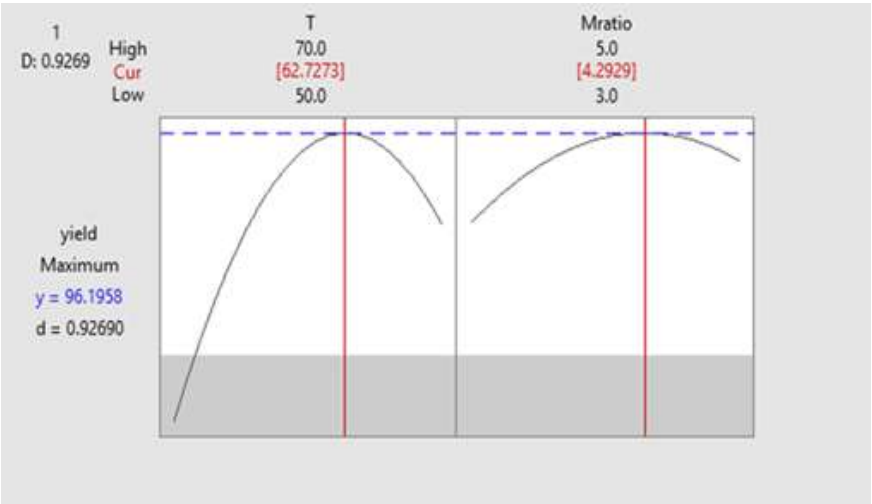

Figure I.11: The optimal conditions

Table I.6: Numerical optimization criteria for maximum biodiesel production.

Criteria	Goal	Lower limit	Higher limit
Temperature	In range	50°C	70°C
Molar ratio	In range	3	5
Efficiency	Maximum	86%	97%

Optimization process was carried out to determine the optimum value of biodiesel production yield, after performing a screening of factors and their interactions, the response surface analysis was carried out. The maximum biodiesel production yield obtained is 96.2%, The optimal conditions resulting from this optimization were a reaction temperature 62.72°C and Molar ratio 4.3.

ANOVA results had shown that both factors Temperature and oil to alcohol and their interactions are significant and have a strong effect on the biodiesel yield.

I.3 Results Comparison

The aim of this study is the Noticing Table I.7 that compares the results we had with the article reference that we are working on to improve, we can clearly notice better Results, which is something we successfully achieved.

Table I.7: Results comparison.

	My results	Article results
R^2	99.64 %	99.2 %
R^2 (adj)	99.41 %	98.7 %
Press	4.64	7.79
Lack of fit	0.81	0.34
Desirability	0.926	0.608
Temperature	62.72	62.83
Molar ratio	4.3	4.3
Yield	96.2%	96.08%

Noticing the huge change in R^2, R^2 (adj), Press and lack of fit that would make a big difference in the model strength, However the desirability changed from 0.608 to 0.926, Moreover the yield was enhanced to 96.2%. we can say that we Found a better results.

❖ Conclusion:

The aim of this study was modelling and optimization of biodiesel production, the Response surface methodology based on the Central Composite Face-Centered Design was Applied to study the effect of temperature and Oil:alcohol molar ratio on the biodiesel production, Anova results showed that both temperature and molar ratio and their interaction have a great effect on the transesterification reaction.

Finding better results than the article results was done successfully, by enhancing R^2, R^2 (adj) Desirability, lack of fit, and the Yield, which indicate that we had a better model. The optimal values obtained from the numerical-statistical evaluation, reaction temperature of 62.72°C and 4.3 oil: Alcohol molar ratio of 4.3, which gave the highest biodiesel production yield 96.2%.

Finally, modelling and optimization of biodiesel production yield were done successfully.

CHAPTER II: *Biodiesel production from waste cooking oil.*

❖ Introduction

According to the statistics, huge amount of cooking oil are being wasted forasmuch the huge consumption of oils around the world and its importance in humans food.

Instead of throwing waste cooking oil in the nature and cause various type of damages in the environment, we adopted the transesterification reaction to convert the waste cooking oil into a useful, clean and renewable biodiesel, Using methanol alcohol and KOH catalysts.

II. Material and methods

II.1 Method

Transesterification reaction is a costless and traditional reaction, it was carried out to produce biodiesel using methanol alcohol and KOH catalyst. Methanol alcohol is a pricless alcohol with good physical and chemical characterizations that help for an effective productivity and the oil used was wasted sunflower oil. The figure II.1 shows the transesterification reaction progress:

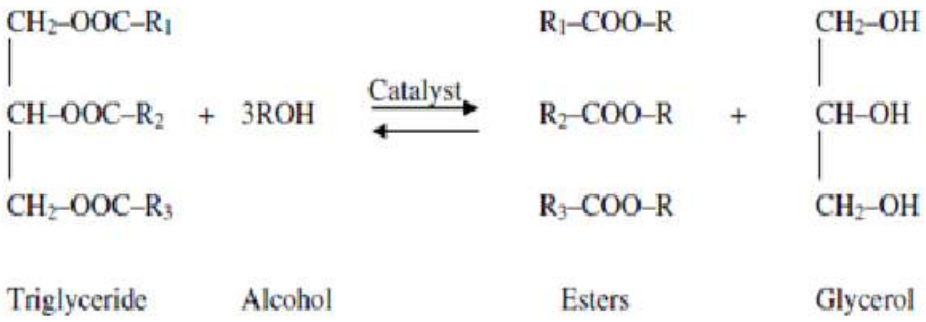

Figure II.1: Transesterification reaction

II.2 Materials and equipment

Table II.1. : materials and products used In the biodiesel production .

Products	Materials	Devices
- Methanol. - Waste cooking oil. - KOH. - Distilled water.	- Thermometer. - Balance . - Erlynmayer flask. - Watch glass. - Funnel. - Stand and clumb. - Beaker. - Magnetic stirrer with hot plate. - Separature funnel . - Oven . - Magnet.	- Ph meter.

II.3.Experimental Procedure

- **Waste cooking oil preparation**

The Waste Cooking Oil (WCO) has food particles, polymer and decomposition products, that are very unfavorable for the transesterification and would affect the Biodiesel production, Thus, the pretreatments of WCO including physical and chemical treatments are necessary before starting the reaction

  - Firstlly, the WCO was filtered by using filter paper folded into a cone in a glass funnel to get rid of any food particles or products that can be present in the WCO.

  - Secondly, WCO was heated to 80°C remove any water drops that may be contained in the oil.

- **Reaction**

  - 10 ml of methanol were mixed with 1g of potassium hydroxide KOH in a beaker, placed on a magnetic stirrer until the KOH is totally solved in the methanol, and acquire the methoxide solution.

  - 30 ml of the prepared oil were cooled to the reaction temperature 45°C to 60°C, then the produced methoxide was added to the oil, placed on the magnetic stirrer with hot plate at 65°C, The stirrer is switched on during the reaction at a speed of 400 rpm. The reaction lasts up to 2 hours.

- **Separation**

After the transesterification, the mixture obtained was is poured into Separator funnel where the mixture rests for 3 hours, incrementally, two phases appear as shown in figure II.2

The upper phase is the biodiesel obtained, and the lower phase is glycerine.

Glycerine can be used in many other productions like soap and many other important productions.

By opening the separator funnel van cautiously, the glycerine is allowed to fall into a beaker, and close the van quickly when only biodiesel is left the the separation funnel.

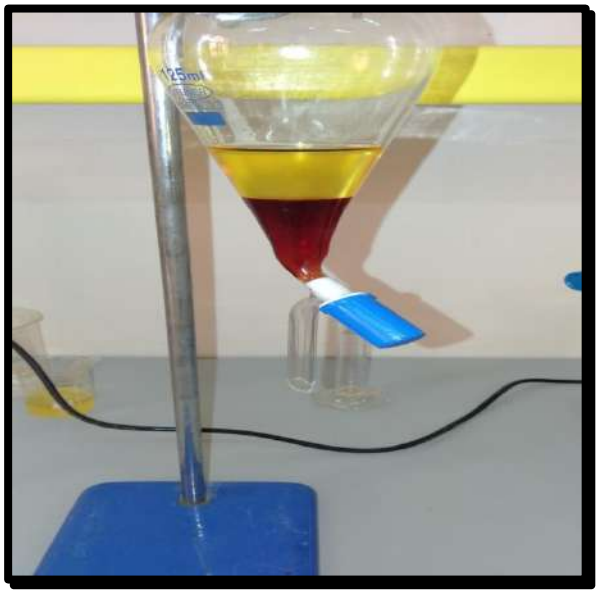

Figure II.2: Biodiesel separation.

II.4 Washing biodiesel

- Wasing biodiesel is a necessary step to remove the residues of methanol, KOH, soap and glycerine, by washing the biodiesel carefully several times by hot distilled water, with one minute shaking.

- Washed biodiesel must rest for 2 hours to separate the water and biodiesel.

II.5 Drying Biodiesel

The biodiesel obtained was dried in the oven at 100°C for 2 hours.

❖ Conclusion

The transesterification was used to produce biodiesel from waste cooking oil in this work, by using methanol alcohol and koh catalyst, acrossing five important steps, WCO preparation, Transesterification reaction, separation, biodiesel washing and drying.

The transesterification of WCO is a costless way to produce clean biofuel and afford the need of energy in the world.

GENERAL CONCLUSION

General conclusion

For the sic of our environment and saving the earth from different kind of pollutions, we have to move quickly, and using biodiesel is one of the strategies that we have to start working on to reduce both air and water pollution. Also, using biodiesel produced from waste cooking oil will not just reduce gas emissions in the air or reduce the amount of oils thrown in the water problem, which water treatment stations are facing, But it's also a costless source of energy.

We can easily produce biodiesel from waste cooking oil that we can get from houses or restaurants of even companies, those oils could be sunflower oil, soja oil, corn oil, seed oil, and many other kinds of vegetable cooking oil that are widely produced in the world, and their production increase by the increase of human population.

Transesrefication is the most used method in biodiesel production, However, Ethanol and methanol are the most used alcohols in this reaction, and that's according to their physical and chemical proprieties and low cost, sodium hydroxide NAOH and potassium hydroxide KOH can be used as catalysts in this reaction since they are both available in almost every laboratory, Moreover, many factors could effect this reaction that should be always considered such as oil to alcohol molar ratio, reaction temperature, reaction Time and many others.

Biodiesel production from waste cooking oil follows the important steps bellow: 1- Transeterification reaction.
2- Separation.
3- Washing and drying. 4- Biodieselanalyses.

While the last one is an important step to make sure, the biodiesel produced follows the international standards.

Using design of experiments played a huge role in enhancing both biodiesel quality and yield, however, creating a great model is necessary to achieve the goal. RSM was applied in this thesis using CCF design, where a greater model than the article model was created, By having better results such as R^2 R^2 adj , PRESS , S, Lack of fit, desirability and the yield.

After using CCF design 14 experiment were ran, where Temperature and Oil to alcohol molar ratio were considered as factors while biodiesel production yield as a response, the results found were great and satisfying, R^2 and R^2 adj were found 99.64% and 99.41% respectively, 4.64 as PRESS and 0.81 as lack of fit, while desirability enhanced to reach 0.926, Importantly yield was found 96.2% with the optimum conditions 62.72°C for temperature and 4:3 oil to alcohol molar ratio.

References

References

[1]: Melissa Denchak. “Fossil Fuels: The Dirty Facts”, June 29, 2018, https://www.nrdc.org/stories/fossil-fuels-dirty-facts.

[2]: Kumar, I.S. Sundari, S. Sen, N. Dasgupta, R. Chidambaram “Animal Fat- and Vegetable Oil-Based Platform Chemical Biorefinery” , , second edition, University Vellore, Tamil Nadu, India, 367p, 2016.

[3]: John R. WagnerJr , Harold F. GilesJr., “In Extrusion”, 2014, Second Edition, 291p.

[4]: Melissa Petruzzello “Diesel fuel” 2018, https://www.britannica.com/technology/diesel-fuel.

[5]: Demshemino S. Innocent,O’Donnell P. Sylvester, Muhammad F.Yahaya,IsiomaNwadike, and Linus N. Okoro. “COMPARATIVE ANALYSIS OF BIODIESEL AND PETROLEUM DIESEL” 2013, International Journal of Education and Research , Vol. 1 No. 8.

[6]: Eloisa Torres-Jimenez a , Marta Svoljšak Jerman b , Andreja Gregorc b , Irenca Lisec b , M. Pilar Dorado c,1 ,Breda Kegl “Physical and chemical properties of ethanol–diesel fuel blends” 2011 , University of Maribor slovenia , Universidad de Cordoba , spain .24-3.

[7]: Mohamed F. Al_Dawodya, S.K. Bhatti “Experimental and Computational Investigations for Combustion, Performance and Emission Parameters of a Diesel Engine Fuelled with Soybean Biodiesel-Diesel Blends” 2013, Biofules journal, Volume 7-6.

[8]: World power, 01 April 2015 “What are the advantages and disadvantages of the different types of fuel?” //www.worldpowerfaqs.com/en/categories/fuel.

[9]: M.M. Gui, K.T. Lee and S. Bhatia ‘‘Feasibility of Edible Oil vs. Non-Edible Oil vs. Waste Edible Oil As Biodiesel Feedstock’’2008, Energy, Malaysia, Vol. 33, N°11,1646–1653.

[10]: Muhammad Naqvi and Jinyue Yan “First-Generation Biofuels” 2015, African Journal of Biotechnology - 9 (7).

[11]: A. DEMIRBAS1 “Potential Resources of Non-edible Oils for Biodiesel” 2009, Journal Energy Sources, Volume 4, N°3.

[12]: Tushar Jasha “Biodiesel production from used vegetable oil collected from shops selling fritters in Kolkata Nabanita Banerjeea, Ritica Ramakrishnana” 2013 4th International Conference on Advances in Energy Research, ICAER.

[13]: X. L. Zhang J. Chen Z. Wu S. Yan R. D. Tyagi J. Li W. Dong R. Y. Surampalli “Microalgae Oil Biodiesel ” 2019, second edition, University of Iowa Libraries. 176pp.

[14]: Marie-Josée Dumont n, Michael Ngadi , Peter Adewale “Recent trends of biodiesel production from animal fat wastes and associated production techniques” 2014, Renewable and Sustainable Energy Reviews, Canada, 45:574-588.

[15]: Hayder A. Alalwana,, Alaa H. Alminshidb and Haydar A.S. Aljaafaric “Promising

evolution of biofuel generations" 2019, Renewable Energy Focus journal, Volume 28, Number 00.

[16]: Roland Arthur Lee, Jean-Michel Lavoie "Challenges of producing a commodity from a biomass of increasing complexity" 2013, Animal Frontiers ,Canada, Volume 3 page 6–11.

[17]: Bawadi Abdullaha, Syed Anuar Faua'ad Syed Muhammadb, Zahra Shokravic, Shahrul Ismaild,Khairul Anuar Kassime, Azmi Nik Mahmoodb, Md Maniruzzaman A. Aziz "Fourth generation biofuel: A review on risks and mitigation strategies", 2019, Renewable and Sustainable Energy Reviews, vol. 107, issue C, 37-50.

[18]: Á. PÉREZ A. CARRERO, "Advances in biodiesel quality control", 2012, First edition Woodhead Publishing Limited spain, 99pp.

[19]: Guomin Xiao and Lijing Gao "First Generation Biodiesel" 2011 , Biofuel Production-Recent Developments and Prospects ,P. R. China, 46-47.

[20]: Nora Traviss , Brett Amy Thelen, Jaime Kathryn Ingalls, Melinda Dawn Treadwell , "Biodiesel versus Diesel: A Pilot Study Comparing Exhaust Exposures for Employees at a Rural Municipal Facility" 2010 , ournal of the Air & Waste Management Association 60(9):1026-33.

[21]: T. Wang "Global biodiesel production by country 2018" 2019. https://www.statista.com/statistics/271472/biodiesel-production-in-selected-countries/.

[22]: Homa Hosseinzadeh-Bandbafhaa , Meisam Tabatabaeib,c , Mortaza Aghbashloa, Majid Khanalia , Ayhan Demirbas "Energy Conversion and Management" ,2018, A comprehensive review on the environmental impacts of diesel/biodiesel additives , page 579.

[23] Food and Agriculture Organization "BIOFUELS: PROSPECTS, RISKS AND OPPORTUNITIES" 2008, first edition, page 55.

[24]: Catherine Bowyer, Senior Policy Analyst "Anticipated Indirect Land Use Change Associated with Expanded Use of Biofuels and Bioliquids in the EU – An Analysis of the National Renewable Energy Action Plans" ,2010, institute of European environmental policy, Belgium.

[25]: Da Silva, V. T., & Sousa, L. A,"Catalytic Upgrading of Fats and Vegetable Oils for the Production of Fuels. The Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals", 2013, First edition Universidade Federal do Rio de Janeiro, Brazil, 67–92pp.

[26]: F.J. Sánchez-Muniz, C. Cuesta, "SUNFLOWER OIL" (Second Edition), in Encyclopedia of Food Sciences and Nutrition, Spain. 2003.

[27]: Jacqueline B. Marcus MS, RD, LD, CNS, FADA, "Lipids Basics: Fats and Oils in Foods and Health", Third edition, 2013.

[28]: Dupont, J., White, P. J., Carpenter, M. P., Schaefer, E. J., Meydani, S. N., Elson, C. E., Gorbach, S. L. "Food uses and health effects of corn oil. Journal of the American College of Nutrition", 1990,USA, first edition, 438pp.

[29]: Walter F. Baughman and George S. Jamieson. "THE CHEMICAL COMPOSITION OF CORN OIL" Contribution from the oil, fat and wax laboratory, Bureau of chemistry, U.S departement of Agricultur, 2696pp, 1921.

[30]: Massimo Mozzon, Roberta Foligni and Urszula Tylewicz "Chemical Characteristics and Nutritional Properties of Hybrid Palm Oils" 2017, DOI: 10.5772/intechopen.75421.

[31]: Charis M. Galanakis ,Özge Seçmeler " Olive Fruit and Olive Oil", in Innovations in Traditional Foods, second edition, University of Istanbul, Turkey, 2019.

[32]: Dimitrios Boskou, Georgios Blekas, and Maria Tsimidou "Olive Oil Composition", first edition, pp41, 2006.

[33]: S.M. Ghazani, A.G. Marangoni "Healthy Fats and Oils", second edition, Academic Press, 2016.

[34]: Dérick Rousseau , Saeed Mirzaee Ghazani , Alejandro Gregorio Marangoni "12 Chemical Interesterification of Food Lipids: Chemistry, Nutrition, and Biotechnology"; Fourth Edition, 252pp, 2017.

[35]: Mangesh G. KulkarniAjay K. Dalai "Industrial & Engineering Chemistry Research", First edition, 2901 -2902pp, 2006.

[36]: M. Shahbandeh, "Vegetable oils: global consumption by oil type 2013/14 to 2019/2020" 31 jan 2020. https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/.

[37]: sellina wamucii "Algeria Sunflower Oil Market Insights" 2018, "https://www.selinawamucii.com/insights/market/algeria/sunflower-oil/."

[38]: Angelo Maria Giuffrè "Analytical characteristics of olive oil produced with three different processes in Algeria", 2010, Rivista Italiana Delle Sostanze Grasse, 87(3):186-195.

[39]: Mangesh G. KulkarniAjay K. Dalai "Industrial & Engineering Chemistry Research", first edition, 2901 -2902pp, 2006.

[40]: Diyar I. Ahmed 1,a, S. Kasolang 1,b, Basim A. Khidhir 2,c, N.R. Abdullah1,d "Application of Response Surface Methodology to Predict Oil-Film Friction in Journal Bearing" ,2013, Applied Mechanics and Materials 393, DOI: 10.4028/www.scientific.net/AMM.393.931.

[41]: Ahmed Badr Eldin "General Introduction to Design of Experiments (DOE)",2011, Wide Spectra of Quality Contro, DOI: 10.5772/23878.

[42]: Viktor P. Astakhov "Design of Experiment Methods in Manufacturing: Basics and Practical Applications" 2012, second edition 1-54pp.

[43]: Behzad Shiroud Heidaria , Erfan Oliaeia , Hadi Shayestehb , Seyed Mohammad Davachia, , Iman Hejazia, Javad Seyfic, Mozhgan Bahramid, Hamid Rashedie "Simulation of Mechanical Behavior and Optimization of Simulated Injection Molding Process for PLA based Antibacterial Composite and Nanocomposite Bone Screws Using Central Composite Design", 2016, Journal of the Mechanical Behavior of Biomedical Materials,Volume 65, Pages 160-176.

[44]: Jaimon D. Quadros a, S. A. Khan b , and Antony A. J. "Modelling of Suddenly Expanded Flow Process in SupersonicMach Regime using Design of Experiments and Response Surface Methodology" 2018, Vol. 49 page 160.

[45]: M.W. Mumtaz, M. Danish, "Biodiesel Production Through Chemical and Biochemical Transesterification in Clean Energy for Sustainable Development", 2017, Advanced Biofuels, 443-471pp.

[46]: Widayata,b, Agam Duma Kalista Wibowoa, Hadiyantoa, "Study on production process of biodiesel from rubber seed(hevea brasiliensis) by in situ (trans)esterification method with acid catalyst", 2012, Energy Procedia 32(7):64–73.

[47] : Eman Ali Ateeq Supervisor Prof. Issam Rashid Abdelraziq Co - Supervisor Prof. Sharif Mohammad Musameh "Biodiesel Viscosity and Flash Point Determination", Master's Thesis in Energy system , An–Najah National University - Nablus, Palestine, 2015.

[48]: Zaloa Ares Gondra "STUDY OF FACTORS INFLUENCING THE QUALITY AND YIELD OF BIODIESEL PRODUCED BY TRANSESTERIFICATION OF VEGETABLE OILS" , master thesis, University of Gavle, Sweden, 2010.

[49]: J. Braz. Chem. Soc "Transesterification of Vegetable Oils" 1998, Journal of Aircraft, vol.9 no.3,741–750.

[50]: Mohamad Firdaus Mohamad Yusoff • Xuebing Xu • Zheng Gu "Comparison of Fatty Acid Methyl and Ethyl Esters as Biodiesel Base Stock: a Review on Processing and Production Requirements", 2014, ACS Catal, Vol 6, 10, 6762–6769pp.

[51] : Marchetti, J. M., Miguel, V. U., J.M. Marchetti, V.U. Miguel, A.F. & Errazu, A. F. "Possible methods for biodiesel production",2005. Renewable and Sustainable Energy Reviews, 11(6), 1300–1311.

[52]: Ivan J. Stojković a , Olivera S. Stamenković b , Dragan S. Povrenović a , Vlada B. Veljković b,n "Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification" 2014 , Renewable and Sustainable Energy Reviews, 32, 1–15.

[53] : Amit Sarin "Biodiesel: Production and Properties", First edition, 2012 .

[54] :Mehulkumar L. Savaliya a , Bhaveshkumar D. Dhorajiya a & Bharatkumar Z. Dholakiya 2013 "Current Trends in Separation and Purification of Fatty Acid Methyl Ester: A Review", Journal Separation & Purification Reviews,Volume 44, 2015 - Issue 1.

[55]: Mushatq Ahmad1, Shoaib Ahmed2, Fayyaz-Ul-Hassan3, Muhammad Arshad4, Mir Ajab Khan1, Muhammad Zafar1 and Shazia Sultana1 "Base catalyzed transesterification of sunflower oil biodiesel" 2010 , African journal of biotechnology, 9(50).

[56]: Rizal Alamsyaha, Enny Hawani Loebisaa Conference and Exhibition Indonesia Renewable Energy & Energy Conservation, "Design and Technical Testing for Crude Biodiesel Reactor Using Dry Methods: Comparison of Energy Analysis" ,2014, Indonesia EBTKE CONEX 2013, 235 – 241pp.

[57]: Jln. Ir. H. M.Mathiyazhagan and A.Ganapathi , "Factors Affecting Biodiesel" 2011, journal of research of plant biology, VOL 1 NO 2.

[58]: Jagadale S. S., Jugulkar L. M. "Review of Various Reaction Parameters and Other Factors Affecting on Production of Chicken Fat Based Biodiesel" 2012 Department of Automobile Engineering, Maharashtra, Vol.2, Issue.2 , 407-411pp.

[59]: Atadashi, I. M., Aroua, M. K., Aziz, A. R. A., & Sulaiman, N. M. N. "Refining technologies for the purification of crude biodiesel" 2011 Applied Energy, 88(12), 4239–4251.

[60]: Hoekman, S. K., Broch, A., Robbins, C., Ceniceros, E., & Natarajan, M. "Review of biodiesel composition, properties, and specifications. Renewable and Sustainable Energy Reviews", 2012, 16(1), 143–169.

[61]: Qi, D. H., & Lee, C. F "Influence of soybean biodiesel content on basic properties of biodiesel-diesel blends." 2014, Journal of the Taiwan Institute of Chemical Engineers, 45(2), 504–507.

[62]: Bhale, P. V., Deshpande, N. V., & Thombre, S. B. "Improving the low temperature properties of biodiesel fuel. Renewable Energy", 2010, 34(3), 794–800.

[63]: Atadashi, I. M., Aroua, M. K., Aziz, A. R. A., & Sulaiman, N. M. N,"Refining technologies for the purification of crude biodiesel",2011, Applied Energy, 88(12), 4239–4251.

[64]: Boris Ramos "Production of biodiesel from vegetable oils", Master thesis, Institute of technology, Stockholm, Sweden, 2012.

[65]: M. F. Elkady, Ahmed Zaatout, and Ola Balbaa "Production of Biodiesel from Waste Vegetable Oil via KM Micromixer" 2015, Journal of Chemistry, https://doi.org/10.1155/2015/630168.

[66] :John R. WagnerJr , Harold F. GilesJr., "in Extrusion", (Second Edition), 291pp.2014.

[67]: L. A. Sarabia and M. C. Ortiz "Comprehensive Chemometrics: Chemical and Biochemical Data Analysis", 2009, second edition, University of Burgos, 346pp.

[68]: M.Mount, John R.WagnerJr.Eldridge, Harold F.GilesJr. "Extrusion" Second Edition, 292pp, 2014.

[69]: Carl James Schwarz "Designed Experiments" 344pp. 2012.

[70]:D. Granato, V. M. d. A. Calado and B. Jarvis, “Observations on the use of statistical methods in Food Science and Technolog”, 2014, Food Research International, vol. 55, 137–149pp.

[71]: Jacques Goupy “Introduction to design of experiments”, Third edition,sas press, pp7, 2007.

[72]: Das, A. K., & Dewanjee, S. “Optimization of Extraction Using Mathematical Models and Computation. Computational Phytochemistry” 2018, Vol.12 No.1, 83pp.

[73]: Kauko Leiviskä “Introduction to Experiment Design”, 2013, University of Oulu Control Engineering Laboratory, Finland.

[74]: Anderson, M. J., & Whitcomb, P. J, “Design of Experiments. Kirk-Othmer Encyclopedia of Chemical Technology.” 2010, doi:10.1002/0471238961.0405190908010814.

[75]:Arzu Eren ,Senaras “Sustainable Engineering Products and Manufacturing Technologies”,First edition , Academic Press Turkey,189pp, 2019.

[76]: K. Chandrasekarana , P. Marimuthub, K. Rajaa “Prediction Model for CNC Turning on AISI316 with Single and Multilayered Cutting tool Using Box Behnken Design” , 2012, DOI: 10.5829/idosi.ije.2013.26.04a.09.

[77]: Kathleen M. Carley, Natalia Y. Kamneva, Jeff Reminga “Response Surface Methodology1 CASOS Technical Report”, first edition, NASA, 2004.

[78]:Khairul Anwar Mohamad Said , Mohamed Afizal Mohamed Amin “Journal of Applied Science & Process Engineering” ,2015, Vol. 2, No. 1.

[79]: Izabela Polowczyk, Tomasz Kozlecki “Central composite design application in oil agglomeration of talc” 2017, vol. 53(2).

[80] :Ait-Amir, B., Pougnet, P., & El Hami, A “Meta-Model Development. Embedded Mechatronic Systems” 2015, Physicochem. Probl. Miner. Process, volume 2, pp 155.

[81]:J. Prakash Marana, S. Manikandanb, K. Thirugnanasambandhama, C. Vigna Nivethaa, R. Dinesh “Box–Behnken design based statistical modeling for ultrasound-assisted extraction of corn silk polysaccharide”, 2013 , Carbohydrate Polymers, vol 92, 604-611.

[82]: Wilmina Mary Marget “Experimental designs for multiple responses with different models”, first edition Iowa State University, 2015.

[83]: Steven F. Sawyer, PT, PhD “Analysis of Variance: The Fundamental Concepts” ,2010, volume 17 n° 2, 28pp.

[84]: Howard J. Seltman “Experimental Design and Analysis”, first edition, 190pp, 2009.

[85]: jhon zeily and sons “Mathematical and Statistical Methods in Food Science and Technology”, first edition, 2014.

[86]: Babatunde Olawoye “A COMPREHENSIVE HANDOUT ON CENTRAL COMPOSITE

DESIGN (CCD)", first edition, 40pp, 2016

[87]: Theodore T. Allen "ntroduction to Engineering Statistics and Lean Sigma: Statistical Quality" 2010, first edition, 321pp.

[88]: Masoud Moradi1 , Mehdi Fazlzadehdavil2 , Meghdad Pirsaheb3 , Yadollah Mansouri3 ,Touba Khosravi3 , Kiomars Sharafi "Response surface methodology (RSM) and its application for optimization of ammonium ions removal from aqueous solutions by pumice as a natural and low cost adsorbent",2016, Vol. 42 no. 2, 33–43 pp.

[89]: Rajab Suliman "Response Surface Methodology and Its Application in Optimizing the Efficiency of Organic Solar Cells", 2017,doctorat thesis, south Dakota university .

[90]: Ridha Lessouad, Fatiha Souahi, Leonor C .Pelaezb "Modelization and statical optimization of coagulation flocculation treatrment of an old leachate" , 2017, DOI: 10.2175/106143017X14839994523703.

[91]: S.H. Pishgar-Komleh, A. Keyhani, M.R. Mostofi-Sarkari and A. Jafari "Application of Response Surface Methodology for Optimization of Picker-Husker Harvesting Losses in Corn Seed", 2012, iran Iranica Journal of Energy & Environment 3 (2): 134-142.

[92]: Isa Martins Fukuda1, Camila Francini Fidelis Pinto1, Camila dos Santos Moreira 1, Alessandro Morais Saviano1, Felipe Rebello Lourenço1, "Design of Experiments (DoE) applied to Pharmaceutical and Analytical Quality by Design (QbD)" 2018, Brazilian Journal of Pharmaceutical Sciences, http://dx.doi.org/10.1590/s2175-97902018000001006.

[93]: Antony, J. "A Systematic Methodology for Design of Experiments. Design of Experiments for Engineers and Scientists", second edition, Elsevier, 33–50pp,2014.

[94]: minitab INc "Meet MINITAB" ,14 edition, 3-7pp, 2004.

[95]: Nivedita Jaiswal , Om Prakash, Mahe Talat, Syed Hadi Hasan "Application of Response Surface Methodology for the Determination of Optimum Reaction Conditions (Temperature and pH) for Starch Hydrolysis by a-Amylase" 2011, 6(4):357-365.

[96]: Cristian J. B. de Lima, Luciana F. Coelho and Jonas Contiero "The Use of Response Surface Methodology in Optimizationof Lactic Acid Production: Focus on MediumSupplementation, Temperature and pH Control" 2010, Food Technology and Biotechnology, Vol. 48 No. 2.

[97]: Donya Ghafourzadeh "***Visualization and Geometric Interpretation of 3D Surfaces***" 2013, Master thesis, Linköping University,Sweden.

[98]: S. Mohajeri, H.A. Aziz, M.H. Isa, M.A. Zahed, M.N. Adlan, J. Hazard. Mater "Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique" ,2010, 15;176(1-3),749-58pp.

[99]: Banik, A, Dutta, S, Bandyopadhyay,T. K., & Biswal, S. K. "Prediction of maximum

permeate flux (%) of disc membrane using Response Surface Methodology (RSM)" 2018. 46(6): 299-307pp.

[100]: A.M. Joglekar, A.T. May, "Product excellence through design of experiments, Cereal Foods World", First edition, 857–868pp. 1987.

[101]: Adio, S. O., Omar, M. H., Asif, M., & Saleh, T. A."Arsenic and selenium removal from water using biosynthesized nanoscale zero-valent iron: A factorial design analysis. Process Safety and Environmental Protection",2017, volume 107, 518–527pp.

[102]: Saleh, T. A., Adio, S. O., Asif, M., & Dafalla, H. "Statistical analysis of phenols adsorption on diethylenetriamine-modified activated carbon",2018, Journal of Cleaner Production, 182, 960–968pp.

[103]:Ahmad, R., & Hasan, I. "Optimization of the adsorption of Pb (II) from aqueous solution onto PAB nanocomposite using response surface methodology." ,2016, Environmental Nanotechnology Monitoring & Management 6:116-129pp.

[104]: Gopikrishnan, P, Akbar, A., Asokan, A., Bhaskar, B., & Sumesh, C. S. "Numerical Modelling and Optimization of Surface Finish during Peripheral Milling of AISI 4340 Steel using RSM.", 2018, Materials Today: Proceedings Volume 5, Issue 11, Part 3, 24612-24621pp.

[105]: G. Venkatesan a, N. Kulasekharan b, V. Muthukumar c, S. Iniyan 2015 "Regression analysis of a curved vane demister with Taguchi based optimization" 2015, DOI: 10.1016/j.desal.2015.05.011.

[106]: Ganna anitha, pandey PV 2018 "Enantioseparation and purity determination of ondansetron by amylose based chiral HPLC method: A chemometric approach " nternational Journal of Research in Pharmaceutical Sciences 9(3):706-716pp.

[107]: Wan Nur Aifa Wan Azahara, Mastura Bujanga, Ramadhansyah Putra Jayaa, Mohd Rosli Hainina, Azman Mohameda, Norzita Ngadib, Dewi Sri Jayan "The potential of waste cooking oil as bio-asphalt for alternative binder – An overview" 2015, Journal teknologi, vol 78(4).

[108]: William DuMouchel "The Future of Statistical Software: Proceedings of a Forum" First edition, The national academic,1990