



Biogasoline Production by Catalytic Cracking of Waste Cooking oil

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PREFACE

The research contained in this dissertation was completed by the candidate while based in the discipline of Engineering, School of Chemical Engineering of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College, Durban, South Africa. The research was financially funded by the University of KwaZulu-Natal: Strategic Funds and Fee Remission as well supervisor's cost centre.

The contents of this work have not been submitted in any form to another university and except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

Signed: Prof Amir H. Mohammadi

Date: 7 July 2022

DECLARATION: PLAGIARISM

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As the candidate's supervisor, I agree to the submission of this dissertation:

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Prof Amir H. Mohammadi

Date

DEDICATION

To the maker of the universe, invisible and visible. You are God, and there is no one like you, my Yahweh.

“Unless Yahweh builds a house (career, degree, opportunities...), the work of builders is wasted. Unless Yahweh protects a city (someone’s life), guarding it with sentries will do no good. It is useless for you to work so hard from early morning until late night, anxiously working for food to eat or to build a career; for Yahweh gives rest to his loved ones.” Psalm 127:1 – 2 (NLT).

“Trust in Yahweh with all your heart and lean not on your own understanding; in all your ways acknowledge Yahweh, and He shall direct your path. Do not be wise in your own eyes; fear Yahweh and depart from evil” Proverbs 3: 5 – 7 (NKJV).

I am aware of my limitations that why I have never stopped seeking knowledge and asking for help,
I know that I cannot win all the battles that lie ahead of me, and some of them are not worth fighting,
I also know that I have nothing to prove, yet I have all to improve

Ditunga Patient N. Kabasele

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ABSTRACT

Government, Heads of State, and international organizations gather from time to time to investigate and implement strategies required to eradicate global warming and address environmental issues. The principal causes of global warming and ecological issues are industrializations, excavation, cutting down of trees, and production of fossil fuels, to mention only a few.

Besides global warming and climate change, it is essential to know that the other issue related to fossil fuels is that they generate from a finite source. This source is dwindling as time passes. The potential disappearance of fossil fuels is also a cause of the high prices of crude oil, primarily in the regions with less or without crude oil. The reasons mentioned prove that there is a need to alter to a renewable source of energy-generating from an infinite source.

Several investigations are taking place at international and national (South Africa) levels to develop the production of biofuels considered clean fuels. In an attempt to improve the quality of biofuels, many works are taking place behind the scenes regarding feedstock quality, feedstock source, feedstock transportation, and technologies required to produce biofuels.

Regarding biofuels, products like biodiesel and bioethanol, including biogas, are at an advanced stage of development in terms of technologies and commercialization in specific locations such as America (USA), Brazil, and Canada. However, biogasoline production is not yet advanced, even though many vehicles use gasoline. Biogasoline has the quality to be blended or to be used as a replacement for conventional gasoline (fossil-based gasoline) in vehicles' engines.

This project investigates the feasibility of manufacturing biogasoline from waste cooking oil, one of the available feedstocks. Waste cooking oil is converted to biogasoline via catalytic cracking, thermal cracking, and a two-step (hybrid) method. All the methods mentioned earlier see their applications in this research study.

The methods requiring a catalyst were conducted using nanocatalysts which carry out the reactions effectively in an optimized way. The nanocatalysts' structure causes the enzyme to be motionless. The dormant state of enzymes affects the biocatalytic efficiency through the increased load of enzymes and surface area. The nanocatalyst was composed of Ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ and cobalt nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$, including γ -aluminium oxide. After mixing the catalyst samples, they were dried and calcined. Then the catalyst samples were analysed

using the following techniques: x-ray diffraction, inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning and transmission electron microscopy. The thermogravimetry analyser (TGA) method was used to determine the regeneration temperature of the nanocatalyst. The TGA results showed that the regeneration temperature for three nanocatalyst samples is 600°C. However, the nanocatalyst calcined at 600°C is selected for this study since it has a completed regeneration cycle. The regeneration cycle at this temperature starts from the evaporation of water. Then there is an increase of inorganic compounds caused by partial oxidation, and finally, coke combustion. These three processes show that the regeneration cycle of the nanocatalyst at the selected temperature is complete.

After preparing the nanocatalyst, the waste cooking oil underwent pre-treatment to remove salt and food particles. The remaining sulphur after cleaning is 4%, roughly 71% of which is removed from the oil.

Pre-treatment of waste cooking oil concluded, and the resulting product was used to conduct the thermal cracking at varying reaction temperatures (400, 450, and 500°C) and reaction times. This method's highest biogasoline is 24.96%, obtained at 500°C and 60 minutes, respectively, reaction temperature and reaction time. The optimum reaction time is 60 minutes. The catalytic cracking and two-step methods were conducted at a constant reaction time of 60 minutes (optimum time) while varying the catalyst load (1, 3, and 5 grams) and the reaction temperature. For catalytic cracking, the percentage yields increase with the reaction temperature at a constant catalyst load of one gram. The highest percentage yield is 12.7% at a reaction temperature of 550°C. The optimum waste cooking ratio of oil is one gram of nanocatalyst to 44 grams of waste cooking oil. The biogasoline percentage increases with the reaction temperature for the two-step process (hybrid method). The highest biogasoline percentage yield is 29.63% at reaction temperature and catalyst load of 550°C and 3 grams, respectively.

One of the aims of this research was to investigate the effects of the calcination temperature of the nanocatalyst at a constant reaction temperature of 475°C. The experimental procedure yields 42.36% of biogasoline for 5 grams catalyst load. The calcination temperature of the catalyst used is 700°C.

The catalytic processes (catalytic cracking and two-step process) were optimized. The optimized results for cracking are 11.51%, 3.35g, 482°C, and 0.28h⁻¹, respectively; biogasoline percentage yields, catalyst weight, reaction temperature, and weight hourly space velocity. The optimized results for the two-step process are 41.78%, 4.32g, 567.2°C, and 0.22h⁻¹, respectively, biogasoline yields, catalyst weight, reaction temperature, and hourly space velocity.

It is vital to conduct further studies in biogasoline production using thermal cracking methods (with and without catalysts) and the two-step process method. The study must include the addition of metals such as copper and nickel to nanocatalysts and consider changing the operating conditions such as temperature and carried gas pressure. These techniques provide a great platform to step up biogasoline production at an industrial scale and conduct a techno-economic assessment.

It is also vital to conduct a techno-economic assessment of biogasoline production to establish its production cost and selling price. Documenting the production method, the suitable catalyst, and the feedstock is essential. The studies have proved that lignocellulosic biomass is affordable and environmentally sane to produce biogasoline.

LIST OF ACRONYMS

ANOVA: Analysis of variance

ASTM: American Society for testing and Material

BBD: Box-Behnken Design

BOCLE: Ball-on-cylinder lubricity evaluator test

Cat. Weight: Catalyst weight.

C_n: Number of carbons

CO: Carbon monoxide

Co: Cobalt

CO₂: Carbon dioxide

Cv: Calorific value

DIME: Dimethyl ether

DM: Doehlert Matrix

EDX: Energy dispersive x-ray analysis

EtOH: Ethanol

FAME: Fatty acid methyl

FGBs: First-generation biofuels

FP: Flash point

FTL: Fischer-Tropsch liquid

GC: Gas chromatography

GC-MS: Gas chromatography-Mass spectrometry

GHG: Greenhouse gas

HCl: Hydrochloric acid

HFRR: High-frequency reciprocating rig test

HNO₃: Nitric acid

H₂SO₄: Sulfuric acid

H₂S: Hydrogen sulfide

ICP-OES: Inductively Coupled Plasma Optical Emission Spectroscopy

KOH: Potassium Hydroxide

Mo: Molybdenum

NaOH: Sodium Hydroxide

NaOCH₃: Sodium methoxide

ON: Octane Number

OPEC: Organization of the petroleum exporting countries

SEM: Scanning electron microscopy

SGBs: Second-generation biofuels

TEM: Transmission electron microscopy

TGA: Thermogravimetric analyzer

WCO: Waste cooking oil

WHSV: Weight hourly space velocity

WWTPs: Wastewater treatment plants

XRD: X-ray diffraction

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CHAPTER ONE: Introduction

1.1. Research background

The world faces several issues, including an energy crisis, food shortage and numerous environmental issues. Interms of energy, it is vital to know that petroleum crude oil is the world's primary energy source. However, this energy source is on the verge of extinction. As a result, the price of fossil fuels is increasing by day. This predicament affects global energy and transportation in general.

Thus, finding an alternative energy source is the solution to the current global environmental and energy issues, such as the energy crisis, carbon dioxide emissions and greenhouse gas emissions.

In recent years, several studies demonstrated that biomass could be an energy source suitable for the production of markable biofuel; therefore, there is a need to consider and focus on producing fuels using biomass materials as feedstock.

Biomass is a renewable organic material from plants and animals such as castor, soybean, canola, cotton, and palm oil. It is often used in power stations to generate electricity [1, 2]. This study makes use of biomass material to produce biofuels in general and biogasoline.

Biofuels can potentially compete with fossil-based fuels and are renewable energy. Biofuels are generally liquid and gaseous. Several investigations assessed whether biofuel production could transform biomass into hydrocarbon; as a result, biomass as feedstock is considered a viable option for producing transportation fuels such as biodiesel and bio-gasoline [1].

A range of biomass feedstocks, such as vegetable oils, both edible and non-edible, is used to produce biofuels. The feedstock is chosen based on its availability, selling price, and favourable climate for cultivation. The abovementioned criteria strongly dictate the feedstock choice to produce bio-gasoline and other biofuels [1]. After choosing the feedstock is essential to find suitable methods to convert biomass into biofuels (biogasoline in the case of this research study).

The production of bio-gasoline has been reported using several methods. Catalytic cracking is one of the methods used to produce bio-gasoline from biomass. Catalytic cracking is a conversion process that converts high molecular weight oil components into lower molecular weight components utilizing a catalyst. The catalyst is responsible for the cracking reaction that yields more of the desired higher-octane hydrocarbon products to generate higher-octane gasoline [1]. Other methods include thermal cracking and transesterification. Transesterification uses to make biodiesel [3, 4]. And the novel method is the hybrid

method. The latter method merges catalytic cracking and transesterification. This method is still new, and its application is understudied.

The hybrid method is used in two steps: transesterification and catalytic cracking. Transesterification is used as an advanced pre-treatment step to remove remaining impurities from the feedstock. The transesterification is used as a progressive pre-treatment step simply because waste cooking oil cannot be converted into biogasoline solely through transesterification.

Using catalytic cracking process, including thermal cracking and two-step processes, this study investigates the optimum conditions for producing biogasoline from waste cooking oils. The investigation will extend to catalytic cracking activity in order to determine the effects of the reaction temperature, the weight hourly space velocity (WHSV), and the catalyst weight.

1.2. Problem statement

Biogasoline is a promising renewable energy source source for spark engines that can be blended with conventional gasoline or as a replacement it entirely, without requiring any modifications to the engine's materials. To produce sufficient biogasoline, the appropriate biofuel process and catalyst must be utilized. What specific method and catalyst are required depends on various factors, such as the feedstock used and the desired properties of the final product.

1.3. Importance of the topic

The production of petroleum products using crude oil, originating from fossil fuels, has negatively impacted the environment.

Agarwal [5] outlined the problems encountered by using crude oil as a raw material in producing fossil-based or conventional fuels. Using traditional fuels (fossil fuels) led to modifying the earth's surface layer and subsidence of the ground surface after extraction. There are emissions of solid particles into the atmosphere through pollution. These particles have increased carbon dioxide (CO₂) levels in the atmosphere from 280 ppm in the pre-industrial era to 350 ppm in this new era. The rise of carbon dioxide (CO₂) in the atmosphere caused by the utilization of fossil-based fuels and the calcination of ores results in greenhouse gas (GHG) effects, acid rain, smog, and climate change [1].

Traditional fuels are at the centre of numerous issues, such as global warming, increasing prices, and their source, which is on the verge of disappearing. It is essential to consider shifting to the use of biofuels to protect human lives and the Earth. The consideration and potential usage of biofuels are outgrowing conventional (traditional) fuels [6]. Biofuels are considered cleaner fuels, generated from an infinite energy

source, containing fewer sulfur elements that tend to be harmful and corrupt the environment than conventional fuels [7].

It is still unclear whether biofuels reduce overall greenhouse gas emissions as their life cycle span analysis is still under investigation. Nevertheless, if the land-use changes due to biofuel production are significant, it is noticed that there are fewer greenhouse emissions compared to when fossil fuels are used [6].

Another concern about the production of biofuels is that they can compete with the food supply, given that biofuels' primary feedstock is the crops that also serve as nourishment for humankind [8].

The most exciting aspect of the feedstocks is the possibility of using waste materials to produce biofuels. It is convenient to generate biodiesel and bio-gasoline from waste cooking oil and biogas derived from sewage. It is essential to note to produce biodiesel using waste cooking oil using other methods since transesterification is not the most appropriate method to make good quality biodiesel from waste cooking oil.

This study investigates biogasoline production by the catalytic cracking of waste cooking oil. It also optimizes the catalytic cracking's parameters such as temperature, catalyst load, oil-to-catalyst ratio, and weight, hourly space velocity (WHSV). Knothe [9] stated that several studies investigate the production of a range of biofuels (bio-gasoline in the context of this study) using edible and non-edible feedstocks such as vegetable oil, palm oil, and waste cooking oil.

Biofuels, in general, are valuable and essential products since they can massively reduce greenhouse gas emissions. However, bio-gasoline is not yet at an advanced stage in its production compared to biodiesel and biogas. Bio-gasoline can potentially overtake the output of petro-gasoline fuel (conventional gasoline or fossil-based gasoline) after optimizing the operating parameters at the industrial level.

1.4. Aim & Objectives

1.4.1. Aim:

This study's primary purpose is to investigate biogasoline production from catalyst cracking using waste cooking oil. The catalyst of interest is a nano-cobalt molybdenum-based catalyst.

1.4.2. The Objectives of this work include the following:

- Synthesize the catalyst.
- Assessment of the effect of calcination on the activity of the catalyst

- Assessment of operating parameters' effect on bio-gasoline production in the thermal cracking method. The operational parameters investigated are:
 1. The effect of reaction temperature
 2. The effect of reaction time
- Evaluation of operating parameters used to produce bio-gasoline via the catalytic cracking method, including:
 1. The effect of catalyst calcination temperature
 2. The effect of reaction temperature
 3. The effect of reaction time
 4. The effect of oil/catalyst ratio
 5. The weight hourly space velocity (WHSV)
- To compare the results obtained from the catalytic and the thermal cracking methods.

1.5. Research contributions

Bio-gasoline production is developed as much as it is with its bio-gasoline counterparts (bioethanol, biodiesel, biogas, etc.). Firstly, the investigation of biogasoline output aims to provide data, methods, and techniques that will assist in the development of the production of bio-gasoline at an industrial scale. The second purpose of this investigation is to provide scientific data.

1.6. Overview of the thesis

Chapter one provides an overview of the investigated topic and the global economic and environmental challenges facing energy in general, particularly in the transportation sector. Furthermore, this chapter explores the research objectives and motivations that drive the investigation of biogasoline production using waste cooking oil (WCO).

Chapter two focuses on the literature and the evolution of biofuels from the first generation to the fourth generation. This chapter also focuses on different feedstocks used to produce biofuels, their characteristics, and their challenges and limitations. This chapter also reviews the processes associated with producing biofuels, particularly biogasoline. Typical catalysts and operating conditions are discussed. The chapter is concludes with a deep analysis of biogasoline.

Chapter three briefly describes the materials and equipment used to conduct catalytic cracking, thermal cracking, and a two-step process to produce biogasoline and the laboratory setup. The schematic representation and the actual laboratory setup are presented.

Chapter four underlines the experimental procedures and technical analysis used in biogasoline production. This chapter presents the techniques used in the laboratory to produce biogasoline.

Chapter five discusses the results of different analyses. The first set of discussions focuses on catalyst characterization. The X-ray diffraction (XRD) analysis conducted on the catalyst is discussed, followed by the inductively coupled plasma optical emission spectroscopy (ICP-OES) results. Then, scanning and transmission electron microscopy results are reviewed. The catalyst characterization section concludes with a discussion of the regeneration temperature. The second section of the discussion focuses on the pre-treatment and post-treatment of waste cooking oil.

Furthermore, chapter five discusses the different methods used to produce biogasoline. Thermal stability and optimization are also discussed in this chapter. The chapter will concentrate briefly on the physical properties of biogasoline and compares them to conventional or fossil-based gasoline.

Chapter six focuses on the conclusion and the essential suggestions to consider to improve biogasoline production.

CHAPTER TWO: Literature Review

2.1. Introduction

As fossil-based fuel production harms the environment and the oil supply fluctuates, there is an urgent need to find an alternative fuel to fossil-based fuel; therefore, biofuels in general and biogasoline are under investigation. Another fact about fossil-based fuels is that they are generated from a finite source, which dwindles with time.

This chapter briefs the properties of raw materials, biogasoline properties, the different processes used to produce biofuels, the factors affecting bio-gasoline production, the world fuel climate, and the evolution of biofuels throughout various generations, and the manufacturing processes of biofuels (bio-gasoline in this study). Then it will tackle biogasoline, the main topic of this study, and the types of reactions. Finally, the catalysts used to produce biogasoline are to be discussed.

The world relies on fossil-based fuels for its energy demands. The statistical analysis predicts that the world will continue relying on fossil fuels until 2030 [10]. After 2030, fossil-based fuels will disappear. Fossil-based fuels count for all fuels generated underground after animals or plants of the past geologic age have been preserved under severe pressure and temperature conditions over millions of years. Products like coal, gas and all crude oils are in the category of fossil-based fuels.

Table 2. 1: World's central fossil fuel reserves [10]

Region	Fossil fuel reserve (Giga tons of oil equivalent)				Fossil fuel reserve (%)			
	Oil	Coal	Gas	Sum	Oil	Coal	Gas	Sum
North America	8	170	7	185	0.86	18.2	0.75	19.81
South America	15	13	6	34	1.61	1.39	0.64	3.64
Europe	2	40	5	47	0.21	4.28	0.54	5.03
Africa	16	34	13	63	1.71	3.64	1.39	6.75
Russia	18	152	52	222	1.93	16.27	5.57	23.77
Middle East	101	0	66	167	10.81	0	7.07	17.88
India	1	62	1	64	0.11	6.64	0.11	6.86
China	2	76	2	80	0.21	8.14	0.21	8.57
Australia & East Asia	2	60	10	72	0.21	6.42	1.07	7.71
Total	165	607	162	934	17.67	64.99	17.34	100

There is a hope that the abovementioned figures will increase; however, the main concern remains the extent to which these figures will increase (the estimated increase is not yet known) [11]. The author

Maugeri [12] stated that despite the discoveries, these would only cover one-fourth of the world's energy consumption, hence why there is a genuine need to find an alternative energy source to relieve humanity from its reliance on fossil fuels.

Another observation is that the distribution of fossil fuels on Earth is unequal. In some regions, fossil fuels are scarce; in other areas fossil fuels are abundant. Bearing in mind that the entire globe relies on fossil-based fuels as a source of energy, the disproportionality in the distribution of fossil fuels results in the dependency of the entire planet on rich countries for energy. Countries with immense reserves of fossil-based fuels decide on the prices with organizations like the Organization of the Petroleum Exporting Countries (OPEC); consequently, countries without crude petroleum reserves are not part of the consultations to decide on the selling prices [13]. The facts above indicate that countries with scarce fossil-based fuel reserves require an alternative and accessible source of fuel to supply their needs.

Besides the fact that crude oil is disproportionally distributed, several studies show that fossil fuels have significantly impacted the global environment. According to Mampuru [4], using fossil fuels such as petroleum products results in modifying the Earth's surface layer and subsidence of the ground surface after extraction. There is an augmentation of carbon dioxide in the atmosphere. The concentration of CO₂ has increased from 280 ppm to 350 ppm in the industrial era [4]. The rise in CO₂ levels in the atmosphere is directly proportional to the number of fuels used, leading to the greenhouse effect, acid rain, and climate change.

The following paragraph will discuss the biorefinery concept.

2.2. Biorefinery concept

A biorefinery is an industrial process like a fossil-based (petroleum) refinery that converts biomass into various chemical compounds. There are four principal subcategories of biorefinery processes. The existence of these processes depends on [14]:

- The chosen platforms or essential intermediate products and processes,
- The manufactured products, whether it is energy production or compounds
- The feedstock of choice
- The processes used

The following paragraph will discuss in detail the different platforms.

2.2.1. Conversion platforms

Conversion platforms are methods or techniques that convert biomass into a set product. According to Maugeri [12], there are three conversion platforms: biochemical or biological, thermochemical, and hybrid.

2.2.1.1. Biochemical and biological conversion platforms

These conversion techniques facilitate the microorganisms, enzymatic and fermentation processes to convert the pretreated raw material (biomass) into a range of products (desired products).

2.2.1.2. Thermochemical conversion platform

On the other hand, a thermochemical conversion technique platform generally uses chemical processes to convert raw material (biomass) into desired or targeted products.

2.2.1.3. Hybrid conversion platform

The hybrid conversion platform combines three conversion platforms (biochemical, biological, and thermochemical) to produce valuable biomass products. The technique considers the combined techniques' strengths of different conversion platforms to process biomass into valuable products. The hybrid method uses thermochemical conversion for the pre-treatment step, whereas the biological conversion technique converts the pretreated biomass into required products [15, 16]. The resulting biomass products will then be purified to remove impurities. The impurities are either by-products or the material used in the fermentation process. The purification of the products is conducted utilising a distillation column (trays or packed columns) and evaporation. The distillation column purifies the products based on the difference in the boiling points of the components in the mixture. The heavy part is withdrawn from the bottom, and the light produced is from the top of the column. According to [15], the performance (efficiency and energy necessity) of the downstream processing step (DSP) depends on the previous steps (purification). The solid particles are separated or removed from the desired products using filters, centrifuges, and membrane techniques. If the products are required to be delivered in a particle form, additional units are added downstream for the following processes: crystallization, drying, and milling [17].

This research uses thermochemical conversion platforms to convert biomass into bio-gasoline.

2.2.2. Feedstocks

Various types of raw materials are used to produce biofuels and materials. This paragraph presents the different kinds of feedstocks available to produce biofuels.

2.2.2.1. Lignocellulosic

Several studies indicate the usefulness of the lignocellulosic biomass feedstock type. Lignocellulosic biomass has been used to produce biofuels and their related by-products. The biomass lignocellulosic type is justified because of its abundant occurrence regardless of the process of converting biomass into any product (material, fuel, or energy) [18].

Lignocellulosic biomass comprises lignin, hemicellulose, and cellulose (see Figure 2). The percentage of constituents of lignocellulosic biomass depends on the source of biomass.

2.2.2.2. Green Biomass

Green biomass mainly comprises living, herbaceous, and wet biomass such as grasses and clover [19]. The grasses originate from pasture lands, roadside cuttings, and (private) gardens and parks. Clover, which is named after a cover crop and green manure, prevents the soil from erosion and runoff by its root system during the uncultivated period of the land. The clovers belong to the Leguminosae group, characterized by the symbiotic Rhizobia bacteria in their root nodules. The Rhizobia stabilizes atmospheric nitrogen, hence fertilizing the soil. The harvested grasses and clovers can be cultivated to feed animals; however, a significant part is less utilized than expected [19, 20].

2.2.2.3. Biowaste

Biowaste is becoming the principal source of biomass because many investigations have been carried out using this source of biomass. The waste biorefineries provide double benefits. They possess biorefining capacities, and they can also be considered waste processors. Waste biorefineries are sourced from variety of industrial waste destined for landfills.

Agricultural biowaste sources provide two types of components: the lignocellulosic and green biomass, illustrated respectively by corn stover and clovers. The food industry is an essential source of biowaste, considering that it provides grains and filter cakes from breweries, bagasse, and molasses from the sugar industry. The other source of biowaste worth mentioning is urban municipalities. From this source, an essential quantity of biowaste is produced. Urban municipalities' wastes are diversified compared to the other waste feedstocks investigated.

The feedstock size and composition are problematic tasks that waste-based or other biorefinery faces. The biorefineries industry will be a significant energy source once its chain supplier and overall logistic network become efficient [21, 22].

This study investigates the production of bio-gasoline from cooking and vegetable oil. The first feedstock is purely biowaste feedstock, meaning biowaste is this study's focal point.

2.3. Classification of biofuel generations

Biofuels are fuels produced from biomass for transportation and heating purposes [23]. The production of biofuels will create an energy source to substitute conventional energy sources (fossil-based fuels), and their use is gaining momentum. Escobar et al. [7] presented biofuels as a cleaner fuel source with fewer harmful elements than fossil-based fuels containing high Sulphur concentrations. Sulphur compounds are environmentally toxic substances.

Low sulfur concentrations in biofuels do not spare the production of biofuels from being harmful to some extent. There are still environmental issues concerning the production of biofuels and whether these different generations of biofuels lessen overall greenhouse gas emissions since the life cycle analysis of biofuels is still under consideration.

Several investigations conducted on biofuels reveal that by using biomass in the production of biofuels as feedstock, the emission of greenhouse gases is less than reproducing during the production of fossil-based fuels using crude oil. The statement becomes relevant only if biomass cultivation does not influence the land or if biomass cultivation has an insignificant influence on the ground [6].

Different generations of biofuels have been recorded throughout the years. These generations do not differ from a structural point of view. Still, their difference is relative to the source and the characteristics of feedstocks used from one biofuel generation to the other.

There are four generations of biofuels; a brief description of each generation is underlined in the following paragraphs.

2.3.1. First-generation biofuel

First-generation (FG) produces biofuels using agricultural resources such as starch, sugar, animal fats, and vegetable oil as feedstocks. The well-known first-generation biofuel is ethanol (biodiesel) [24].

Biorefinery uses conversion platforms to produce biofuels. First-generation used biochemical and biological conversion platforms. The manufacturing process used in biochemical and biological conversion platforms is fermentation [24].

The feedstock used to produce first-generation biofuels is mainly composed of agricultural resources. The utilization of agricultural resources to manufacture biofuels affects food production. Additionally, it combats food supply and the proliferation of carbon emissions because of excessive growth necessity when planted out of the season of traditional agricultural [24].

Regarding product yields, the first-generation biofuel extracted biodiesel from the crops through fermentation [24].

The concern regarding the production of first-generation biofuel is the uncertainty of this generation decrease greenhouse gas (GHG) and carbon emissions. The author Olganatha [24] stated that the amount of carbon dioxide liberated throughout the production of most first-generation, when compared to their feedstock cultivation, results in a net energy loss.

The other issue related to first-generation biofuels, besides the greenhouse gas and carbon emission, is the "food vs fuel" competition. There is a potential augmentation of food prices on a global scale as the demand for biofuels is increasing, setting a high quantity of crops used for biofuel production. Consequently, the population will famish as more crops will be dedicated to producing biofuels [24].

The future and development of first-generation biofuels are jeopardized, considering crops' growth and production depending on several parameters, such as agricultural prices, season changes, market speculation, and extreme weather patterns [24].

The drawback related to first-generation biofuels pushes researchers to seek alternative feedstocks.

2.3.2. Second-generation biofuel

Inventing second-generation biofuels was to solve the issues linked to first-generation biofuels. It is essential to underline that the feedstock used to produce first-generation biofuels is mainly agricultural, forest residues and non-edible food crops. The production of second-generation biofuels saw the light of life to overcome the limitations of the first-generation. Second-generation biofuels are produced from plants, waste material, or non-edible plants [25].

The consideration of second-generation biofuels is down to the inability of first-generation biofuels to solve the issues linked to fossil-based fuels. Nevertheless, the first-generation biofuels added problems and did not provide enough solutions to environmental concerns; instead, they impacted food security, they increased competitiveness with the food industry and prices [26, 27].

Second-generation biofuels use a different source of biomass in comparison to first-generation. Second-generation biomass consists mainly of lignocellulosic biomass, woody biomass, and inedible seeds such as *Jatropha curcas* and waste cooking oil. The feedstock used in the manufacturing process of second-generation biofuels is available and cheaper [26, 27]. According to Naik et al. and Mohammadi et al. [26, 27], the source of second-generation is either food industry remnants or those produced during the manufacturing process of the first-generation biofuels.

Second-generation biofuels are different from one another. The difference is in the conversion platforms used to produce fuels. There are two sets of second-generation biofuels, which are biochemical and Thermochemical second-generation biofuels.

A thermochemical conversion platform is a novel technology that produces biofuels. The conversion platform that makes second-generation biofuels has no first-generation analogue [28].

The mechanisms used in producing second-generation biofuels via the thermochemical conversion platform and those used in producing fossil-based fuels are similar. Figure 2.1. illustrates the similarity between fossil-based fuels and thermochemical second-generation biofuel production.

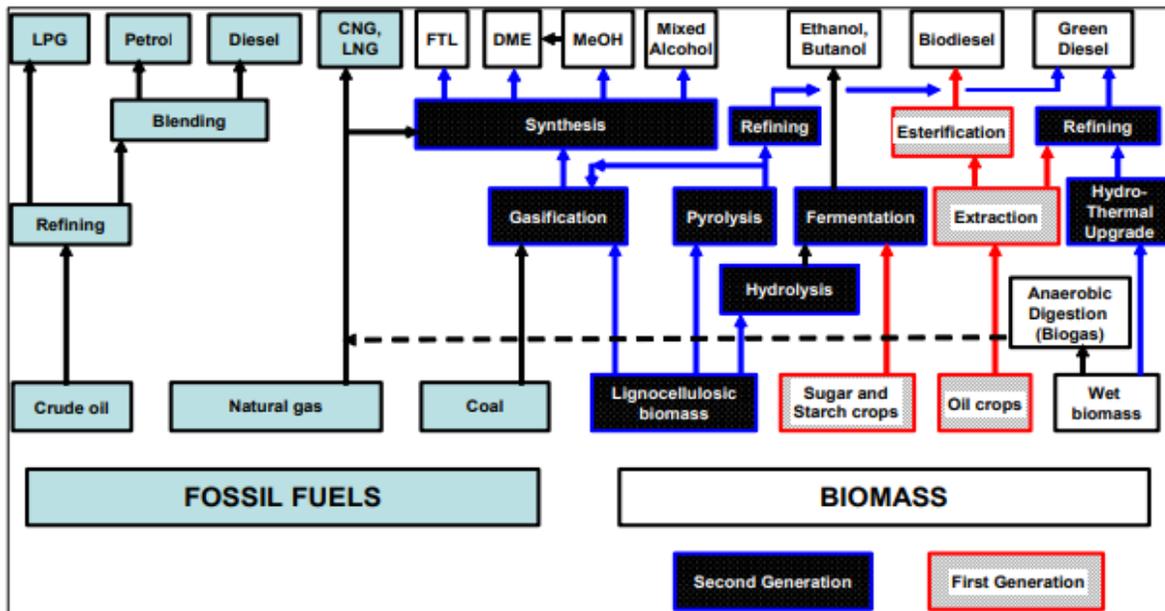


Figure 2. 1: Production pathways to liquid fuels from biomass and, for comparison, from fossil fuels [28]

2.3.2.1. Second-generation biochemical biofuels

The feedstock used to produce first-generation biofuels (FGBs) presents no difference in properties from the one used to produce second-generation biofuels (SGBs). However, the methods or techniques used are different. Second-generation biofuels produced using lignocellulosic biomass are generally called cellulosic biofuels [21].

The second-generation biofuels (SGBs) production via the biochemical conversion platforms uses the following steps: pretreated, saccharified, fermented, and distilled. The feeds are pretreated to separate three main components of biomass: cellulose, hemicellulose, and lignin, into simple sugars to allow the enzyme to catalyze through the addition of water which decomposes carbohydrate molecules parts "cellulose and hemicellulose" [22]. Cellulose is a crystalline lattice composed of long chains of glucose C₆ sugar molecules. The decomposition of cellulose into simple has never been easy, resulting in difficulty fermenting cellulose. The disintegration of biomass enables a quick fermentation process using microorganisms. However, the fermentation of hemicellulose is challenging. It isn't easy to convert biomass consisting of C₅ sugar molecules to biofuels. It is a complex process despite the hemicellulose being less tenacious and easy to decompose. The newly developed microorganisms have helped to ease the fermentation process of hemicellulose [22].

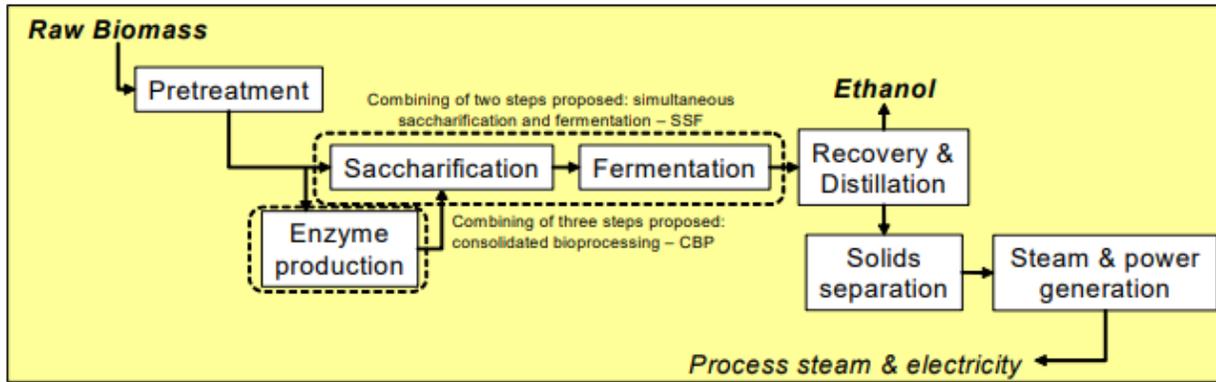


Figure 2. 2: Simplified depiction of process steps for the production of second-generation fuel ethanol [28]

The investigation of an alternative energy source has been ongoing for an extended period resulting in the production of biodiesel and biogas at the industrial level. However, bio-gasoline production is still staggering [29].

Several process designs have been elaborated and proposed regarding the production of second-generation biofuels via a biochemical conversion platform, including the production of bioethanol. One of the innovations is the combination of saccharification and fermentation to produce bioethanol. The well-conceived conversion platform makes second-generation bioethanol presented in figure 2.2 [29]. Besides the above-modified technologies, the consolidated bioprocessing technology has also seen the light of the day in producing second-generation biofuels. The latest technology merges enzyme production from biomass with saccharification and fermentation [30].

It is worth highlighting that the technologies developed have been solely used to produce bioethanol. There is a possibility to extend the use of these technologies to process other second-generation biofuels.

2.3.2.2. Second-generation thermochemical biofuels

A thermochemical conversion platform produces second-generation biofuels at extremely high pressure and temperature [28].

The thermochemical conversion platform is an essential technique. It can accommodate several feedstocks and yield a variety of finished biofuels compared to the biochemical conversion platform. Another advantage of the thermochemical conversion platform is the quality of its end products. The thermodynamical conversion platform yields clean-finished fuel ready for engines. Gasification or pyrolysis is the first thermochemical process used; this process is not cost-effective. Therefore, it needs a considerable scale for the best economy [28].

The gasification process is an exciting step through which different biofuels are produced, including Fischer-Tropsch Liquids (FTL), dimethyl ether (DME), and various alcohols. Gasification uses combustion to convert biomass to gas; the transformation of biomass to gas results in combustible and non-combustible gases. The impurity in the gas is purged, followed by specific processes by adjusting, which performs using the "water-gas shift" reaction of the synthesis gas, also known as syngas, to prepare it for additional downstream treatment (figure 2.3).

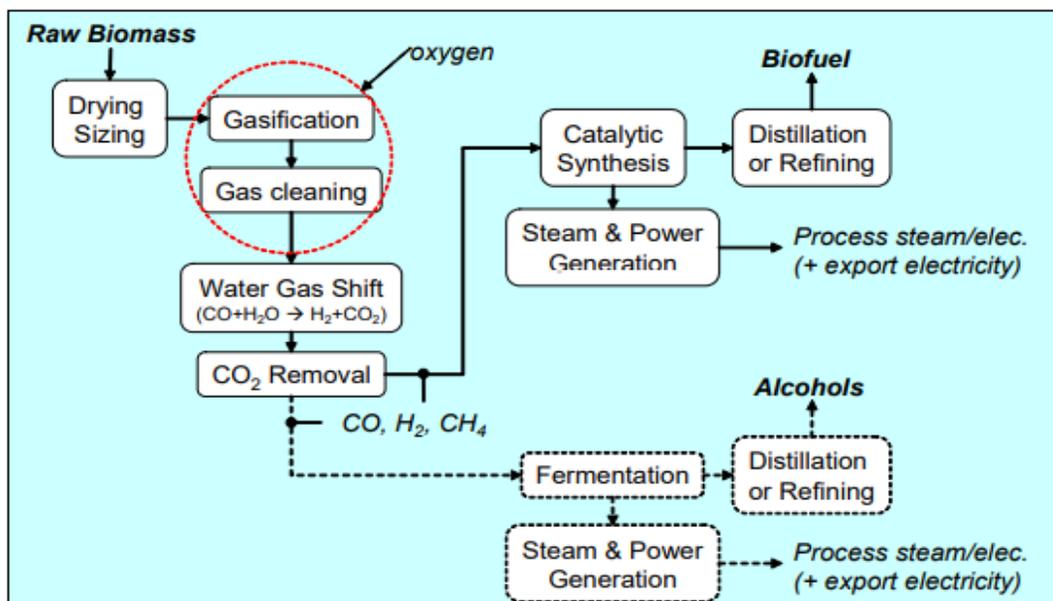


Figure 2. 3: Simplified depiction of process steps for thermochemical biofuel production [28].

The downstream inlet stream consists of a mixture of a solution of syngas and a selected solvent. Mixing the syngas and the solvent is to sequester carbon dioxide through its dilution. The sequestration of carbon dioxide in the syngas facilitates a series of reactions downstream. After cleaning the mixture of syngas and solvent, the resulting syngas consists mainly of carbon monoxide (CO), hydrogen, and a small quantity of methane (CH₄) [28].

The outlet stream comprising CO, H₂, and a small quantity of methane undergoes a catalytic process to produce biofuel. Methane is inert in this process. The catalyst is the main element on which biofuel production depends. This process has the disadvantage of incomplete syngas conversion to biofuel in most plants; therefore, some syngas does not convert to biofuel. The unreacted portion of syngas is used as an energy supplier to run the facility and sometimes exports electricity to the grid. Syngas can be converted to liquid through fermentation using microorganisms (figure 2.3), even though this technology is not yet at an advanced stage commercially compared to the catalytic cracking process [28]. The equipment required to convert biomass to fuel through catalytic synthesis is readily obtainable. However, progress is necessary

for feeding biomass into a large-scale pressurized gasifier and cleaning the raw gas produced by the gasifier [28].

This study investigates biogasoline production using second-generation biomass. The conversion platform of interest is the thermochemical and its variety.

2.3.3. Third-generation biofuel

The third-generation biofuel is an interesting one. Third-generation biofuel does not use either crops or biowaste. However, it uses algae and aquatic biomass as feedstock to make biofuel [24].

Algae grow in marine (saltwater) or freshwater environments. Algae have so many advantages, including being the fastest-growing plants. They convert sunlight, water, carbon dioxide (CO₂), and other nutrients into energy and biomass and release large amounts of oxygen into the atmosphere [31].

There are at least five methods used to convert algae and aquatic biomass into biofuel: Open Pond system, Hybrid system, modular closed photobioreactor, heterotrophic fermentation, and sophisticated integrated system [24].

2.3.3.1. Environmental Benefits of Algae Cultivation

Several benefits come with the cultivation of algae. It requires small arable land; therefore, competition with food crops is low. In contrast to previous generations of biofuel feedstocks, algae-based biofuel feedstock does not require cultivation on non-arable land, increasing consumer food security. The other advantage linked to the cultivation of algae-based biofuel feedstock is that it uses less water [32].

Applying methods such as bio-fixation and bioremediation enhances water quality and provides a cost-effective treatment method for wastewater treatment. Other advantages associated with the cultivation of algae are the mitigation of eutrophication and dead zones, the fixation of around 40% of global carbon, and it can lessen and prevent industrial greenhouse gases [32]. Finally, algae cultivation slows down deforestation and releases carbon into the atmosphere [33].

The additional benefit of algae is that they are currently catalysts in carbon dioxide capture and sequestration.

2.3.4. Fourth-generation biofuels

Fourth-generation biofuels are produced using artificial plants or biomass with more minor cellulosic breakdown barriers or excellent yields [24]. In addition, there is no destruction of biomass since the cultivation of the plant or biomass does not require the land and water used in crop agriculture. Furthermore, the plants or the biomass used to produce fourth [24, 34].

The fourth generation used methods similar to those used in refineries. One of the methods used is hydro-processing [24]. The use of biofuel is finding a suitable one that must have a tremendous environmental benefit over fossil-based fuel, be cost-effective, and the quantity produced should satisfy the energy demands [24]. Fourth-generation biofuel has the potential to be environmentally suitable and economical.

An additional key fact to consider regarding the fourth generation is that the net energy obtained from the feedstock needs to be more significant than the amount necessary for production. Considerable net power derives from the feedstock when the eucalyptus trees are designed to accumulate three times more carbon dioxide than expected, increasing the chance of reducing greenhouse gases and rescuing the current state of global warming [24].

The use of microbes or microorganisms seems to be an excellent opportunity for substituting conventional fuel feedstock because of the following characteristics: short life cycle, lower labour requirements, reduced influence by location, season, and climate, and the ease of scaling up production [24].

Regarding biofuel feedstock generation, this study investigates bio-gasoline production using second-generation, non-edible feedstocks. The investigation produces bio-gasoline through catalytic cracking, thermal cracking, and hybrid (two-step process) methods.

2.4. Review of biofuel products.

This section reviews biofuel products and their technologies.

2.4.1. Bioethanol

Bioethanol is a biofuel from biomass crops feedstock. It is an alcohol, typically ethyl alcohol, represented chemically by C_2H_5OH (EtOH). The blend of bioethanol and gasoline is considered a replacement/substitute for transportation fuels [35].

The feedstocks used to produce bioethanol are wheat, sugar beets, corn, straw, and wood. When biomass lignocellulosic is the feed to produce bioethanol, the process consists of three steps: pre-treatment, polysaccharide hydrolysis to shorten long-chain sugars to simple or bit sugars, and finally, fermentation of short-chain sugar to bioethanol (ethanol) [36]. The biomass constituents play a significant role during biomass conversion to bioethanol, the primary element among three main components: Cellulose, Hemicellulose, and lignin; lignin plays the part of cementing agent binding individual fibres together. According to [37] and [38], lignin hinders different conversion steps from proceeding since it is present at the cell walls.

There are advantages and disadvantages to producing bioethanol.

Advantages of bioethanol [35]:

- Higher octane number (108)
- Larger flammability limits
- Higher flame speeds
- Higher heat of vaporization.

The disadvantages of bioethanol [35]:

- Low energy density
- It is corrosive
- It has a low-flame luminosity
- Low vapour pressure
- Miscibility with water
- Toxicity to ecosystems
- Increase in exhaust emissions of acetaldehyde
- Increase in vapour pressure

2.4.2. Biogas

Biogas is a valuable renewable source of energy, potentially used in vehicles as fuel and as a source of energy production. Biogas produces electricity as an energy source and is possibly injectable into the natural gas grid.

Organic matter biodegrades under anaerobic conditions to produce biogas. The biodegradation process occurs following hydrolysis, acid-genesis, acetogenesis/dehydrogenation, and methanation. The completion of biodegradation requires a combination of multiple microorganisms [4]. The sewage sludge from wastewater treatment plants (WWTPs) is the most used organic matter in biogas production instead of its counterparts' organic matter since it is easily accessible. Its anaerobic digestion is an exciting process that yields energy.

Biogas production undergoes a pre-treatment stage, which is imperative since it removes impurities and improves methane concentration (CH_4). The end-use of biogas decisively affects its purification—the purification of biogas, regardless of its end use, decreases the concentration of hydrogen sulfide due to its nuisance. The H_2S is toxic and flammable, causes corrosion, damages equipment, and harms the environment because it emits sulfide dioxide (SO_2). Finally, H_2S is dangerous to life and health [18].

Biogas production utilizes numerous materials to allow the activity of an enzyme. Among the materials used as primary substrates are sewage sludge from wastewater treatment plants (WWTPs), livestock manure, waste from the agri-food industry, and the organic fraction of municipal solid waste.

The resulting gas product is gas-rich in methane (CH₄) in the proportion of 45-75% and carbon dioxide in the proportion of 20-50%. The composition of the resulting gas product depends mainly on the type of feedstocks and the digestion system. In addition to methane and carbon dioxide, the product gas contains other compounds such as hydrogen, nitrogen, and hydrogen sulfide [5-10].

Biogas purification uses two genetic methods: physicochemical and biological processes. The resulting biogas after the purification process is known as biomethane. This name is due to the high concentration of methane in the biogas.

2.4.3. Biodiesel.

Biodiesel is an environmentally friendly and renewable fuel. The need to produce biodiesel rises because of the unavailability and the market price increase of fossil-based diesel [39].

According to Marchetti [40], biodiesel is a fatty acid methyl or ethyl ester (FAME) produced from vegetable oils or animal fats. Biodiesel serves as fuel for diesel engines as well as heating systems. The production of biodiesel, also known as fatty acid methyl esters, is carried out through the transesterification of vegetable oil and animal fats.

The transesterification technique uses methanol in the presence of a suitable catalyst to form alkyl esters (biodiesel) and glycerin. Transesterification uses two types of catalysts used in transesterification: acidic (H₂SO₄ and HCl) and alkaline (NaOH, KOH, NaOCH₃).

Industrial processes use these catalysts because of their performance, and they yield high reaction and conversion rates. Another type of catalyst available is a biological catalyst (lipase). Regarding biological catalyst utilization, only a small quantity is necessary since it is faster than transesterification [40].

According to Churasia [41], potassium hydroxide (KOH) is a catalyst for biodiesel production using methanol transesterification. The catalyst reaction produces biodiesel (alkyl esters) and glycerin. Furthermore, the products contain unreacted glycerides such as mono-, di- and tri-acyl [41]. The transesterification technique is named methanolysis since methanol is used [39].

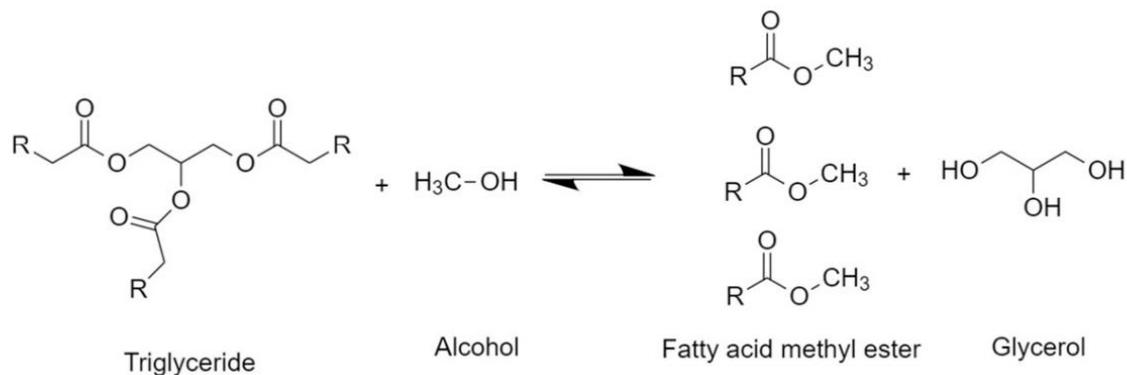


Figure 2. 4: General scheme for transesterification of triglycerides [42]

2.4.4. Biogasoline

Towards the end of the 18th century, European countries discovered a particular fuel produced using vegetable oils and related materials. Numerous studies have been conducted on biofuel production. Nevertheless, biogasoline production is less advanced than biodiesel, biogas, and ethanol. Due to the commercial production of the other biofuels, the investigation of biogasoline output is a relevant topic to explore [13].

Different studies reveal similarities between bio-gasoline and commercial gasoline (fossil fuel gasoline)[43]. Biogasoline is also compatible with conventional gasoline, cars, and infrastructure [13].

The method used to produce biogasoline is similar to that used in the petroleum refinery industry. Bio-gasoline production from vegetable oils uses fluidized catalytic cracking. Fluidized catalytic cracking is used in petroleum refineries to produce fossil-based fuels. The biogasoline made from vegetable oils leads to severe competition with food consumption. Hence, biorefineries use non-edible vegetable oils, animal fats, and waste cooking oils as feedstocks [44].

Several investigations show the possibility of manufacturing and commercialising biogasoline to compete with conventional gasoline (fossil-based gasoline), using non-edible vegetable oils.

2.4.4.1. Major components of bio-gasoline

Table 2. 2: Biogasoline composition

Components	Percentage composition	Other possible components
n-alkanes		Octane enhancers
C ₅	3	Methyl t-butyl ether (MTBE)
C ₆	11.6	t-Butyl alcohol(TBA)
C ₇	1.2	Ethanol,
C ₉	0.7	Methanol
C ₁₀ - C ₁₃	0.8	

Total of n-alkanes	17.3	Antioxidants
Branched alkanes		N,N*-dialkylphenylenediamines
C ₄	2.2	2,6-dialkyl and 2,4,6-trialkyl phenols
C ₅	15.1	Butylated methyl,
C ₆	8	Ethyl and dimethyl phenols
C ₇	1.9	Triethylene tetramine
C ₈	2.1	Methal deactivators
C ₁₀ - C ₁₃	1	N,N*-disalicylidene-1,2 ethanediamine
Total of branched alkanes	32	N,N*-disalicylidene-propanediamine
Cycloalkanes		N,N*-disalicylidene-cyclohexanediamine
C ₆	3	disalicylidene-N-methyl-disalicylidene-N-
C ₇	1.4	methyl-dipropylene-triamine
C ₈	0.6	Ignition Controllers
		Tri-o-cresylphosphate (TOCP)
Total of cycloalkanes	5	Icing inhibitors
		Isopropyl alcohol
Olefines		Detergents/dispersants
C ₆	1.8	Alkyl phosphates
Total of olefines	1.8	Poly-isobutene amines
		Long chain alkyl phenols
Aromatics		Long chain alcohols
Benzene	3.2	Long chain carboxylic acids
Toluene	4.8	Long chain amines
Xylenes	6.6	Corrosion inhibitors
ethylbenzene	1.4	Carboxylic acids
C ₃ -benzenes	4.2	Phosphoric acids
C ₄ -benzenes	7.6	Sulfuric acids
Others	2.7	
Total of aromatics	30.5	

2.4.4.2. Properties of biogasoline feedstocks

Biogasoline production uses hydrocracking, thermal cracking with a catalyst (catalytic cracking), or without catalytic. Recently catalytic cracking and transesterification have produced biogasoline using waste cooking oil as feedstock. Transesterification accounted for an advanced pre-treatment stage of waste cooking oil [45].

Biogasoline can be processed using edible or non-edible oil, animal fat, microalgae, and fungi oil as feedstock through the above-mentioned methods.

The feedstock of interest for this study is waste cooking oil (WCO), a non-edible oil.

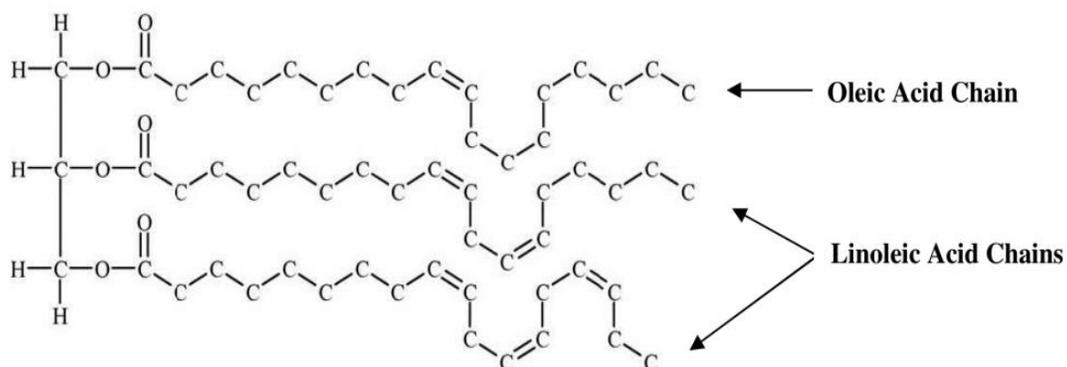


Figure 2. 5: Molecular structure of triglyceride (vegetable oil) molecule consisting of oleic and linoleic acid chains [45]

Table 2. 3: Physicochemical properties of different oils [46]

Feedstock (oil)	Heating value MJ/Kg	Density Kg/m ³	Kinematic viscosity at (38°C) mm ² /s	Flash point	Pour point	Cetane number	Reference
Corn	39.5	909.5	34.9	277	-40.0	37.6	[47]
Cottonseed	-	915	33.7(40°C)	234	-15	33.7	[48]
Linseed	39.3	923.6	27.2	241	-15	34.6	[49]
Peanut	-	903	40 (40°C)	271	-6.7	34.6	[48]
Rapeseed	39.7	-	37	246	-31.7	37.6	[50]
Safflower	39.5	914.4	31.3	260	-6.7	41.3	[47]
Sesame	39.3	-	35.5	260	-9.4	40.2	[50]
Soya bean	39.6	913.8	32.6	254	-12.2	37.9	[49]
Sunflower	39.6	916.1	33.9	274	-15.0	37.1	[50]
Palm	-	918.8	39.6	267	-	42.0	[47]
Babasu	-	946	30.3	150	-	38	[49]
Satropa	39-40	912	55(30°C)	240	-	40-45	[50]
Karanja	-	936.5	43.6(40°C)	-	-	-	[51]
Neem	-	918.5	50.3(40°C)	-	-	-	[51]
Castor	37.4	955.0	251 (40°C)	-	-	42.3	[51]
Mahua	36	960	24.5(40°C)	232	-	-	[51]
Tallow	-	903	51.2 (40°C)	201	-	40.2	[48]

The kinematic viscosity of castor oil is exceptionally high (251 mm².S⁻¹ at 40°C). Castor oil has high kinematic viscosity because its chemical composition comprises ricinoleic acid. Ricinoleic acid constitutes around 90% per weight of castor oil. Besides the presence of ricinoleic acid in castor oil, the other factor

that causes high viscosity is the method used to extract castor oil. The extraction of castor oil through cold pressing yields low acid content, low iodine content, lighter colour, and high saponification value, consequently lowering its viscosity. The physicochemical properties of castor oil, extracted using the cold pressing (mechanical) method, differ slightly from their properties when solvent extraction is used to produce castor oil [52].

Table 2. 4: Feedstock [53]

Group	Source of oil
Non-edible	Babassu tree, Copaiba, Jatropha, jojoba, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk-cotton tree, and castor
Major oils	Coconut (Copra), Corn (maize), cotton seed, canola (a variety of rapeseed), Olive, peanut (groundnut), Safflower, Sesame, Soybean, and Sunflower,
Nut oils	Almond, Cashew, Hazelnut, macadamia, pecan, pistachio, and walnut
Other edible oils	Amaranth, apricot, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod, cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lemon seed, meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pine nut, poppy seed, prune kernel, quinoa, rice bran, tallow, tea (camellia), thistle and wheat germ,

Table 2. 5: Physical properties of different oils [54]

Oil	Saponification value	Iodine Value	Acid value mgKOH/Oil	References
Canola	188 – 193	109 – 126	0.6 – 0.8	[55]
Olive	184 – 196	75 – 94	0.9 – 2.2	[56]
Corn	187 – 198	103 – 140	0.1 – 5.7	[55]
Jatropha curcas	177 – 189	92 – 112	11.6 – 43	[55]
Palm	186 – 209	35 – 61	6.9 – 50.8	[55]
Rapeseed	168 – 187	94 – 120	0.2	[57]
Soybean	189 – 195	117 – 143	0.1 – 0.2	[55]
Sunflower	186 – 194	110 – 143	0.2 – 0.5	[55]

Table 2.6: Composition of fatty acid (wt%) in different feedstocks[54]

Oil	Myristic C _{14:0}	Palmistic C _{16:0}	Stearic C _{18:0}	Oleic C _{18:1}	Linoleic C _{18:2}	Linolenic C _{18:3}	Reference
Edible							
Sunflower		5 – 8	2.6	15 – 40	30 – 70	3 – 5	[58]
Rapeseed		1 – 3	0 – 1	10 – 15	12 – 15	8 – 12	[58]
Soybean		6 – 10	2 – 5	20 – 30	50 – 60	5 – 11	[58]
Peanut		8 – 9	2 – 3	50 – 65	20 – 30	-	[58]
Olive		9 – 10	2 – 3	72 – 85	10 – 12	0 – 1	[58]
Palm	0.5 – 2	39 – 48	3 – 6	36 – 44	9 – 12	-	[58]
Mustard	-	-	1 – 2	8 – 23	10 – 24	8 – 18	[58]
Coconut	16 – 21	7 – 10	2 – 4	5 – 10	1 – 2.5	-	[58]
Almond	-	6.5	1.4	70.7	20	0.9	[59]
Walnut	-	7.2	1.9	18.5	56	16.2	[59]

Sesame	-	13	4	53	30	-	[59]
Non-edible						-	
Linseed	-	4 – 7	2 – 4	25 – 40	35 – 40	25 – 60	[58]
Neem	-	13 – 16	-	49.1-61.9	-	-	[58]
Jatropha	14 – 15	0 – 13	-	34.3–45.8	14 – 15	0 - 0.3	[58]
Cotton seed	-	23 – 28	0.8 – 0.9	13.3 – 18.3	-	0.2	[58]
Rubber	2.2	10.2	8.7	24.6	39.6	16.3	[60]
Karanja	-	3.7 – 7.9	2.4 – 8.6	44.5 – 71.3	10 – 18	-	[60]
Pongamia	11.6	-	-	51.5	11.6	-	[54]
Stillingia	0.1	7.5	2.3	16.7	31.5	41.5	[60]
Other							
Chicken fat	3.1	19.8	3.1	37.62			[54]
Waste	-	8.5	3.1	21.2	55.2	5.9	[54]
Cooking Oil							
Tallow	23.3	19.3	42.4	2.9	0.9	2.9	[59]
Brown grease	1.6	22.8	12.5	42.3	12.1	0.8	[60]
Microalgal	12 – 15	10 – 20	-	-	-	-	[54]
Yellow grease	2.4	23.2	12.9	44.3	6.9	0	[60]

2.4.4.3. Biogasoline properties

2.4.4.3.1. Viscosity

There are two types of viscosities: dynamic viscosity and kinematic viscosity. This paragraph explains in-depth kinematic viscosity, defined as the resistance a flowing liquid experiences, also considered as the degree of the thickness of the fuel or the thickness that fuel would have. Viscous fuel affects its injection system due to clogging. Since the fuel is viscous, this fuel quality may not experience complete combustion. Several studies revealed that the kinematic viscosity depends on the feedstock utilized to process the fuel and the technique used to determine the kinematic viscosity.

The kinematic viscosity of bio-gasoline is not well known since this type of biofuel is not yet at an advanced stage of production compared to other biofuels, such as biodiesel. In terms of biodiesel, the American Society for Testing and Materials (ASTM) predicted that it is in the range of 19-6mm²/s (ASTM D445) (Test of kinematic viscosity for transparent and opaque liquids) for pure biodiesel using numerous feedstocks. The insertion of the feedstock pre-treatment in the production of biofuels aims at decreasing the kinematic viscosity of biofuels since several studies reported that the kinematic viscosity of the biofuels is elevated compared to the kinematic viscosity of conventional fuels, also known as fossil-based fuels [61].

2.4.4.3.2. Octane Number or Octane rating

The Octane Number (ON) or Octane rating is a number that symbolizes the degree to which a gasoline blend can withstand early detonation. The octane rating also indicates that the gasoline blend can burn in the combustion chamber of an engine without knocking and pinging. These knockings and pinging might be produced by engine dysfunctionality and the fuel's inability to burn at the appropriate point in the engine cycle, resulting in reduced power out and damage to engine parts such as valve pistons bearings.

Engineers put together processes and designs to yield the mixture of hydrocarbons to provide less likelihood of causing knockings and pinging [62].

To establish the octane number (octane rating), two organic compounds: n-Heptane and Isooctane, were used. Each organic compound was assigned an octane number, respectively 0 and 100. Zero was attributed to n-heptane because this compound produces severe knockings and 100. It burns smoothly without creating knockings. To determine the octane rating of specific gasoline by comparing its knockings in a test engine to a mixture of n-heptane and Isooctane. For instance, for a blend of 89%, the remaining is n-heptane. An average is calculated in the following manner:

$$\text{ON(Unknown mixture)} = 100 \times 0.89 + 0 \times 0.11 = 89$$

The degree of detonation is determined or measured when the fuel is subjected to severe pressure and temperature conditions. The explosion occurs in the combustion internal chamber.

Octane Enhancers: The purpose is to produce a fuel with the required characteristics and specifications to avoid problems such as corrosion, damage to engine fuel system parts, and environmental issue, hence why engineers developed substances called Octane enhancers. These substances, such as tetraethyl lead $[(\text{CH}_2\text{H}_5)_4\text{Pb}]$, methyl t-butyl ether, and ethanol, are octane enhancers.

Ethanol produced from a renewable source is used to enhance the octane rating of gasoline instead of the previous enhancers since they had adverse impacts on the engine's operations, the fuel, and the environment, to mention a few: corrosion, toxicity, and groundwater contamination.

Table 2. 7: Octane rating of the chemical compound [46]

Name	Condensed structural formula	Octane rating
n-Heptane	$\text{CH}_3-(\text{CH}_2)_5-\text{CH}_3$	0
n-Hexane	$\text{CH}_3-(\text{CH}_2)_4-\text{CH}_3$	25
n-pentane	$\text{CH}_3-(\text{CH}_2)_3-\text{CH}_3$	62
Isooctane	$(\text{CH}_3)_3-\text{CCH}_2\text{CH}(\text{CH}_3)_2$	100
Benzene	C_6H_6	106
Methanol	CH_3OH	107
o-xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	107

Ethanol	CH ₃ CH ₂ OH	108
t-Butyl alcohol	(CH ₃) ₃ COH	113
p-xylene	C ₆ H ₄ (CH ₃) ₂	116
Methyl t-butyl ether	H ₃ COC(CH ₃) ₃	116
Toluene	C ₆ H ₅ CH ₃ or C ₇ H ₈	118

2.4.4.3.3. Flash point

The flashpoint is a minimum temperature at this condition of temperature. The fuel experiences an ignition when it is exposed to a flame or spark. The flashpoint varies depending on the fuel; not all fuels ignite at the same temperature. The larger the flashpoint, the higher the temperature required to ignite that fuel of interest [61].

Regarding the engine's operating condition, it is essential to have fuel that ignites at a low flash point; however, for transportation safety, it is necessary to have fuel that ignites at a higher flashpoint for safety [61].

Biogasoline ignites at a temperature of -28°C, whereas conventional gasoline (fossil-based fuel) ignites at a temperature of -24°C. The figure shows that bio-gasoline ignites at low temperatures than fossil-based gasoline. The lower flash point in biogasoline is a function of the fuel's constituent. The biogasoline does not contain long unsaturated chains such as C_{18:1}. These long chains are responsible for a higher ignition temperature experience with biodiesel in the range of 110°C – 180°C than the ignition temperature of conventional diesel, which is from 55°C to 60°C [40].

Catoire et al. [63]'s investigations and studies established an empirical model to evaluate the ignition temperature (flash point). This empirical model explained why an elevated flash point in the fuel contains more extended carbon chain compounds.

$$FP = 1.477T_b \times \Delta H_{vap}^{0.16845} \times C^{0.05948}$$

FP: is the flash point

T_b: is the boiling point of the compound (K)

ΔH_{vap}⁰: is the standard enthalpy of vaporization of the compound at 298.15K in [$\frac{kJ}{mol}$]

C: is the number of carbon atoms in the fuel molecule

2.4.4.3.4. Cloud point and Pour point

Cloud point and Pour point are physical fuel properties. The cloud point is a temperature at which fuel displays a less transparent colouration. At this temperature, fuel is unclear, which is caused by the presence of wax [63]. The crystal in a specific fuel appears when the fuel is cooled. Cloud point is evaluated using

ASTM D2500 (Test Method for cloud point of Petroleum Products). Other methods used to perform cloud point calculations are D5771, D5772 or D5773 [63].

The pour point, on the other hand, is a temperature at which the fuel loses its fluidity resulting in itself-solidification. To measure the pour point, ASTM D97 is used (Standard Test Method for Pour Point of Petroleum Products) and D5950 or D5949 [63].

The cloud and pour points relate to the quantity of saturated fatty acids. The cloud point is directly proportional to the amount of saturated fatty acids. The cloudier and more solidified fuel means the fuel's cloud and pour points are higher.

The bio-gasoline demonstrates a cloud point ranging from -22 to 0°C and a pour point from -19°C to -17°C [61].

2.4.4.3.5. Calorific Value (CV)

It is a rate of energy per mass of fuel, also known as the heating value. The heating value is measured using ASTM D240 (Standard Test Method for heat combustion of liquid hydrocarbon fuels by a bomb calorimeter).

The heating value or the quantity of energy contained in the fuel is the quantity of energy released when a specific volume of a particular fuel experiences combustion [64].

Biogasoline releases less energy (caloric value or heating value) than conventional gasoline (fossil-based fuel). The biogasoline and fossil-based gasoline heating values are 45.9MJ/kg and 47.8MJ/kg [44].

2.4.4.3.6. Lubricity

Lubricity is the lubrication quality of fuel to flow easily. The lubricity of a particular liquid substance is determined after measuring its viscosity [65].

To determine the lubricity of fluid, a thin film of the fluid of interest is used to assess its capacity to prevent two metal surfaces from severe corrosion [65].

There are many methods which are common in the computation of lubricity. Some of those methods are: a high-frequency reciprocating rig test (HFRR), a ball-on-cylinder lubricity evaluator test (BOCLE), and a four-ball wear test; these are ancient methods modelled around 1933 [65]. Lastly, the standards for the wear test are ASTM D2266 for grease and ASTM D4172 B for lubricants.

2.4.4.3.7. Sulfur Content

Sulfur content is one of the significant components of fuel's properties. It is a requirement for fuel to contain less sulfur since it severely affects human health, the environment, and engine performance.

Environmental effect: Sulfur present in fuels is responsible for the nanoparticles emitted in the exhaust gas. These nanoparticle matters cause significant pollution, leading to global warming [66].

Engine performance: It has been discovered that the excess sulfur in fuels cause corrosion inside the engine cylinder [66].

Besides corrosion in the engine cylinder, the excess sulfur produces a series of chemical reactions. These reactions occur during fuel combustion to primarily form sulfur dioxide (SO₂), then the SO₂ is oxidized to SO₃, and SO₃ reacts with water. The late reaction yields sulfuric acid (H₂SO₄). Sulfuric acid causes severe corrosion, damage, and failure to the engine parts. The issues mentioned happen when sulfuric acid condensation occurs on the metal engine's part [67].

Health issue: Gaseous sulfur emission affects humankind's health. The emission of gaseous sulfur causes breathing problems, and prolonged exposure will result in heart disease and eventually cause death [66].

These reasons are enough to alter biogasoline since it provides better qualities than conventional gasoline.

Table 2. 8: Properties of waste engine oil bio-gasoline and commercial (conventional) gasoline [44]

Property	Waste engine bio-gasoline	Commercial gasoline	Test
Octane number or rating	96	89	ASTM D2699
Density at 288K (kg/m ³)	0.732	0.735	ASTM D1298
Sulfur content (%w/w)	0.003	0.002	ASTM D1266
Higher heating value (MJ/kg)	45.9	47.8	ASTM D2015
Flashpoint (K)	245	249	
Dynamic viscosity at 300K (mm ² /s)	1.13	1.17	
Colour	Yellow	Yellow	
Initial boiling point (K)	304	312	
Endpoint (K)	445	454	

2.5. Biogasoline production processes

Several techniques are available for the production of biogasoline. Most methods used to produce biogasoline resemble those used in the petroleum industry with minor modifications [68]. The amendments are experienced on process variables (temperature, pressure, and catalyst) to accommodate the biomass feedstocks with distinctive characteristics to crude oil.

Each biofuel type uses a different production method to convert biomass feedstock since each feedstock requires different approaches. For instance, in biodiesel production from vegetable oil, the

transesterification reaction easily converts vegetable oil to biodiesel [69]. However, transesterification is ineffective in converting waste cooking oils to biodiesel since the impurity in waste cooking oil poisons the catalyst and forms soap. Consequently, the catalyst gets neutralized and weakened and cannot be available for transesterification [70]. The impurities present in the waste cooking oil are high free fatty and rancidity. Because of these impurities converting waste cooking oil to biodiesel via transesterification could produce low-quality fuel [69].

The impurity indicates that converting waste cooking oils to biofuels requires a novel technology. The cracking processes are suitable for converting large hydrocarbon molecules into valuable bits of hydrocarbon molecules [71].

Waste cooking oil (WCO) conversion to biogasoline uses the following processes: catalytic cracking, hydrocracking, and thermal cracking [71].

Cracking methods convert large hydrocarbon molecules into small and valuable molecules. Cracking processes differ based on the conditions used. For instance, catalytic cracking converts biomass into biofuels from moderate to the high-temperature at low pressure. In contrast, thermal cracking converts biomass into biofuel at high pressure and temperature conditions without a catalyst [71].

2.5.1. Catalytic cracking

Catalytic cracking is a thermochemical conversion process that converts long carbon chain molecules (high-weight oil components) to shorter carbon chains (lower molecular weight) in the presence of a catalyst. The catalyst speeds up the cracking reaction, producing a large quantity of the desired higher-octane hydrocarbon. And the higher-octane hydrocarbon produced higher-octane gasoline [71].

Catalytic cracking of waste cooking oil into biofuels is an effective process since the waste cooking oil contains fatty acids such as 10-octadecenoic acid and hexadecenoic acid. These long chains are broken into shorter and smaller carbon chains resembling fossil fuels using catalytic cracking. The cracker has no exact reaction since breaking the long chain results in an unexpected mixture of small functional hydrocarbon molecules [69].

There are several advantages linked to the catalytic cracking technique, such as [72]:

1. It converts biomass into biogas, organic liquid products (OLP), water, and coke. It is essential to know that the large molecules in the waste cooking oil cannot penetrate deep inside the catalyst pores, hence why cracking is restricted to the small reaction site at the catalyst surface.

2. Regarding reaction temperature, the catalyst cracking operates lower than the pyrolysis reaction. Catalytic cracking breaks larger molecules into smaller molecules through dehydration, dehydrogenation, deoxygenation, and decarboxylation.
3. Catalytic cracking is a cost-effective process in terms of energy consumption
4. The presence of the catalyst speeds up the reaction rate and selectivity of the yields.

The catalytic methods or techniques used to produce biofuels yield various products.

2.5.2. Hydrocracking

The hydrocracking catalytic method is used in the refinery to break down the hydrocarbons from low to moderate conditions. Hydrocracking uses a catalyst in gas form, notably hydrogen, to produce shorter-chain hydrocarbon molecules [73]. The shorter chain molecules represent different varieties of petroleum products. According to Mohanty et al. [75], due to the numerous products that yield from hydrocracking, it is not easy to singularize the reaction occurring during this process.

Hydrocracking facilitates the combination of multiple feedstocks, catalysts, reactor configurations, and reaction conditions to yield various products. A pattern that assembles different kinetic models and reaction mechanisms for each set of combinations of states settled through a series of studies [74].

For this research, the use of hydrocracking is not relevant.

2.5.3. Thermal cracking

Thermal cracking is a high-temperature process in which more significant hydrocarbon compounds are converted into more minor chain hydrocarbon compounds without the implication of catalysts [75]. In this process, nitrogen gas is used as a carrier gas at low to moderate pressure. Thermal cracking has been immensely used in the petroleum industry to process crude oil by refining it into lighter products. The modern-day thermal cracking process is used in the production of biofuels. This technique breaks carbon-carbon and hydrogen bonds under severe conditions [75].

The products yielded from thermal cracking are small compared to the reactants. The thermal cracking products are alkanes and alkenes and rarely alkynes. The thermal cracking process is endothermic, requiring considerable energy to break the bonds. Thermal cracking is suitable for temperatures ranging from 400°C to 850°C, with a pressure of 70atm [76].

Modern-day thermal cracking reduces the fuel's viscosity in the so-called visbreaking process. The other version of thermal cracking used in gasoline production is thermal gasoline. Using **thermal gasoline** reduces the gasoline viscosity and yields a maximum recovery of the products (gasoline) [77].

Thermal cracking **delays the coking**, which implies yield maximisation [77].

2.5.4. Two-step process (Hybrid process)

The hybrid method combines transesterification and catalytic cracking to produce biogasoline. Thus, the technique is called a two-step process.

Transesterification

Transesterification is a pre-treatment step before catalytic cracking to enhance bio-gasoline quality. Its purpose is to eliminate toxic compounds such as acrolein and triolein and to decrease coke production, lowering the oil's viscosity.

Transesterification is the primary technique used to produce biodiesel from vegetable oils. It is also essential to know that vegetable oil can potentially replace diesel fuel in engines without being converted via any process. The issue with vegetable oils is their high viscosity. The viscosity is responsible for poor atomization in the engine's combustion chamber, causing an operational problem [72, 78].

It is necessary to use a suitable method to remedy the deficient performance of vegetable oils in diesel engines, hence the induction of transesterification. It is induced by a simultaneous dilution of oils and enhances the resulting fuel's properties [72, 78].

Transesterification is a catalytic method used in the production of biodiesel. Different catalysts are used to enhance the quality of the desired diesel products. The catalyst can be acidic, alkaline, or both in homogeneous and heterogeneous forms; enzymatic catalysts can also be applied in transesterification [79].

Biodiesel production is performed either in batch or continuous mode using transesterification and catalysts in the industry [78]. Alkaline homogeneous catalysts support transesterification. The following catalysts are preferred to convert biomass to biodiesel: sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide. They provide incredible performance, high biodiesel yields and low residence time [78, 80].

The side reactions, neutralization and saponification, cause the catalyst to underperform and render them inefficient. Moreover, these side reactions result in the entrapment of the produced biodiesel in the soap. The amount of soap in the process must remain low to prevent the intensification of side reactions [78].

This study does not consider transesterification as a method that converts waste cooking oil into biogasoline. It is used merely as an advanced pre-treatment step of waste cooking oil before catalytic cracking. Hence, the combination of transesterification and catalytic cracking processes is referred to as a two-step or hybrid method.

2.5.5. The catalyst used in the production of bio-gasoline

The vegetable oils are cracked and converted into bio-gasoline in the presence of a selected catalyst, hence why the process is called catalytic cracking [3, 4].

Several studies used zeolite catalysts to convert vegetable and other oils into bio-gasoline. Zeolites are extremely useful as catalysts. Their characteristics allow them to adapt to reactions involving organic molecules, such as cracking, isomerisation and hydrocarbon synthesis. Zeolites increase the activity of numerous catalytic reactions, including acid-base and metal-induced reactions [81].

Catalytic cracking breaks down fatty acids under moderate conditions of temperature and pressure. The catalytic cracking technique aims to break down fatty acids, which are directed and changed with different reaction paths [82].

A catalyst is first used as an active site to crack or break down fatty molecules. Later, the catalyst acts as an additional source of hydrogen atoms for the chains [3, 4].

The choice of the catalyst proves to be fitting and encouraging in transforming triglycerides into bio-gasoline [83]. Xu et al. [84] emphasized that using catalysts in biogasoline production prevents the additional cost of purchasing other chemicals, such as ethanol and methanol.

The table below presents the type of catalyst, operating conditions, the reactor used, and yield.

Table 2. 9: Biogasoline production from vegetable oil by the catalytic cracking process using zeolite catalyst[85]

Feed	Catalyst	Operating Condition Temperature	Operating Time (Hour)	Type of reactor	Biogasoline Yield	Reference
Palm Oil	HZSM-5	360-420	2-4	FBR	40-70%	[86]
Palm Oil	HZSM-5, β -zeolite, USY	350-450	1-4	FBR	28%	[87]
Palm oil	HZSM-5	400-450	2.5-4.5	FBMR	44.4% wt	[88]
Palm oil	REY Zeolite	400-500	10s, 20s, 30s	TRR	59.1% wt	[89]
Palm oil	REY Zeolite	450	20s	TRR	30-40%	[90]
Bio-oil	Zeolite, ZSM-5	450-500	15min	HPR	91.67%	[91]
Palm oil	HZSM-5	350-500	2	FBMR	28.87%	[92]
Coconut	HZSM-5, HY	450	30s – 30h ¹	FBR	26.9 – 40,1%	[93]
Palm oil	HZSM-5	350-500	2	FBMR	17.11%	[94]
Jatropha oil	HZSM-5	400	1	FBR	11.6%	[94]

Rapeseed oil	HZSM-5	550	1-3	FBD FR	11.6%, 32-41% (C ₅ -C ₁₀)	[95]
Microalga chlorella	ZSM-5	350	30min	FBR	19.4%	[96]
Soybean	USY, β -zeolite, HY, ZSM-5	360	7h ⁻¹	FBR	70%	[97]
Rubber Seed oil	HZSM-5	400-440	1,5,2	PR	50.9%	[98]
Bio-oil	NaY/USY				63.6-71.8%	-
	HZSM-5, Zeolite	340-430	15-20min	FBR	29.9%	[99]
Cotton Seed oil	Y-Zeolite	480-540	30min	FBR	46-55%	[100]
Rapeseed oil	ZSM-5, HZSM-5	550	1-3	FBD FR	>32%	[95]
Palm oil	HZSM-5	420	2	BR	14.8%	[101]
Sunflower oil	Na/HZSM-5	450-550	1	TBR	Liquid product, >80%	[102]
Waste tire	Natural zeolite	300-600	25, 30, 60, 85min	BR	Light hydrocarbon (biogasoline, biodiesel) 12%	([103])
Soybean oil	NaZSM-5, HZSM-5	453	2	FBR	50.77%	[104]

Table (2.9) above shows that using a zeolite catalyst yields a significant amount of bio-gasoline; however, none of these studies used waste cooking oil as feedstock to produce bio-gasoline from the catalytic cracking process.

To produce biogasoline from catalytic cracking using WCO. The catalyst of interest was synthesized using two inorganic compounds and γ -aluminium oxide, like some catalysts used to make bio-gasoline from the hydrocracking process. Table (10) below shows that no studies used waste cooking oil as feedstock.

Table 2. 10: catalyst used to produce biogasoline via hydrocracking [3, 4].

Feeds	Catalyst	Bio-gasoline Yield	Reference
Fresh cooking oil	Commercial catalyst	10%	[105]
Used cooking oil	Commercial catalyst	8	[105]
Calophyllum inophyllum oil	Co-Mo/ γ -Al ₂ O ₃	25.63	[106]
Calophyllum inophyllum oil	Co-Mo/ γ -Al ₂ O ₃ -SiO ₂		[106]
Vacuum	ASA/Ni-MO+ β	23.4	[107]

Tables (2.9) and (2.10) suggest that the performance of catalysts used to produce biogasoline is not satisfying since the yield is low. Asri et al. [94] proposed the modification of the zeolite catalyst by adding metals such as copper, nickel, and zinc to improve the catalyst's performance. These metals' presence significantly affects biogasoline yields [85, 108].

Table (2.11) presents the studies conducted following the recommendation suggested by Asri et al. [94].

Table 2. 11: Biogasoline production from vegetable oil by the catalytic cracking process using modified zeolite catalyst with the addition of metals [85]

Feed	Catalyst	Temperature (°C)	Reaction time(hour)	Reactor	Biogasoline yield (%)	Reference
Palm oil	NiMo/zeolite	300-320	1, 1.5, 2	BR	11,93	[92]
Palm oil	Au/HZSM-5	330-550	1	FBMR	4 – 15	[85]
Palm oil	Zn/HZSM-5	350-500	2	FBMR	28,38	[94]
	Cu/HZSM-5				18,05	
	Ni/HZSM-5				17,55	
Rapeseed oil	Ni/HZSM-5	550	1 – 3	FBDFR	32 – 37	[95]
	Mo/HZSM-5					
Palm oil	HZSM-5	350-550	2min	FBR	9 – 23	[109]
	Pd/HZSM-5					
	Pt/HZSM-5					
Carinata oil	Zn/Na-ZSM-5	450, 500, 550	0,2; 0,6; 1	FBR	Hydrocarbon biofuel	[110]
Rapeseed oil	Ni/ZSM-5	550	1 – 3	FBDFR	32 – 41	[111]
	Ni/HZSM-5					
Camelina oil	Zn/ZSM-5	450, 500, 550	1.0 h ⁻¹	FBR	Hydrocarbon biofuel	[110]
Callophyll uminnophyllum L. oil	NiMo/zeolite	350	2	ABR	n-paraffin (C ₁₀ – C ₁₉) 59,5	[112]
Callophyll uminnophyllum L. oil	NiMo/zeolite	350	2	ABR	< 15	[113]
Coconut oil	Ni/MNZ	360, 410, 450, 500	-	FBR	11,73	[114]
Cerbera manghas	Co-Ni/HZSM-5	300 – 375	2	BR	1,97	[115]
Palm oil	Zn/HZSM-5	300, 400	1	FBR	2.54	[116]

Budianto et al. [109] used two metals, lead (Pb) and platinum (Pt), to improve catalyst performance. Pb and Pt are transitional metals [84], and the mobility of their peripheral electrons facilitates reaction, especially in breaking covalent bonds during the cracking process [85]. In search of improving catalyst performance, the zeolite catalyst undergoes other modifications by adding elements such as sodium. However, they did not yield biogasoline, as seen in Table (2.11) with the investigation by Zhao et al. [110], resulting in hydrocarbon biofuels [117].

2.6. Biogasoline optimization

Several tools have been designed and developed recently to provide a helping hand in the optimization of analytical methods, mainly when multivariate techniques are used in an experimental procedure.

The benefit of using these tools is that they reduce the number of experiments, and consequently, fewer reagents and less laboratory work. In addition, the optimization techniques assist building mathematical models. The mathematical models developed are used to assess the consistency of the results and the statistical representation of the effects studied and evaluate the interaction effects between factors [118].

The constraint to using the optimised univariate factors' interaction effect to model the multivariate factors' interaction effect is that these interactions must not be significant; otherwise, they differ from the correctness of the result provided. Suppose the interaction effects of the univariate optimized factors are substantial. The result implies a difference between the univariate and multivariate strategies [118].

In case of a significant interaction effect of the optimized factors, the univariate optimisation results will be considered inconsistent and discarded. The inconsistency of univariate optimization results is down to the fact that the effect of one variable can be dependent on the level of the others involved in the optimization, hence why experiment designs are optimized using the multivariate optimization techniques since these techniques yield consistent and reliable results [118].

In the investigation of bio-gasoline production, the box-Behnken design multivariate optimization design tool is of interest.

2.6.1. Box-Behnken design optimization method (technique)

Box-Behnken design (BBD) is a rotatable second-order design based on three-level incomplete factorial designs.

For three factorial box-Behnken design methods, two graphical representations are considered [118]:

- A cube is a method with three points, one positioned in the centre (a midway point) and the other in the middle of the cube's edges.
- A figure of three interlocking 2^2 factorial designs as well as a central point

In the Box-Behnken model, the number of experiments is defined by the following correlation [118]:

$$N = 2k(k - 1) + C_o$$

With: N : number of run,

k : number of factor

C_0 : number of central point

There are quite a few surface design multivariate methods, to mention a few: central composite, Doehlert Matrix (DM), and three-level complete factorial design; however, BBD is an efficient model regardless of the number of factors considered or computed. Techniques such as three-level full factorial designs cannot cope with the higher number of factors that surpass two. Furthermore, the application or use of BBD does not necessarily require the implication of all factors simultaneously used at their highest or lowest levels. For these reasons, this method is crucial since it can assist in eradicating experiments performed under severe conditions, resulting in unsatisfactory results [118].

The BBD scheme can optimize various methods: electroanalytical, chromatographic, and capillary electrophoresis.

2.6.2. Optimization model

Often, the theoretical model that links dependent variables (factors) to a response is not always available. The available model is complex because an empirical model relates dependent variables to their response [119].

The optimization concerns the following factors: reaction temperature, nitrogen flow rate and weight hourly space velocity (WHSV). WHSV is the ratio of the nitrogen flow rate to the catalyst weight.

These factors affect the cracking process of WCO and influence the organic liquid product quality.

The regression model was used to predict the response based on a second-order polynomial model [1]:

$$Y_{biogasoline(\%)} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{1,2} X_1 X_2 + \beta_{1,3} X_1 X_3 + \beta_{2,3} X_2 X_3 + \beta_{1,1} X_1^2 + \beta_{2,2} X_2^2 + \beta_{3,3} X_3^2$$

$Y_{biogasoline(\%)}$: response

β_0 : constant coefficient

$\beta_i, \beta_{i,i}, \beta_{i,j}$: are interaction coefficients of linear, quadratic and second order terms respectively

$X_{i,ii,ij}$: independent variables

2.7. Reactor Unit

The pyrolysis reactor is the fixed bed reactor investigating bio-gasoline production by catalytic cracking of waste cooking oil. The cracking methods require an elevated temperature to break down heavy and light

hydrocarbon molecules. Waste cooking oil contains heavy hydrocarbons. Heavy hydrocarbons have several disadvantages that prevent vegetable oil from being considered fuel without being processed [120].

One of the disadvantages related to the use of vegetable oil is its high viscosity. That is why bio-gasoline production by catalytic cracking of waste cooking oil uses a fixed bed reactor. The fixed bed reactor unit comprises a fixed bed containing the feeds (waste cooking oil). The reactor operated in batch mode [120].

The fixed bed reactor can process both solids and liquids. When solid particles are processed, the reactor's feed capacity can contain ± 45 grams in the material weight to be processed. Regarding liquid material, the maximum volume of material to be processed cannot exceed 100ml. The feed's density determines the weight and volume of the material to fit in the reactor. The energy required to process the material can reach a maximum temperature of 1200°C [120].

Aziz et al. [121] stated that the conception and design of the fixed bed reactor are reliable and straightforward to process feeds such as waste cooking oil. Aziz et al. and Van Rensburg et al. [121, 122] added that the feedstock system of the fixed bed reactor is suitable for small-scale projects.

According to Van Rensburg et al. [123], the products are formed through thermal devolatilization. Thermal volatilization yields heavy oil and volatile components (condensable, non-condensable or permanent gases). The condensable volatile is sent to the condenser to be cooled. The resulting products from the condensable volatiles are organic liquid products (OLP) and permanent gases.

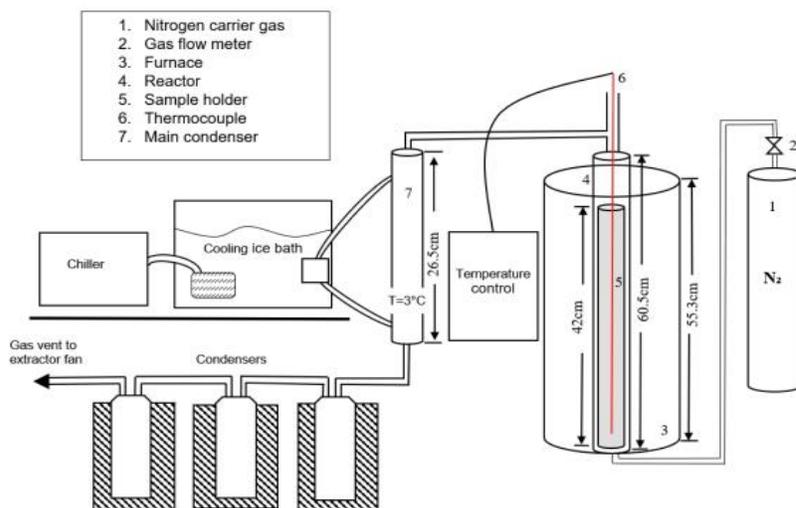


Figure 3. 1: Schematic set-up [122]

CHAPTER THREE: Equipment Description

3.1. Introduction

This chapter aims to represent the experimental setup and briefly overview the materials that facilitated biogasoline production using waste cooking oil.

3.2. Materials used

Table 3. 1: Raw materials

Raw material	Supplier	Purity
Waste cooking oil	Collected after domestic used	
Chlorine acid (HCl)	Merck	37.5%
Sulfuric acid	Merck	95 – 99
Nitric acid	Associated chemical enterprises (ACE)	55%
Methanol (CH ₃ OH)	Sigma – Aldrich	≥ 99.8 %
Iso propanol	-	99%
Potassium Hydroxide (KOH)	Merck	56.11%
Cobaltous nitrate hexahydrate	Associated chemical enterprises (ACE)	Analytical grade (AR)
Ammonium molybdate tetrahydrate	American chemical society (ACS)	Analytical grade (AR)
Aluminium oxide	Associated chemical enterprises (ACE)	Analytical grade (AR)
Nitrogen gas	Afrox	≥ 99.5%
Ice cube	-	-
Dry Ice	Afrox	-

3.3. Equipment used

Table 3. 2: Equipment

Equipment	Description
Crucible	Uses to hold the catalyst for the calcination process
Pipette	Measures acids volume accurately and safer
Propipette (Pipette filler)	Uses as a vacuum source to fill acids through the pipette
Micropipette	Measures micro-volume during the preparation of standard solution for ICP-OES analysis
Microfilter (0.45 μ m)	Facilitates filtration of bio-oil produced before GC-MS analysis and catalyst solution before ICP-OES analysis
Hot plate	Facilitate heating of the solution
Measuring cylinder (25, 50, 500ml)	Facilitates volumetric measurement of waste cooking oil and other liquid
Separation funnel	It separates the oil, water, and aqueous solution mixture during the pre-treatment stage. It was also used to separate glycol and ester after transesterification in two steps process.
Stirrer bar	Ensuring the homogeneity of the solution. Used in the preparation of solution to use for ICP-OES analysis.
Thermometer	Enables suitable temperature adjustment to maintain isothermal conditions.
Water bath	Supplies cold water to condenser to facilitate condensation oil vapour.

3.4. Experimental Setup



Photograph 3. 1: Laboratory set-up used to produce biogasoline

The reactor is designed with a tube that contains the sample to be processed. The process is a high-temperature process without oxygen [123].

Nitrogen gas flows into the reactor under a constant flow rate, temperature and pressure to create an inert environment. Nitrogen gas plays a double role in the study: an inert environment creator and gas carrier. During the reactor's operation, chemical and physical transformations occur as the reaction proceeds, and the resulting product separates into small hydrocarbon molecules.

The cooling system used in the setup was composed of a chiller and an ice bath connected to the condenser to create a cold environment at 5°C. The products were collected in three receivers or collection flasks. Two of the three receivers were immersed in ice to condense the volatiles condensable to organic liquid products from waste cooking oil feedstock. The additional receivers or collection flasks were necessary to prevent loss of liquid fraction. The non-condensable gases flowed through a vent into an extractor fan.

CHAPTER FOUR. Experimental Procedures and Analysis Techniques

4.1. Introduction

This chapter aims to describe the steps taken in the laboratory to produce bio-gasoline. There are steps used in making bio-gasoline by catalytic cracking of waste cooking oil: pre-treatment of waste cooking oil, catalyst synthesis, thermal cracking, catalyst cracking, combined catalyst cracking and transesterification (two-step process), and catalyst characterization.

4.2. Waste cooking oil pre-treatment

The oil used for this study contained impurities since it was used and contained particles. It was required to remove those impurities as they are a potential nuisance to the catalyst performance by blocking active sites and taking part in some reactions. The waste cooking oil needed to undergo pre-treatment to prevent the catalyst from being poisoned in the case of catalytic cracking and poor yield in the case of thermal cracking.



Photograph 4. 1: waste cooking oil

The pre-treatment process is conducted to purify waste cooking oil (WCO). The flowsheet below was used to pre-treat waste cooking oil.

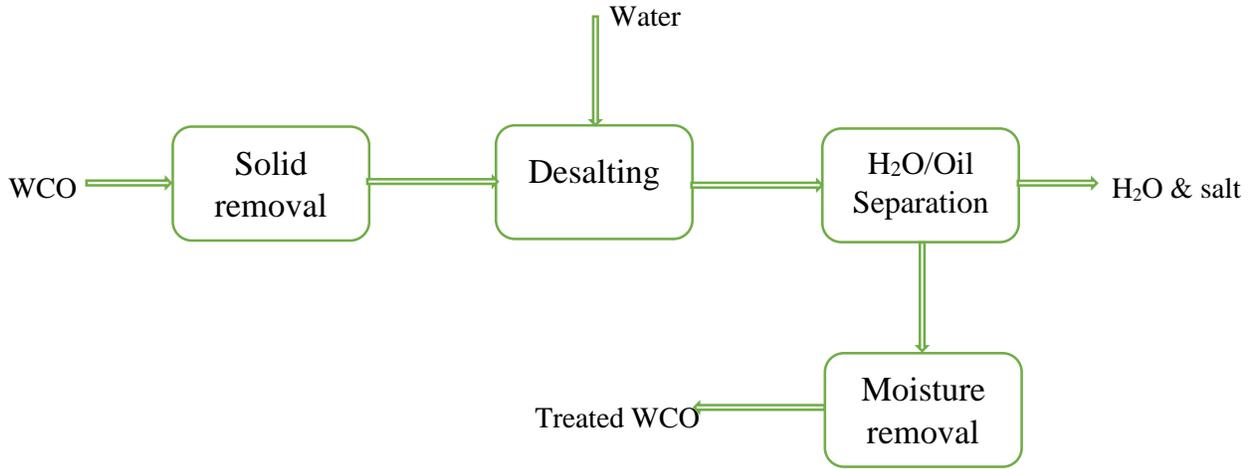


Figure 4. 1: Waste cooking oil pre-treatment process [3, 4]

4.2.1. The solid particles removal

Three sieves were set as follows: 1000, 425, and 300 μ m, the purpose of sieving the oil was to remove any solid particles in the oil. The sieves were set up on the pulverisette used in the mineral processing for pre-crushing. The large aperture sieve was placed on top of the setup, and the small aperture size sieve was placed at the bottom. The pulverisette was timed for 10 minutes.

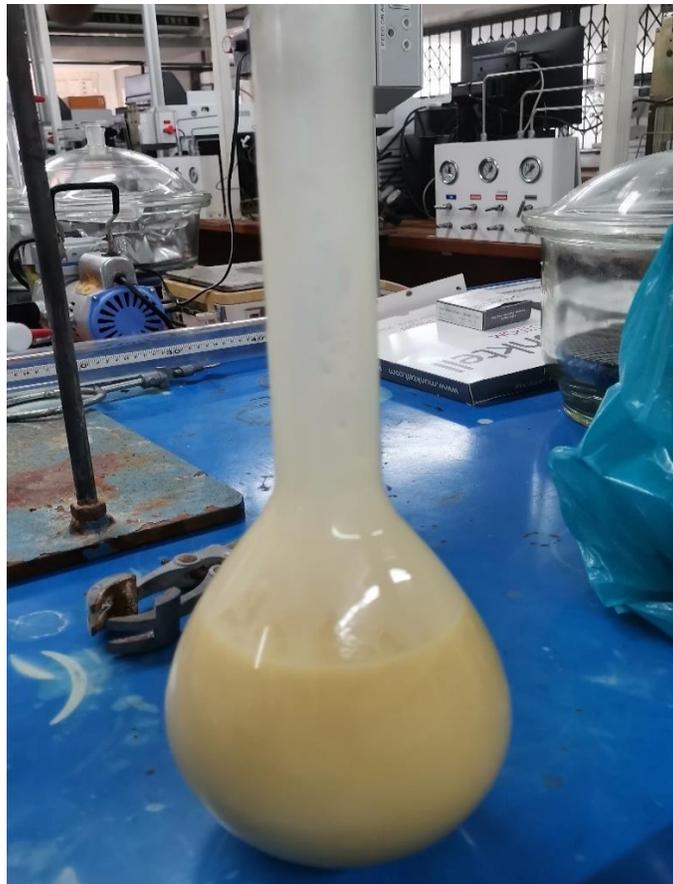


Photograph 4. 2: Solids particles removal set up

4.2.2. Desalting

Waste cooking oil contains salt, and salt is poisonous to catalysts. The removal of salt from the oil prevents catalysts from poisoning. The oil must be clean of all impurities to yield a better catalyst performance, and salt in the catalyst can harm the fuel's quality.

The desalting process is performed by adding water to the oil. Salt is dissolved, and one litre of waste cooking oil dissolves in two litres of water. After adding water to the oil, the mixture was vigorously shaken and left for 24 hours to allow the Salt to move from the oil to an aqueous solution before decanting. The oil-treated and separated was then heated at 100°C for 30 minutes to remove any remaining water.



Photograph 4. 3: Mixture of oil and water



Photograph 4. 4: Decantation: separation of oil and water



Photograph 4. 5: Heating of oil to remove the remaining water

4.3. Catalyst preparation

This study used a cobalt-molybdenum catalyst supported on aluminium powder. In preparing the catalyst of interest, the impregnation technique of the aluminium oxide with a solution composed of dissolved cobalt and Molybdenum was used [124].

As mentioned in the catalyst review paragraph that zeolites are either acidic or alkaline. For this study, the catalyst used is an acidic zeolite. An HCl solution of 37% concentration in mass was diluted in water to make the required acidic solution (pH=2).

After preparing the acidic solution, five samples of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ and cobalt nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$ were weighed in different mole ratios, respectively (1:1, 1:2, 1:3, 2:1, 3:1). Each mole ratio was dissolved in the acidic solution (pH=2).

After the dissolution, aluminium oxide (Al_2O_3) was added to the dissolved solution to form five slurries formed. The size of aluminium oxide added ranges from 63-200 μm .

The aluminium oxide powder impregnated the catalyst, considered a compensator for void volume. The void volume was calculated using the equation provided below. Considering that the impregnation consisted of sufficient support wetting, the quantity of aluminium oxide used was enough to cover the void. It has been found that 10g of Al_2O_3 contained a void volume of 7.5 ml. That was the amount of solution added to synthesize the catalyst.

$$\text{Voidage volume} = \text{measured } \text{Al}_2\text{O}_3 - \frac{\text{Al}_2\text{O}_3 \text{ measured mass}}{\text{Al}_2\text{O}_3 \text{ density}}$$

The slurries were then placed in the oven at 120°C for 24 hours to remove water, and then the catalyst samples were dried. The catalyst sample calcination temperature was 600°C for 4 hours in the furnace.

Different analytical techniques characterised the catalyst samples to determine the equimolar metal mole ratio. After deciding, the equimolar metal ratio was calcined at different temperatures ranging from 300°C to 700°C at an increment of 100°C.

The catalyst can be moist when exposed to open air since the humidity can potentially deactivate the catalyst when it reacts with sulfuric trioxide in the catalyst to produce sulphuric acid. Sulphuric acid production deforms and degrades the catalyst [125]. For this reason, the catalyst was stored in a desiccator.

4.4. Thermal cracking

The pyrolysis reactor is the unit used to perform a thermal cracking process at elevated temperatures.

- 50ml of waste cooking oil was poured into the tube for each run, and
- The reactor was switched on; the reactor temperature was set,
- The nitrogen gas (carrier gas) knob was turned. The carrier gas was used to transport the gaseous products to the condenser. The gaseous product was condensed into an organic liquid product (OLP).
- The OLP was collected in three receivers or collection flasks. The first receiver sets in an ice bath, the second in an ordinary ice bath, and the third in a dry ice bath for the entire experimental procedure.

This conclusion is based on the estimation for conventional gasoline that boils in the range of 30-220°C (Government of Canada, n.d).

The thermal cracking method ran at temperatures ranging from 400 to 500°C at an increment of 50°C. The thermal was performed to study the effect of the reaction time at different temperatures. Since the carrier gas flow rate does not affect the product, the gas pressure and temperature were constant, 50kPa and 25°C. The cooling system consisted of a bath, and the chiller operated at 5°C. The system setup was monitored to prevent any gas leaks.

The variables for this study were furnace temperature and reaction time.

4.5. Catalytic cracking

The catalytic cracking method was carried out at elevated temperatures as performed in the previous process; however, the catalytic cracking used a catalyst to break long chains.

- The catalytic cracking was carried out at the atmospheric pressure with a temperature range of 400-550°C and the carrier gas pressure at 50kPa using a fixed bed reactor.
- The temperature varied at a rate of 75°C.
- The waste cooking oil and the catalyst were mixed in different portions before the reaction.
- The experiment was conducted at different reaction temperatures, catalyst calcination temperatures, reaction times, and catalyst/oil ratios.
- The oil volumetric flow rate was kept constant while the catalyst mass varied from 1 to 5 grams.
- The reactor effluent was carried to the condenser system by the nitrogen gas used as carrier gas. The reactor effluent was cooled to 5°C and collected in a receiver or collection flask at room temperature.

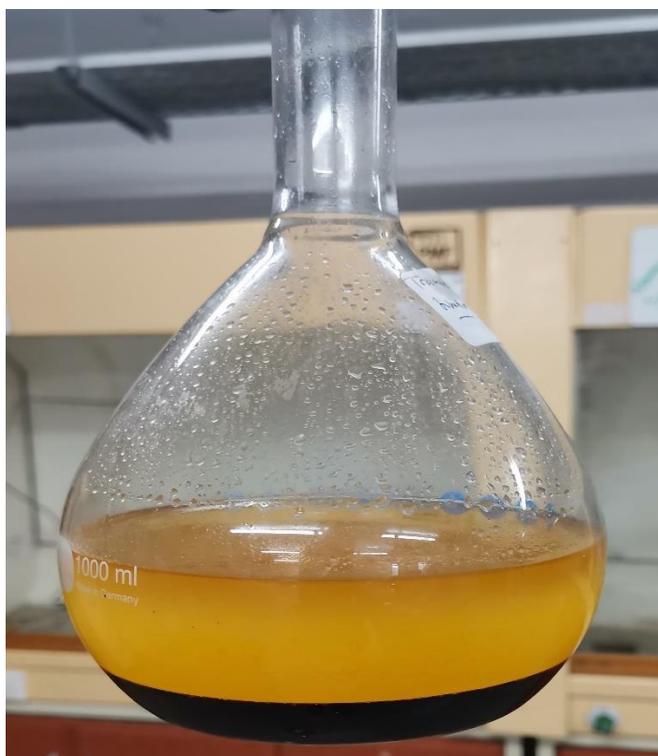
This method investigated the reaction temperature, the calcination temperature, the ratio of catalyst oil, and the weight hourly space velocity.

The organic liquid product was then analyzed using the gas chromatography-mass spectrum (GC-MS).

4.6. Two-step process (Hybrid method)

The so-called hybrid technique, as mentioned, it is a combination respectively of transesterification and catalytic cracking. The waste cooking oil has undergone further treatment before the catalytic cracking in the fixed-bed reactor.

- Two hundred millilitres of methanol were measured and poured into a flask. 8.5 grams of potassium hydroxide was weighed and poured into the methanol flask.
- The mixed stirred and heated up at 60°C for a complete dissolution of potassium hydroxide. The solution obtained was mixed with the oil.
- The mixture was left to settle for 24 hours.
- The mixture underwent the standard catalytic cracking procedure to produce bio-gasoline, as mentioned in paragraph 3.4.



Photograph 4. 6: Transesterification product (mixture bio-oil and soap)



Photograph 4. 7: Decantation: separation of bio-oil and soap prior to the catalytic cracking process



Photograph 4. 8: Final transesterification product (bio-oil)

4.7. Technical analysis

Several technical analyses were carried out on the catalyst, the reactor effluents, and the raw materials (waste cooking oils).

The following analyses were performed on the catalyst synthesized:

- X-ray diffraction (XRD): composition analysis of the catalyst
- Inductively coupled plasma optical emission: spectroscopy (ICP-OES): Elemental compositions
- Scanning and Transmission Electron Microscope (SEM): Morphology

The following techniques were used to analyze the waste cooking oil and reactor effluents (products):

- Gas Chromatography-Mass Spectroscopy (GC-MS): composition
- Volume and Mass measurement: Density
- Viscosity measurement
- Thermogravimetric analysis

4.7.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is an analytical technique for investigating materials and thin films. The application of XRD is practical, depending on having a crystalline material. XRD is a bulk-sensitive analytical method. Its application can be extended to investigate surface changes in appropriate circumstances [126].

The instrument used to conduct the analysis is an OEM Rigaku MiniFlex 600. The following parameters were adjusted to perform the XRD:

- Scan range: 10 – 90 2theta
- Step size: 0.02 2theta
- Scan rate: 10 2theta
- Cu radiation.

4.7.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The ICP-OES analytical technique is a laboratory technique that analyses the composition of the element containing several metals. The use of ICP-OES is to quantify the ratio of metal in the catalyst.

This technique is two steps analysis. The first step is the preparation of samples, and the second is preparing the standard solutions.

4.7.2.1. Samples preparation

The samples preparation follows the steps below:

- One gram of nanocatalyst was diluted in 20ml of nitric acid and sulfuric acid, respectively, 16ml of nitric acid (55% concentrated) and 4ml of sulfuric acid (98% concentrated).
- Adding 80ml of deionized water to make it 100 ml
- Heating the mixture for 40minutes
- Cooling the mixture at room temperature
- Finally, filter the mixture with 10 ml of deionized water.

The samples were prepared to undergo standardization since the ICP-OES function of the standard solution.

4.7.2.2. Standard solution preparation

The standardization follows the steps below:

- Dilution of 70ml nitric acid (HNO₃) into 800ml of deionized water and mix well by shaking.
- Steady the flask and cool the solution at room temperature
- Addition of deionized water to make the final 1000ml volume

The dilution relationship needed to prepare the standard solution:

$$V_s = \frac{C_w x V_f}{C_s}$$

C_s: Concentration of primary solution (stock solution)

C_w: Desire concentration of working standard solution (in ppm)

V_f: desire final volume (in ml) of working standard solution

V_s: volume (in ml) of primary standard (stock) solution required to be diluted with de-ionised water to prepare standard solution

4.7.3. Scanning and Transmission Electron Microscopy (SEM & TEM)

Microscopy analysis is vital to other analytical techniques, such as X-ray diffraction. This technique envisages a particle's structure and assigns a function to each form and vice versa.

The quality of the image depends on the resolution of the equipment used to analyze the sample. There are two image resolution types: higher resolution power and light microscope. Higher resolution power is used to image cellular components' ultrastructure [127].

The law of Ernst Abbe states that the limit resolution of an optical system is a function of the numerical aperture and the wavelength of light. This law is also applicable to an electron whose speed determines its wavelength. Through this law, we can conclude that a better resolution results in the remarkable speed of the electron and a smaller wavelength [128].

This study examines two variants of microscopy tests: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In scanning electron microscopy (SEM) analysis, a bulk sample is scanned with a focused electron beam, resulting in a surface view of the material's structure of interest. In transmission electron microscopy (TEM) analysis, the electrons transmit a thin sample to form a projected sample image. These methods use the acceleration voltage to analyse materials.

The acceleration voltage is the parameter used in microscopy analysis to determine the speed of the electron. The study runs at an acceleration voltage of 100kV, the resolution in transmission electron microscopy is approximately 0.5nm, and the resolution in scanning electron microscopy is about 1nm.

The current analysis yields better resolution than biological specimens because of the preparation of the material. The SEM and TEM were conducted in the following manner:

4.7.3.1. Scanning electron microscopy (SEM)

- The sample was mounted onto aluminium scanning electron microscopy studs with double-sided adhesive carbon tape. These studs were gold coated with a Quorum K150 RES sputter coater.
- The samples were imaged with a Zeiss Ultra Plus FEG SEM.
- EDX was performed, and EDX was obtained with an Oxford X-Max EDX detector.

4.7.3.2. Transmission electron microscopy (TEM)

- Approximately 10ug (micrograms) of catalyst was placed in an Eppendorf tube with 500ul(microlitres) of ethanol used as a solvent (100%).
- The tube was sonicated for 10 minutes
- A carbon-coated formvar transmission electron microscopy grid was dipped into the solution and allowed to air dry
- Images were captured on the JEOL 2100 HRTEM (Japan)

4.7.4. Gas Chromatography and Mass Spectrometry (GC-MS)

Gas chromatography and mass spectrometry (GC-MS) is an analytical technique used to analyse and determine different molecules contained in a substance. GC-MS is used to analyse various substances, including biological samples. The GC-MS analytical approach is appropriate for analysing lesser molecules

in substances such as fatty acids, aromatics, alcohols, and benzene. Several institutes use GC-MS, including the US National Institute of standards, for the conclusive methods standard reference.

Waste cooking oil and reactor effluent underwent two different analyses: GC-pyrolysis and GC-MS.

The GC-MS(PEGA/PY-3030D) has the following features DB5+MS:

- Rapid heating (600°C/min) and cooling (100°C/min)
- High-temperature pyrolysis up to 1050°C
- Superior performance due to exact temperature control, an inert sample pathway, no dead volumes, no cold spots
- Dedicated samplers for sample induction, e.g. Micro Reaction Sampler. UV Sampler

For the waste cooking oil (treated and untreated), 1.5µL of each sample was analyzed using the pyrolysis side of the GC-MS under the following conditions:

For bio-oil, 0.3µL of each sample was analyzed to determine the composition of the products. For the waste cooking oils, the analysis determined whether the sulphur content and other impurities were eliminated or decreased.

Table 4. 1: GC-MS operating conditions

Initial temperature	Temperature rate	Final temperature	Final time	Total time
100°C	50°C	500°C	1minute	9minutes

4.7.5. Volume and Mass measurement: Density

Mettler Toledo is the instrument used to measure the density of biogasoline produced. It is necessary to calibrate the device before measuring the density. Isopropanol was used to calibrate and clean the instrument after each run, then dry it. Drying the subsequent measurement was required to prevent the device from getting a wrong reading.

The measurement was conducted at 20°C, and to inject the sample in the Mettler Toledo density 10ml syringe was used.



Photograph 4. 9: Density meter

4.7.6. Viscosity measurement

The Brookfield viscometer was used to measure the viscosity of biogasoline produced. Before conducting the measurement, it is necessary to assemble the different parts of the instrument and set the device in operating mode. Standalone was the operating mode set for this experiment because the viscometer was used with any external device, such as a computer.

The viscometer device operated under the following conditions: spindle speed of 30RPM and temperature of 21.6°C.



Photograph 4. 10: Viscometer

4.7.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is thermal testing investigating changes in substance weight with changes in temperature conditions [129].

This analytical technique investigates the thermal stability of the organic liquid oil and the regeneration cycle of catalysts. The analyzed substance is thermally stable if there is no significant change in its properties during heating at a given temperature or time. Thermal stability indicates the quantity of volatile matter present in the material analyzed. The property under consideration during TGA is weight loss. The change in weight of the material under consideration is a function of temperature or time[129]. The weight loss vs temperature or time graph generates a curve to identify the temperature (or time) at which the most apparent weight loss is [1].

Thermogravimetric analysis is a vital technique used in research and testing since it determines the characteristics of materials to determine degradation temperature [1].

Two types of analyses are carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry. These two valuable techniques (methods) examine the consumed catalyst's combustion characteristics over temperature.

4.7.7.1. Thermal stability

The analysis conducted for this study was performed using 20mg of organic oil at the rate of 20°C per minute for a temperature range of 100°C to 800°C (373K to 1073K).

4.7.7.2. Catalyst regeneration temperature investigation

The material used in laboratory research and industry to control the rate and selectivity of a chemical reaction is called a catalyst. The design of a catalytic process intends to use the catalyst without changing its mechanical, physical, and chemical properties; unfortunately, these properties have altered. The alternation (modification) that the catalyst undergoes affects its activity and, more often, its selectivity. The technical name for the alternation experiences by a catalyst is deactivation. Both heterogeneous and homogeneous catalysts deactivate. Attention to heterogeneous catalysts is vital since this type contains several metals. Numerous parameters affect the stability of the solid catalysts, and through these parameters, the catalyst deactivates.

The catalyst deactivates through:

- Poisoning: this phenomenon occurs when strong chemisorption of species deposits on the activated site of the catalyst. The species that poison the catalyst is often in the feed.

- The formation of coke deposits on the catalyst occurs either by fouling or by the catalyst itself or else via coking (formation of coke). The formation of coke is a thermal transformation of feed components.
- The chemical composition and structure of catalysts change during metal sintering which is caused by sulfur poisoning, dealumination, and collapse of zeolite. The changes mentioned take place at elevated temperatures in an aqueous solution.
- Mechanical degradation of a catalyst can result from intentional or unintentional mechanical stresses. A catalyst can be subject to various types of mechanical stresses that lead to deactivation, including crushing, attrition, abrasion, and erosion.
- Leaching of active species takes place when fine particles in the liquid phase are synthesized.

Catalysts can undergo two types of deactivation: reversible and irreversible. Reversible deactivation happens when the catalyst's active site is leached out over time. Irreversible deactivation occurs when the catalyst can no longer be recycled or used again.

Catalysts can be rejuvenated or regenerated through treatment in the same or different reactor unit used for the catalytic process under similar or different operating conditions.

A catalyst's regeneration cycle involves determining the appropriate regeneration temperature and calcination temperature for the production of biogasoline via catalytic cracking of waste cooking oil.

CHAPTER FIVE: Results and Discussion

5.1. Introduction

The main objective of this chapter is to provide a comprehensive analysis of the experimental work conducted, and to compare the results, whenever applicable, with existing literature. The results of this chapter include the different techniques used for catalyst synthesis analysis, feedstock analysis, biogasoline analysis, and various methods used for biogasoline production.

5.2. Catalyst characterization

The catalyst synthesis used in this study underwent different characterization techniques to determine the composition, morphology, size, and regeneration temperature.

5.2.1. X-ray diffraction (XRD)

The catalyst samples were analyzed using X-ray diffraction (XRD) to determine the crystallinity and different phases present. XRD analysis involved two categories of samples: catalyst samples with varying calcination temperatures and the catalyst sample with a varying mole ratio of metal ions.

5.2.1.1. Variation in calcination temperature of the catalyst samples

X-ray diffraction (XRD) analysis was used to investigate the effect of varying calcination temperatures on the catalyst sample. The first set of graphs represents the different calcination temperatures.

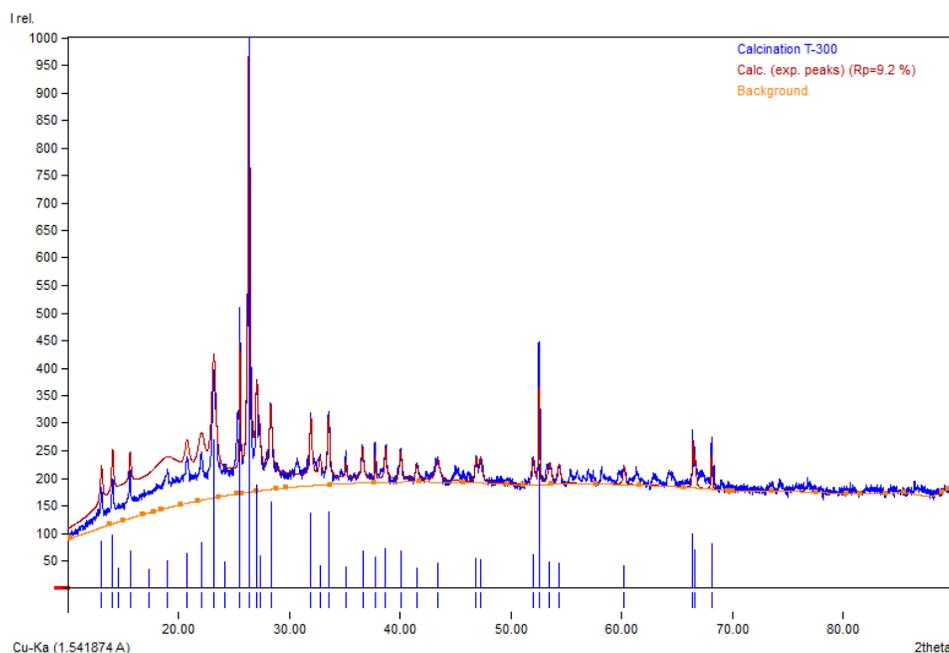


Figure 5. 1: Catalyst calcined at 300°C at a constant mole ratio

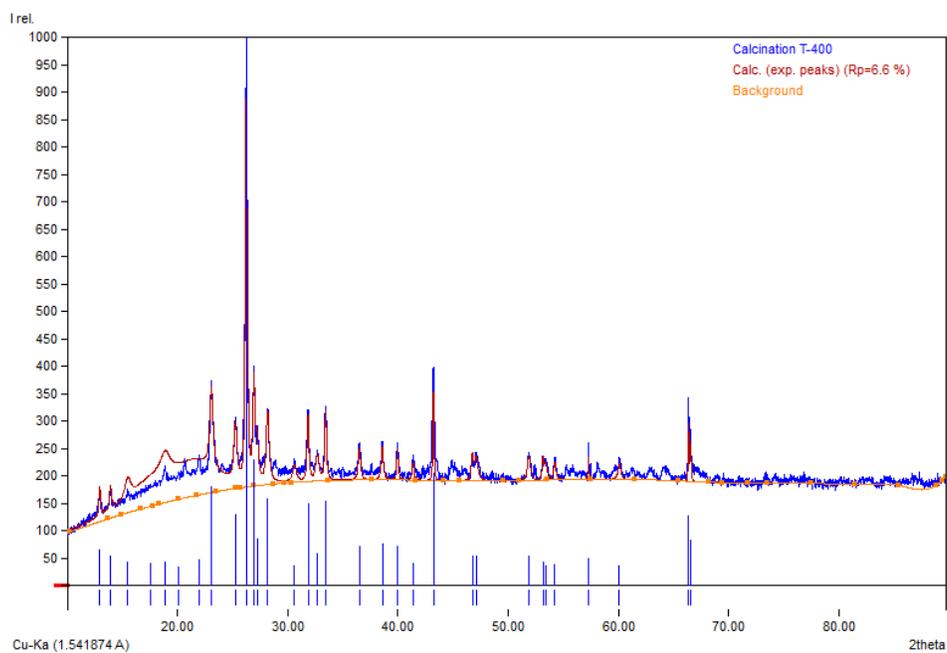


Figure 5. 2: Catalyst calcined at 400°C

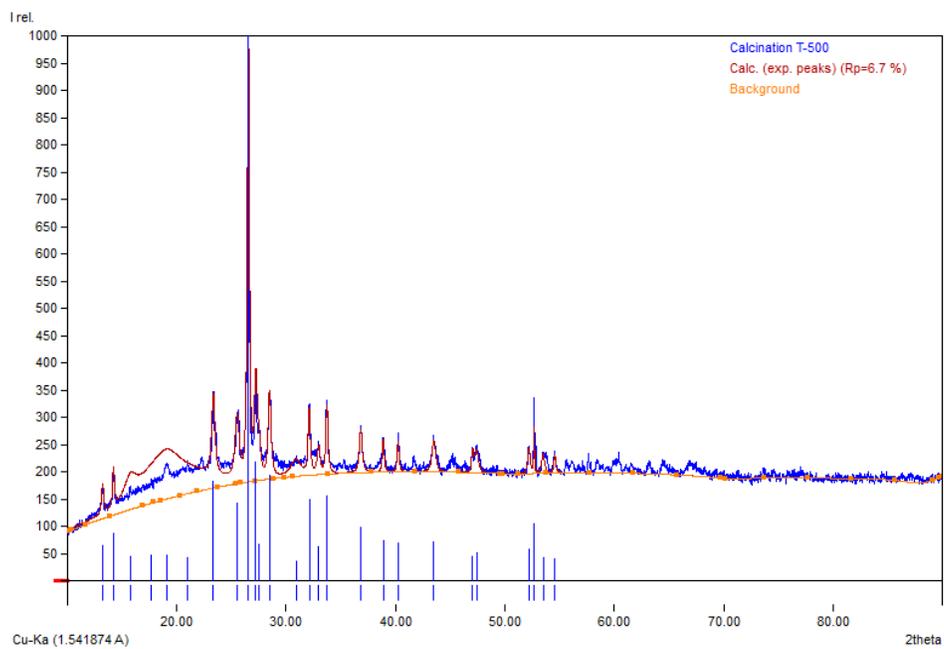


Figure 5. 3: Catalyst calcined at 500°C

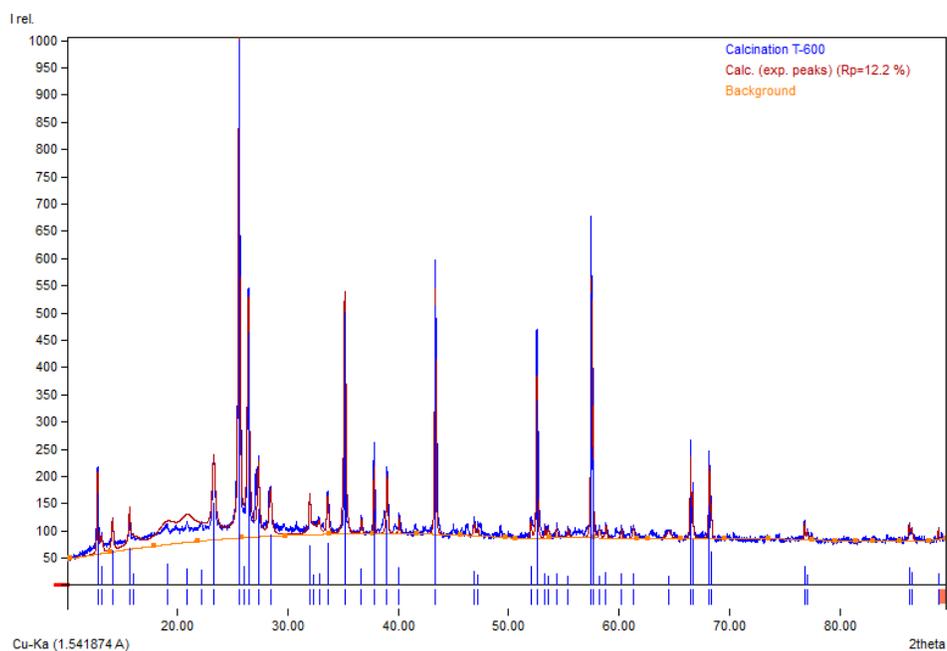


Figure 5. 4: Catalyst calcined at 600°C

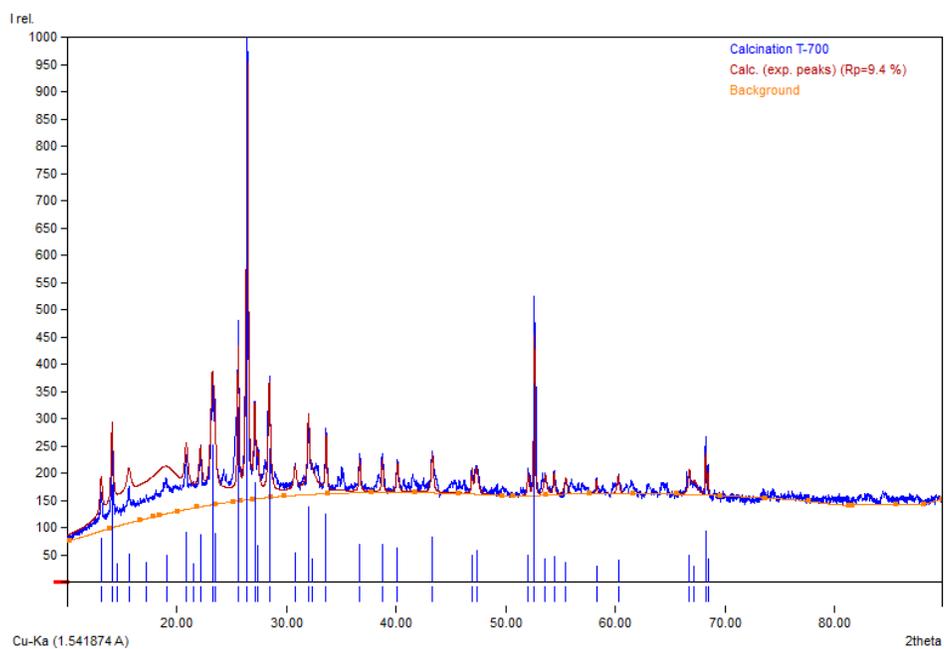


Figure 5. 5: Catalyst calcined at 700°C

Boehmite and aluminium oxide hydroxide complex crystalline were found on the surface of the catalysts calcined at low temperatures (300°C and 400°C) due to incomplete dehydration. Therefore, it is recommended to calcine the catalysts at 500°C or above to achieve complete dehydration and avoid boehmite formation. Boehmite presence leads to poor yields and ineffective cracking [3, 4].

The above reasons lead to producing bio-gasoline using catalyst calcined at 500°C, 600°C, and 700°C.

5.2.1.2. Variation of mole ratio of metal ions

Five samples with varying cobalt and molybdenum mole ratios were analyzed to investigate the effect of different metal ion mole ratios on the intrinsic characteristics of the catalyst using X-ray diffraction (XRD) analysis. The generated graph depicted the results.

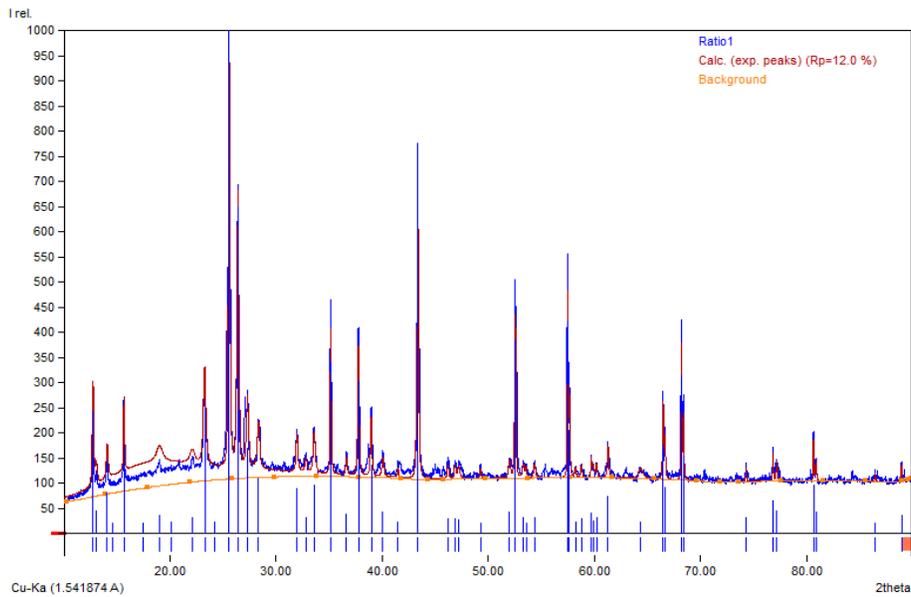


Figure 5. 6: Catalyst calcined at 300°C, equal mole ratio

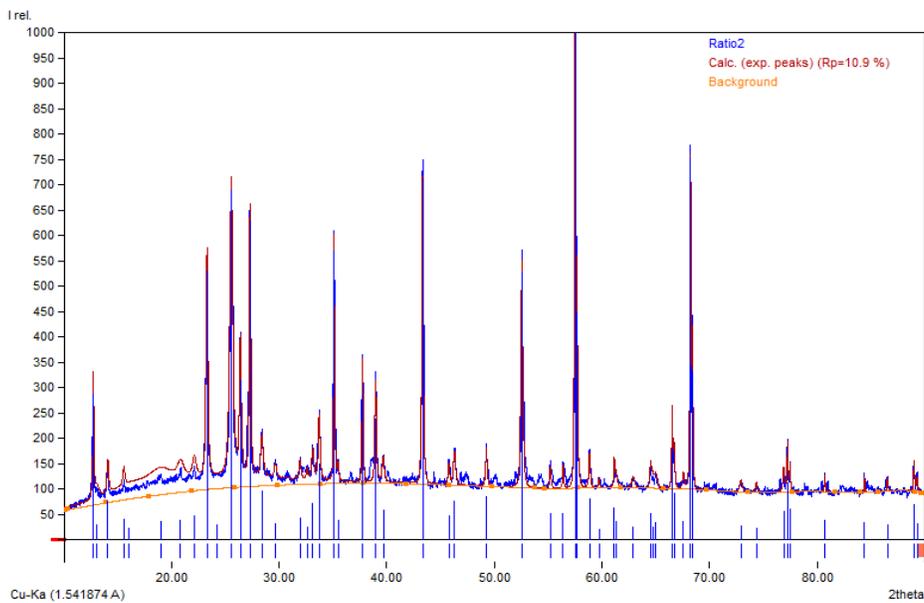


Figure 5. 7: Catalyst calcined at 400°C one (Co) to two mole ratios (Mo)

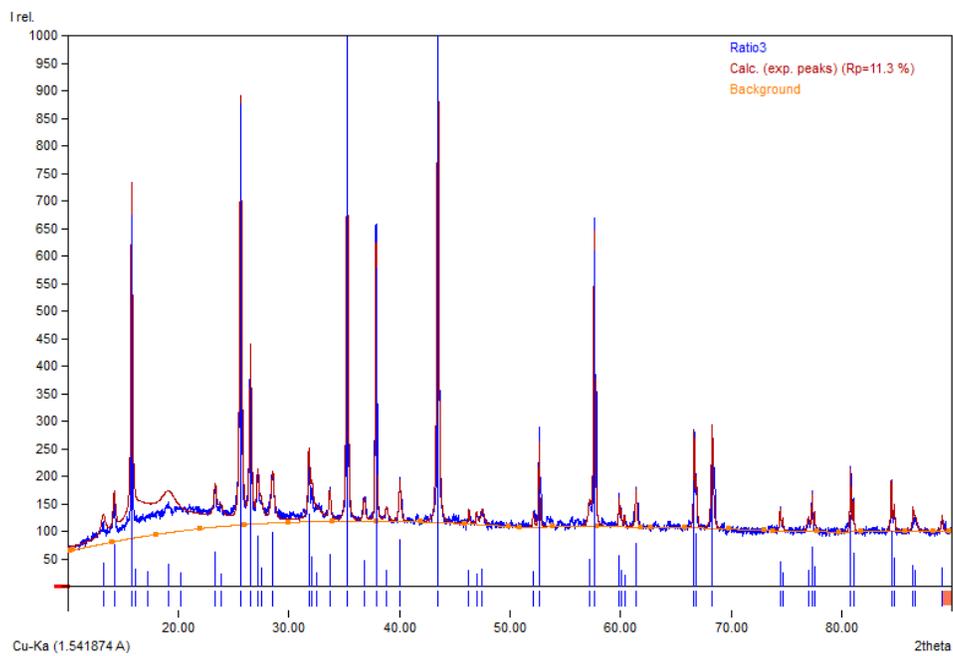


Figure 5. 8: Catalyst calcined at 500°C one (Co) to three-mole (Mo)

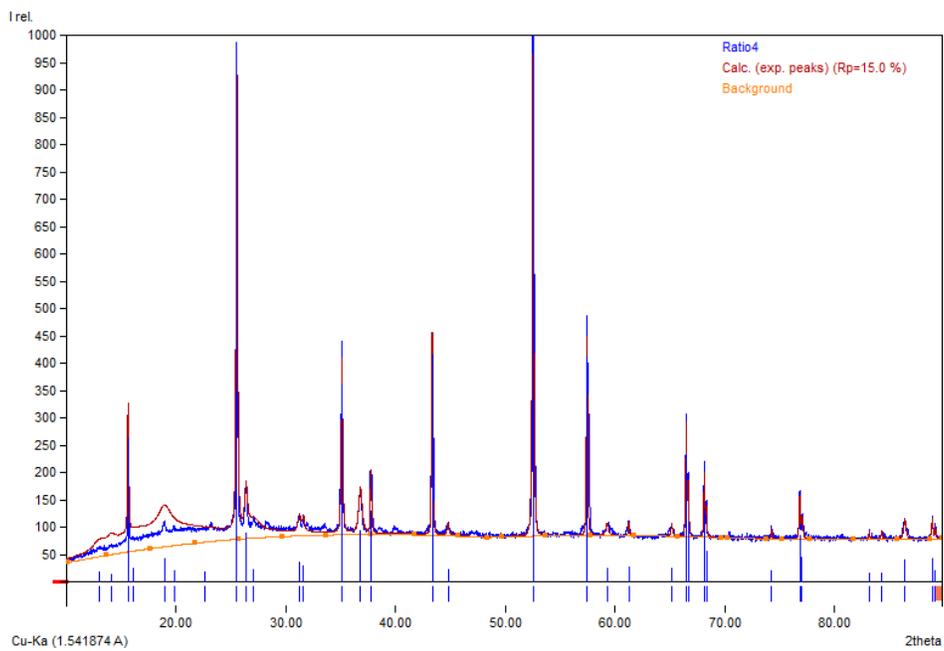


Figure 5. 9: Catalyst calcined at 600°C two (Co) to one-mole (Mo)

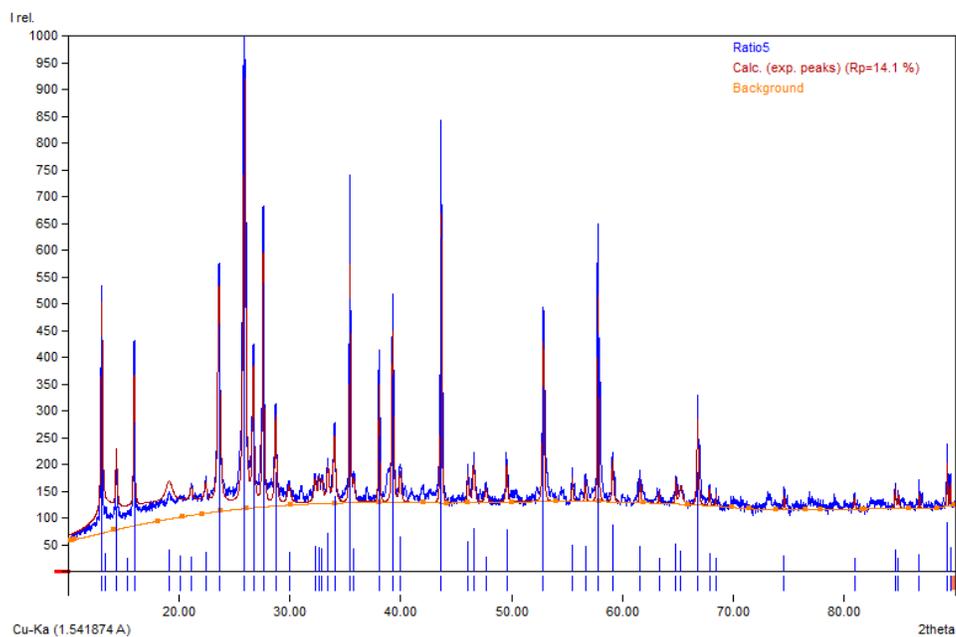


Figure 5. 10: Catalyst calcined at 700°C three (Co) to one-mole (Mo)

The resulting graphical representations exhibit similarities and have peaks at identical positions. Furthermore, the structure of these graphs remains consistent across all five samples. Mabika [3, 4] made the same observation regarding the peaks' behavior for different mole ratios of metal ions. Mabika [3, 4] noted that this trend is due to X-ray diffraction (XRD) being a qualitative analysis and not displaying the variation in metal ions' concentration in the catalyst samples. Quantitative analysis, such as inductively coupled plasma optical emission spectroscopy, is necessary to determine the exact variation in metal ion concentration. It is essential to emphasize that, although the graphs are similar, the catalyst sample contains different compounds, including cobalt oxide, molybdenum, and aluminum oxide.

5.2.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used in this study to quantify cobalt and molybdenum in the catalyst. Choi et al. (2004) state that the desired cobalt-molybdenum ratio is one-to-one (1:1) (equimolar ratio).

The tables below give a brief overview of different mixing and the ICP-OES results.

Table 5. 1: Catalyst mole ratio determination

Mixing ratio	Moles in the sample after ICP-OES analysis		Calculated ratio as per ICP-OES analysis		Error %	
	Cobalt	Molybdenum	Cobalt	Molybdenum		
1	1	0.49	0.51	0.98	1.02	+/-2
1	2	0.36	0.64	1	1.78	11
1	3	0.21	0.79	1	3.73	24
2	1	0.17	0.83	0.2	1	-90
3	1	0.58	0.42	1.38	1	-54

Table 5.1 displays the selected catalyst ratio used to produce biogasoline through the cracking method, which falls within the recommended cobalt-molybdenum ratio. The percentage error is 4%, which is lower than the maximum allowable error of 10%. According Choi et al [124], producing biogasoline through oil cracking requires a catalyst with an equal ratio of principal elements.

Table 5. 2: Catalyst metal concentration and standard deviation

Cobalt concentration g/L	Molybdenum Concentration g/L	Standard deviation [Co]	Standard deviation [Mo]	Relative Standard deviation [RSD][Co]	Relative Standard deviation [RSD][Mo]
359.30	367.15	0.40	0.38	0.11	0.10
472.88	835.65	2.93	3.44	0.62	0.38
176.62	659.02	1.13	2.56	0.64	0.36
145.36	692.90	0.74	3.35	0.51	0.45
383.00	278.85	0.99	0.70	0.26	0.25

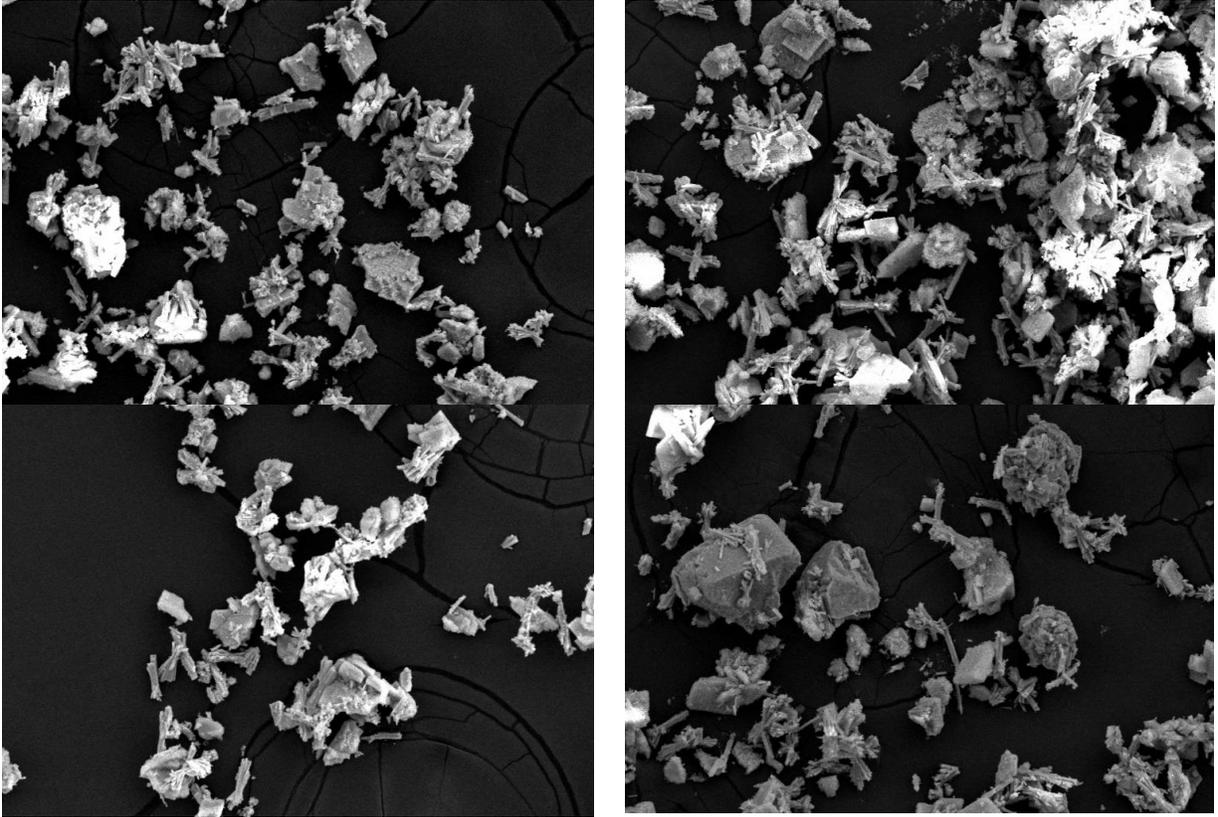
Table 5.2's statistical data reveals that the catalyst sample utilized in the study to investigate biogasoline production has a low standard deviation for the metals cobalt and molybdenum. The data is tightly clustered around the mean value and demonstrates consistency.

5.2.3. Scanning and transmission electron microscopy

Scanning and transmission electron microscopy analyses were performed to investigate the effect of temperature on the texture at both low and high magnifications. The composition of the catalyst was identical for all the samples analyzed.

5.2.3.1. Scanning electron microscopy (SEM)

The SEM images presented below were captured at low magnifications, ranging in the region of 1kx. The observations indicate that the samples looked similar, as presented in photograph (5.1)



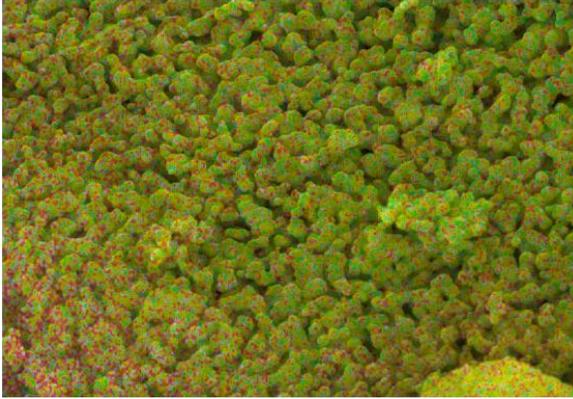
Photograph 5. 1: Low magnification of CoMo/Al₂O₃

The SEM images presented below were captured at high magnifications, ranging in the region of 50kx. SEM images indicate dissimilarity, with nanoparticles appearing on the catalysts as the calcination temperature increased. The tiny nanoparticles observed at high magnification led to a change in texture as the calcination temperature varied. Mabika [3, 4] reported the same observation.

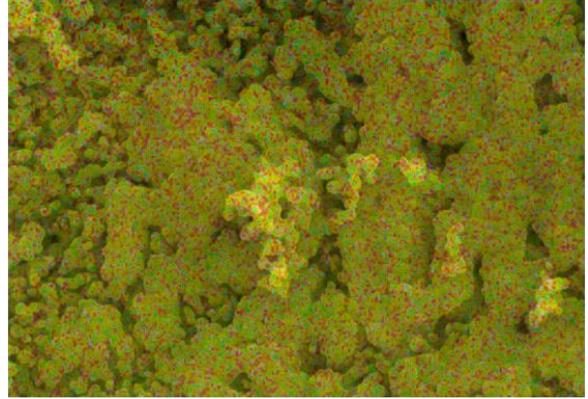
The SEM photographs indicate that cracks in the catalyst are dependent on the calcination temperature, resulting in the development of holes on the catalyst surface. The breaking of the nanocatalyst is attributed to the expansion of calcination temperature. The benefits of cracks are that they allow the feed to penetrate the nanocatalyst through the holes created, resulting in reaction rate [3, 4].

The SEM photographs reveal the presence of microscopic holes, which enable better penetration of feed and improved cracking of waste cooking oil.

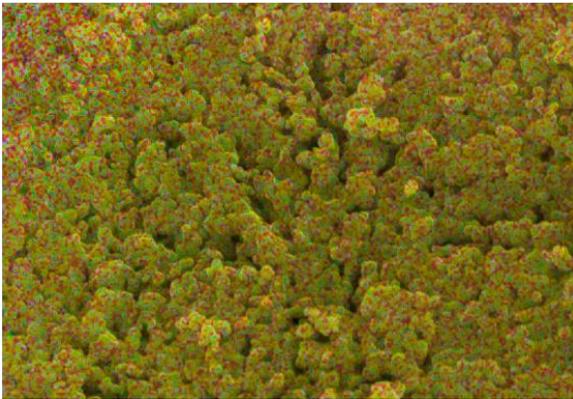
300



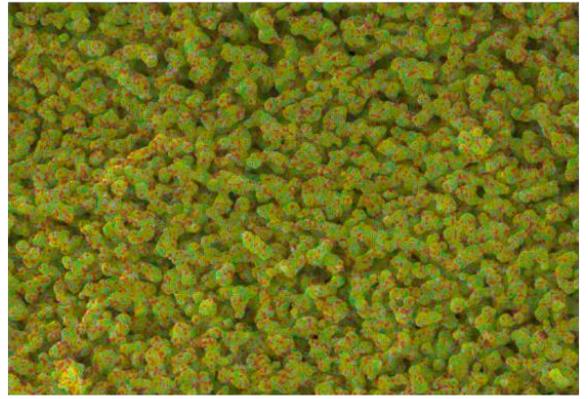
400



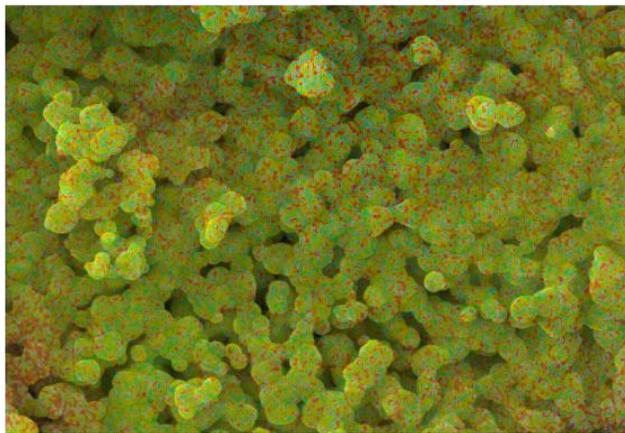
500



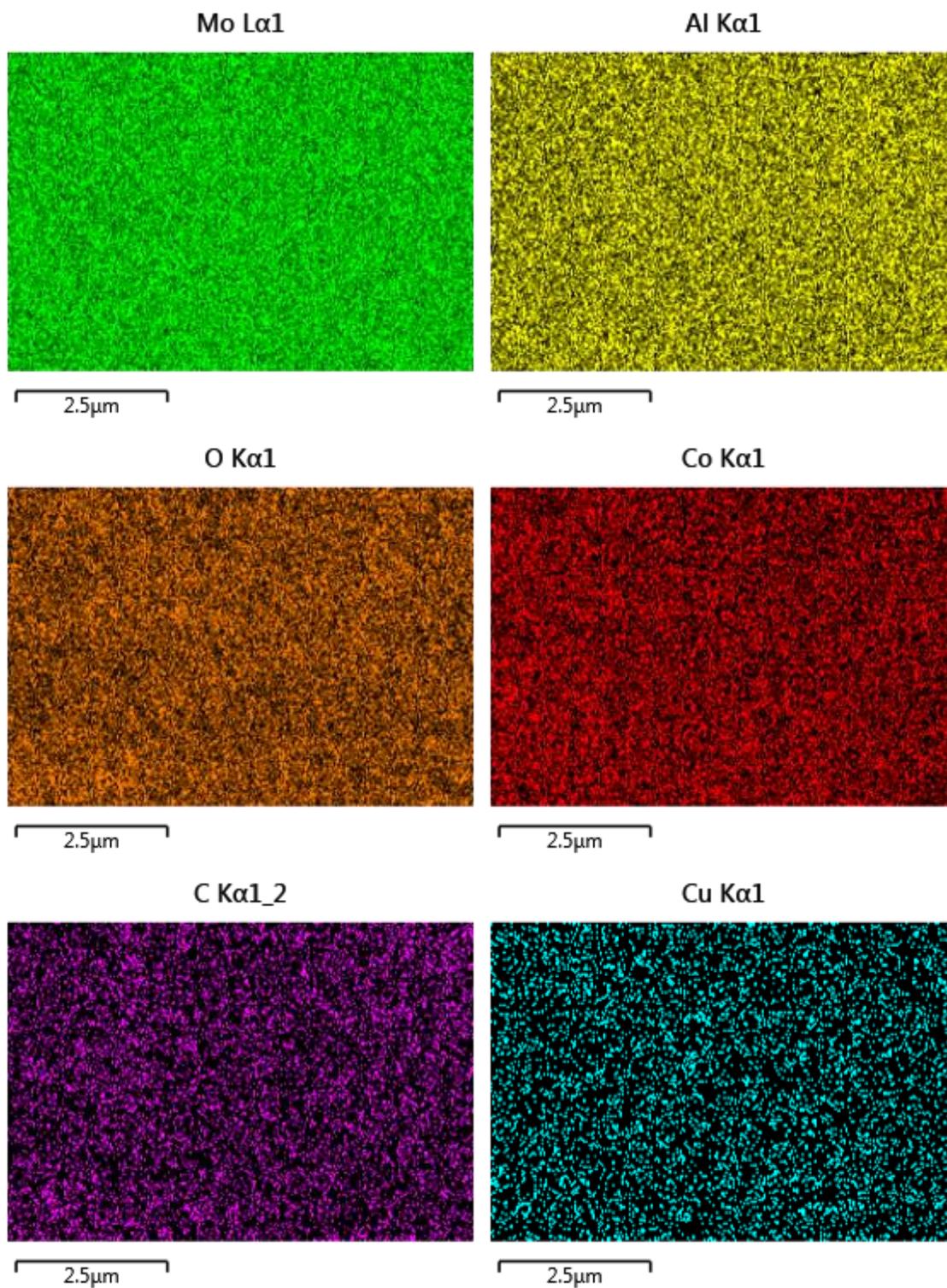
600



700



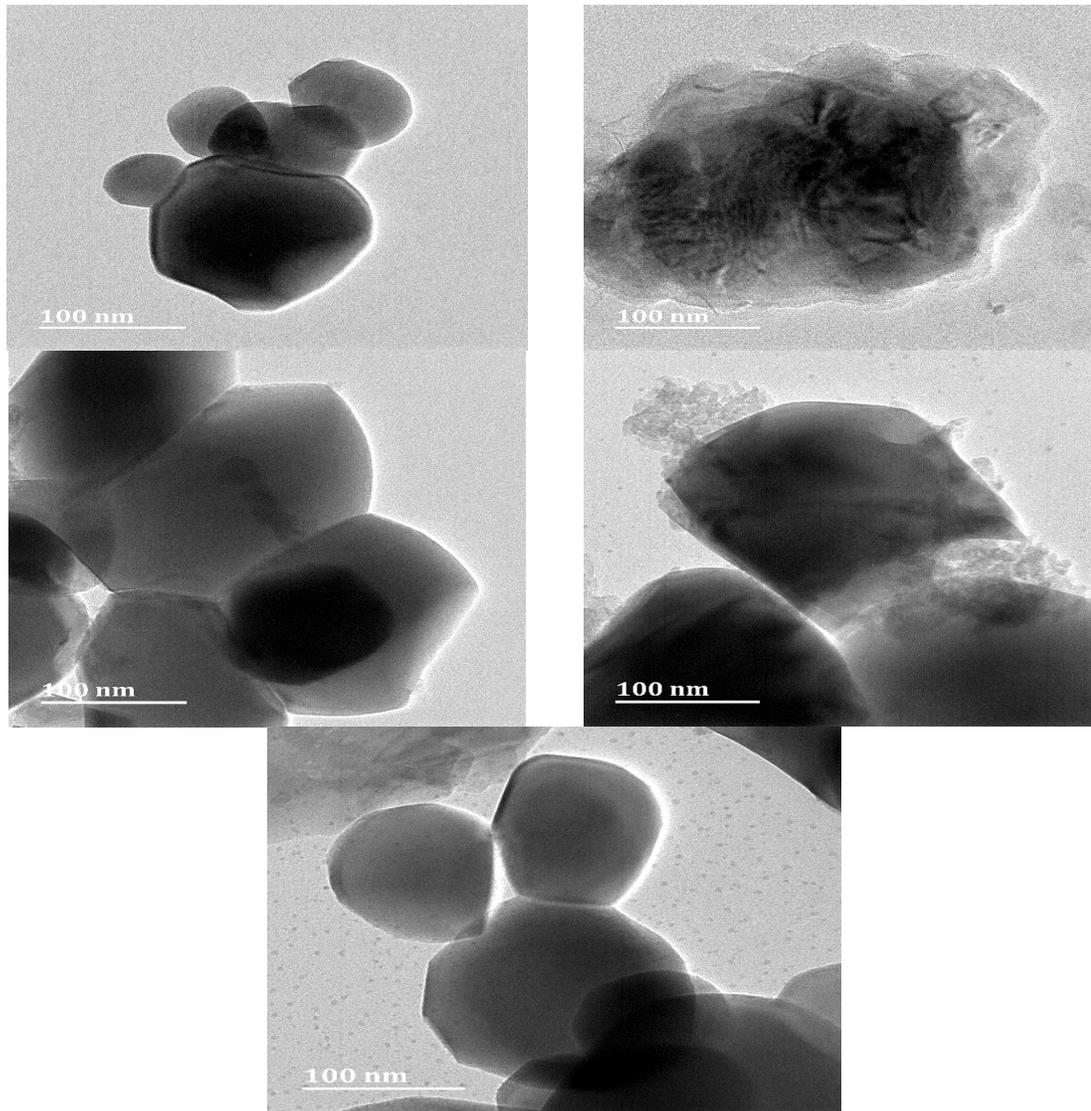
Photograph 5. 2: SEM Images for varying calcination temperature at high magnification



Photograph 5. 3: EDX Images showing the chemical composition of the catalyst sample

The scanning EDX analysis indicates that the catalyst sample is composed of Aluminum, Carbon, Cobalt, copper, molybdenum, and oxygen.

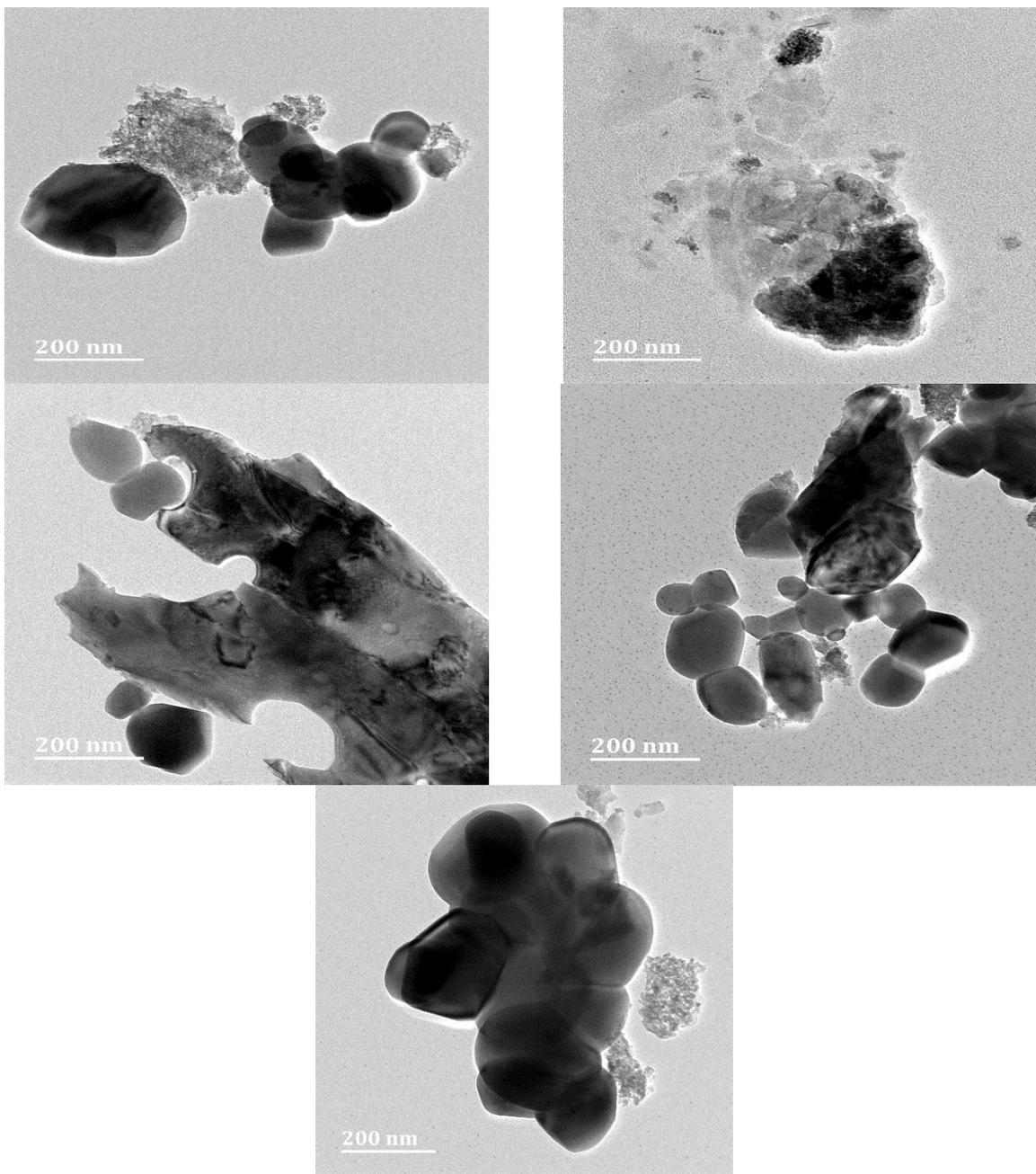
5.2.3.2. Transmission electron microscopy (TEM)



Photograph 5. 4: TEM Images for varying calcination temperature at low magnification

The TEM photograph reveals that the calcination of catalysts is a crucial step in catalytic cracking. Calcination causes the catalysts to break, allowing for easier access to the catalyst during catalytic cracking.

The conclusion drawn from the SEM photographs is also applicable to the TEM images. Despite the different calcination temperatures, the catalysts exhibit no significant changes in their texture, except for variations in shape and size of cracks and holes.



Photograph 5. 5: TEM Images for varying calcination temperature

Observations from photograph (5.5) indicate a change in texture and structure as the temperature increases in the high magnification TEM images. The catalyst undergoes significant breaking at a calcination temperature of 600°C. This image supports further investigation of biogasoline production using the nanocatalyst calcined at 600°C, as previously reported by Mabika [3, 4], breaking up the catalyst is advantageous because it creates space for raw materials to access the catalyst, which can increase the reaction rates. This is because the breaking of the catalyst creates more active sites where the reactions can occur. Additionally, the increased surface area resulting from the breaking of the catalyst also provides more opportunities for the reactants to interact with the catalyst, which can further enhance the reaction rates.

5.2.4. Determination of regeneration temperature

Regeneration is a crucial industrial process that aims to restore the activity of a spent catalyst. Over time, the catalyst's surface can become fouled with organic materials, which can poison and deform the structure of the catalyst. This results in reduced activity and selectivity, which can ultimately lead to decreased efficiency and increased costs. Regeneration involves removing the fouling materials from the catalyst's surface, either through chemical or thermal treatment, in order to restore the catalyst's activity and prolong its useful life [3, 4, 130]. Organic materials that accumulate on the surface of a catalyst during its use are typically referred to as coke. These materials can build up and eventually block the active sites on the catalyst, reducing its effectiveness. Regeneration involves removing this coke through various methods such as burning it off with oxygen or steam.

The nature of the cokes deposited on the catalyst's surface determines whether the catalyst is deactivated or destroyed. If the catalyst is deactivated, the regeneration process can be initiated, but if the catalyst is poisoned, it is impossible to regenerate it [130].

The regeneration process can be defined as a coke-removing process from the catalyst surface through an oxidation reaction with air or other oxidizing agents [130]. This reaction can restore the catalyst's activity, but it is important to carefully control the temperature and other conditions to avoid damaging the catalyst. The regeneration process investigates the regeneration temperature of the catalyst in biogasoline production.

To determine the regeneration temperature of the catalyst used in the investigation of biogasoline production through catalytic cracking, three samples calcined at 500°C, 600°C, and 700°C were subjected to a regeneration process using TGA and DSC analysis. TGA analysis determines the percentage weight per unit mass, while DSC determines the percentage of weight per minute. The results from DSC analysis assist in determining the most suitable catalyst sample for this investigation.

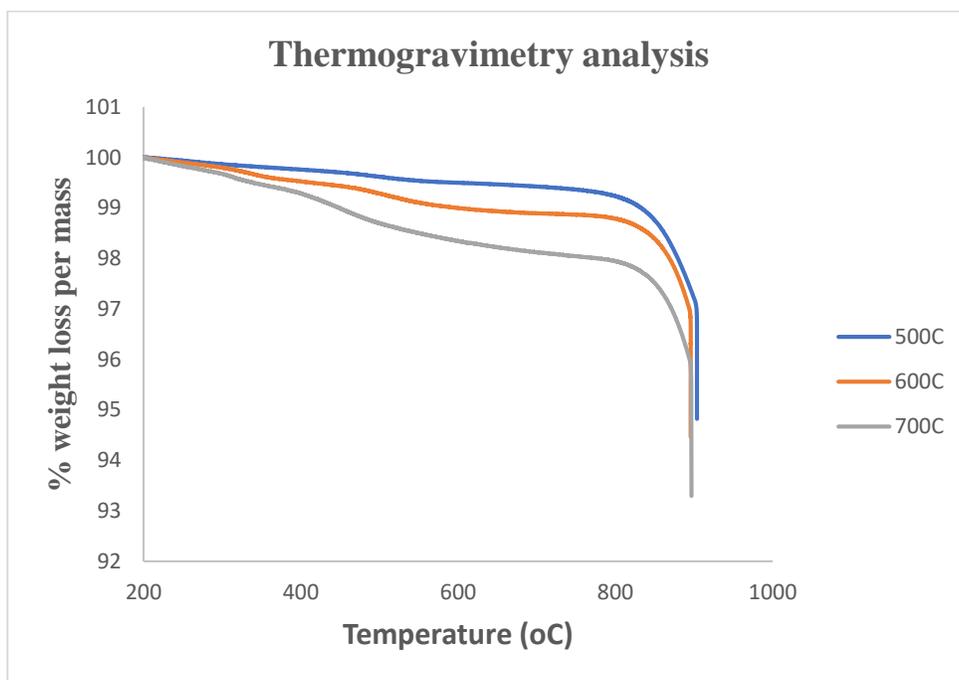


Figure 5. 11: Thermogravimetry analysis

Figure (5.11) does not give enough information about selecting the calcination temperature since TGA is a thermo-analytical technique used to determine a sample's weight changes as a function of temperature or time. It can provide information about the thermal stability and composition of a sample. However, it cannot directly determine the regeneration temperature of a catalyst. DSC, on the other hand, is a technique that measures the heat flow of a sample as function of temperature or time. It can provide information about the thermal properties of a sample, including the regeneration temperature of a catalyst. Therefore, both techniques are useful to fully understand the thermal behavior of a catalyst.

The use of the TGA enables quantifying the significant difference in material constituents, studying decomposition and thermal stability, and identifying the material in the sample. Since TGA cannot investigate the regeneration temperature, it is essential to use differential scanning calorimetry (DSC). The DSC generates the derivative curves.

The derivative curves obtained from DSC analysis at different calcination temperatures (500°C, 600°C, and 700°C) assist in investigating and determining the suitable regeneration temperature for the catalyst. The reason for considering these three temperatures is to evaluate the effect of calcination temperature on the coke removal process during regeneration. The goal is to find the temperature at which the catalyst can be effectively regenerated and restore its activity for further use in biogasoline production. The result of the regeneration process, in turn, can inform the selection of the appropriate catalyst for biogasoline production.

It is possible that a catalyst calcined at a temperature lower than 500°C may perform as well as catalysts calcined at higher temperatures. It is important to note that the optimal calcination temperature for a catalyst may vary depending on the specific application or reaction being studied. The regeneration process is the criteria used to select the appropriate catalyst to make biogasoline.

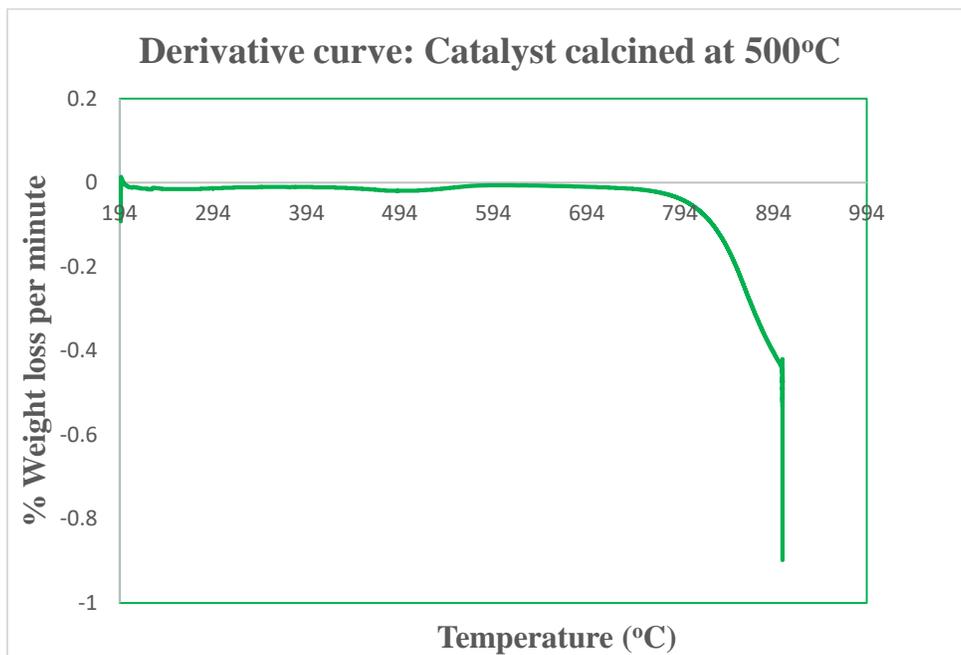


Figure 5. 12: Weight loss per minute vs temperature for catalyst calcined at 500°C

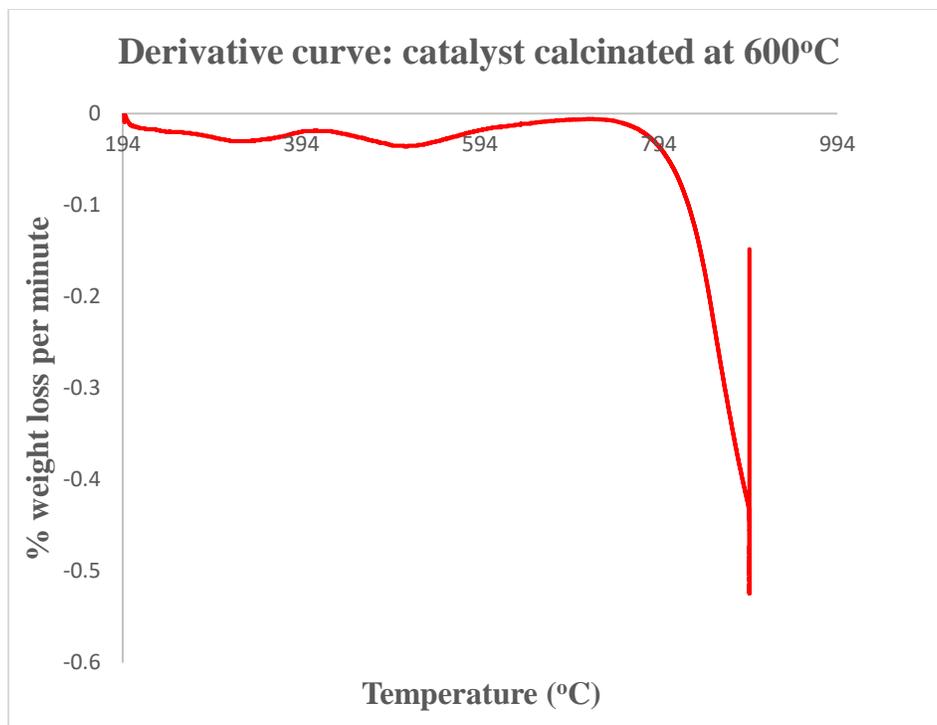


Figure 5. 13: Weight loss per minute vs. temperature for catalyst calcined at 600°C

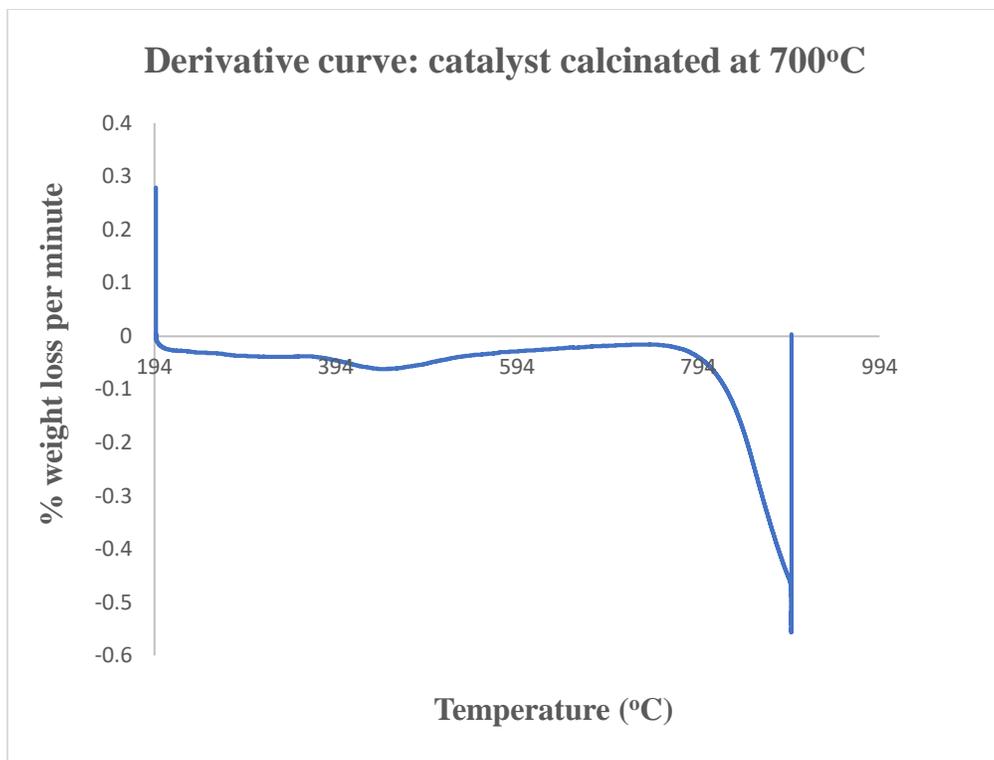


Figure 5. 14: Weight loss per minute vs. temperature for catalyst calcinated at 700°C

The removal of the organic material from the catalyst's surface reacted through combustion with air. The following reaction takes place during the process:

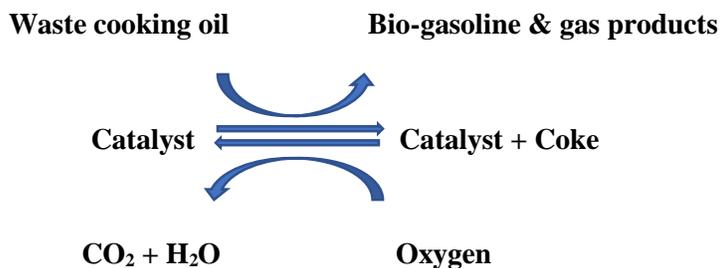


Figure 5. 15: Oxidation reaction taking place during combustion [3, 4]

The first instance of mass loss per minute marks the evaporation of water content from the catalyst combustion. The schematic oxidation reaction shown in Figure 5.15 illustrates that the combustion process results in partial coke oxidation. Due to the partial nature of the reaction in each derivative curve, there are cycles where the weight per minutes increases and decreases.

Devaraj et al. [128] showed that the increase in mass observed in the derivative curve is due to the partial oxidation of organic compounds on the surface of the catalyst, resulting in oxygenation. The same study reported that the negative trend observed in the derivative curve is due to the combustion of different coke properties on the catalyst surface [130].

The derivative curve of nanocatalyst calcined at 600°C, as shown in Figure 5.13, is an excellent graph that illustrates the various regeneration steps, starting with the evaporation of water, followed by an increase due to the partial oxidation of organic compounds, and then a negative trend due to the combustion of other coke properties.

According to Jiménez-Morales et al. [131], the regeneration cycle of the catalyst increases due to the combustion of coke on its surface. The peak begins and reaches its maximum, where the catalyst regenerates to its original sharpness, and then decreases. The regeneration of the samples started at around 594°C and went up to the maximum. At the maximum, the regeneration curve touches the x-axis for the samples calcinated at 500°C and 600°C. The regeneration cycle is instrumental in determining the temperature at which the catalyst will regenerate. To establish regeneration temperature, it is essential to thoroughly analyze the reaction-rejuvenation cycle.

Figure 5.12 depicts the catalyst calcined at 500°C. For this catalyst, it is difficult to differentiate between water evaporation and oxidation reactions. The regeneration cycle is not well defined, although it started around 594°C, reaches its peak, and then decreases. The regeneration curve does not show all the steps with clarity.

Figure 5.13 represents the catalyst calcinated at 600°C. The derivative curve generated is smooth, and the significant steps of the reaction-regeneration cycle are clearly visible. It is easy to distinguish between the evaporation step, the oxidation step of an organic compound, and the negative trends due to both combustions of different coke properties and to complete combustion of organic compounds, as reported by Jiménez-Morales et al. [131]. The regeneration cycle starts around 594°C and ends when the derivative curve intersects with the x-axis.

Figure 5.14 depicts the catalyst calcinated at 700°C. The derivative curve generated shows a rigorous deactivation. The curve displays a complete deactivation, which is not desired for many reasons, including economic reasons. The derivative curve indicates the evaporation of the partially oxidized organic compounds, the negative trend due to the combustion of different coke properties, and the negative trends due to the complete combustion of organic compounds [131]. During the reaction-regeneration cycle, the catalyst calcinated at 700°C did not show complete rejuvenation. There is a clear indication that the catalyst calcined at 700°C cannot be regenerated after its use. Economically, it is not worth producing biogasoline

with a catalyst calcined at such a temperature. For this reason, many researchers, including Mabika [3,4] and Chuaykleang et al. [1], suggest that the catalyst be calcined at 600°C.

As mentioned earlier, nitrogen was used as a carrier gas in this study. Additional analysis was conducted using nitrogen gas to compare the deactivation trend observed during biogasoline production. Figure 5.16 shows the catalyst deactivation trend caused by nitrogen for the samples calcined at 600°C and 700°C, and it is clear again that the catalyst calcined at 700°C does not regenerate.

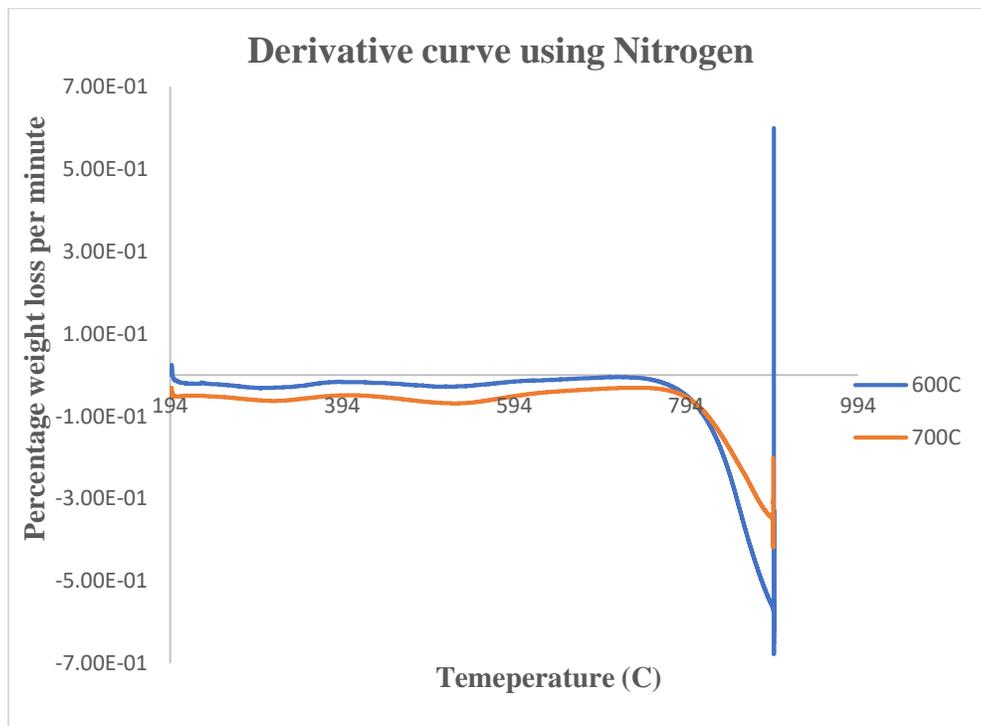


Figure 5. 16: Weight loss per minute vs. temperature for catalyst calcined at 600 and 700°C using nitrogen gas

Figure 5.16 shows that the deactivation trend of the overused catalyst due to nitrogen gas is similar to the deactivation trend caused by coked decomposition. The nitrogen gas compound was found to be responsible for the deactivation, while the effect of combustion was negligible due to high purity of the feed used in the study [131]. The study used air and nitrogen gas for the analysis of the regeneration cycle.

the catalyst sample calcined at 600°C achieved a regeneration conversion was 100% when the reaction-regeneration cycle curve intersected with the temperature axis at approximately 600°C. Based on the completion of the regeneration cycle at 600°C for both catalysts and the equivalent amount of coke in the samples calcined at 600 and 700°C, it can be inferred that the regeneration temperature is 600°C. However, the catalyst calcined at 700°C cannot be used for further production as its regeneration is impossible.

Ren et al. [130] stated after the complete reaction-regeneration cycle a new regeneration process can begin. This means that after the catalyst has been used and then regenerated, it can be used again to produce more biogasoline. Figure 5.16, which shows the deactivation trend caused by nitrogen for the catalyst samples calcined at 600°C and 700°C, supports this idea. The regeneration conversion was 100% for the catalyst calcined at 600°C, indicating that it can be fully regenerated and used again. This demonstrates the accuracy of Ren et al.'s conclusion that a new regeneration process can begin after the complete process.

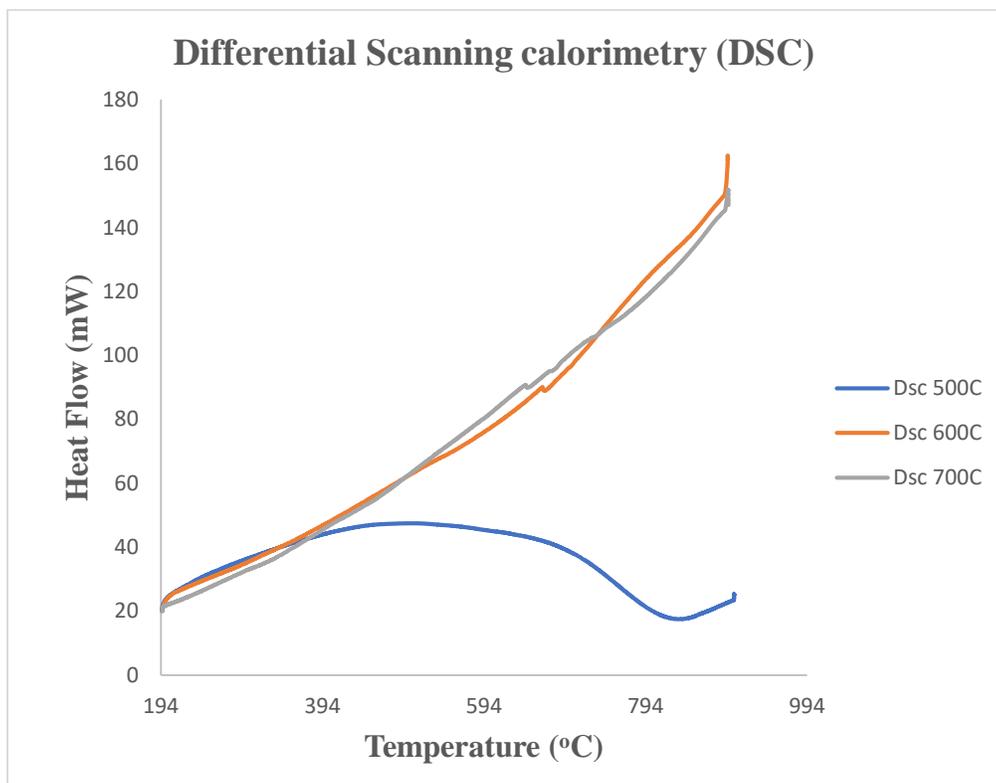


Figure 5. 17: Heat flow vs temperature

Figure 5.17 depicts the coke yield during the calcination process. The results show that the amount of coke generated is similar for the catalyst samples calcined at 600°C and 700°C, while the catalyst calcined at 500°C generated less coke than the other two. Furthermore, Jiménez-Morales et al. [131] noted that the equivalent amount of coke deposited both catalysts at 600°C and 700°C implies that the severe deactivation observed at 700°C is not solely due to the coke deposition on the catalyst surface. According to Jiménez-Morales et al. [131], there is a slow combustion rate observed for the remaining coke at 600 and 700°C.

5.3. Waste cooking oil pre-treatment

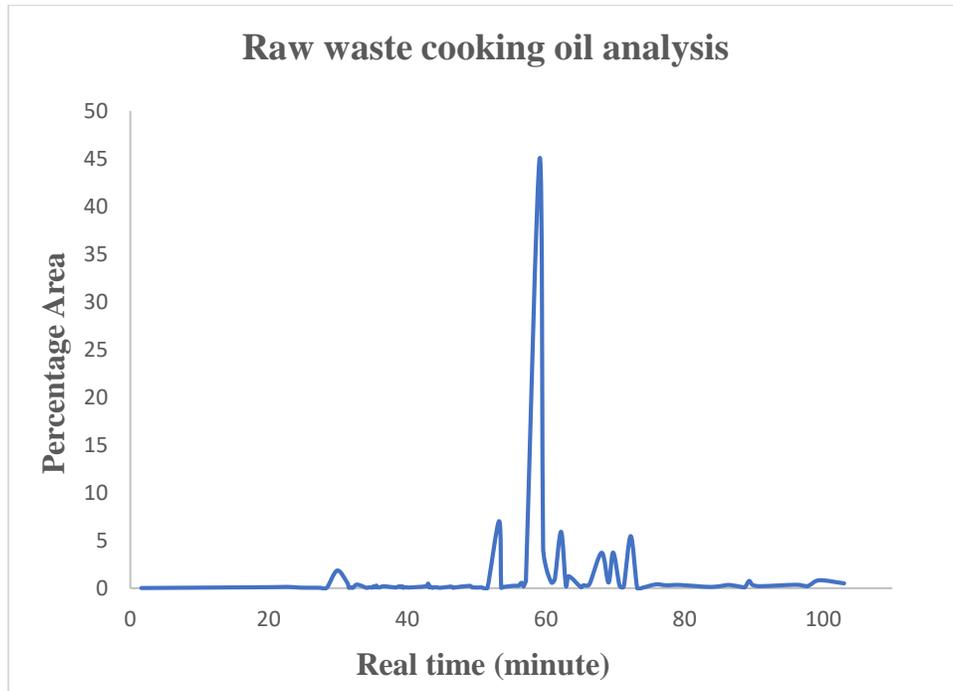


Figure 5. 18: Untreated waste cooking oil chromatogram

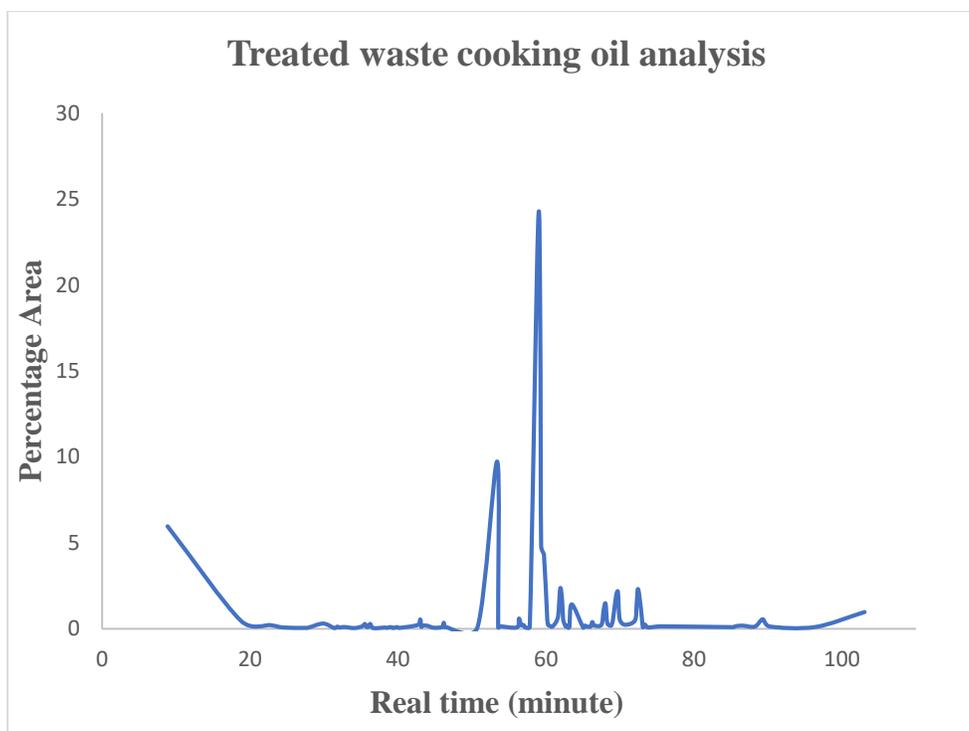


Figure 5. 19: Treated waste cooking oil chromatogram

The composition and the purity of the feed play a crucial role in determining the catalyst's activity, selectivity, and longevity. The feed's impurities and contaminants can cause deactivation, reduce the catalyst's selectivity, and shorten the catalyst's lifespan. On the other hand, high-purity feed can enhance the catalyst's performance and longevity, leading to more efficient and cost-effective processes. Therefore, it is essential to ensure high-quality and consistent feed in the biogasoline production process to maximize the catalyst's performance and efficiency.

In order to achieve better catalyst performance, it was found to be necessary to remove salts and food particles, as well as reduce compounds containing halogen elements and sulfur (bromide, chloride, and fluoride) in the waste cooking oil used as feedstock. According to Mabika's [3, 4] research, the pre-treatment step resulted in 33% reduction in impurities (from 13.18% to 4.37%), in this study, the pre-treatment reduced the impurities in the waste cooking oil to 37%, which is slightly higher than the 33% reduction achieved in Mabika's study. However, the post-treatment impurity level in this study was still within the recommended range of being within 5% of the initial level. Therefore, the difference of 4% in impurities between the pre and post-treatment results is considered reasonable.

It is beneficial for the catalyst to eliminate impurities from waste cooking oil, particularly salts. As per Figueiredo et al. [132], salts can crystallize in catalyst pores during the catalytic reaction, leading to pore blockage and ultimately reducing the catalyst's activity.

It appears that the shapes of figures 5.18 and 5.19 demonstrate that not only were the abovementioned impurities removed from the feed, but many other compounds were also removed and enriched, such as oxygen and other compounds.

5.4. Bio-gasoline product

5.4.1. Bio-oil percentage yield

In each run of the experiment, 50 ml of waste cooking oil was measured using a cylinder for accurate volume measurement. The table below shows the bio-oil recovered:

Table 5. 3: Bio-oil recovery

Temperature	Volume (ml) Input	Volume (ml) Out	Percentage yield
400	50	10	20
450	50	30	60
475	50	35	70
500	50	32.5	65
550	50	35	70

5.4.2. Bio-oil analysis

GC-MS was used to analyze the bio-oil and organic liquid products obtained from thermal cracking, catalytic cracking, and hybrid technique known as two stages process. The latter involves transesterification followed by catalytic cracking. The analysis revealed that the organic oil product (OLP) is composed of various compounds, including paraffins, olefins, aromatic, cyclic compounds, alcohol, and carboxylic acid. Moreover, the bio-oil analysis showed the presence of biodiesel, biogasoline, biokerosene, and heavy oil.

The size of the molecules in biodiesel, biogasoline, and biokerosene differ. According to some authors biogasoline is classified as hydrocarbon-containing carbon compounds ranging from C₄-C₁₁, biokerosene from C₁₂-C₁₅, and biodiesel from C₁₄-C₁₈. However, other authors classify biogasoline as hydrocarbon-containing carbon compounds ranging from C₄-C₁₃, biokerosene from C₁₄-C₁₈, and biodiesel from C₁₆-C₂₄ [61].

In this study, the biofuels are classified as follows: biogasoline from C₄-C₁₃, biokerosene from C₁₄-C₁₈, and biodiesel from C₁₉-C₂₄. Please refer to Table 2.2, for the biogasoline composition.

5.4.3. Thermal cracking method

Thermal cracking is a catalyst-free method used to produce biogasoline and its by-products. In biogasoline production, the variables of interest are the reaction temperature and time. The paragraphs below discuss the results of this method.

5.4.3.1. Reaction time variation

The objective of this study is to examine and establish the relationship between the reaction time and the biogasoline produced via the thermal cracking method. The reaction time is varied while maintaining constant temperature and nitrogen pressure. Typically, the bio-oil produced is directly proportional to the reaction time. However, this was not the case for producing biofuels, for reasons that became apparent during the study.

As shown in the following figure, increasing the reaction time does not necessarily lead to an increase in biogasoline product yield.

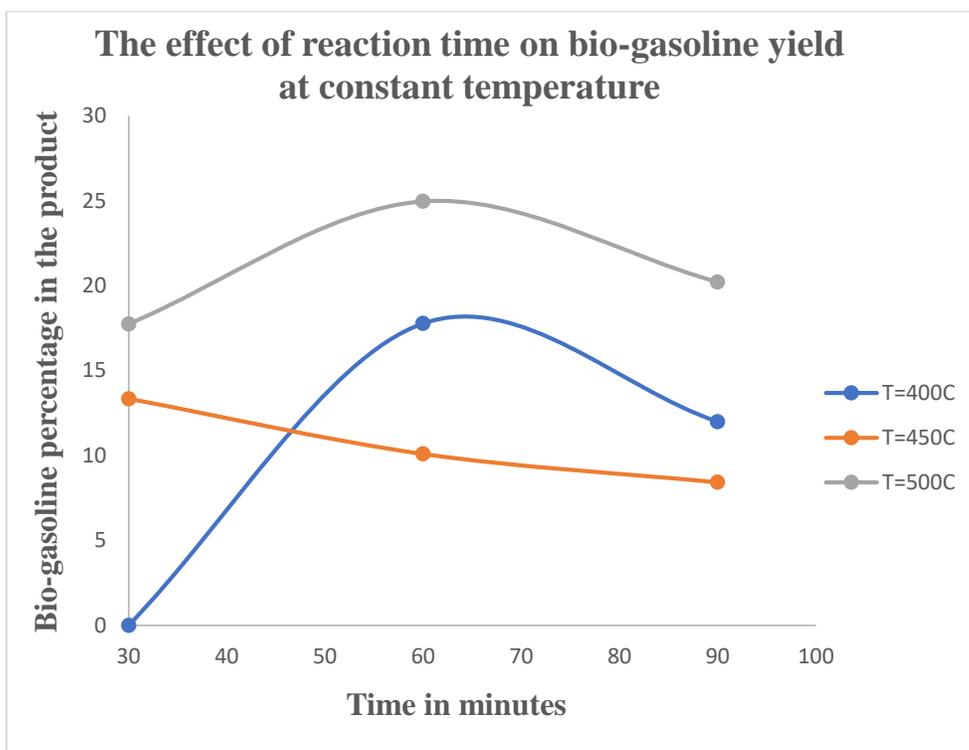


Figure 5. 20: Biogasoline percentage yields vs reaction time at a constant reaction temperature

The production of biogasoline increases as the reaction time is increased for the process runs at 400°C and 500°C, up to 60 minutes reaction time. After that; there is a drop in the biogasoline percentage in the product. Muhammad et al. [133] reported that the biogasoline rate decreases after 60 minutes of reaction time because 60 minutes is the optimum time. Mabika [3, 4] also found that the optimum reaction time is 60 minutes.

Based on Al Mashhadan’s research [61], it has been observed that the production rate of biogasoline decreases when the reaction time exceeds 60 minutes at temperatures of 400 and 500°C. This decline in

production rate is believed to be caused by the formation of undersirable compounds like non-condensable gases, water, and organic compounds. Therefore, it is crucial to produce biogasoline within the optimal reaction time to maintain its quality, as an increase in reaction time can negatively impact the product. It is worth noting that the specific optimal reaction time and temperature reaction may vary depending on the process and conditions employed for biogasoline production. Nonetheless, ensuring an optimal reaction time is vital for producing high-quality biogasoline.

5.4.3.2. Reaction temperature variation

The experimental setup for thermal cracking involved maintaining a constant reaction time and nitrogen pressure while varying the temperature between 400°C to 500°C at the rate of 50°C.

The resulting data, depicted in Figure 5.21, indicates that when the reaction time is limited to 30 minutes, the percentage of biogasoline in the product is directly proportional to the increase in temperature.

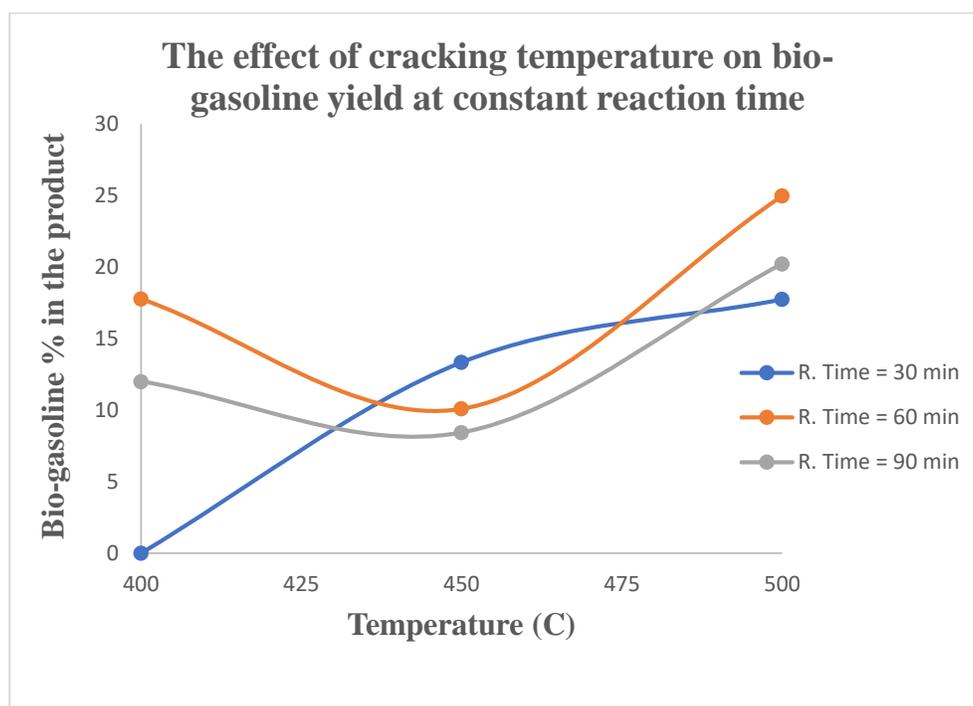


Figure 5. 21: Biogasoline percentage yields vs temperature at constant reaction time

Based on the experimental results, it appears that increasing the temperature during thermal cracking can result in higher yields of biogasoline, as longer chains can break down into shorter chains that make up the biofuel. However, the data obtained for waste cooking oil processed at 450°C does not entirely support this prediction. Nevertheless, the biogasoline percentage yield observed at 500°C aligns with the forecast, particularly at the optimal reaction time.

According to Tamunaidu et al. [89], the low percentage of biogasoline yield observed in the case of waste cooking oil may be attributed to other components present in the feedstock. Therefore, it is crucial to optimize the process by finding the optimal temperature at which a significant quantity of the desired product is formed.

5.4.4. Catalytic cracking method

Waste cooking oil (WCO) is composed of carboxylic acid components with long chains. These chains vary in length and may include octanoic acid, hexadecenoic acid, 9,12-hexadecanoic acid, and other fatty acids. The presence of long-chain fatty acids in the WCO increases the heating value of the oil. However, to process WCO efficiently, it is necessary to lower its heating value or boiling point using catalytic techniques. One such technique is catalytic cracking, which involves a combustion reaction that occurs in the vapor phase. This process converts long-chain components of WCO into lighter fractions, making it easier to process. By breaking product down the long chains into shorter chains, the resulting product can be used as a source of biofuel, including biogasoline [134].

In the production of biogasoline, the catalytic cracking method was employed using nanocatalyst. The production process involved varying the weight of the catalyst, the reaction temperature, and the calcination temperature. Unlike thermal cracking, the variation of reaction time was deemed unimportant for catalytic cracking since the optimum reaction time had already been established as 60 minutes. Consequently, the catalytic cracking process was carried out for a fixed reaction of 60 minutes, while other parameters such as catalyst weight, calcination temperature, and reaction temperature were varied.

5.4.4.1. Catalyst calcination temperature variation

During the production of biogasoline using catalytic cracking, the impact of calcination temperature was examined. The experiment was conducted while maintaining the catalyst weight, reaction time, reaction temperature (475°C), and the carrier gas (nitrogen) flow rate and pressure constant. The only variable that was modified in this experiment was the calcination temperature, and its effect on biogasoline was observed.

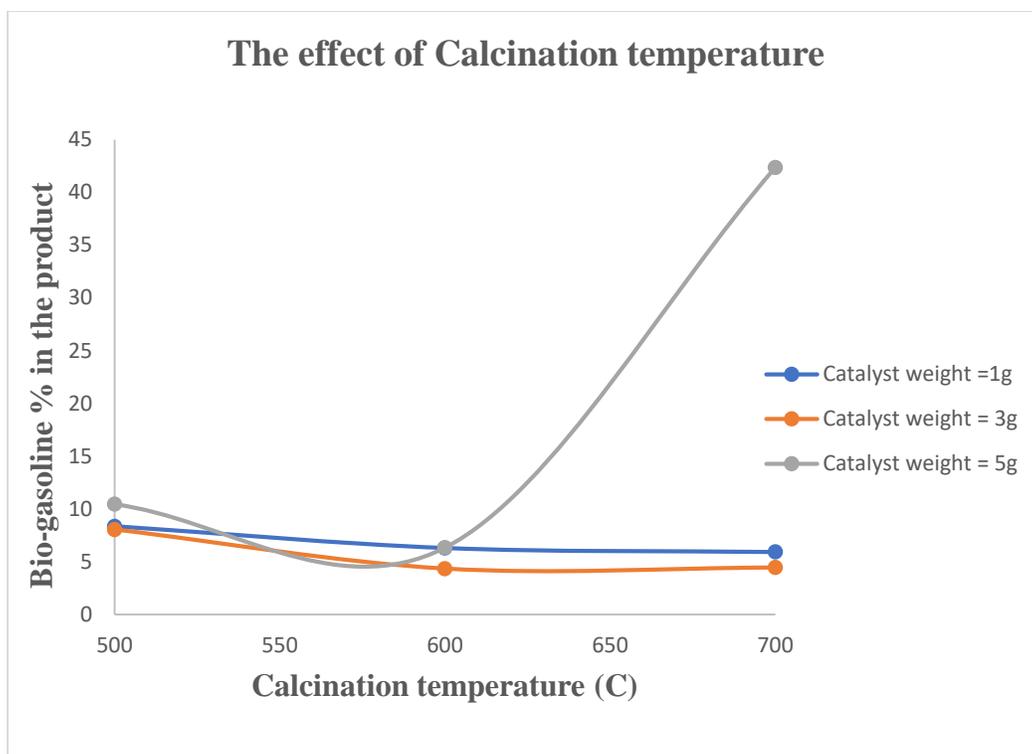


Figure 5. 22: Biogasoline vs. calcination temperature at constant reaction temperature (475°C)

Figure 5.22 displays the decline in biogasoline yields for catalyst loads of 1 and 3 grams, as the calcination temperature is increased, while maintaining a constant reaction temperature. However, when a catalyst load of 5 grams was utilized, a substantial product was produced as the calcination temperature increased. It was observed that the biogasoline percentage in the product increased with increasing catalyst calcination temperature. Nonetheless, further investigation is required to determine the parameter responsible for the observed shift during biogasoline production at elevated calcination temperature and 5 grams catalyst load.

5.4.4.2. The effect of reaction temperature variation

The cracking temperature, also known as the reaction temperature, is directly proportional to the load of cooling system. The temperature plays a significant role in determining the quality of the product yield. Whether it is catalytic cracking, the two-step process (hybrid cracking technique) that combines transesterification and catalytic cracking, or thermal cracking, the temperature difference leads to a variation in the quality of product yield [133]. The load of the cooling system contributes to a difference in the biogasoline product quality. As the cooling load increases, the dew point is reached, resulting in different quantities. In addition to the difference in product yields caused by the difference variation, it is important to note that non-condensable gases generated during cracking also impact the quality of the liquid produced [133].

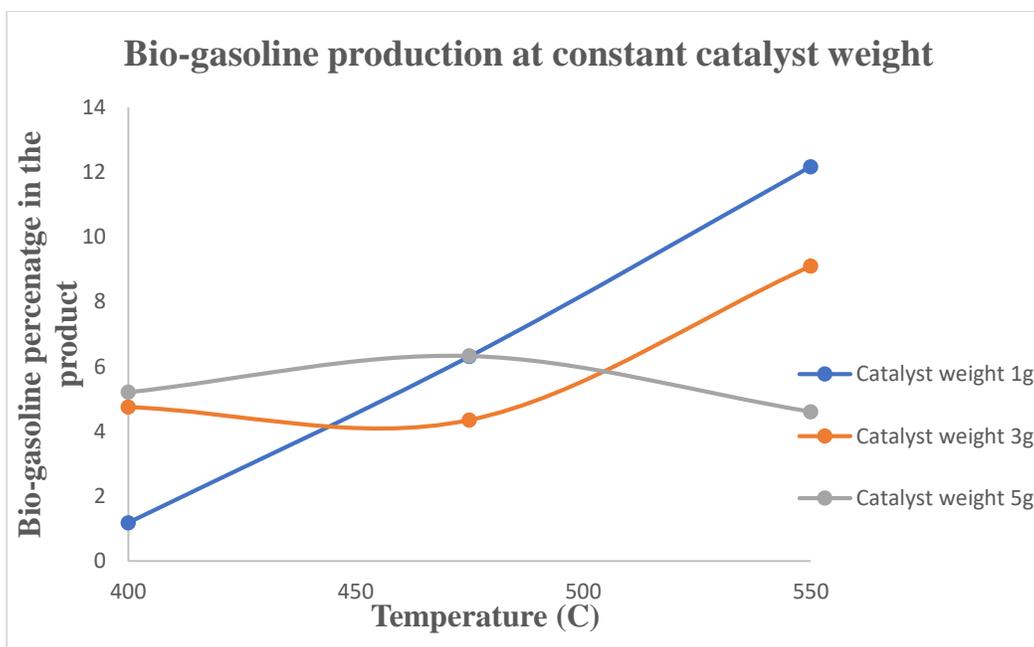


Figure 5. 23: Biogasoline percentage vs temperature at constant catalyst weight

Figure (5.23) shows an increase in biogasoline yield at a constant catalyst weight of 1 gram as temperature increases. The highest product quantity is 12.7% of biogasoline obtained at 550°C. This investigation yields the best results compared to the other studies under the same conditions; for instance, the research conducted by Hassan et al. [135] produced 4.5% of biogasoline.

The experiment at a constant catalyst load of 3 grams showed a slight change in product from 450°C to 475°C; the biogasoline yield increased with temperature. The highest product quantity is 9.1% at 550°C.

The experiment at a constant catalyst of 5 grams showed a decrease in product quantity as the temperature increased from 475 to 550°C. Tamunaidu et al. [89] found that the cause of low biogasoline yield at high temperatures is the formation of other organic compounds which are not listed among the organic compounds in bio-oil. The listed biofuels are biodiesel, biokerosene, and heavy oil.

It is important to note that the formation of different biofuels is influenced by various factors such as reaction temperature, catalyst load, and cooling system. While Hassan et al. [135] stated that different reaction temperature yields fewer biogasoline products due to the formation of other biofuels, it is not always the case. As seen in the experiments discussed earlier, an increase in temperature resulted in increase in biogasoline yield at constant catalyst load of 1 gram, while a decrease in product quantity was observed at a constant catalyst load of 5 grams. Therefore, the relationship between temperature and biogasoline yield is complex and is influenced by several variables. Additionally, the presence of other biofuels such as biodiesel and biokerosene does not necessarily imply a lower biogasoline yield, as seen in the

experiments with a constant catalyst load of 3 grams where the highest biogasoline yield was obtained at 550°C.

5.4.4.3. The effect of the ratio of catalyst weight to WCO weight

The use of a catalyst to produce biogasoline lies within several parameters, including activity, selectivity, use time, and ease of regeneration. The production of biogasoline from catalyst using waste cooking oil was carried out using a nanocatalyst. The catalyst consisted of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, cobalt nitrate hexahydrate $[\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}]$ impregnated in aluminium oxide. The catalyst used controls the activity, selectivity, and ease of regeneration. However, the biogasoline percentage in the product is not significant.

The effect of the catalyst weight ratio was investigated at a constant temperature, reaction time (60 minutes), and gas flow rate. The proportion varied in the following manner 1/44, 3/44, and 5/44.

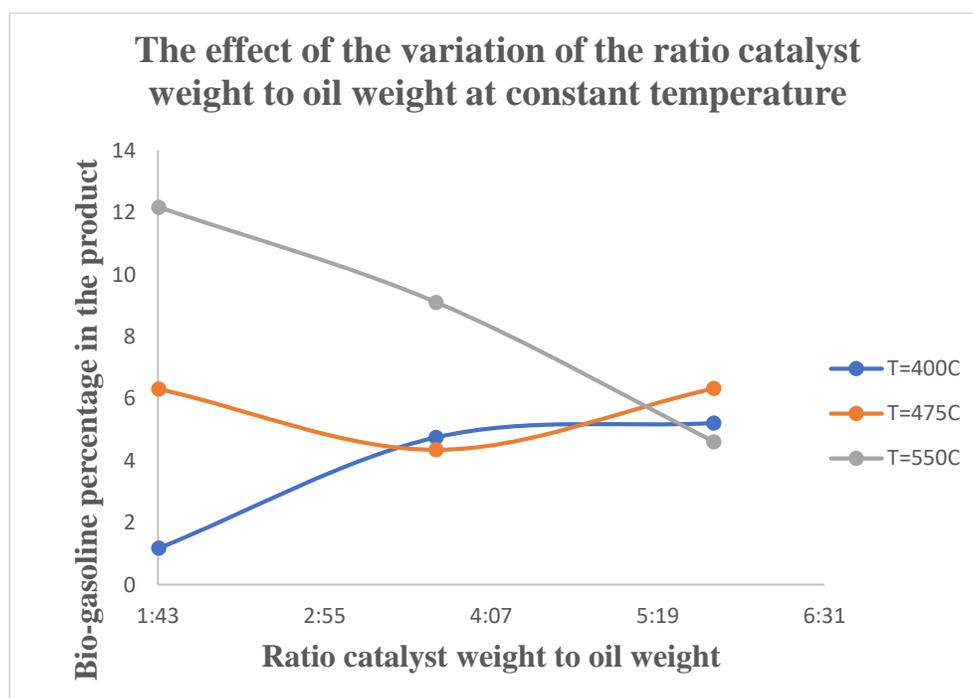


Figure 5. 24: Biogasoline percentage vs catalyst weight ratio to WCO weight at a constant temperature.

Zeolite catalyst is the most used catalyst in the production of biogasoline. Haryani et al. [85] found that the addition of copper, nickel and zinc to zeolite catalyst can enhance their performance in the production of biogasoline. The modified catalysts showed increased activity and selectivity towards gasoline range hydrocarbons, which resulted in higher biogasoline yields.

It appears that the initial percentage yields of biogasoline using zeolite catalyst were low, ranging from 4 to 15%. However, the modification suggested by Haryani et al. [85] and applied by Martínez et al. [136] resulted in significantly higher biogasoline percentage yields, ranging from 32 to 41%. This modification likely involved impregnating the zeolite catalyst with nickel metal, which has been shown to enhance the catalyst's performance for biogasoline production.

It is noteworthy that the performance of zeolite catalyst with nickel metal impregnation is reported to be comparable to that of the nanocatalyst used, indicating that the modified zeolite catalyst may be a cost-effective alternative for biogasoline production. However, more research is needed to fully evaluate the performance and feasibility of the modified zeolite catalyst in biogasoline production.

Based on the results reported, it seems that the actual biogasoline percentage yield obtained using the zeolite catalyst were consistent with the prediction made by Haryani et al [85]. However, in one particular experiment conducted at a catalyst weight to oil ratio of 1:44 and a temperature of 400°C, the biogasoline percentage was slightly lower than the predicted minimum of 4%.

On the other hand, the use of the nanocatalyst for biogasoline production yielded higher percentage yields ranging from 1.18 to 12.17%. The highest percentage yield was obtained at a catalyst weight to oil of 1:44 and a temperature of 550°C. These findings suggest that the nanocatalyst may be a more efficient catalyst than zeolite for biogasoline production from waste cooking oil.

Overall, these results support the potential use of both zeolite and nanocatalysts for biogasoline production from waste cooking oil. However, further studies are necessary to compare the performance of both catalyst under different reaction conditions and to evaluate their economic and environmental viability for large-scale biogasoline production.

5.4.5. Two-step process (Hybrid Method)

The two-step process, as described, is a hybrid technique for producing biofuels from feedstocks such as vegetable oils or animal fats. In this process, the feedstock undergoes two stages of chemical reactions. The first stage is transesterification, which converts the triglycerides in the feedstock into fatty acids methyl esters (FAME), also known as biodiesel. Transesterification typically requires the use of a catalyst and a source of alcohol, such as methanol.

In the second stage of the two-stage process, the FAME produced in the first stage is subjected to catalytic cracking. Catalytic cracking is a process in which a catalyst is used to break down larger molecules into smaller ones, typically by the application of heat.

The result of catalytic cracking is a mixture of smaller hydrocarbon molecules that can be used as a biofuel.

The use of transesterification as an advanced pre-treatment stage in two-step process is intended to improve the efficiency and the overall process. By converting the triglycerides in the feedstock into FAME before subjecting them to catalytic cracking, the second stage of the process is able to operate more effectively. This because the FAME produced in the first stage is more easily cracked than the larger triglyceride molecules.

Overall, the two-step process is a promising technique for producing biofuel from variety of feedstocks. While there still some technical and economic challenges associated with the process, ongoing research is focused addressing these issues and improving the viability of the technology [102].

The main difference between the two-stage process and the catalytic cracking is that in the two-stage process, transesterification is used as an advanced pre-treatment stage, whereas in catalytic cracking, it is not. The other parameters in the process remain unchanged.

5.4.5.1. The effect of temperature variation

The two-stage process involved two consecutive steps conducted at different temperature of 400°C, 475°C, and 550°C respectively, with a constant reaction time of 60 minutes. The gas flow rate was kept constant throughout the process.

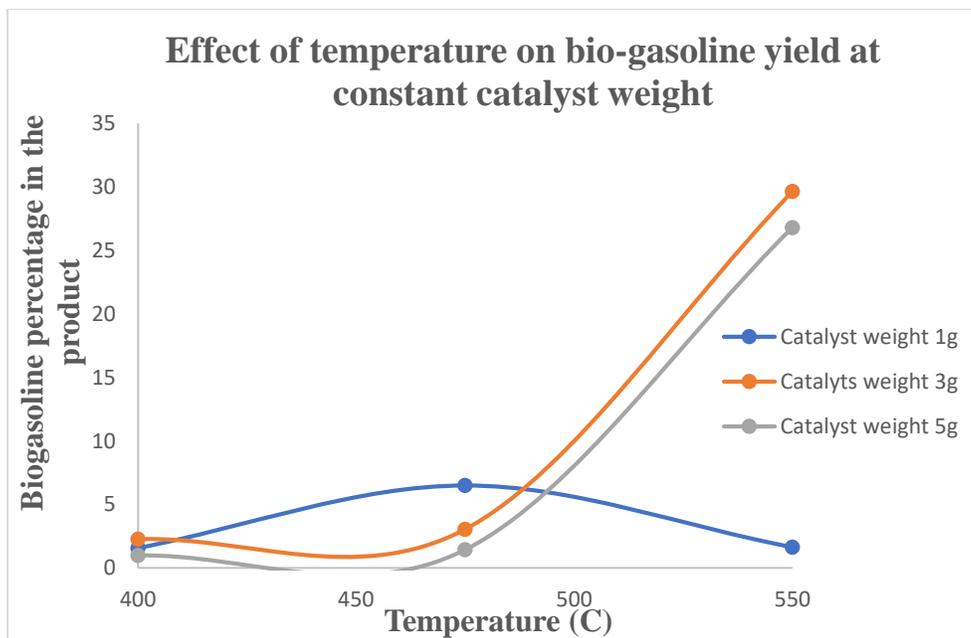


Figure 5. 25: Biogasoline percentage vs temperature at constant catalyst weight (two-step process)

The percentage yield of biogasoline in the product increased with increasing reaction temperature up to 475°C, when using a constant catalyst weight of 1 gram. However, at high temperature, the biogasoline

yield began to decrease. Normally an increase in reaction temperature would result in an increase in biogasoline percentage in bio-oil produced, but this was not observed in this study. Further investigation is vital to determine the cause of the decrease in biogasoline yield observed in the temperature range from 475°C to 550°C when using a minimum amount of catalyst (1 gram). Understanding the factors contributing to this drop will be important for optimizing the process and improving the yield of biogasoline from bio-oil.

In experiments where the two stages process was conducted with 3 grams and 5 grams of catalysts, the percentage biogasoline in the bio-oil product increased with increasing reaction temperature, but the relationship was not linear. At the maximum reaction temperature of 550°C, the biogasoline percentage was 29.63% for 3grams and 26.79 % for 5 grams of catalyst load, respectively.

Two stages process or hybrid method, shows significantly improvement in biogasoline percentage yield in bio-oil at high reaction temperatures and with considerable catalyst load. However, further investigation is needed to explore its application, as the biogasoline percentage yield obtained using this method are still in the range of 32-41% reported by Haryani et al. [85], who achieved these yield by modifying the zeolite catalyst's intrinsic characteristics with nickel.

5.4.5.2. The effect of the ratio catalyst weight to WCO weight

This study investigated the effect of catalyst weight on waste cooking oil by varying weight from 1 to 5 grams at 2-gram intervals. The weight of waste cooking oil was kept constant, as well as the reaction time (60 minutes) and gas flow rate, while the reaction temperature varied at an increment of 75°C.

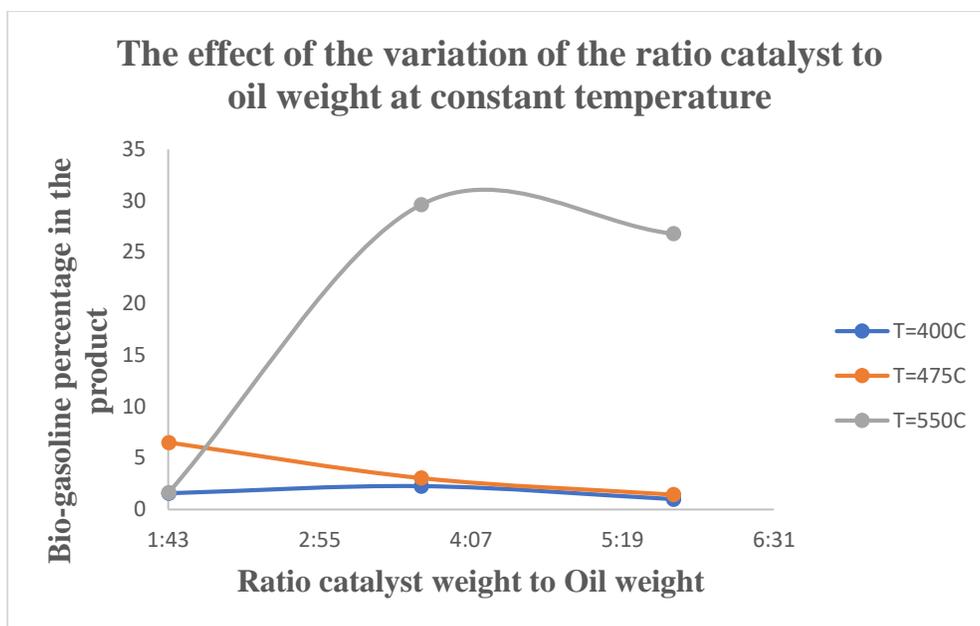


Figure 5. 26: Biogasoline percentage vs ratio of catalyst weight to WCO weight at constant temperature (two-step process).

Figure 5.26 shows that the biogasoline percentage in the product decreases as the catalyst weight ratio to the weight of waste cooking oil increases at low temperatures. However, for the experiment conducted at 550°C, the percentage yield increased as the ratio increased. The highest biogasoline yield of 29.63%, was obtained for a ratio of 3 grams of catalyst weight to 44 grams of waste cooking oil weight, which was slightly reduced to 26.79% for a ratio of 5 grams of catalyst weight to 44 grams of waste cooking oil weight.

Compared to previous methods, the two-stage process appears to be the best for producing biogasoline at elevated temperatures, followed by thermal cracking without catalyst and catalytic cracking.

5.5. Thermal stability of bio-gasoline

Thermogravimetric analysis (TGA) is a technique that measures the weight of a sample as it is heated or cooled over time. In the case biogasoline, TGA can be used to determine the temperature at which the fuel begins to degrade or decompose. This information is important because it allows researchers to assess the fuel’s thermal stability, which is a critical factor in its performance and safety [1]. The production of biogasoline involves various chemical reactions such as hydrolysis, fermentation, distillation, isomerization, and reforming. These reactions play an essential role in determining the properties of the resulting fuel. They can affect several factors, including the fuel’s thermal stability, composition, kinetics decomposition, moisture and volatiles content, transition temperature, the heat of fusion, and melting and boiling points. Ultimately, the reactions that occur during biogasoline production are crucial in determining the quality and effectiveness of fuel.

This paragraph analysis the thermal stability of the fuel.

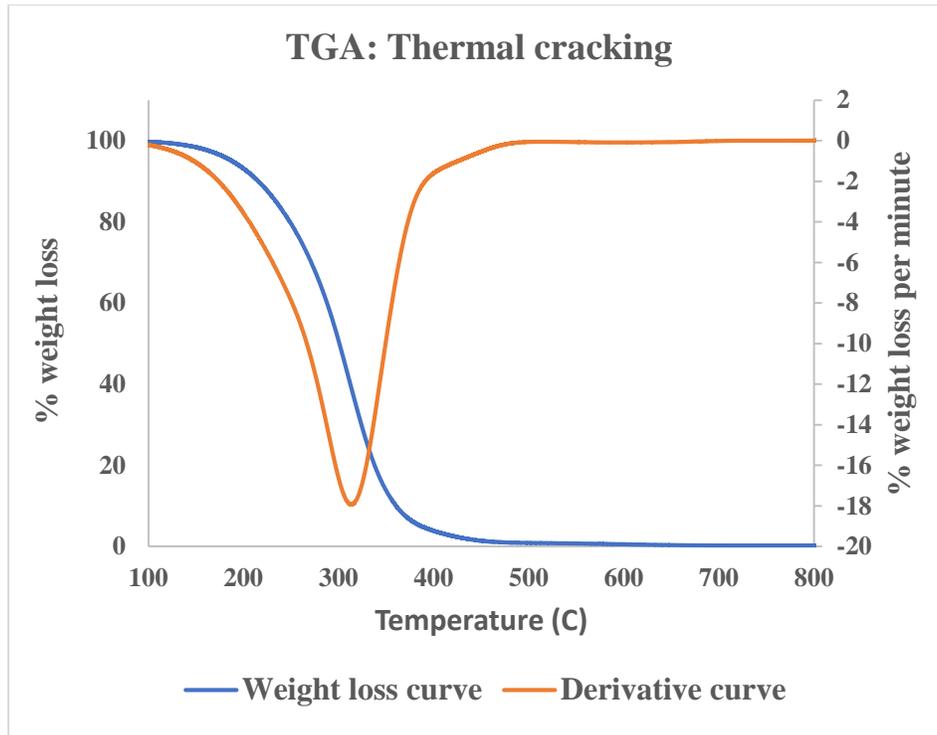


Figure 5. 27: Derivative curve and weight loss curve vs temperature (thermal cracking)

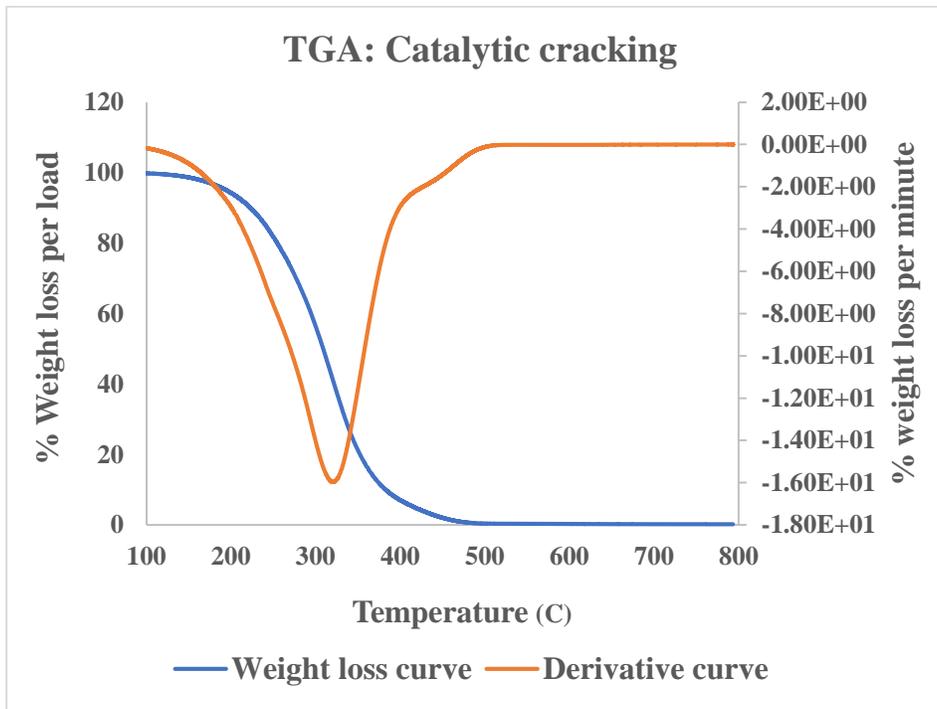


Figure 5. 28: Derivative curve and weight loss curve vs temperature (catalytic cracking)

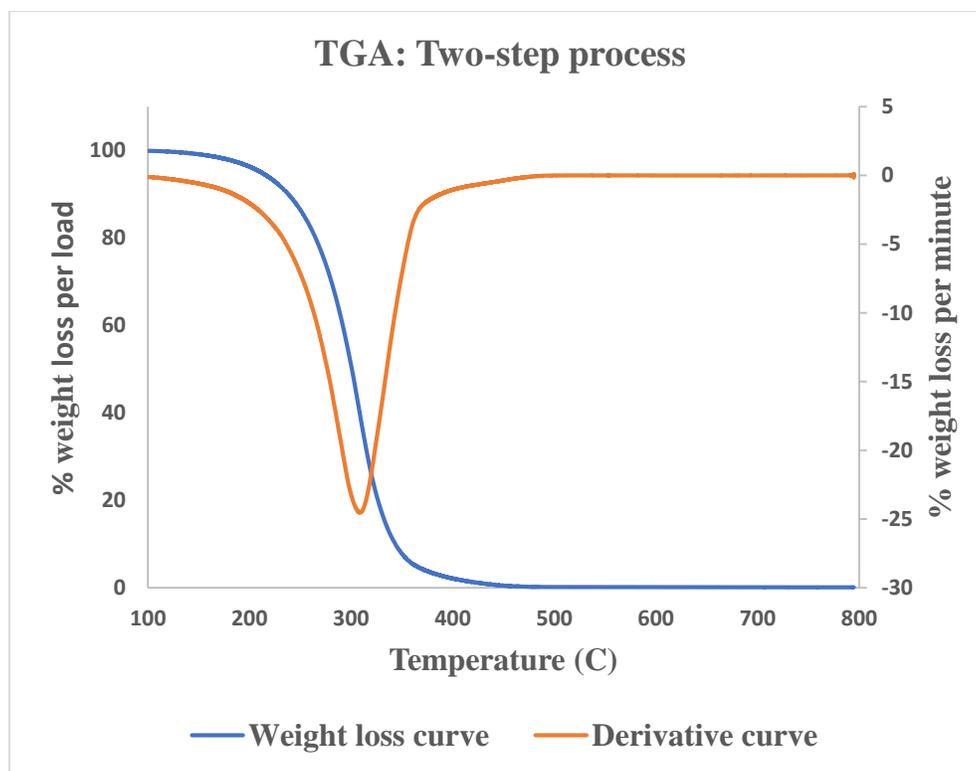


Figure 5. 29: Derivative curve and weight loss curve vs temperature (two-step process)

The thermal stability of biogasoline was studied concerning three different production methods. Regardless of the method used, a derivative curve shift was observed at 300°C in the graphical representation of the data above. This suggests that the thermal stability of biogasoline may be influenced by factors common to all production methods.

Each method yields a different weight loss percentage, causing the derivative curves to end at different points than the weight loss curves, except for thermal cracking curves. The weight loss curves show the amount of mass lost as a function of temperature, while the derivative curves show the rate of mass loss as a function of temperature. The presence of non-condensable gases can affect the rate of mass loss, resulting in differences in the derivative curves. Additionally, the difference in weight loss can be attributed to the presence of difference compounds in the fuel, such as water or non-condensable gases, which can affect the overall weight loss percentage [133].

Furthermore, the presence of water in the fuel can affect the biogasoline's properties and quality, such as octane number, energy content, and stability. Water can also promote the formation of acids, aldehydes, and ketones, which can lead to corrosion of fuel system components and negatively impact engine performance. Therefore, it is essential to control the water content in biogasoline during the production process to ensure its optimal performance and stability [137].

Hence, the weight loss curve is constant in the early stage of thermogravimetric analysis before it decreases as temperature increases. As the temperature increases with time, the water contained evaporates.

In addition to water, biogasoline products also contain oxygenated compounds and acids, which can affect the fuel's intrinsic characteristics and reduce its thermal stability. Carbonylation and hydrogen oxidation reactions form these compounds during the cracking processes. It should be noted that these reactions are not entirely anaerobic [133].

All three processes used to produce biogasoline demonstrate excellent thermal stability. The weight loss curve exhibits changes at a temperature close to 300°C, while the derivative curve varies between 300-800°C. These temperature ranges are consistent with those found by Chuaykleang et al [1].

In their study, the weight loss curve began to change around 350°C, and the derivative curve changed between 350-800°C.

The result shows that the bio-gasoline produced is thermally stable.

5.6. Optimization

In investigating the impact of reaction variables on the percentage yield of biogasoline, it is crucial to identify significant variables and their effects on the response. However, it should be noted that the nitrogen flow rate does not significantly affect the process. Its response is neglected and therefore suppressed from the regression model. Then the empirical equation is reduced to:

$$Y_{biogasoline(\%)} = -260.55 + 1.245X_1 - 11.35X_3 - 0.00136X_1^2 - 0.308X_3^2 + 0.02773X_1X_3$$

X₁ and X₃ represent respectively the response factors of temperature and catalyst weight

The empirical model was used to optimize biogasoline percentage yield. Then the data were regressed to find the optimum reaction temperature and catalyst weight.

5.6.1. Catalytic cracking

Table 5. 4: Catalytic cracking optimized result

Temperature (C)	Cat. Weight (g)	Experimental data%	Optimized data	Error Square
400	1	1.18	1.189	6.59E-05
400	3	4.75	4.273	0.0125
400	5	5.21	6.276	0.0288
475	1	6.31	6.252	8.58E-05
475	3	4.35	6.404	0.1029
475	5	6.33	5.476	0.0243
550	1	12.17	11.511	0.0033
550	3	9.1	8.732	0.0018
550	5	4.61	4.872	0.0029

From table 5.4, the optimized data are within the required range since the error is within the +/- 15%. The experimental data match the optimized data. Therefore, the assumption that the nitrogen flow rate does not affect the result is correct. The optimized biogasoline yield is 11.511% recovered at 550°C and 1g catalyst load.

Table 5. 5: Regression data for catalytic cracking**Regression Statistics**

Multiple R	0.685
R Square	0.469
Adjusted R Square	0.292
Standard Error	2.437
Observations	9

The R-Square value is an indicator of how well the data fit in the model used. It is a value between 0 and 1, where a higher value indicates a better fit. In the regression statistics table 5.5, the R-squared value is 0.469, which means that the model can explain about 47% of the variation in the data. While a high R-squared value (above 0.9) is generally desirable, it depends on the specific context and goals of the analysis. In some cases, a lower R-squared value may still be considered acceptable, particularly if the model is statistically significant and provides useful insights into the relationship between the variables as for the actual study.

Table 5. 6: ANOVA data for catalytic cracking

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	15320.746	15320.746	5.819	0.0466
Residual	7	18429.254	2632.751		
Total	8	33750			

From the ANOVA table, the significance of the F value explains that the regression of data was good since the importance of the F value is less than the α value ($\alpha = 0.05$).

The operating temperature and catalyst weight is 482°C and 3.35 grams, respectively.

5.6.2. Two steps process (hybrid process)

Table 5. 7: Two steps process optimization data

Temperature (C)	Cat. Weight (g)	Experimental data (%)	Optimized data	Error Square
400	1	1.56	1.578	0.000
400	3	2.26	2.328	0.000
400	5	0.98	0.971	0.000
475	1	6.5	5.690	0.020
475	3	3.04	16.616	0.668
475	5	1.43	25.434	0.891
550	1	1.63	1.688	0.000
550	3	29.63	22.780	0.090
550	5	26.79	41.780	0.024

The error square values for the process carried at 475°C and high catalyst weight (3 and 5 grams) are high, reaching the maximum percentage error of 89.1%. These data are not within the acceptable maximum 15% error, and the process is carried out at 550°C and with low catalyst weight.

The processes carried out at low temperatures are within the maximum acceptable error for all catalyst weights. The process carried at 550°C and the high catalyst weight (3 and 5 grams) are within reasonable ultimate mistake. The optimized biogasoline yield is 41.78% recovered at 550°C and 5g catalyst load.

Table 5. 8: Regression data for two steps process (Hybrid method)

Regression Statistics	
Multiple R	0.909
R Square	0.825
Adjusted R Square	0.770
Standard Error	5.165
Observations	9

The model explains about 82.5% of data even though the R. Square value is lower than the required value, which must be above 90% (R. Square >0.9). The model used is deemed fit for the regression of two steps process method.

Table 5. 9: ANOVA data for two steps process (hybrid process)

ANOVA					
	df	SS	MS	F	Significance F
Regression	2	757.086	378.543	14.191	0.005
Residual	6	160.045	26.674		
Total	8	917.131			

The significance of F for the two-step process is lower, which explains the observed regression.

The operating temperature and catalyst weight were measured at 567.2°C and 4.32grams

5.7. Weight hourly space velocity (WHSV)

The weight hourly space velocity is a critical parameter in biogasoline production, defined as the ratio of the nitrogen flow rate to the catalyst weight, with a unit of per hour (h^{-1}) [1].

The optimum weight hourly space velocity for catalytic cracking and the two-step process are respectively $0.28h^{-1}$ and $0.22h^{-1}$.

5.8. By-products

GC-SM analysis reveals the presence of two other components in addition to the biogasoline in bio-oil produced during the cracking of waste cooking oil. The composition of bio-oil is known to vary, and after investigation, the following products were found in the bio-oil: biogasoline, biodiesel, biokerosene, and heavy bio-oil. Interestingly, an increase in the percentage of biogasoline led to a decrease in the percentage of other biofuels.

The tables below represent different categories of biofuels present in the bio-oils after the cracking of WCO.

Table 5. 10: Catalytic cracking products

Temperature	Catalyst Weight	Bio gasoline	Biodiesel	Kerosene
400	1	1.18	73.34	23.93
400	3	4.75	9.61	65.8
400	5	5.21	9.19	77.93
475	1	6.31	7.4	80.72
475	3	4.35	6.38	82.14
475	5	6.33	11.13	76.81
550	1	12.17	8.41	75.33
550	3	9.1	9.99	75.74
550	5	4.61	7.35	81.15

The amount of biodiesel produced is higher at low temperatures and low catalyst weight, while an increase in reaction temperature leads to a rise in the percentage of biogasoline and biokerosene. Moreover, increasing the catalyst load results in a higher percentage of biogasoline and biokerosene, but a lower percentage of biodiesel.

At moderate temperatures, the percentage of biogasoline produced remains similar at both low and high catalyst loads, whereas the percentage of biokerosene increases from low to medium catalyst load. Additionally, the percentage of biodiesel increases with the increase in catalyst load.

At high temperatures, the percentage of biogasoline decreases with increasing catalyst load, while the percentage of biokerosene increases.

Table 5. 11: Two steps process (Hybrid method)

Temperature	Catalytic Weight	Bio gasoline	Biodiesel	Kerosene
400	1	1.56	74.2	23.45
400	3	2.26	37.17	57.47
400	5	0.98	76.22	22.09
475	1	6.5	19.38	69.39
475	3	3.04	30.61	59.98
475	5	1.43	68.09	29.01
550	1	1.63	75.25	22.25
550	3	29.63	27.57	36.41
550	5	26.79	28.71	39.25

The percentage of of biodiesel in bio-oil is significant, as the two-step process uses transesterification as an advanced pre-treatment step to produce biogasoline. An increase in the biodiesel percentage leads to a decrease in both the biogasoline and biokerosene percentages.

At low to moderate temperatures, a higher percentage of biodiesel and biokerosene is produced. However, at high temperature and from moderate to high loads, the biofuels are produced in almost equivalent portions.

5.9. Physical properties of biogasoline

5.9.1. Introduction

This chapter aims to provide some essential physical properties of biogasoline produced and compare them with the physical properties of conventional gasoline (fossil-based biofuel).

5.9.2. Colour

Colour is a physical property that can be distinguished easily. Bio gasoline shares the same colour as gasoline which is yellow. Bio-oil produced is not entirely yellow since it contains more than one biofuel. The product is not yellow, so distillation is a requirement.

5.9.3. Density

Gasoline has a density of 0.735 kg.m^{-3} , as reported by Demirbas [139] at 15°C . Demirbas [139] reported biogasoline density to be 0.732 kg.m^{-3} .

The bio-oil produced during this investigation has a density of 0.887 kg.m^{-3} at 20°C . A discrepancy exists between the density reported by [139] and the density measured. The density measured is within biodiesel and biokerosene density. The density measured is roughly 17.47% of the biogasoline density reported by Demirbas [139]

5.9.4. Viscosity

Demirbas [139] reported that biogasoline's dynamic viscosity is in the region of 1.13cP, and the dynamic viscosity of conventional gasoline (fossil-based gasoline) is in the region of 1.17cP. Yet, the dynamic viscosity measured is between 2 to 3.5cP.

The measured viscosity of biogasoline is within the reported viscosity range of biodiesel and biokerosene, which is expected since the bio-oil consists of biodiesel, biogasoline, and biokerosene. The reported viscosity values are therefore considered accurate. The properties measured proved that the properties of biogasoline produced are within the range of those reported. It is necessary to measure these properties after the purification of bio-oil produced.

Table 2.8 provides more information regarding biogasoline properties and conventional gasoline properties.

CHAPTER SIX: Conclusions and Recommendations

7.1. Conclusions

According to the X-ray diffraction analysis, calcination at low temperatures results in poor yield due to incomplete dehydration, which causes the formation of boehmite. The presence of boehmite makes the catalyst ineffective during the waste cooking oil cracking stage. Therefore, it is necessary and practical to perform the calcination process at elevated temperatures, as this allows for complete dehydration. Cracking can then occur successfully, resulting in better yield.

A second X-ray diffraction analysis was carried out to evaluate the impact of the component mole ratio on the catalyst samples. The graphical representation of the data indicates that the different samples exhibit peaks located at the same position regardless of the component's mole ratio. This result demonstrates that X-ray diffraction analysis is primarily qualitative and cannot detect differences in mole ratio based on the chromatogram alone.

The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was performed to identify the optimal mixture, as it was suggested that the ideal combination should consist of metal ions in an equimolar ratio. The results of the ICP-OES analysis indicate that the catalyst sample used was within the recommended range, as the difference between the cobalt and molybdenum ratio required to achieve equimolar was within an acceptable margin of error.

Both scanning and transmission electron microscopy (SEM & TEM) analyses were performed at low and high magnifications. At low magnification, the sample images obtained from both analyses were similar. However, at high magnification, the SEM images showed significant changes in the catalyst samples as the temperature increased. The samples appeared to break up and develop cracks at high temperatures. This breaking and cracking within the catalyst samples facilitated the penetration of raw materials, leading to better cracking of waste cooking oil. Therefore, the catalyst was calcined at high temperatures ranging from 500°C to 700°C to perform catalytic cracking of waste cooking oil.

The transmission electron microscopy (TEM) image of the catalyst calcined at 600°C exhibited significant breakage, providing evidence to support the majority of authors' recommendation of using the catalyst calcined at 600°C.

The EDX images confirmed the presence of all the metals in the catalyst.

Thermogravimetric analysis (TGA) was used to identify the the regeneration temperature of the catalyst. The catalyst sample undergoes a regeneration cycle that involves calcination and several reactions,

including evaporation, partial oxidation, combustion, and complete catalyst regeneration. Three catalyst samples calcined at 500°C, 600°C, and 700°C were analyzed to determine the optimal catalyst for biogasoline production. The graphical representation indicated that the catalyst calcined at 600°C underwent the regeneration cycle more effectively than the other two catalyst samples. The regeneration temperature for all three catalysts was 600°C. Therefore, the catalyst calcined at 600°C with a smooth regeneration reaction curve was deemed suitable for producing biogasoline through catalyst cracking using waste cooking oil.

The catalyst sample calcined at 700°C has a rigorous regeneration reaction curve. This abnormality could be linked to the amount of coke deposited on the catalyst during calcination. The analysis based on the amount of catalyst deposited on the catalyst revealed that the same amount of coke was deposited on both catalysts calcined respectively at 600°C and 700°C. Hence, it was concluded that the rigorous nature of the regeneration reaction curve is not linked to the coke deposited on their surface. The rigorous regeneration curve at 700°C can be related to heat load.

The regeneration reaction curve did not follow the conventional regeneration reaction cycle, so it is recommended to use catalyst calcines at elevated temperatures above 500°C.

Waste cooking oil comprises many impurities. After its pre-treatment, the chromatograph () shows that cleaning eliminates impurities, and the sulfur portion decreases from 13% to 4%. The remaining 4% of contaminants were within an acceptable percentage.

It is essential to monitor the following parameters because they are the ones that control the recovery: the reaction temperature, reaction time, and process. The recovery percentage of bio-oil ranges from 10% to 70%. There was no biogasoline produced at low reaction temperature and short reaction time. The 10% was the minor bio-oil recovered at low temperatures, and 70% was the highest at elevated moderate and elevated cracking temperatures (70%).

Thermal cracking used three reaction times, respectively 30, 60, and 90 minutes, to investigate biogasoline production. Figure (5.20) shows that the biogasoline yields reach their maximum at a reaction time of 60 minutes. After that, biogasoline production decreases due to the formation of non-condensable gases, ashes, and other organic compounds present in the product.

For the thermal cracking method, the highest biogasoline percentage yields (24.96%) at the reaction temperature of 500°C with a reaction time of 60 minutes. Biogasoline yields increase with the temperature increase at the optimum reaction temperature and decrease as the reaction time increases. The following

biogasoline yields produce at the reaction temperature of 500°C, 17.74%, 24.96, and 20.21, respectively, at 30, 60, and 90 minutes.

The catalytic cracking process was conducted at a constant reaction time since the reaction time was set from thermal cracking.

The catalytic cracking was conducted based on the calcination temperature, the catalyst weight load, and the reaction temperature.

Based on the investigation of the biogasoline production at the constant reaction temperature (475°C) while varying the calcination temperature, the biogasoline percentage yield increased with the calcination temperature. 42.36% biogasoline was produced using 5 grams of catalyst load for a calcination temperature of 700°C. As the catalyst load is lowered, the biogasoline percentage also decreases.

The biogasoline percentage increases with the reaction temperature at a constant catalyst weight of 1 gram. The highest biogasoline percentage yield (12.7%) was obtained at 550°C.

One gram of catalyst to 44 grams of oil was found suitable for biogasoline production.

The biogasoline percentage increases with the reaction temperature reaction for the two steps process (hybrid method). 29.63% of biogasoline was yielded at the reaction temperature of 550°C and 3 grams catalyst load.

Figures (5.27), (5.28), and (5.29) were used to investigate the thermal stability of biogasoline produced. It was concluded that the biogasoline produced was thermally stable since there was no weight loss at low temperatures, and the shape of the curves changed in the region from 350°C to 800°C.

The optimum temperatures and the catalyst weight after statistical analysis for catalytic cracking and two steps process to be respectively 482°C and 3.35grams (for the catalytic cracking) and 567.2°C and 4.32grams (for the two-step process). The optimum biogasoline yields for catalytic cracking and the two-step process are 11 and 41%.

The optimum weight hourly space velocity for catalytic cracking and two-step process are respectively 0.28h⁻¹ and 0.22h⁻¹.

7.2. Recommendations

Improving the reactor flowsheet by adding a preheating system for excellent conversation of waste cooking oil is recommended. Using the pyrolysis reactor alone without preheating caused the reactor to continue increasing after the temperature reading reached the set reaction temperature. The preheating system before

the catalytic reaction will allow the formation of the gaseous reactor's effluent to be fed to the catalytic reactor for better conversion because gas-phase reactions are known to have higher conversions, given that there is an excellent transfer phase.

It is recommended to perform thermal cracking without a catalyst at high temperatures ranging from 500 to 800°C at a reaction time of one hour because thermal cracking seems to have an excellent conversion rate at high temperatures.

It is recommended to further research on catalytic cracking at high temperatures and low to moderate catalyst weight load.

It is recommended to research the two-step technique further. It is a future technology, and its conversion rate at high temperatures is promising. The recommended temperature must range from 550°C to 800°C. These types of temperatures will require sophisticated equipment able to withstand high temperatures.

The technology used to produce the biogasoline yielded an excellent percentage of fuel and some by-products. Further research is recommended, and modification of parameters for excellent quality and biogasoline percentage yield. The improvement of conversion rate is linked to the improvement of catalyst performance. It is recommended to improve the catalyst performance through the addition of metals such as Copper (Cu), Nickel (Ni), and gold (Au). It must be mentioned that the use of gold in the catalyst will command high fees, so it is reasonable to improve the catalyst with affordable chemicals.

It is recommended to carry out thermal and two-step processes at moderate to high pressure to improve weight hourly space velocity, a vital parameter in converting biomass to biogasoline.

It establishes a proper production pathway (method or technique) and the production cost of the biogasoline.

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Appendix

Appendix A: Waste cooking oil composition

Table A. 1: Untreated WCO

Peak#	R.Time	Area%	Name	Similarity	Base m/z
1	1.585	0.02	Oxygen	94	31.95
2	20.171	0.11	Cyclopentene,1-hexyl-	90	67.05
3	22.713	0.14	Octanoic acid	77	60
4	24.546	0.06	6-Dodecyne	89	54
5	26.865	0.05	Nonanoic acid	92	60
6	27.296	0.04	5-Tridecene, (E)-	84	81
7	27.471	0.04	1-Tridecene	95	43.05
8	28.371	0.06	2,4-Decadienal, (E,E)-	97	81.05
9	29.86	1.85	3-Allyl-6-methoxyphenol	97	164.1
10	31.277	0.62	n-Decanoic acid	96	73
11	31.552	0.06	Oleyl alcohol, trifluoroacetate	88	55
12	31.774	0.09	1-Pentadecene	94	55.05
13	32.129	0.05	Tetradecane	94	57.05
14	32.727	0.38	Caryophyllene	97	93.05
15	34.095	0.04	Cyclopentane, decyl-	93	69.05
16	34.287	0.07	Cyclopentene, 1-octyl-	83	67.05
17	34.602	0.09	Undecylenic acid	91	55.05
18	34.785	0.07	Nortricyclyl formate	75	92.05
19	34.921	0.07	Undecanoic acid	77	105.1
20	35.117	0.21	1,13-Tetradecadiene	90	55.05
21	35.375	0.09	Vinyl caprylate	70	57.05
22	35.503	0.28	Oleyl alcohol, trifluoroacetate	92	55
23	35.655	0.14	n-Tridecan-1-ol	93	69.05
24	35.913	0.08	n-Pentadecanol	94	55
25	36.231	0.15	Heptadecane	96	57.05
26	36.636	0.21	Phenol, 2-methoxy-4-(2-propenyl)-, acetate	94	164.1
27	38.247	0.07	n-Nonylcyclohexane	95	83.05
28	38.433	0.09	1,8,11-Heptadecatriene, (Z,Z)-	88	67.05
29	38.786	0.2	Dodecanoic acid	94	73
30	38.945	0.13	Cyclohexene, 1-decyl-	75	81.05
31	39.058	0.11	1,7-Hexadecadiene	95	67.05
32	39.289	0.2	1-Hexadecanol	89	69.05
33	39.425	0.04	7-Pentadecyne	84	67.05
34	39.522	0.08	1-Hexadecanol	94	69.05

35	39.843	0.11	1-Heptadecene	96	83.1
36	40.139	0.07	Hexadecane	96	57.05
37	42.666	0.21	cis-13,16-Docasadienoic acid	91	67.05
38	42.993	0.49	3-Heptadecene, (Z)-	95	69.05
39	43.135	0.09	5-Heptadecene, 1-bromo-	81	67.05
40	43.216	0.2	1-Hexadecanol	91	83.05
41	43.587	0.04	1-Nonadecene	93	83.05
42	43.86	0.11	Heptadecane	97	57.05
43	44.712	0.04	6,9-Heptadecadiene	88	67.05
44	44.818	0.05	Oleyl alcohol, trifluoroacetate	87	69.05
45	45.935	0.14	6,9-Heptadecadiene	88	67.05
46	46.09	0.18	Tetradecanoic acid	95	73
47	46.237	0.15	1,7-Hexadecadiene	94	81.05
48	46.499	0.14	n-Nonadecanol-1	92	55.05
49	46.605	0.03	1,7-Hexadecadiene	87	67.05
50	46.743	0.07	1-Hexadecanol	92	83.05
51	48.994	0.25	cis-10-Heptadecenoic acid	88	55
52	49.405	0.08	cis-13,16-Docasadienoic acid	87	67.05
53	50.75	0.08	2-Heptadecanone	87	43
54	51.542	0.04	Hexadecanoic acid, methyl ester	95	74
55	53.238	7.03	n-Hexadecanoic acid	97	73
56	53.525	0.06	9,17-Octadecadienal, (Z)-	92	67.05
57	53.785	0.12	cis-9-Hexadecenal	94	55.05
58	55.219	0.25	Oleic Acid	89	55.05
59	56.076	0.27	cis-13,16-Docasadienoic acid	90	67.05
60	56.323	0.5	Octadecanoic acid, 2-propenyl ester	85	43.05
61	56.564	0.55	Henicos-1-ene	95	97.1
62	56.75	0.18	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	88	67.05
63	56.993	0.59	9-Octadecenoic acid, methyl ester, (E)-	95	55.05
64	57.1	0.75	Nonacosane	85	57.05
65	59.105	45.08	6-Octadecenoic acid, (Z)-	91	55.05
66	59.58	4.37	Octadecanoic acid	94	73
67	60.052	2.06	9,12-Octadecadienoic acid (Z,Z)-	90	67.05
68	60.825	0.57	(R)-(-)-14-Methyl-8-hexadecyn-1-ol	89	67.05
69	61.279	0.98	9,12-Octadecadienoic acid (Z,Z)-	93	67.05
70	62.177	5.91	9-Hexadecen-1-ol, (Z)-	91	96.1
71	62.871	0.27	Octadecanoic acid, 2-propenyl ester	88	100.05
72	63.275	1.26	Glycidyl palmitate	67	98.05
73	65.025	0.12	iso-Propyl 9-.cis.,11-.trans.-octadecadienoate	79	67.05
74	65.373	0.31	(R)-(-)-14-Methyl-8-hexadecyn-1-ol	90	67.05
75	66.262	0.41	9-Hexacosene	94	97.1

76	68.039	3.72	Oleoyl chloride	89	55
77	69.025	0.59	Octadecanoic acid, 2,3-dihydroxypropyl ester	83	98.05
78	69.695	3.74	Glycidyl oleate	89	129.05
79	70.625	0.25	Glycidyl palmitate	88	57.05
80	71.225	0.18	9,12-Octadecadienoic acid (Z,Z)-, 2,3-dihydrox	84	67.05
81	72.231	5.46	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	92	67.05
82	73.172	0.03	Oleyl alcohol , acetate	88	96.1
83	73.963	0.06	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	88	67.05
84	75.859	0.4	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	82	67.05
85	77.326	0.31	7-Hexadecenal, (Z)-	87	97.1
86	79.398	0.34	1,22-Docosanediol	72	173.05
87	82.95	0.15	Oleic acid, 3-(octadecyloxy)propyl ester	79	98.05
88	84.481	0.16	2-Methylhexacosane	85	57.05
89	85.483	0.26	Diethyl n-hexadecylmalonate	68	173.05
90	86.517	0.34	(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5R)-5,6	81	382.35
91	88.224	0.13	Stigmasta-3,5-diene	85	396.4
92	88.728	0.12	9,19-Cyclolanostan-3-ol, 24-methylene-, (3.beta	72	55
93	89.313	0.76	Stigmasta-3,5-diene	90	396.4
94	89.825	0.34	Stigmasta-5,22-dien-3-ol, acetate, (3.beta.)-	71	296.25
95	90.873	0.21	Tetrapentacontane, 1,54-dibromo-	84	57.05
96	96.091	0.36	.gamma.-Sitosterol	91	414.4
97	97.628	0.21	E,E,Z-1,3,12-Nonadecatriene-5,14-diol	87	55.05
98	98.093	0.34	E,E,Z-1,3,12-Nonadecatriene-5,14-diol	80	55.05
99	99.495	0.84	1,6,10,14,18,22-Tetracosahexaen-3-ol, 2,6,10,1	85	69.05
100	103.024	0.51	Oxirane, hexadecyl-	77	57.05

Table A. 2:Treated WCO

Peak#	R.Time	Area%	Name	Similarity	Base m/z
1	8.854	5.96	Hexanal	88	44
2	18.769	0.46	Heptanoic acid	90	60
3	22.735	0.21	(3E,5Z)-1,3,5-Undecatriene	78	79.05
4	24.567	0.07	6-Dodecyne	89	54
5	27.486	0.05	1-Tridecene	96	43.05
6	27.855	0.06	Tetradecane	96	57.05
7	29.883	0.3	Eugenol	97	164.1
8	31.393	0.04	n-Decanoic acid	93	73
9	31.789	0.12	1-Pentadecene	96	55.05
10	32.137	0.07	Tetradecane	97	57.05
11	32.739	0.1	Caryophyllene	95	93.05
12	34.108	0.04	Cyclopentane, decyl-	94	69.05

13	35.156	0.14	cis-9-Tetradecen-1-ol	92	67.05
14	35.523	0.28	(Z)6-Pentadecen-1-ol	91	67.05
15	35.664	0.14	n-Tridecan-1-ol	93	69.05
16	35.923	0.09	1-Pentadecene	96	83.1
17	36.244	0.28	Heptadecane	96	57.05
18	36.641	0.04	Phenol, 2-methoxy-4-(2-propenyl)-, acetate	92	164.1
19	38.261	0.07	n-Nonylcyclohexane	96	83.05
20	38.441	0.05	5-Heptadecene, 1-bromo-	84	67.05
21	38.828	0.08	Dodecanoic acid	93	73
22	38.945	0.1	Cyclohexene, 1-nonyl-	77	81.05
23	39.065	0.08	1,7-Hexadecadiene	95	81.05
24	39.245	0.05	Bicyclo[5.3.0]decane	81	82.05
25	39.31	0.07	1-Tetradecanol	90	69.05
26	39.532	0.05	1-Hexadecanol	95	69.05
27	39.858	0.1	1-Heptadecene	96	83.05
28	40.151	0.05	Hexadecane	95	57.05
29	42.677	0.22	cis-13,16-Docasadienoic acid	91	67.05
30	43.006	0.54	3-Heptadecene, (Z)-	95	69.05
31	43.15	0.11	cis-13,16-Docasadienoic acid	78	67.05
32	43.229	0.17	3-Heptadecene, (Z)-	93	83.05
33	43.871	0.18	Heptadecane	97	57.05
34	44.829	0.06	Oleyl alcohol, trifluoroacetate	88	69.05
35	45.941	0.1	6,9-Heptadecadiene	88	67.05
36	46.184	0.35	Tetradecanoic acid	94	73
37	46.265	0.09	1,13-Tetradecadiene	93	55.05
38	46.507	0.09	9-Tricosene, (Z)-	92	55.05
39	50.755	0.1	2-Heptadecanone	93	58
40	53.395	9.73	n-Hexadecanoic acid	97	73
41	53.538	0.08	9,17-Octadecadienal, (Z)-	93	67.05
42	53.791	0.14	cis-9-Hexadecenal	94	55.05
43	56.081	0.08	9,12-Octadecadien-1-ol, (Z,Z)-	89	67.05
44	56.338	0.59	Octadecanoic acid, 2-propenyl ester	86	43.05
45	56.573	0.3	Henicos-1-ene	96	97.1
46	56.666	0.2	Octadecyl trifluoroacetate	88	57.05
47	56.995	0.21	9-Octadecenoic acid, methyl ester, (E)-	94	55.05
48	57.165	0.08	2-Nonadecanone	93	58
49	57.81	0.11	17-Octadecynoic acid, methyl ester	78	43.05
50	58.937	23.57	9,12-Octadecadienoic acid (Z,Z)-	91	67.05
51	59.226	17.81	Octadec-9-enoic acid	93	55.05
52	59.347	4.81	9,12-Octadecadienoic acid (Z,Z)-	90	67.05
53	59.727	4.31	Octadecanoic acid	94	73

54	60.178	0.49	9,12-Octadecadienoic acid (Z,Z)-	89	67.05
55	60.29	0.22	9,12-Octadecadienoic acid (Z,Z)-	88	67.05
56	60.45	0.18	Naphthalene, 1,2,3,4,4a,5,8,8a-octahydro-4a-m	78	96.1
57	60.835	0.12	(R)-(-)-14-Methyl-8-hexadecyn-1-ol	88	67.05
58	61.323	0.36	9,12-Octadecadienoic acid (Z,Z)-	93	67.05
59	61.651	0.75	Isopropyl linoleate	85	67.05
60	61.93	2.35	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (86	55.05
61	62.183	1.64	Z-9-Tetradecen-1-ol formate	91	96.1
62	62.321	0.54	9-Octadecen-1-ol, (Z)-	90	96.1
63	62.547	0.24	cis-13,16-Docosadienoic acid, methyl ester	90	67.05
64	62.68	0.12	Glycidyl oleate	78	129.05
65	62.886	0.19	Octadecanoic acid, 2-propenyl ester	92	43.05
66	63.023	0.05	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (79	265.25
67	63.167	0.1	1-Hexacosanol	94	97.1
68	63.477	1.42	Glycidyl palmitate	94	98.05
69	65.023	0.07	iso-Propyl 9-.cis.,11-.trans.-octadecadienoate	82	67.05
70	65.26	0.18	6,9-Octadecadienoic acid, methyl ester	84	67.05
71	65.511	0.13	Oleyl alcohol , acetate	92	96.1
72	66.043	0.13	Oleyl alcohol , acetate	91	96.1
73	66.266	0.39	1-Hexacosanol	96	97.1
74	66.535	0.19	1-Hexacosanol	94	97.1
75	67.5	0.23	Isopropyl linoleate	83	43
76	67.79	1.08	9,12-Octadecadienoic acid (Z,Z)-, 2-hydroxy-1	88	43
77	68.054	1.46	Oleoyl chloride	91	55.05
78	68.282	0.33	Propyleneglycol monooleate	87	55.05
79	68.787	0.17	Octadecanoic acid, ethenyl ester	78	43.05
80	69.039	0.48	Stearic acid chloride	84	98.05
81	69.468	1.9	1,8,11-Heptadecatriene, (Z,Z)-	84	67.05
82	69.718	2.16	Glycidyl oleate	89	129.05
83	69.961	0.56	E,E,Z-1,3,12-Nonadecatriene-5,14-diol	87	55.05
84	70.647	0.23	Glycidyl palmitate	89	57.05
85	72.011	0.47	Methyl 5,11,14-eicosatrienoate	87	67.05
86	72.248	1.39	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	92	67.05
87	72.444	2.31	13-Docosen-1-ol, (Z)-	92	96.1
88	72.822	1.21	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	90	67.05
89	73.08	0.09	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	84	67.05
90	73.182	0.1	cis-13,16-Docosadienoic acid	89	96.1
91	73.38	0.24	1-Hexacosanol	95	97.1
92	73.638	0.1	Nonadecyl trifluoroacetate	90	97.1
93	73.959	0.07	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	88	67.05
94	75.63	0.14	9,12-Octadecadien-1-ol, (Z,Z)-	89	67.05

95	85.33	0.09	trans,trans-9,12-Octadecadienoic acid, propyl e	87	67.05
96	85.503	0.13	4-Trifluoromethylbenzoic acid. 4-hexadecyl es	69	173.05
97	86.52	0.18	(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5R)-5,6	78	382.35
98	88.218	0.12	Stigmasta-3,5-diene	87	396.35
99	89.311	0.55	Stigmasta-3,5-diene	90	396.35
100	90.24	0.13	Oleyl oleate	79	55.05
101	96.399	0.1	16-Hentriacontanone	96	239.2
102	103.069	0.97	Oxirane, hexadecyl-	78	57.05

Appendix B: Bio-oil composition

Table B. 1:Thermal cracking

Peak#	R.Time	Area%	Name	Similarity	Base m/z
1	1.92	3.69	Methylene chloride	97	49
2	2.093	0.25	Acetic acid	98	43
3	2.917	0.16	1-Heptene	91	56.05
4	3.023	0.13	Heptane	97	43.05
5	4.793	0.24	1-Octene	97	55
6	5.044	0.3	Octane	96	43.05
7	8.479	0.52	1-Nonene	93	43.05
8	8.861	0.43	Nonane	96	43.05
9	13.267	0.49	1-Decene	95	43.05
10	13.429	0.31	Hexanoic acid	91	60
11	13.708	0.26	Decane	95	57.05
12	16.46	0.11	Benzene, n-butyl-	89	91.05
13	18.333	0.86	1-Undecene	96	43.05
14	18.415	0.78	trans-1,2-Diethyl cyclopentane	60	55
15	18.56	0.13	3-Methyloctanoic acid	61	60
16	18.606	0.36	Heptanoic acid	89	60
17	18.764	0.27	Undecane	97	57.05
18	19.038	0.38	1-Undecanol	94	55
19	19.461	0.19	1-Undecene	94	55.05
20	20.021	0.26	Cyclopentene,1-hexyl-	91	67
21	21.53	0.21	Benzene, pentyl-	95	91.05
22	23.105	0.46	1-Heptanol, 6-methyl-	80	57.05
23	23.199	0.31	Octanoic acid	96	60
24	23.289	0.23	1-Dodecene	95	43.05
25	23.699	0.28	Dodecane	97	57.05
26	27.42	0.48	n-Decanoic acid	62	131

27	27.46	0.29	Nonanoic acid	58	60
28	27.505	0.17	8-Methylnonanoic acid	71	73
29	27.569	0.51	Nonanoic acid	95	60
30	27.99	0.37	1-Tridecene	96	55.05
31	28.367	0.43	Tridecane	96	57.05
32	32.093	5.65	n-Decanoic acid	96	73
33	32.421	0.58	1-Tetradecene	96	55
34	32.773	0.55	Tetradecane	98	57.05
35	34.765	0.16	Cyclopentane, nonyl-	92	69.05
36	35.05	0.22	Cyclopentene, 1-octyl-	83	67
37	35.73	0.56	Undecanoic acid	90	73
38	35.919	0.44	Undecylenic acid	94	55.05
39	36.22	0.14	1-Pentadecene	90	55
40	36.318	0.4	11,14-Eicosadienoic acid	85	67
41	36.381	0.28	1-Pentadecene	93	69.05
42	36.606	0.41	1-Pentadecene	96	83.05
43	36.923	1.42	Pentadecane	96	57.05
44	38.913	0.29	n-Nonylcyclohexane	96	83.05
45	39.548	0.28	Dodecanoic acid	90	73
46	39.685	0.19	Cyclohexene, 1-nonyl-	80	81.05
47	39.805	0.26	5-Tetradecen-1-ol, acetate, (Z)-	89	82.05
48	39.96	0.17	1,7-Hexadecadiene	86	82.05
49	40.048	0.2	Pentafluoropropionic acid, 4-hexadecyl ester	88	83.05
50	40.265	0.27	Dichloroacetic acid, 4-hexadecyl ester	93	83.1
51	40.557	0.49	1-Nonadecene	97	83.05
52	40.849	0.44	Heptadecane	95	57.05
53	43.259	0.25	n-Nonadecanol-1	85	83.1
54	43.609	0.16	Carbonic acid, ethyl tetradecyl ester	75	92.05
55	43.739	1.31	3-Heptadecene, (Z)-	95	83.05
56	43.962	1.08	3-Heptadecene, (Z)-	95	83.1
57	44.309	0.29	1-Nonadecene	95	83.05
58	44.576	1.19	Heptadecane	97	57.05
59	46.622	0.17	cis-13,16-Docosadienoic acid	90	67
60	46.864	0.55	Tetradecanoic acid	95	73
61	47.011	0.15	9-Octadecen-1-ol, (Z)-	94	55
62	47.251	0.28	Oleyl alcohol, trifluoroacetate	93	55
63	47.49	0.26	9-Tricosene, (Z)-	89	83.05
64	47.861	0.14	n-Nonadecanol-1	95	97.1
65	48.112	0.16	Eicosane	94	57.05
66	50.63	0.17	Oxirane, hexadecyl-	86	57.05
67	51.485	0.2	Heneicosane	89	57.05

68	51.546	0.27	2-Heptadecanone	86	58
69	53.861	11.5	n-Hexadecanoic acid	96	73
70	54.135	0.71	1-(+)-Ascorbic acid 2,6-dihexadecanoate	67	83.05
71	54.345	0.96	Pentadecafluorooctanoic acid, hexadecyl ester	81	83.1
72	54.505	0.51	Behenic alcohol	88	97.05
73	54.715	0.4	Eicosane	90	57.05
74	57.128	0.34	Oxirane, hexadecyl-	81	43.05
75	57.306	0.54	Henicos-1-ene	94	97.1
76	57.375	0.28	9-Tricosanol, acetate	90	83.05
77	57.783	0.28	Heneicosane	93	57.05
78	57.952	0.24	2-Nonadecanone	91	58
79	58.935	0.45	o-Dodecylphenol	86	107.05
80	59.468	25.05	9-Octadecenoic acid, (E)-	92	55
81	60.174	8	Octadecanoic acid	91	43.05
82	60.86	0.46	3,7,11,15-Tetramethylhexadecane-1,2,3-triol	66	105.1
83	61.06	0.36	2-Methylhexacosane	77	57.05
84	62.885	0.58	Palmitoyl chloride	82	239.1
85	63.082	1.68	9-Octadecen-1-ol, acetate, (Z)-	92	96.05
86	63.431	0.65	(6Z,9Z)-6,9-Tricosadiene	89	96.05
87	64.052	0.39	9-Tricosene, (Z)-	93	97.1
88	66.478	0.28	13-Docosen-1-ol, (Z)-	91	96.05
89	67.198	1.47	Tetracosan-10-yl acetate	95	97.05
90	67.466	1.12	Tetracosan-10-yl acetate	94	97.1
91	69.16	0.63	1-cis-Vaccenoylglycerol	91	55
92	69.398	0.37	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl	88	55.05
93	70.116	0.42	Stearic anhydride	84	267.15
94	73.43	2.96	9-Octadecen-1-ol, acetate, (Z)-	92	96.1
95	73.751	1.87	13-Docosen-1-ol, (Z)-	91	96.05
96	73.878	1.35	Linoleyl acetate	84	81.05
97	74.355	0.77	1-Hexacosanol	95	97.05
98	74.61	0.55	Docosyl heptafluorobutyrate	90	57.05
99	89.352	0.42	Stigmastanol, 2-ethylbutyrate	82	398.25
100	91.166	0.52	.beta.-Sitosterol acetate	92	396.2

Table B. 2: Catalytic cracking at 550oC and 3grams of catalyst

Peak#	R.Time	Area%	Name	Similarity	Base m/z
1	1.781	0.05	Pentane	89	43.05
2	1.87	0.43	Methylene chloride	97	48.95
3	2.011	0.26	Ammonium acetate	98	43
4	2.046	0.1	1-Hexene	96	56.05

5	2.082	0.1	n-Hexane	97	57.05
6	2.651	0.06	Cyclobutane, ethenyl-	87	67.05
7	2.712	0.28	1-Heptene	98	56.05
8	2.801	0.27	Heptane	96	43.05
9	2.878	0.04	2-Heptene	96	56.05
10	4.305	0.33	1-Octene	98	55.05
11	4.525	0.42	Octane	94	43.05
12	4.685	0.19	2-Octene, (E)-	97	55.05
13	4.907	0.1	2-Octene, (Z)-	97	55.05
14	5.27	0.11	1,3-Octadiene	95	54.05
15	6.465	0.07	2,4-Octadiene	84	91.05
16	7.681	0.25	1-Nonene	93	56.05
17	8.054	0.47	Undecane	90	43.05
18	12.325	0.26	1-Decene	95	56.05
19	12.39	0.01	Hexanoic acid	87	60
20	12.766	0.14	Undecane	95	57.05
21	17.343	0.28	1-Undecene	95	55.05
22	17.596	0.31	Heptanoic acid	91	60
23	17.784	0.12	Undecane	95	57.05
24	18.028	0.39	5-Undecene	94	55.05
25	18.426	0.23	1-Undecene	93	55.05
26	19.034	0.33	3a,7a-Epoxy-1H-inden-1-one, hexahydro-	88	67.05
27	20.475	0.12	Benzene, pentyl-	95	91.05
28	20.56	0.13	Tricyclo[4.4.0.0(3,8)]decan-2-one	79	79.05
29	22.317	0.12	1-Tridecene	95	55.05
30	22.74	0.14	Dodecane	97	57.05
31	23.938	0.13	6-Dodecyne	90	54.05
32	27.043	0.21	1-Tridecene	96	43.05
33	27.432	0.25	Tetradecane	97	57.05
34	30.835	0.17	Allyl nonanoate	87	41.05
35	30.89	0.39	n-Decanoic acid	83	60
36	31.005	0.45	Oleic Acid	80	55.05
37	31.04	0.33	n-Decanoic acid	77	60
38	31.09	1.09	Octadecanoic acid	84	129.1
39	31.191	0.64	n-Decanoic acid	95	73
40	31.493	0.32	1-Tetradecene	97	43.05
41	31.848	0.23	Tetradecane	97	57.05
42	33.835	0.12	Cyclopentane, decyl-	94	69.1
43	34.046	0.08	Cyclopentene, 1-octyl-	86	67.05
44	34.718	0.17	Undecanoic acid	93	73
45	34.907	0.22	Undecylenic acid	90	55.05

46	35.273	0.34	Cyclopentadecane	91	55.05
47	35.433	0.29	n-Tridecan-1-ol	93	69.05
48	35.687	0.21	1-Pentadecene	96	83.1
49	36.023	1.62	Heptadecane	96	57.05
50	38.035	0.2	n-Nonylcyclohexane	96	83.1
51	38.538	0.09	Dodecanoic acid	80	73
52	38.858	0.06	1,7-Hexadecadiene	95	81.05
53	39.097	0.12	Pentafluoropropionic acid, 4-hexadecyl ester	90	69.05
54	39.325	0.09	1-Hexadecanol	94	69.05
55	39.651	0.21	1-Nonadecene	96	83.1
56	39.947	0.13	Hexadecane	95	57.05
57	42.264	0.16	n-Nonadecanol-1	87	69.05
58	42.806	1.95	3-Heptadecene, (Z)-	95	69.05
59	43.036	1.41	3-Heptadecene, (Z)-	95	69.05
60	43.155	0.1	Z-8-Methyl-9-tetradecen-1-ol formate	82	81.05
61	43.684	1.04	Heptadecane	97	57.05
62	45.74	0.21	6,9-Heptadecadiene	88	67.05
63	45.894	0.62	Tetradecanoic acid	95	73
64	46.312	0.25	1-Octadecene	93	55.05
65	46.56	0.11	1-Nonadecene	93	83.1
66	50.576	0.23	Eicosane	90	57.05
67	52.92	14.27	n-Hexadecanoic acid	94	73
68	52.965	2.92	n-Hexadecanoic acid	96	73
69	55.701	0.13	Heptadecanoic acid	85	43.05
70	56.12	0.61	Octadecanoic acid, 2-propenyl ester	87	43.05
71	56.357	0.53	Henicos-1-ene	96	97.1
72	56.453	0.17	1-Heptacosanol	91	57.05
73	58.435	25.05	6-Octadecenoic acid, (Z)-	92	55.05
74	58.595	11.55	9-Octadecenoic acid, (E)-	93	55.05
75	58.82	0.06	1,1'-Bicyclohexyl, 2-propyl-, cis-	78	69.05
76	59.112	8.54	Octadecanoic acid	94	73
77	59.26	0.37	Cyclopentane, 1-pentyl-2-propyl-	83	69.05
78	59.544	0.37	1,8,11-Heptadecatriene, (Z,Z)-	81	67.05
79	59.862	0.33	Naphthalene, 1,2,3,4,4a,5,8,8a-octahydro-4a-m	79	96.1
80	60.85	0.88	9,12-Octadecadienoic acid (Z,Z)-	92	67.05
81	61.578	1.19	1,2-Oxathiane, 6-dodecyl-, 2,2-dioxide	81	55.05
82	61.87	1.36	13-Docosen-1-ol, (Z)-	91	96.1
83	62.018	0.59	Oleyl alcohol , acetate	92	96.1
84	62.233	0.57	9-Octadecen-1-ol, (Z)-	89	96.1
85	62.577	0.31	Octadecanoic acid, 2-propenyl ester	90	43.05
86	62.865	0.19	Nonadecyl trifluoroacetate	94	97.1

87	62.97	0.09	9-Octadecene, 1,1'-[1,2-ethanediylbis(oxy)]bis	76	55.05
88	65.212	0.2	Oleyl alcohol , acetate	92	96.1
89	65.974	1.24	1-Hexacosanol	96	97.1
90	66.244	0.65	1-Hexacosanol	95	97.1
91	67.689	0.59	Oleoyl chloride	91	55.05
92	67.931	0.27	Oleoyl chloride	90	55.05
93	68.678	0.29	Octadecanoic acid, 2,3-dihydroxypropyl ester	82	98.1
94	71.889	0.26	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	91	67.05
95	72.092	2.12	Oleyl alcohol , acetate	92	96.1
96	72.435	2.2	13-Docosen-1-ol, (Z)-	91	96.1
97	72.667	0.5	13-Docosen-1-ol, (Z)-	90	96.1
98	73.06	0.72	1-Hexacosanol	95	97.1
99	73.326	0.3	1-Hexacosanol	94	97.1
100	88.933	0.18	Stigmasta-3,5-diene	90	396.35

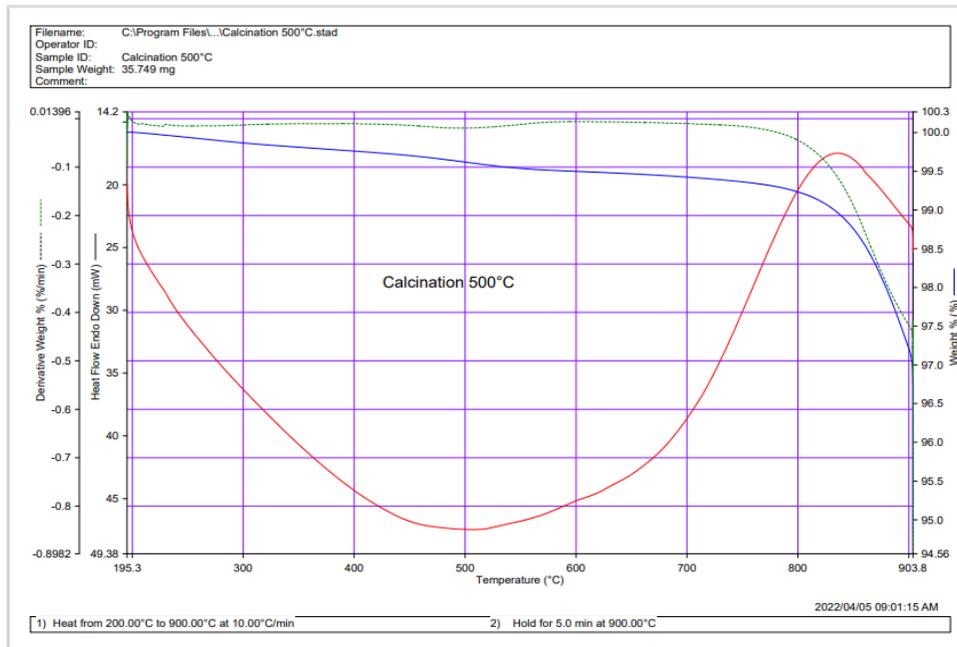
Table B. 3:Two-step process

Peak#	R.Time	Area%	Name	Similarity	Base m/z
1	1.652	21.42	Methyl Alcohol	83	31.05
2	1.782	0.31	Acetone	98	43
3	1.859	0.02	Acetic acid, methyl ester	96	43
4	2.095	0.02	n-Hexane	95	57.05
5	2.157	0.39	Ethyl Acetate	98	43
6	2.28	0.03	Cyclopentane, methyl-	90	56.05
7	2.405	1.71	Propane, 2,2-dimethoxy-	91	73.05
8	2.508	0.08	Hexane, 2-methyl-	96	43.05
9	2.547	0.03	Pentane, 2,3-dimethyl-	94	56.05
10	2.589	0.1	Hexane, 3-methyl-	97	43.05
11	2.691	0.01	Pentane, 3-ethyl-	93	43.05
12	2.821	0.08	Heptane	96	43.05
13	3.862	0.85	Toluene	98	91.05
14	4.93	0.24	Acetic acid, butyl ester	98	43
15	6.524	0.11	Ethylbenzene	98	91.05
16	6.862	0.53	o-Xylene	98	91.05
17	6.915	0.27	p-Xylene	97	91.05
18	7.747	0.3	o-Xylene	98	91.05
19	8.248	0.29	Ethanol, 2-butoxy-	97	57.05
20	52.638	3.65	n-Hexadecanoic acid	96	73
21	56.786	0.1	8-Octadecenoic acid, methyl ester	93	55.05
22	57.92	3.72	9,12-Octadecadienoic acid (Z,Z)-	91	67.05
23	58.229	19.26	Oleic Acid	93	55.05

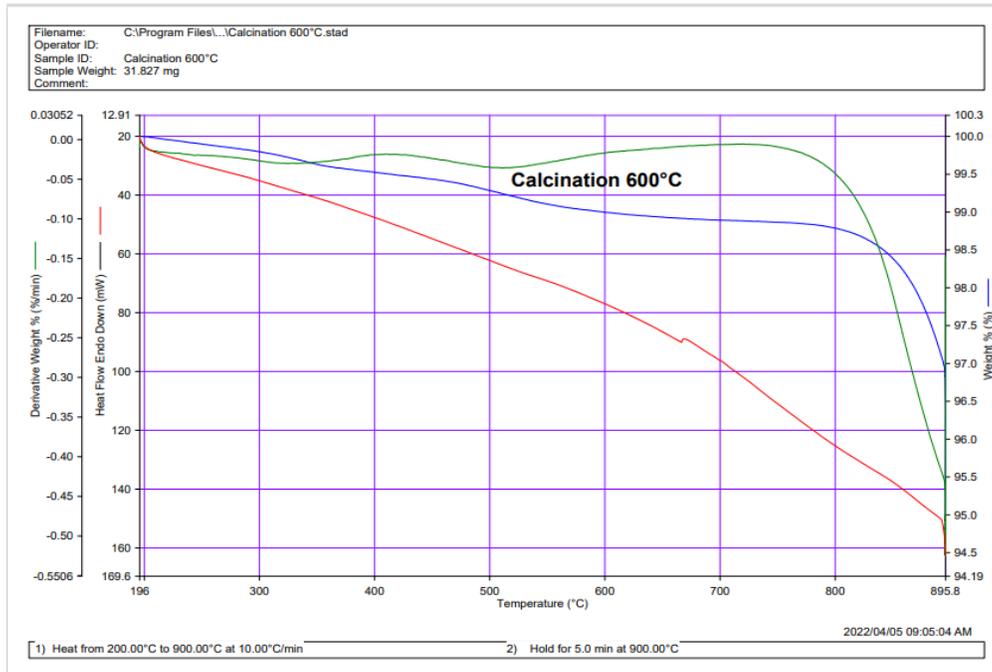
24	58.346	6.28	cis-9-Hexadecenal	91	55.05
25	58.849	2.5	Octadecanoic acid	93	43.05
26	61.603	0.09	Palmitoyl chloride	80	43.05
27	63.168	0.35	Glycidyl palmitate	92	57.05
28	67.493	0.09	9,12-Octadecadienoic acid (Z,Z)-, 2,3-dihydrox	89	67.05
29	67.746	0.19	Oleoyl chloride	90	55.05
30	69.164	0.36	Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	86	67.05
31	69.401	1.14	Glycidyl oleate	91	129.1
32	69.654	0.22	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (87	55.05
33	70.396	0.16	Glycidyl palmitate	86	57.05
34	85.07	0.07	9,12-Octadecadienoic acid (Z,Z)-	81	67.05
35	85.251	0.25	Decyl sulfide	70	173.05
36	89.023	0.09	Stigmast-5-en-3-ol, oleate	84	396.35
37	90.074	18.06	E,E,Z-1,3,12-Nonadecatriene-5,14-diol	85	55.05
38	90.62	1.8	Bromoacetic acid, octadecyl ester	76	97.1
39	90.938	2.98	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16	84	55.05
40	91.295	1.51	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16	78	67.05
41	92.307	3.49	Oxirane, hexadecyl-	78	57.05
42	94.398	2.84	2,5-Di(trifluoromethyl)benzoic acid, 3-hexadec	70	241.1
43	95.813	0.13	.gamma.-Sitosterol	86	414.35
44	96.12	0.17	16-Hentriacontanone	84	239.2
45	96.334	0.4	Sebacic acid, butyl 3-oxobut-2-yl ester	60	241.1
46	97.652	1.27	E,Z-1,3,12-Nonadecatriene	83	67.05
47	102.633	1.66	Oxirane, hexadecyl-	78	57.05
48	103.17	0.23	Z,Z-4,15-Octadecadien-1-ol acetate	65	43.05
49	103.693	0.14	16-Hentriacontanone	78	239.2

Appendix C: Thermogravimetry analysis (TGA)

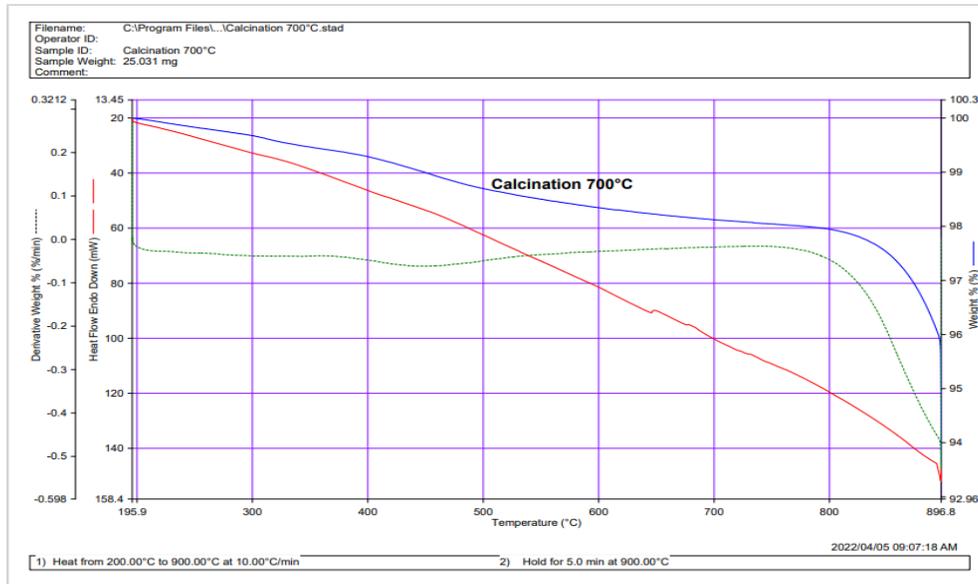
C.1: Determination of temperature raw data



Appendix C. 1: Catalyst calcined at 500°C

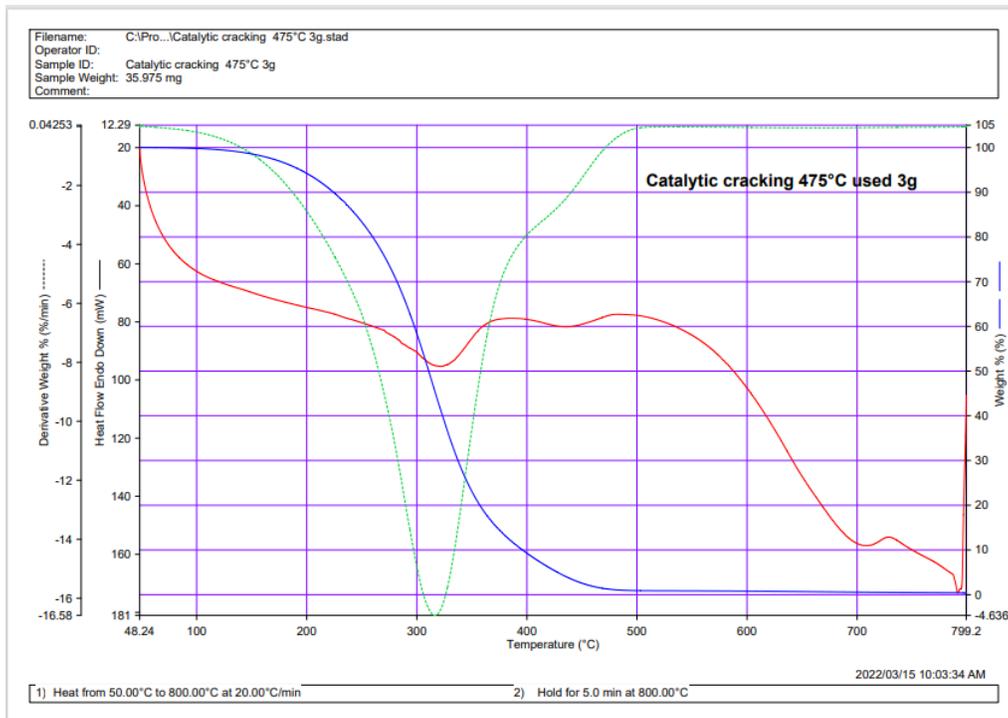


Appendix C. 2: Catalyst calcined at 600°C



Appendix C. 3: Catalyst calcined at 700°C

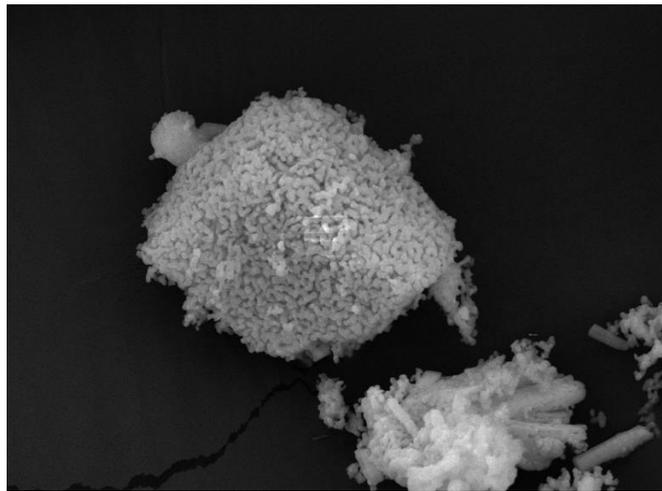
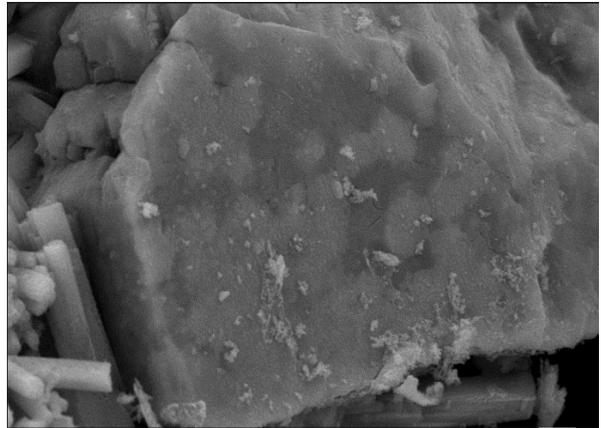
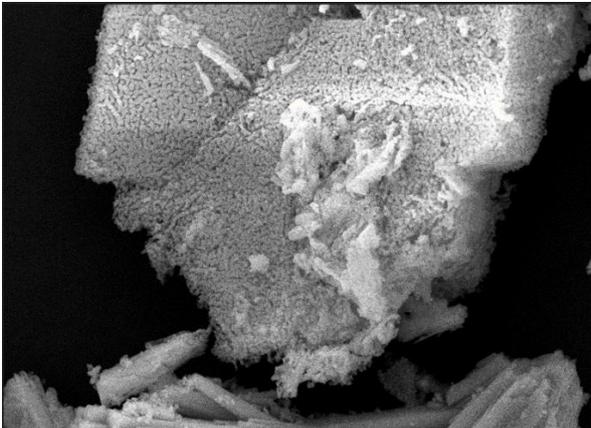
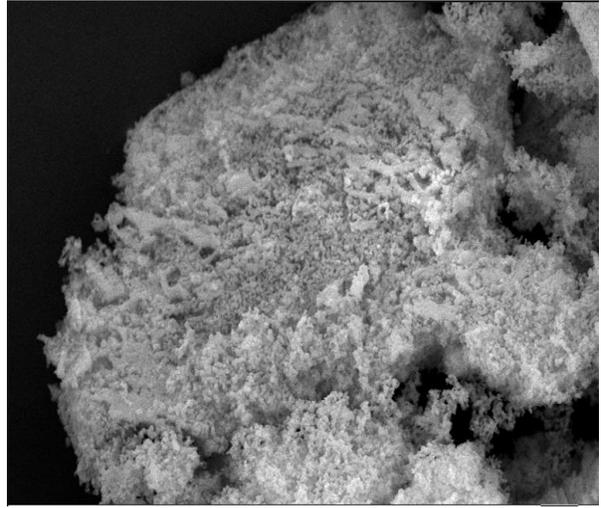
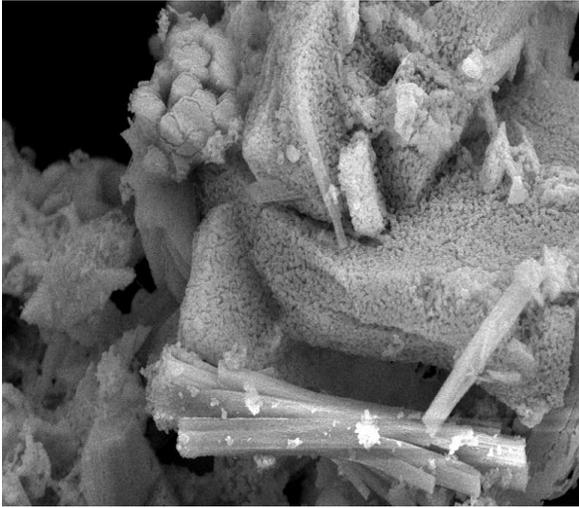
C.2: Thermal Stability of bio-oil



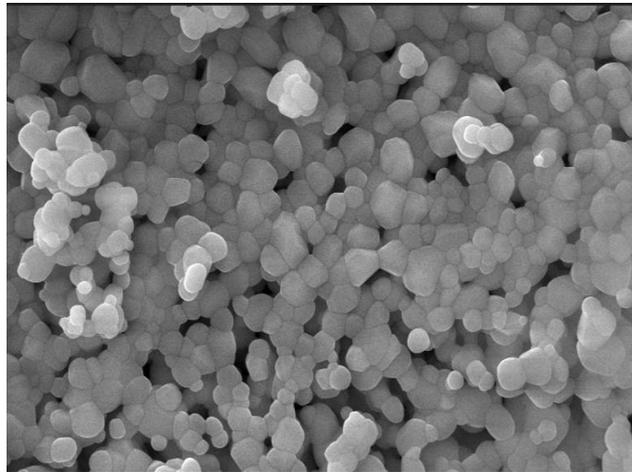
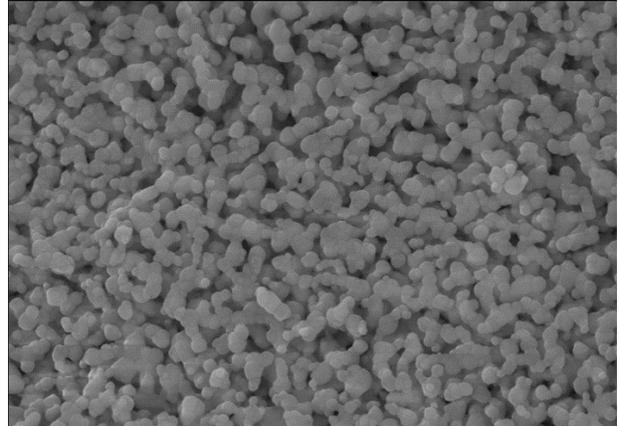
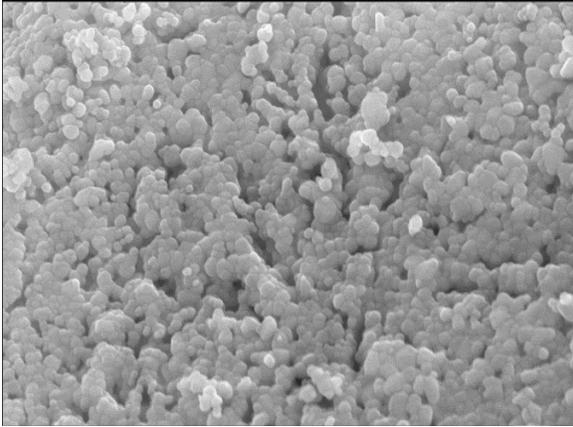
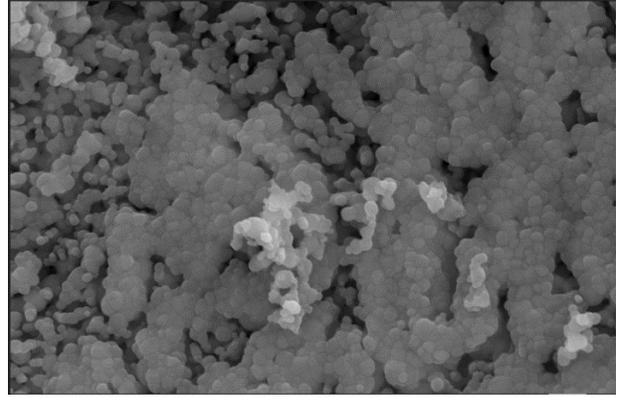
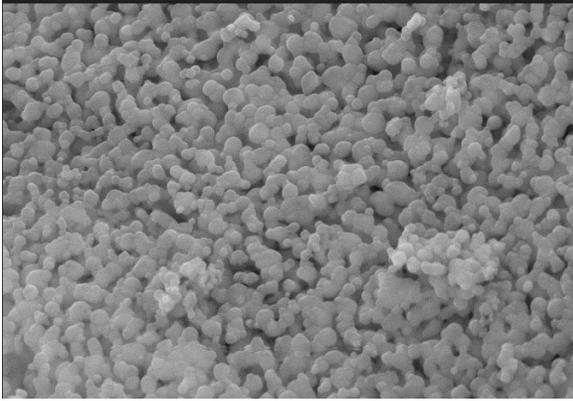
Appendix C. 4: Bio-oil produced at 475°C using 3 grams catalyst

Appendix D: SEM & TEM

D.1: Scanning electron microscopy

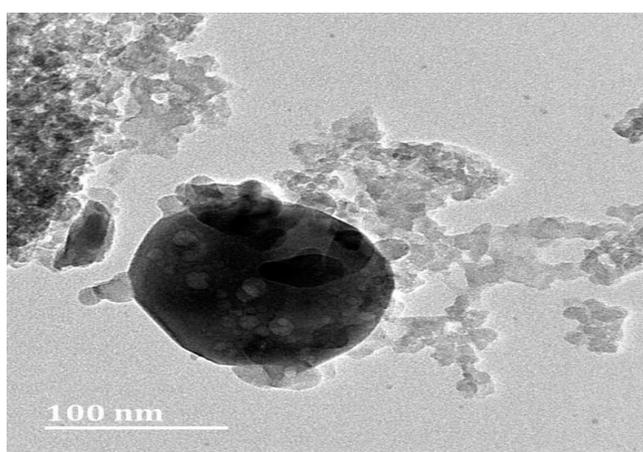
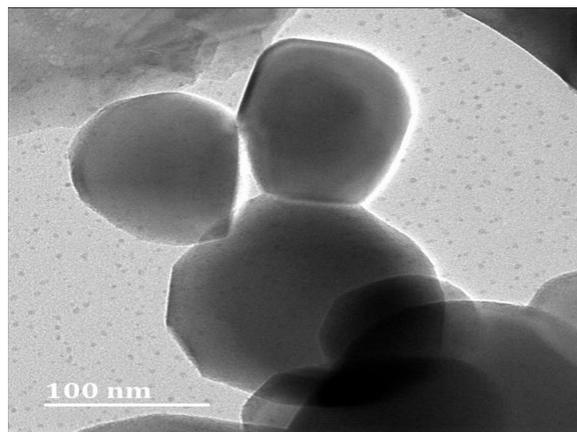
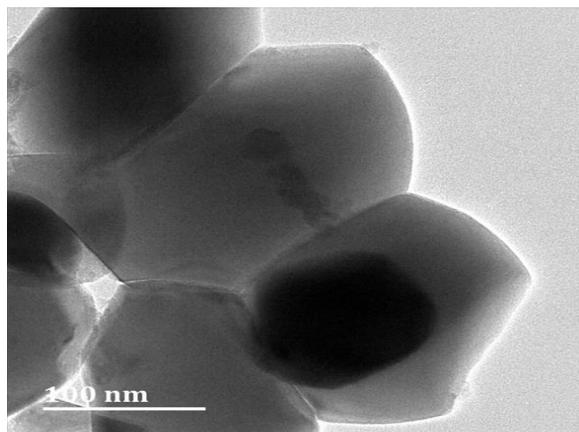
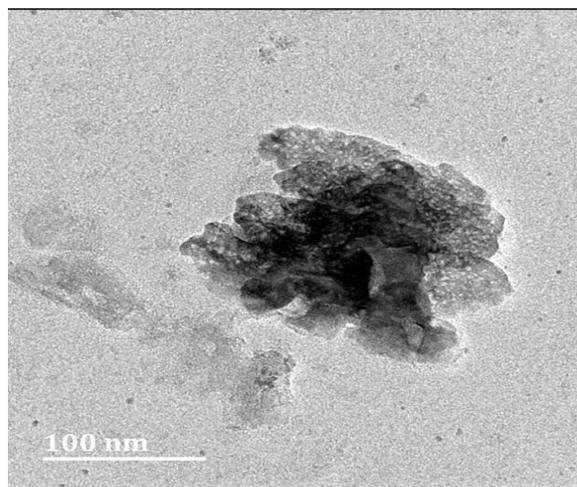
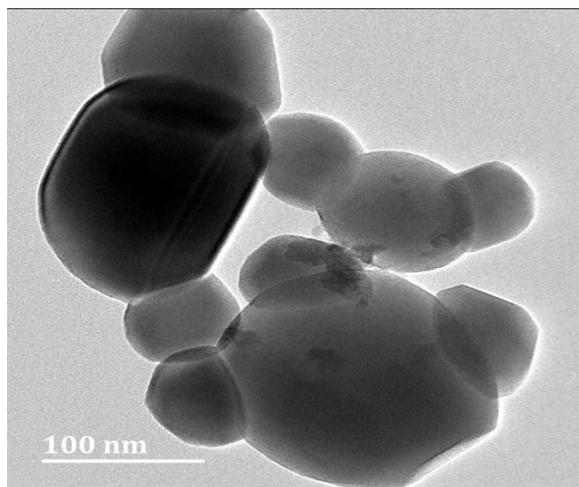


Photograph D. 1:SEM Images Low magnification

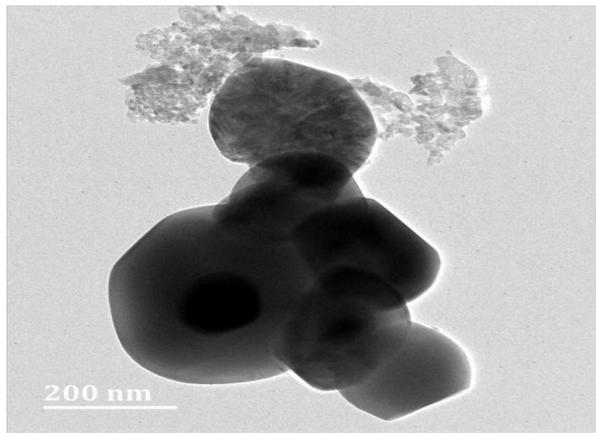
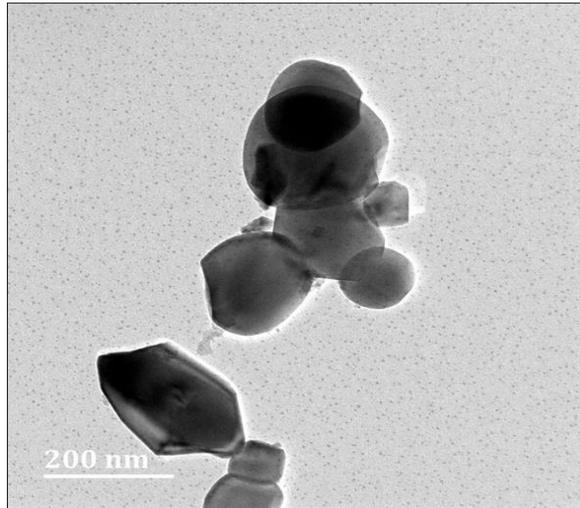
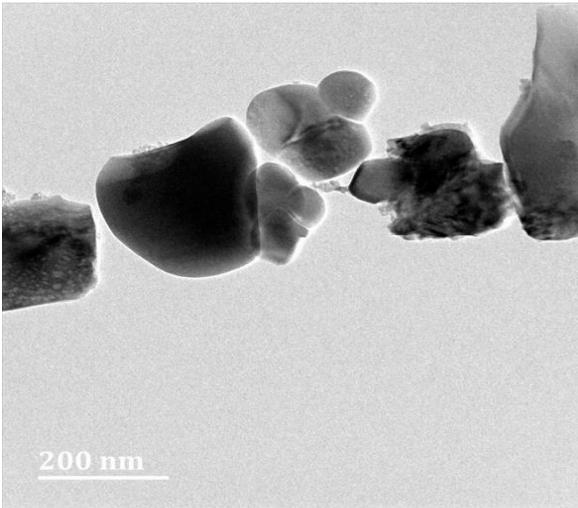
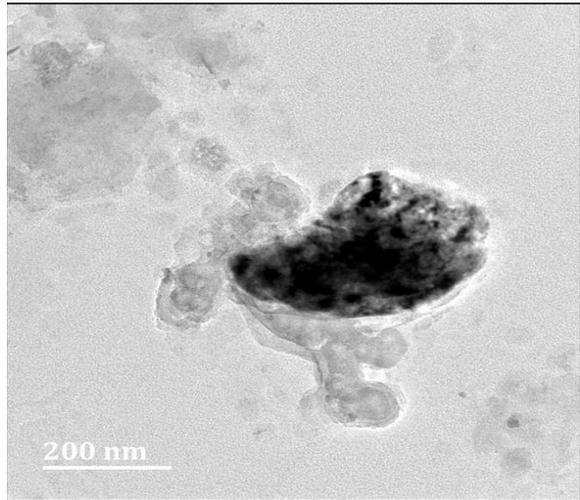
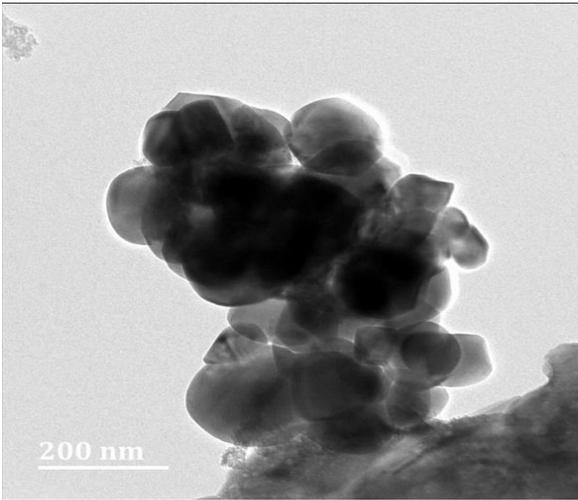


Photograph D. 2: SEM Images high magnification

D.3: Transmission electron microscopy

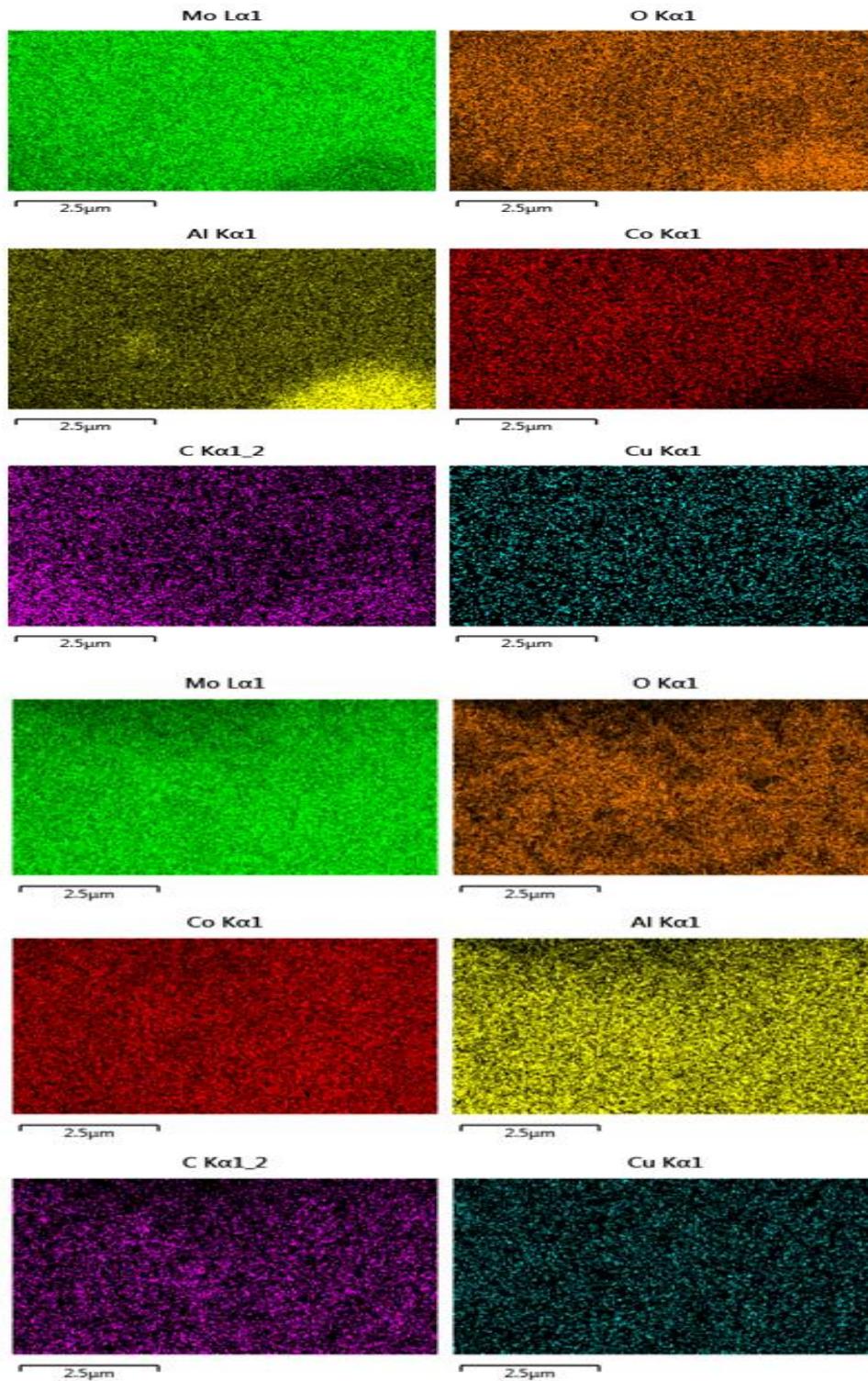


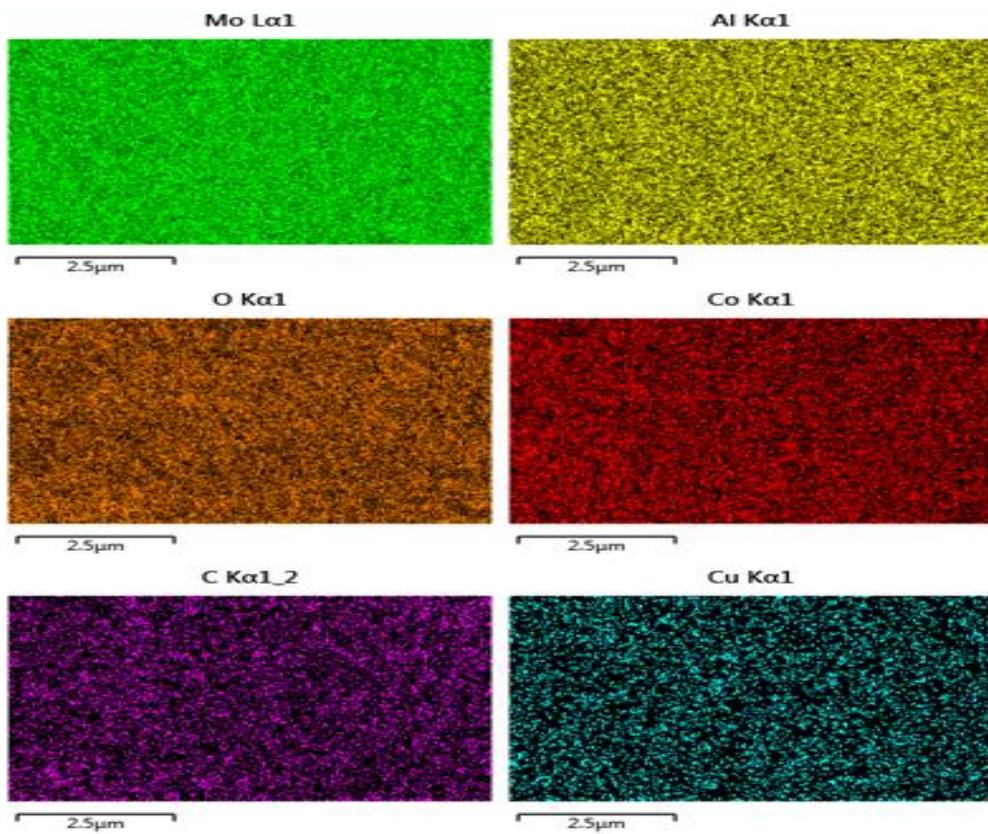
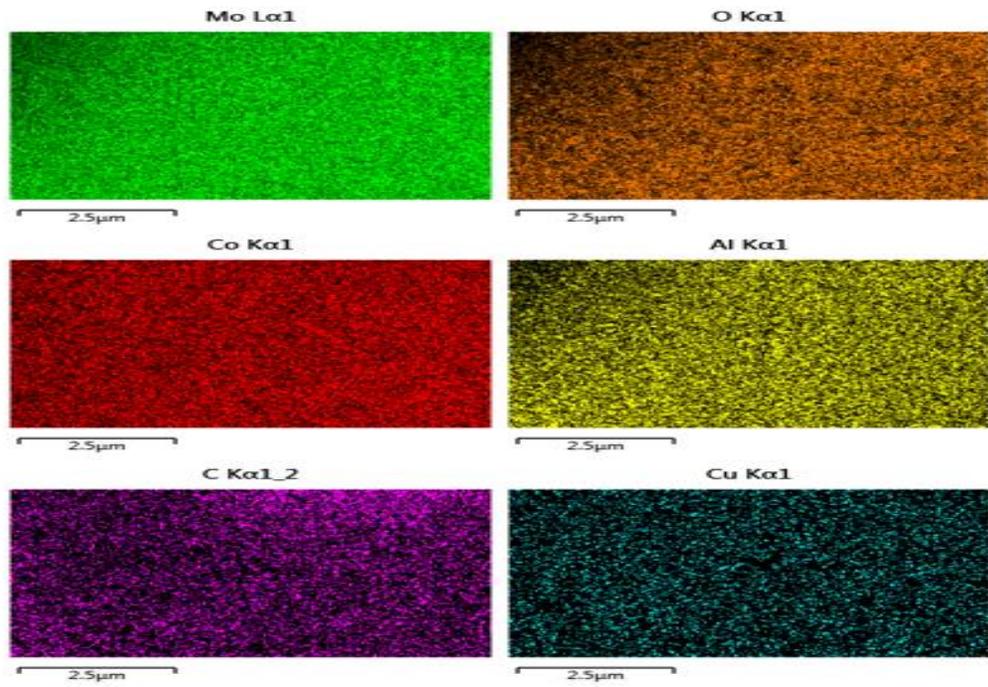
Photograph D. 3: TEM Images low magnification

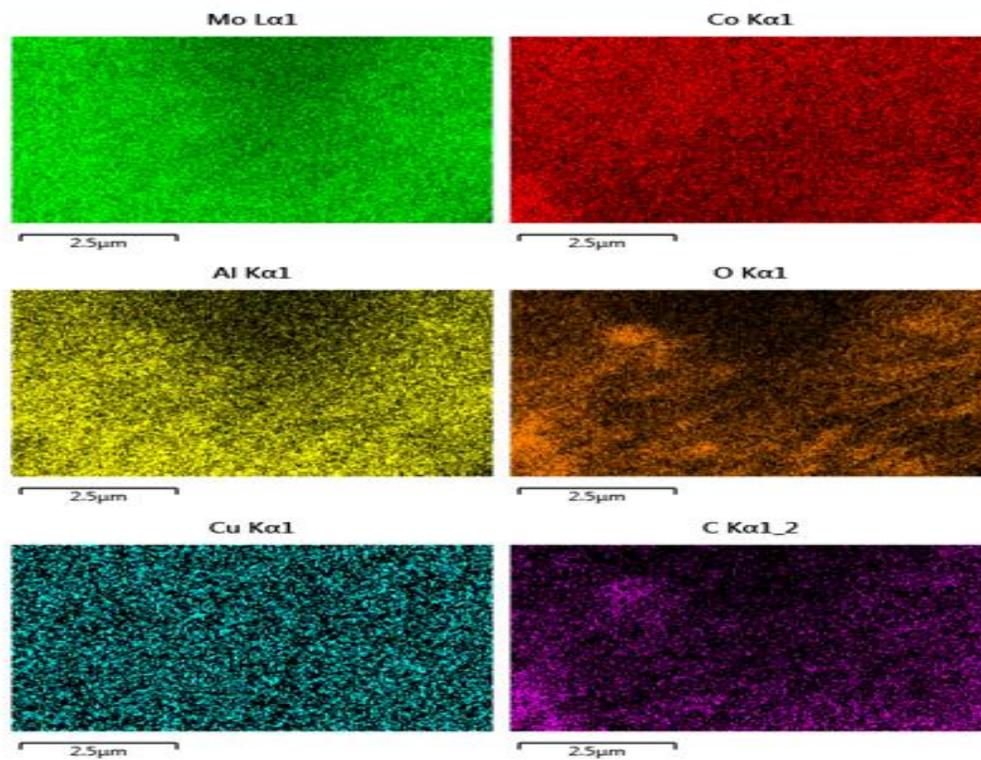


Photograph D. 4:TEM Images high magnification

Appendix E: Energy dispersive x-ray analysis (EDX)







Photograph E. 1: EDX Images