SUDAN UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF GRADUATE STUDIES

PRODUCTION OF BIODIESEL FROM WASTE FRYING OIL USING CALCIUM OXIDE BIO-DERIVED CATALYST FROM WASTE EGGSHELLS

إنتاج الديزل الحيوي من مخلفات زيت التحمير بإستخدام أكسيد الكالسيوم كعامل محفز مشتق حيويا من قشر البيض

A Dissertation Submitted in Partial Fulfillment of the

Requirements for the Award of the Degree of

Master of Science (Chemistry)

By

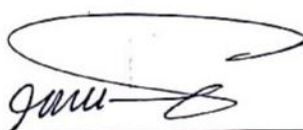Mohammed Hassaballa Abdelrazig

B.Sc. (Honour), Chemistry

Supervisor

Dr. Elfatih Ahmed Hassan

FEBRUARY 2022

EXAMINERS' APPROVAL LETTER

We hereby declare that we have read this dissertation and in our opinion this dissertation is sufficient in terms of scope and quality for partial fulfillment of the requirements for the award of the degree of Master of Science (Chemistry).

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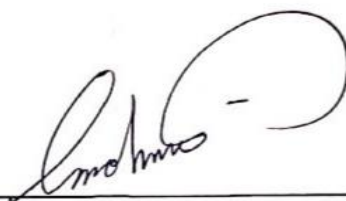Name of Supervisor : Elfatih Ahmed Hassan

Date : 20 Feb. 2022

Signature : _____

Name of External Examiner : Elshiekh. Elgilay

Date : 20.02.2022

Signature : _____

Name of Internal Examiner : Mohamed Abbo

Date : 20/2/2022

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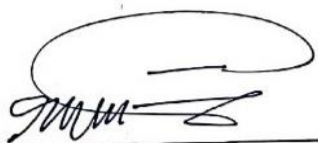Name of Student : Mohammed Hassaballa Abdelzarig
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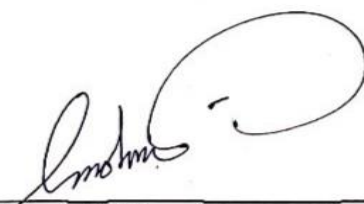Name of Supervisor   : *Elfatih Ahmed Hassan*

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بسم الله الرحمن الرحيم

إستهلال

قال تعالى:

(رَبَّنَا لَا تُزِغْ قُلُوبَنَا بَعْدَ إِذْ هَدَيْتَنَا وَهَبْ لَنَا مِن لَّدُنكَ رَحْمَةً ۚ إِنَّكَ أَنتَ الْوَهَّابُ)

صدق الله العظيم

DEDICATION

Dedicated especially to my parents and my wife for giving me inspiration and support that made this work possible.

ACKNOWLEDGEMENTS

ABSTRACT

Waste Frying Oil (WFO) has significant potential as a raw material for biodiesel production. About 80% of the total production cost of biodiesel goes to feedstock when high-grade oil is used. The objective of this research is to reduce the cost of biodiesel production by utilization of waste materials in the production process. The methodology used in this study is the catalytic transesterification reaction method which was conducted to produce biodiesel using WFO specifically collected from chips frying as a raw material and calcium oxide bio- derived from waste eggshells (Rich in calcium carbonate) as a catalyst. The catalyst was successfully prepared by calcination of waste eggshells at 900°C, and analyzed by IR before and after calcination. The comparison between the spectrums of raw eggshells, calcined eggshells and standard calcium oxide showed that, the obtained peaks in both spectrums of calcined eggshells and standard calcium oxide are identical. Furthermore, preliminary investigations were performed on the WFO and the results showed that the WFO from chips frying has a density of (0.91 g/cm^3), acid value (0.92 mg KOH /g Oil), free fatty acid (0.46%), fatty acid profile, by GC-MS, contains (Saturated fatty acid 25.77 %, Monounsaturated fatty acid 27.58%, Polyunsaturated fatty acid 46.55%) and average molecular weight (877.78 g/mole). Additionally, the corresponding biodiesel fuel properties of the WFO were predicted using the fatty acid profile and biodiesel analyzer software. Almost all the obtained data met the standard specification of biodiesel (ASTM and EN). The most interesting finding in this study was that the free fatty acid (FFA %) of the WFO is (0.46%), this finding meets the reference standard of the FFA% of high- grade oils (< 1% FFA), accordingly, the WFO from chips frying could be considered as high-grade oil. A significance of this finding helped in production of biodiesel through only one step transesterification reaction at mild reaction conditions. Finally, the produced biodiesel was separated, purified and then analyzed. The obtained results showed that the biodiesel has a yield of (85%), density (0.85 g/cm^3), acid value (0.30 mg KOH /g Oil) and, by GS-MC, found that the most abundant esters in the methyl ester profile of biodiesel are (9, 12-Octadecadienoic acid (Z, Z)-, methyl ester 54.66% and 9-Octadecenoic acid (Z)-, methyl ester 31.74%). This study provides an important opportunity to design an inexpensive simple approach for scaling up the production of biodiesel from waste materials.

المستخلص

مخلفات زيت التحميرلها قيمة عالية كمادة خام لإنتاج الديزل الحيوي. حوالي 80 % من إجمالي تكلفة إنتاج الديزل الحيوي مرتبطة بإستخدام زيت عالي الجودة كمادة خام. هدف هذه الدراسة هو خفض تكلفة إنتاج الديزل الحيوي عن طريق إستحدام مخلفات مواد في عملية الإنتاج. المنهجية التي اتخذت في هذه الدراسة هي طريقة تفاعل تحويل الأسترة المحفزة التي أجريت لإنتاج الديزل الحيوي بإستخدام مخلفات زيت التحمير ,تحديدا الذي تم تجميعة من تحمير البطاطس, كمادة خام و أوكسيد الكالسيوم المشتق حيويا من مخلفات قشر البيض (غني بكربونات الكالسيوم) كعامل حفاز . تم تحضير العامل الحفاز بنجاح عن طريق المعالجة الحرارية لمخلفات قشر البيض عند درجة حرارة 900 درجة مئوية وتم تحليله بواسطة جهاز الاشعة تحت الحمراء قبل وبعد المعالجة الحرارية. وأظهرت المقارنة بين أطياف كل من خام قشر البيض, قشر البيض المعالج حراريا وأكسيد كالسيوم قياسي, أن إشارات الإمتصاص المتحصل عليها في طيفي كل من قشر البيض المعالج حراريا و أوكسيد الكالسيوم القياسي متطابقة . بعد ذلك تم إجراء كشوفات أولية على مخلفات زيت الطعام. بينت النتائج المتحصل عليها أن مخلفات زيت تحمير البطاطس له كثافة (0.91 جم /سم³), قيمة حمضية (0.92 ملجم KOH / جم زيت), نسبة أحماض دهنية حرة (0.46 %), بواسطة جهاز كروموتوغرافيا الغاز ـ مطياف الكتلة, ملف تعريف أحماض دهنية يحتوي على (الأحماض الدهنية المشبعة (25.77 %), الأحماض الدهنية الاحادية غير المشبعة (27.58 %), الأحماض الدهنية المتعددة غير المشبعة (46.55 %) و متوسط وزن جزيئ (877.78 جم/مول). بالإضافة لذلك تم التنبؤ بخواص وقود الديزل الحيوي المتوقع إنتاجه من الزيت الخام باستخدام نسب الاحماض الدهنية من ملف تعريف الاحماض الدهنية وبرنامج محلل الوقود الحيوي ووجد أن اغلب النتائج مطابقة للمواصفات القياسية للديزل الحيوي (المواصفة القياسية للجمعية الأمريكية للإختبار والمواد والمواصفة الأوربية). النتيجة الاكثر إهتماما في هذه الدراسة هي ان نسبة الأحماض الدهنية الحرة في الزيت هي (0.46 %), هذه النتيجة تطابق القيمة المرجعية لنسب الأحماض الدهينة للزيوت عالية الجودة (1% >) ,وفقا لذلك ,يمكن إعتبارمخلفات زيت تحمير البطاطس كزيت عالي الجودة. وأهمية هذه النتيجة ساعدت في إنتاج الديزل الحيوي بطريقة سهلة من خطوة واحدة لتفاعل تحويل الأسترة تحت ظروف تفاعل معتدلة. وأخيرا, تم فصل, تنقية ومن ثم تحليل الديزل الحيوي المنتج. وأظهرت النتائج المتحصل عليها أن للديزل الحيوي كثافة تبلغ (0.85 جم /سم³), نسبة أحماض دهنية حرة (0.30%), و باستخدام جهاز كروموتوغرافيا الغازـ مطياف الكتلة, وجد أن الإسترات الأكثر وفرة في ملف إسترات الأحماض الدهنية للديزل الحيوي هي 9-Octadecenoic acid (Z)-, methyl ester 31.74% و 9,12-Octadecadienoic acid (Z,Z)-, methyl ester 54.66%)

توفر هذه الدراسة فرصة هامة لتصميم مخطط مبسط ومنخفض التكلفة لإنتاج الديزل الحيوي بكميات كبيرة من مخلفات مواد.

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Abbreviations	Detail
APE	Allylic Position Equivalent
ASTM	American Society for Testing and Material
BAPE	Bis-Allylic Position Equivalent
BD	Biodiesel
CFPP:	Cold Filter Plugging Point (°C)
CN	Cetane number
CP	Cloud Point (°C)
DU	Degree of Unsaturation
EN	European standard
FA	Fatty Acid
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
HHV	Higher Heating Value
IR	Infrared Spectroscopy
IV	Iodine Value
LCSF	Long Chain Saturated Factor
MUFA	Monounsaturated Fatty Acid
NIST	National Institute of Standards and Technology
OS	Oxidation Stability
PP	Pour Point
PUFA	Polyunsaturated Fatty Acid
SFA	Saturated Fatty Acid
SV	Saponification Value
TG	Triglyceride
WFO	Waste Frying Oil

Chapter One

(INTRODUCTION)

Chapter One

1. Introduction

1.1 Background of study:

One of the most significant current discussions in 21st century are energy sustainability, environmental problems and a rise in the price of petroleum-based fuels. Recently, the energy sustainability has been one of the major challenges for researchers and the scientific community worldwide due to increasing consumption of the world total energy.(Ambat et al., 2018) According to the International Energy Outlook 2016 projection, the total world consumption of marketed energy expands by 48% from 2012 to 2040(Gebremariam and Marchetti, 2018). Today, over 80% of the total energy used in the world is provided by fossil fuels(Hajjari et al., 2017). Conventional fuels (Fossil fuels) has been used as a source for transportation and other energy purposes, this has led to speedy fossil fuel depletion, rising future energy requirement and demand, and climatic changes because of emissions of the fossil fuel(Tseten and Murthy, 2014). Due to the above-mentioned concerns, tremendous efforts have been made to find the best alternative fuels for overcoming the economic and environmental impacts of fossil fuels consumption. Biofuels are very attractive option to overcome the energy crisis which would partly decrease the dependency on petroleum-based fuel around the world(Hajjari et al., 2017).

1.2 Biofuel as an alternative energy resource:

Biofuel defined as a clean renewable fuel, generated from organic biomass.(Gnanaprakasam et al., 2013). In general, the term of "biofuel" refers to solid (bio-char), liquid (ethanol and biodiesel), or gaseous (biogas), Among different types of biofuels, biodiesel is getting more attraction in view of the reasons listed below: (Thanh et al., 2012):

- ✓ The formation process is faster and simpler compared with others.
- ✓ Widely adapted with existing filling-fuel stations; they can be used with current vehicles.
- ✓ There are many benefits to the environment and economy.
- ✓ Easily available from common biomass sources.

1.3 Current biodiesel discussions:

The debates on biodiesel have been intensively discussed in both the scientific world and the media(Atabani et al., 2012). The biodiesel production is increasing globally, which will grow in coming years, therefore it becomes a systemic issue with respect to its economic, ecological, and socio-political impacts. Opportunities, challenges, and even threats have been raised especially for answering questions below(Thanh et al., 2012, Lin et al., 2011):

I. What is the best raw material available that does not increase food prices or deforestation?

II. What is the best production method for a green process by which monoalkyl esters (Biodiesel) can be obtained with a minimal emission of waste and low energy consumption?

1.4 Problem Statement

The problem was to investigate the extent of utilization of waste frying oil (Taken from potato frying "chips") to produce biodiesel via transesterification process where calcium oxide (derived from biomass "waste eggshells") was suggested as a catalyst, a qualitative approach was conducted to examine the efficiency of the chosen catalyst and feedstock on biodiesel production.

1.5 Objective of Study

The objective of this research is to reduce the cost of biodiesel production by recycling waste materials through a simple biodiesel production process which will affect the economic viability of biodiesel industry.

1.6 Significances of study:

The importance of this research is to help the industry field to design a simple approach in scaling up the production of biodiesel from waste materials.

1.7 The knowledge gap in the field of this study:

There are only a few studies in literature that deal with the selection of a specific type of waste frying oil therefore the chips waste oil was suggested as feedstock due to its frying needs slightly low temperature for short frying time compare with chicken and fish waste oils.

1.8 Design of Study

The study was designed as shown below:

1. Collection of WFO (used for potato frying) from household kitchens
2. Pretreatment of WFO:
   - Filtration: to remove solid contaminants.
   - Heating at 110 °C: To reduce water content.
3. Preliminary investigation of WFO (Analysis)
   - Acid value: to determine free fatty acid (FFA).
   - Density: to compare it with the product and literature.
   - Analysis of WFO by GC-MS to achieve the following:
     - ✓ Characterization of the chemical composition of the feedstock (Fatty acid profile).
     - ✓ Estimation of fatty acid content%
     - ✓ Determination of the average molecular weight of the WFO
     - ✓ Prediction of the corresponding biodiesel fuel properties using the fatty acid profile of the WFO and biodiesel analyzer software.
4. Collection of waste eggshells (From restaurants)
5. Pretreatment of waste eggshells:
   - Washing with hot distill water: to remove contaminants.
   - Crushing: to produce powder shape.
6. Preparation of biomass-derived calcium oxide (CaO) Catalyst:
   - Calcination at 900°C: to convert the $CaCO_3$ in waste eggshell to CaO.
7. Analysis of CaO catalyst:
   - Comparing the IR spectrums of (Standard CaO, Calcined eggshell at 900°C and raw eggshell)
8. Biodiesel synthesis and purification through Transesterification reaction
9. Analysis of biodiesel :
   - Acid value
   - Density
   - Yield %
   - GC-MS (Identification FAME profile).

Chapter Two

(LITERATURE REVIEW)

2. Literature review:

2.1 Biodiesel:

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable feedstock i.e.(Oils, Fats and Microalgae) .(Zhang et al., 2003).

2.1.1 History of biodiesel:

Ever since human discovered fire, charcoal, woodchips and cattle dung have been used as a source of energy and still today people used these solid fuels for heating and frying in many parts of the world. In mid 1700s and early 1800s, Oil extracted from whale was broadly used for lighting purposes. For more than a century, biofuel has been around us despite the term "biofuel" came into existence few years back. Rudolph Diesel in late 19th century used peanut oil to generate power and he is the one who started using vegetable oil as a source of energy (Tseten and Murthy, 2014). In 1912, Diesel said, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum products of the present time" .Today throughout the world, countries are renewed interest in using this form of fuel due to its renewable source and reduction in pollution(Owolabi et al., 2012).

2.1.2 Fuel characteristics of biodiesel:

- Just like petroleum-based diesel fuel, biodiesel operates in the compression ignition (diesel) engines. The biodiesel is characterized by determining its physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. In general, biodiesel compares well to petroleum-based diesel as shown in Table.2.1 (Balat and Balat, 2010).

Table 2.1: ASTM standards of maximum allowed quantities in diesel and biodiesel.

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10–C21)	FAME[b] (C12–C22)
Kin. viscosity (mm^2/s) at 313 K	1.9–4.1	1.9–6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (K)	333–353	373–443
Cloud point (K)	258–278	270–285
Pour point (K)	238–258	258–289
Water (vol. %)	0.05	0.05
Carbon (wt. %)	87	77
Hydrogen (wt. %)	13	12
Oxygen (wt. %)	0	11
Sulfur (wt. %)	0.05	0.05
Cetane number	40–55	48–60

a Hydrocarbons. b Fatty acid methyl esters.

- Viscosity is the most important property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has a viscosity close to that of diesel fuels. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors(Balat, 2008).

2.1.3 Chemical Composition of biodiesel

Elemental composition and relative amounts of compounds present in biodiesel and diesel fuel are given in Tables 2.2 and 2.3. Due to presence of electronegative element oxygen, biodiesel is slightly more polar than diesel fuel as a result viscosity of biodiesel is higher than diesel fuel. Presence of elemental oxygen lowers the heating value of biodiesel when compared to the diesel fuel.(Kulkarni et al., 2008).

Table 2.2: Elemental analysis of biodiesel and diesel fuels(Kulkarni et al., 2008)

Elements	Composition (%)	
	Biodiesel	Diesel fuel
Carbon (C)	79.6	86.4
Hydrogen (H)	10.5	13.6
Oxygen (O)	8.6	-
Nitrogen (N)	1.3	-
C/H	7.6	6.5

Table2.3: Composition of biodiesel and diesel fuels(**Kulkarni et al., 2008**)

Type of compounds	Composition (%)	
	Biodiesel	Diesel fuel
n-Aliphatic	15.2	67.4
Olefinics	84.7	3.4
Aromatics	-	20.1
Naphthenes	-	9.1

2.1.4 Biodiesel production around the world:

The overall biodiesel production around the world was estimated to around 15 thousand barrels per day in 2000 which increased to 289 thousand barrels per day in 2008(Atabani et al., 2012). Countries such as USA, Brazil, Germany, Indonesia and France are the top consumers of biodiesel. Table.2.4 shows the list of the top biodiesel producing countries in 2016(Karmakar and Halder, 2019).

Table 2.4: Top 10 countries in terms of biodiesel potential in 2016(**Karmakar and Halder, 2019**).

Country	Biodiesel production (in billion liters)
USA	5.5
Brazil	3.8
Germany	3
Indonesia	3
Argentina	3
France	1.5
Thailand	1.4
Spain	1.1
Belgium	0.5
Colombia	0.5
Canada	0.4
China	0.3

There have been several studies in the literature reporting that the published work in biodiesel production have focused on two topics which are(Thanh et al., 2012).:

    I.   Raw material selection.

    II.   The best production method.

2.2 Biodiesel feedstock (Raw material):

Biodiesel can be produced from different biomass sources such as vegetable oils (that can be edible, non-edible or waste oils), animal fats (mostly edible fats or waste fats) and microalgae oil The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acids (Raqeeb and Bhargavi, 2015).

2.2.1 Triglycerides:

Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amounts of oxygen in its structure. The fatty acids vary in their carbon chain length and in the number of double bonds. The empirical formula and structure of various fatty acids present in vegetable oils are given in Table. 2.5 (Balat, 2008).

Different fatty acids have different physical and chemical properties, and the composition of these fatty acids are the most important parameters influencing the corresponding properties of a vegetable oils and animal fats(Lam et al., 2010). Biodiesel produced from various sources will have different composition and purity(Ambat et al., 2018).

Table 2.5: Chemical structure of common fatty acids**(Balat, 2008):**

Name of fatty acid	Chemical name of fatty acids	Structure *(xx:y)	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucle	cis-13-Docosenoic	22:1	$C_{32}H_{42}O_2$

*Structure (xx:y) represent : (number of carbon atom to number of double bond)

2.2.2 Fuel-related properties of vegetable oils:

The kinematic viscosity of vegetable oils varies in the range of 30 to 40 cSt at 311 K. High viscosity of these oils is due to large molecular mass and chemical structure. Vegetable oils have high molecular weights in the range of 600 to 900, which are three or more times higher than diesel fuels. The flash point of vegetable oils are very high (above 473 K). The volumetric heating values of these oils are in the range of 39 to 40 MJ/kg, which are low compared to diesel fuels (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The cetane numbers are in the range of 32 to 40. The iodine value ranges from 0 to 200 depending upon unsaturation. The cloud and pour points of vegetable oils are higher than that of diesel fuels(Balat, 2008).

2.2.3 Feedstock selection:

- Feedstock selection is a key step in biodiesel production, which affects various factors, including yield, and quality of the produced biodiesel. Feedstock can be screened based on their availability and type of source (edible, non-edible, or waste)(Ambat et al., 2018) .
- To date, the major obstacle in the commercialization of biodiesel is the cost of production. In this regard, the exploitation of waste materials for the production of biodiesel might be useful to reduce the feedstock cost, which makes the process economical(Sadaf et al., 2018).
- The selection of feedstock can be done by analyzing numerous parameters of raw materials such as oil content, suitability, chemical composition and physical properties. (Ambat et al., 2018).
- Previous research has shown that there are more than 350 oil-bearing crops identified as potential sources for biodiesel production. Table.2.6 shows the main feedstocks of biodiesel.

Table 2.6: The main feedstocks of biodiesel(**Atabani et al., 2012**)

Edible oils	Non-edible oils	Animal fats	Other sources
Soybeans (Glycine max)	Jatropha curcas	Pork lard	Bacteria
Rapeseed (Brassica napus L.)	Mahua (Madhuca indica)	Beef tallow	Algae (Cyanobacteria)
Safflower	Pongamia (Pongamia pinnata)	Poultry fat	Microalgae (Chlorellavulgaris)
Rice bran oil (Oryza sativum)	Camelina (Camelina Sativa)	Fish oil	Tarpenes
Barley	Cotton seed (Gossypium hirsutum)	Chicken fat	Poplar
Sesame (Sesamum indicum L.)	Karanja or honge (Pongamia pinnata)		Switchgrass
Groundnut	Cumaru		Miscanthus
Sorghum	Cynara cardunculus		Latexes
Wheat	Abutilon muticum		Fungi
Corn	Neem (Azadirachta indica)		Waste frying oil
Coconut	Jojoba (Simmondsia chinensis)		
Canola	Passion seed (Passiflora edulis)		
Peanut	Moringa (Moringa oleifera)		
Palm and palm kernel (Elaeis guineensis)	Tobacco seed		
Sunflower (Helianthus annuus)	Rubber seed tree (Hevca brasiliensis)		
	Salmon oil		
	Tall (Carnegiea gigantean)		
	Coffee ground (Coffea arabica)		
	Nagchampa(Calophyllum inophyllum)		
	Croton megalocarpus		
	Pachira glabra		
	Aleurites moluccana		
	Terminalia belerica		

From the literature, it has been found that feedstock alone represents 80% of the overall biodiesel production cost, therefore the selection of feedstock has been widely investigated and summarized as shown below (Balat and Balat, 2010, Atabania, 2012).

a) **Edible oil :**

- ✓ Their use raises many concerns such as food versus fuel crisis and major environmental problems(Balat and Balat, 2010).
- ✓ In the last 10 years the prices of vegetable oil plants have increased dramatically which will affect the economic viability of biodiesel industry(Atabani et al., 2012).

b) **Non edible oil**

- ✓ The use of non-edible vegetable oils when compared with edible oils is very significant in developing countries because of the tremendous demand for edible oils as food, and they are far too expensive to be used as fuel at present(Balat and Balat, 2010).
- ✓ The production of biodiesel from different non-edible oilseed crops has been extensively investigated over the last few years, Jatropha appears to have several advantages as a renewable diesel feedstock, because it is both non-edible and can be grown on marginal lands, it is potentially a sustainable bio-fuel that will not compete with food crops but the serious problem with jatropha, in addition to the low yield, it is highly toxic. The comparatively high price of Jatropha is also still a drawback(Van Eijck and Romijn, 2008).

c) **Animal fats:**

- ✓ Compared to plant crops, these fats frequently offer an economic advantage because they are often priced favorably for conversion into biodiesel(Balat and Balat, 2010).
- ✓ Animal fats tend to be low in FFAs and water, but there is a limited amount of these fats available, meaning these would never be able to meet the fuel needs of the world(Sheedlo, 2008)

d) **Microalgae:**

- ✓ Microalgae are the untapped resource with more than 25,000 species of which only 15 are in use.
- ✓ Total world commercial microalgal biomass production is about 10,000 tons per year.
- ✓ Algae contain anywhere between 2% and 40% of lipids/oils by weight.
- ✓ They have much higher growth rates and productivity when compared to conventional forestry, agricultural crops, and other aquatic plants, requiring much less land area than other biodiesel feedstocks of agricultural origin.

- ✓ The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale(Demirbas, 2009).

e) Waste frying oil:
- ✓ Waste frying oil (WFO) is a promising alternative to vegetable oil for biodiesel production(Hameed et al., 2009).
- ✓ WFO would be a good choice as raw material since it is cheaper than virgin vegetable oils. Its price is 2–3 times cheaper than virgin vegetable oils.
- ✓ The amount of WFO generated in each country is huge and varies depending on the use of vegetable oil.
- ✓ An estimate of the potential amount of WFO from the collection in the EU is approximately 0.7–1.0 million tons per year, US restaurants, including all the fast-food chains, produce an estimated 3 billion gallons of WFO per year., Approximately 135,000 tons per year of WFO is produced in Canada and Turkey produces over 350,000 tons of WFO per year..(Balat and Balat, 2010).
- ✓ Therefore, biodiesel derived from WFO has taken a commercial patent as an alternative fuel to petroleum-based diesel fuel for diesel engines in the markets of Europe and the United States. As shown in (Table 2.7).
- ✓ The data on the requirements of diesel fuel and availability of waste frying oil in any country indicate that the biodiesel obtained from waste frying oil may not replace diesel fuel completely. However, a substantial amount of diesel fuel can be prepared from waste frying oil, which would partly decrease the dependency on petroleum-based fuel(Kulkarni and Dalai, 2006).
- ✓ The production of biodiesel from WFO is challenging due to the presence of undesirable components such as FFAs and water.

Table.2.7: Current potential feedstocks for biodiesel worldwide (Shahid and Jamal, 2011, Balat and Balat, 2010, Karmakar et al., 2010, Atabani et al., 2012):

Country	Feedstock
USA	Soybeans/waste oil/peanut
Canada	Rapeseed/animal fat/soybeans/yellow grease and tallow/mustard/flax
Mexico	Animal fat/waste oil
Germany	Rapeseed
Italy	Rapeseed/sunflower
France	Rapeseed/sunflower
Spain	Linseed oil/sunflower
Greece	Cottonseed
UK	Rapeseed/waste frying oil
Sweden	Rapeseed
Ireland	Frying oil/animal fats
India	Jatropha/Pongamia pinnata (karanja)/soybean/rapeseed/sunflower/peanut
Malaysia	Palm oil
Indonesia	Palm oil/jatropha/coconut
Singapore	Palm oil
Philippines	Coconut/jatropha
Thailand	Palm/jatropha/coconut
China	Jatropha/waste frying oil/rapeseed
Brazil	Soybeans/palm oil/castor/cotton oil
Argentina	Soybeans
Japan	Waste frying oil
New Zealand	Waste frying oil/tallow

2.2.4 Challenges of using the WFO as biodiesel feedstock

- During frying, oil is heated for relative long period of time. Continuously using the same oil for frying will cause various physical and chemical changes in the oil, depending on the type of oil and oil composition(Nayak et al., 2016).

- Some physical changes observed in vegetable oil after frying are an increase in viscosity, an increase in specific heat, a change in surface tension and change in color(Lam et al., 2010). The chemical properties of WFO can change depending on the frying conditions, such as temperature and frying time.

- The frying process causes the vegetable oil, Triglyceride to break-down to form, Diglycerides, Monoglycerides, and free fatty acids (FFAs).The amount of heat and water in the frying increases the hydrolysis of triglycerides as shown in (Equation 1.1), and therefore it causes a growth of the free fatty acids (FFAs) in the WFO. Moreover, because of oxidation and polymerization reactions, there is an increase in the viscosity and the saponification number of the WFO when compared with the original oil .Furthermore the transport of matter and heat between the frying food and the vegetable oil occurs and causes a higher content of water in the WFO(Raqeeb and Bhargavi, 2015).

Triglyceride   diglyceride   Fatty acid
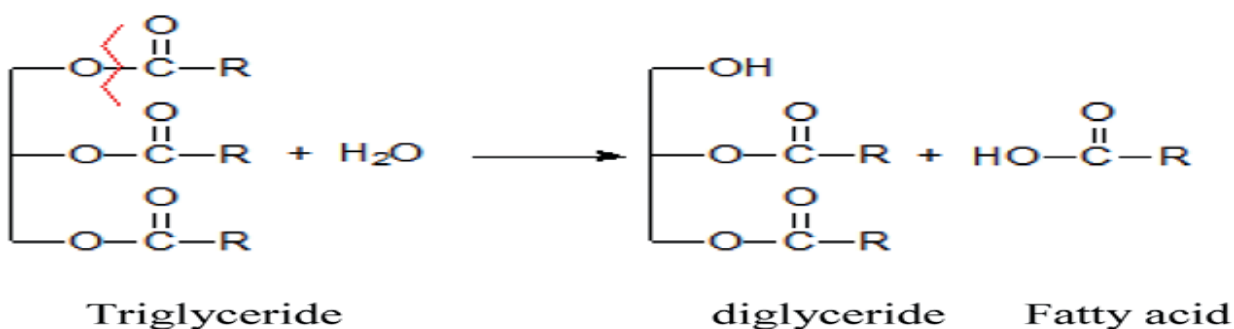
Equation 2.1: Hydrolysis of triglycerides**.**

2.3 Biodiesel production methods:

- Globally, there are many efforts to develop and improve renewable feedstock properties in order to approximate the properties of diesel fuels(Atabani et al., 2012). It is well known that viscosity is the main barrier that prevents the use of direct vegetable oils in conventional diesel engines(Atabani et al., 2013).

- There are four methods used to solve this problems: blending with petro-diesel, pyrolysis, and micro-emulsion (co-solvent blending) and transesterification. Among these methods, the transesterification reaction has been one of the major interesting method due to its low cost and simplicity (Thanh et al., 2012).

- A large and growing body of literature has investigated the advantages and disadvantages of biodiesel production methods as shown in Table.2.8.

  Table. 2.8: Comparison of main biodiesel production technologies(Lin et al., 2011, Atabani et al., 2012).

Methods	Advantages	Disadvantages
Dilution (direst blending or micro-emulsion)	• Simple process.	• High viscosity. • Bad volatility. • Bad stability.
Pyrolysis	• Simple process. • No-polluting.	• High temperature is required. • Equipment is expensive. • Low purity.
Transesterification	• Fuel properties is closer to diesel. • High conversion Efficiency. • Low cost. • It is suitable for industrialized production.	• Low free fatty acid and water content are required (For base catalyst). • Pollutants will be produced because products must be neutralized and washed. • Accompanied by side reactions. • Difficult reaction products separation.
Supercritical methanol	• No catalyst. • Short reaction Time. • High conversion. • Good adaptability.	• High temperature and pressure are required. • Equipment cost is high. • High energy consumption.

It appears from the aforementioned investigations that most attention has been paid to transesterification reaction method.

2.4 Biodiesel production based on transesterification reaction method:

- Transesterification, also called alcoholysis, is the reaction of renewable feedstock (Triglyceride source) with an alcohol to form esters (biodiesel) and glycerol. The basic reaction is showed in Equation 2. 2.
- Transesterification consists of three consecutive reversible reactions viz.; conversion of triglyceride to di-glyceride, di-glyceride to mono-glyceride and mono-glyceride to fatty ester (biodiesel) and glycerol (byproduct),the quality and yield of biodiesel are effected by which feedstock and alcohol used (Chouhan and Sarma, 2011).

$$H_2C-OCOR$$
$$H_2C-OCOR + 3R''OH \xrightarrow{catalyst} 3RCOOR'' + H_2C-OH$$
$$H_2C-OCOR \qquad\qquad H_2C-OH$$
$$Triglyceride + Alcohol \xrightarrow{catalyst} Alkylester + Glycerol$$
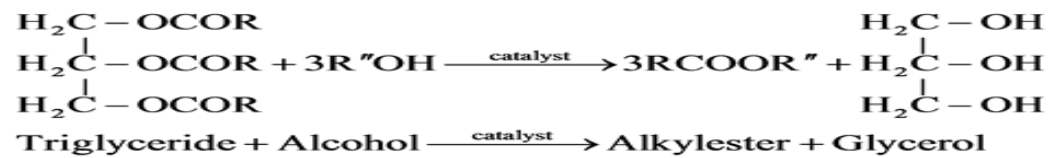
Equation 2.2: General equation of transesterification reaction.

2.4.1 Alcohol in transesterification reaction:

- Alcohols are the primary and secondary monohydric aliphatic compounds having 1‑8 carbon atoms(Helwani et al., 2009b) Many different alcohols can be used in this reaction, including, methanol, ethanol, propanol, and butanol(Talebian-Kiakalaieh et al., 2013).
- Methanol is preferred because of its lower cost and its physical and chemical advantages (polar and shortest chain alcohol) over ethanol(Helwani et al., 2009b), If methanol is used in this process the reaction calls methanolysis(Meher et al., 2006).
- Methanolysis of triglyceride is represented in Equation. 2.3. (R 1, R 2, and R3) are long chains of hydrocarbons and carbon atoms call fatty acid chains. The reaction is based on one mole of triglyceride reacting with three moles of methanol to produce three moles methyl ester (biodiesel) and one mole glycerol (byproduct)(Talebian-Kiakalaieh et al., 2013)

$$R_1\text{-COO}-CH_2 \qquad\qquad R_1\text{-COO}-CH_3 \quad HO-CH_2$$
$$R_2\text{-COO}-CH + 3CH_3OH \rightleftharpoons R_2\text{-COO}-CH_3 + HO-CH$$
$$R_3\text{-COO}-CH_2 \qquad\qquad R_3\text{-COO}-CH_3 \quad HO-CH_2$$

Triglyceride   Methanol   Methyl esters   Glycerol

with R_1, R_2, R_3 = hydrocarbon chain from 15 to 21 carbon atoms
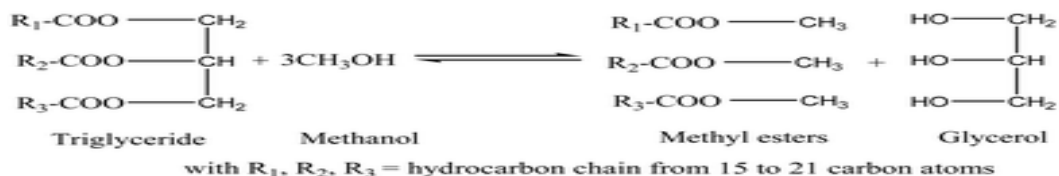
Equation 2.3: Methanolysis of triglyceride.

2.4.2 Undesirable reactions may occur during the transesterification reaction:

1. The presence of water in the reaction medium can lead to hydrolysis of the esters forming free fatty acids and, consequently, soap, which causes problems in the purification of biodiesel(Karmakar and Halder, 2019)

2. Triglycerides with high concentration of free fatty acids neutralize the basic catalyst and form soap, reducing the yield of biodiesel (de Lima and Mota, 2019)

2.4.3 Methods of transesterification reaction

There are two methods in which transesterification can be carried out, which are: (a) with catalyst and (b) without catalyst (supercritical method). The utilization of different types of catalysts improves the rate and yield of biodiesel(Talebian-Kiakalaieh et al., 2013).

2.4.3.1 Transesterification reaction based on supercritical (Non-Catalytic) method:

The supercritical method requires no catalyst and can achieve near complete conversion in a relatively short time. This method is not feasible for large scale production because it requires high temperature and pressure for biodiesel production. These reasons dramatically increase the equipment and production costs. Thus, most researchers have focused on finding new approaches in this method to decrease the reaction temperature and pressure(Talebian-Kiakalaieh et al., 2013).

2.4.3.2 Transesterification reaction based on catalytic method:

- In general the catalysts that can be used for producing biodiesel are divided into three groups: alkaline, acidic and enzymatic. (Gorji and Ghanei, 2014). The reaction is facilitated with a suitable catalyst which is either homogeneous or heterogeneous.(Chouhan and Sarma, 2011).
- . Several factors influence the catalytic process in transesterification reaction which are a) The type of catalyst, b) Selected feedstock, c) Alcohol used and d) The reaction condition(de Lima and Mota, 2019)
- Table 2.9 shows Advantages and disadvantages at different types of catalysts used in biodiesel production.

Table 2.9: Advantages and disadvantages of different types of catalysts used in biodiesel production(Leung et al., 2010).

Type	Example	Advantages	Disadvantages
Alkali Homogeneous	NaOH KOH	• High catalytic activity • Low cost • Favorable kinetics • Modest operation conditions	• Low FF requirement • Anhydrous conditions • Saponification • Emulsion formation • Disposable
Alkali Heterogeneous	CaO CaTiO$_3$ CaZrO$_3$ KOH/Al$_2$O$_3$ Al$_2$O$_3$/KI ETS-10 zeolite alumina/silica supported K$_2$CO$_3$	• Noncorrosive • Environmentally benign • Recyclable • Fewer disposal problems • Easily separation, • Higher selectivity • Longer catalyst lifetimes	• Low FFA requirement • Anhydrous conditions • High molar ratio of alcohol to oil requirement • High reaction temperature and pressure • Diffusion limitations
Acid Homogeneous	Concentrated sulphuric acid	• Catalyze esterification and transesterification simultaneously, • Avoid soap formation	• Equipment corrosion More waste from • Neutralization, • Difficult to recycle, Higher reaction temperature, • Long reaction times, • weak catalytic activity
Acid Heterogeneous	ZnO/I$_2$ ZrO$_2$=SO$_2$ TiO$_2$=SO$_2$ Carbon-based solid acid catalyst	• Catalyze esterification and transesterification simultaneously • Recyclable • Eco-friendly	• Low acid site concentrations • Low micro-porosity, • Diffusion limitations • High cost
Enzymes	Candida antarctica fraction B lipase Rhizomucor mieher lipase	• Avoid soap formation Nonpolluting • Easier purification	• Low acid site concentrations • Low micro-porosity Diffusion limitations • High cost

2.4.4 Choice of using a proper catalyst for transesterification reaction:

The choice of a catalyst for the transesterification mainly depends on the amount of FFA and of raw materials. If the oils have high FFA content and water, the acid-catalyst transesterification process is preferable. However, this process requires relatively high temperatures, i.e., 60–100 °C, and long reaction times, i.e., 2–10 h, in addition to causing undesired corrosion of the equipment(Helwani et al., 2009a). Therefore, to reduce the reaction time, the process with an acid-catalyst is adapted as a pretreatment step only when necessary to convert FFA to esters. In contrast, when the FFA content in the oils is less than(1 wt.%,) many researchers have recommended that only an alkaline-catalyst assisted process should be applied, because this process requires less and simpler equipment than that for the case of higher FFA content mentioned above(Thanh et al., 2012).

2.4.4.1 Bio-derived catalysts for biodiesel production

- Bio-based catalysts have increasingly attracted attention for biodiesel production due to their availability and environmentally friendly nature. Those catalysts are derived from natural sources and divided into 3 types: alkali catalysts, acid catalysts, and biocatalysts (enzymes).
- Each type of catalyst has its advantages and disadvantages for biodiesel production. To synthesize these catalysts, various biomass materials and synthesis methods have been reported. Catalysts derived from different sources possess different catalytic activity(Nguyen et al., 2021).
- Alkali catalysts derived from biomass have attracted considerable interest in biodiesel production due to their ecofriendly nature, low cost, and the availability of biomass as a material for the synthesis of catalysts. Moreover, the use of biomass for catalyst synthesis can solve the environmental problems caused by surplus biomass waste(Teo et al., 2017).

2.4.4.2 Biomass-derived calcium oxide (CaO)

- There are various types of bio-derived alkali catalysts have been studied for transesterification reactions. Biomass-derived calcium oxide (CaO) is one of the most promising solid alkali catalysts used for biodiesel production(Mansir et al., 2018).

- The availability of CaO has been recorded in different types of waste/low-cost materials, mainly from animal-derived biomass, including eggshell , Turbo jourdani shell, oyster shell , Pomacea canaliculata shell , Turbonilla striatula shell , crap shell , mussel (Perna varidis) shell , Grooved razor shell , conch shell , Malleus malleus shells , and animal bone(Mazaheri et al., 2021) .

- The catalytic activities of CaO catalysts vary, depending on the materials used and the synthesis method. Among the materials used, eggshell seems to be one of the most suitable materials and attracted extensive investigations for the synthesis of CaO catalyst since it contains a high level of $CaCO_3$ and is easy to obtain. (Mansir et al., 2018).

Chapter Three

(MATERIALS AND METHODS)

Chapter Three

3. Materials and methods

3.1 Materials:

All chemicals used were of analytical reagent grade (AR): Methanol, Isopropyl alcohol, Potassium hydroxide, Phenolphthalein indicator and calcium oxide.

3.2 Methods:

3.2.1 Collection and pretreatment of the waste frying oil

Waste frying oil (WFO) (Taken from potato frying "chips") was collected from household kitchens as a feedstock and filtered using cloth filter to remove large particles and impurities. Then the WFO was heated using a hotplate at 110°C for 1 hour to reduce the water content. Finally the treated WFO was kept for further steps.

3.2.2. Physicochemical Properties of the WFO:

The Physicochemical Properties were characterized according to standard method described by ASTM. Tests include density (ASTM D1298), acid value (ASTM D974), color (ASTM D974) and the free fatty acid% was calculated using an equation described by Mansir et al, 2018.

3.2.3. Fatty acid profile of the WFO:

The fatty acid profile was determined by methylation (converting the oil into alcohol esters) of fatty acid (The methylation process, does not alter the fatty acids composition of the feedstock) and, by using GS-MS, all the main components in the oil were completely separated and identified by comparing their retention index and mass fragmentation with those available in the GC-MS library (National Institute of Standards and Technology). The relative proportions of the esters were then converted back to corresponding amounts of fatty acids. Then the components and percentages of the fatty acid profile were recorded and used for further calculation.

3.2.3.1. GC/MS Sample preparation:

2ml of WFO was mixed with 7ml of alcoholic sodium hydroxide (2 g of NaOH in 100 ml methanol) then 7 ml of alcoholic sulfuric acid (1ml of H_2SO_4 to 100 ml methanol) was added, and the mixture was mixed for 5 minutes and left to stand overnight. Next, 1 ml of saturated sodium chloride (NaCl) was added and the contents being shaken. Further, 2ml of normal hexane was added and the contents were mixed thoroughly for three minutes. Then, the n-hexane layer (the upper layer of the test tube) was taken using disposable syringe. 5 µl from the n-hexane extract was diluted with 5 ml of diethyl ether .Subsequently, the mixture was filtered through syringe filter 0.45 µm and dried with 1g of anhydrous sodium sulphate as drying agent and 1µl of the diluted sample was injected in the GC.MS instrument.

3.2.3.2. GC/MS Conditions:

 The qualitative and quantitative analysis of the sample was carried out using GC/MS spectrometer model (GC/MS-QP2010-Ultra) from Simadzu, Japan, (serial number 020525101565SA) and capillary column (Rtx-5ms-30m×0.25 mm×0.25µm).The sample was injected using split mode and helium as the carrier gas. The flow rate was 1.61 ml/min, the temperature program was started from 60 °C with rate 10°C /min to 300°C as final temperature, the injection port temperature was 300°C, the ion source temperature was 200°C and the interface temperature was 250°C.The sample was analyzed using scan mode in the range of 40-500 m/z and the total run time was 27 minutes. Identification of components for the sample was achieved and the results were recorded.

3.2.4. Estimation of the prospective biodiesel fuel properties and average molecular weight of the WFO:

Biodiesel properties were estimated using Biodiesel Analyzer© ver. 2.3 (A software for predicting the properties of prospective biodiesel available on http://www.brteam.ir/biodiselanalyzer) (Talebi et al., 2014). The only input data required by the Biodiesel Analyzer is the fatty acid profile of the feedstock oil as determined by GC-MS, the weight percent of the individual fatty acids were entered, and the various calculated properties were estimated and compared with the reference standards. As for the average molecular weight, it was calculated using an online calculator available in https://www.biodieseleducation.org/Production/MolecularweightCalculator.html. The concepts of calculation for both softwares are summarized in appendices A and B.

3.2.5 Preparation of CaO bio-derived catalyst from waste eggshells:

The eggshells were washed with hot water to remove impurities and left to dry overnight at 100 °C in an oven. The dried eggshells were pulverized to obtain finer powder. Next, the powder was placed in a furnace and calcined at 900°C for 2 hours to produce CaO. Then, the catalyst the calcined eggshells was stored away from air and water because the calcium oxide is highly reactive with water and carbon dioxide giving calcium oxide and calcium carbonate, respectively. (Khazaai et al., 2021).

3.2.6 FT-IR analysis of the raw eggshells, calcined eggshells and standard Calcium Oxide:

Firstly, the samples were mixed individually with suitable amount of KBr and then, the functional groups of standard CaO, calcined eggshell and raw eggshell were identified using Infrared Spectra.

3.2.7 Biodiesel synthesis and purification:

The reaction was carried out in 250 mL flask. first, 100g of treated WFO was placed into the reactor and heated up to (55- 60) °C while CaO, methanol were mixed and stirred at room temperature, then the mixture was added to oil in the reactor and stirred at rate of 600 rpm for the desired time. At the end of the reaction, the resulting mixture was transferred to separation funnel and placed to settle down overnight. The reaction conditions were (Methanol to Oil ratio: 15:1- Catalyst loading 3% "with respect to reactants total weight" - Contact Time: 3 hours). The reaction kept in anhydrous condition. Finally, the biodiesel phase was separated and purified using silica gel 2 % (with respect to biodiesel) and stirred gently for 30 minutes. Then the biodiesel was filtered and stored for analysis

3.2.8 Physiochemical properties of biodiesel:

The Physicochemical Properties were characterized according to standard method described by ASTM. Test include acid number (ASTM D974), Density (ASTM D1298) and color

3.2.9. GC-MS analysis of biodiesel (FAME profile):

The qualitative and quantitative analysis of the sample (biodiesel) was carried out by using GM/MS spectrometer. .The sample was analyzed by using scan mode in the range of 40-500 m/z and the total run time was 22 minutes .Identification of components for the sample was achieved by comparing their retention index and mass fragmentation patents with those available in the library of National Institute of Standards and Technology) (NIST).Then, the results were recorded.

Chapter Four

(RESULTS AND DISCUSSIONS)

Chapter Four

4. Results and Discussion

4.1. Physiochemical properties of the WFO (Density, Acid value color and FFA %):

The WFO was characterized by ASTM standard test method as presented in Table4.1, the results obtained are compared with those obtained by other researchers.

Table 4.1. Physiochemical properties of the waste frying oil.

Assay	Result	Reference	Test Method
Density (g/cm^3)	0.91	0.91 (Yaakob et al., 2013)	ASTM D1298
Acid value (mg KOH/g Oil)	0.92	2.47-3.6 (Chai et al., 2014)	ASTM D974
Color	Light Yellow	Yellow or Brown	ASTM D974
Free Fatty acid (FFA)%	0.46 %	> 1% (Yaakob et al., 2013)	(Mansir et al., 2018)

From Table 4.1, it's clear that There was no significant difference of density for the WFO which is similar to that reported in the literature(Yaakob et al., 2013). Density does not present a considerable change for a particular oil, but it is affected by any special treatment that is made to the WFO. Further, acid value usually increases as the WFO is used, due to the heating and cooling processes to which the oil is subjected. The acid value of the WFO was (0.92 mg KOH / g Oil), which is lower than the references (Chai et al., 2014). A possible explanation for this probably because of chips frying needs slightly low temperature for short frying time compare with chicken and fish. The acid value was calculated using Equation 4.1 below:

Acid value (mg KOH/g Oil) $= \{(A - B)*M* 56.1\}/W$

A = KOH solution required for titration of the sample, ml.   M = molarity of KOH, M.

B = KOH solution required for titration of the blank, ml.   W = sample used, g.

Equation 4.1. Calculation formula of the acid value

The observed color was light yellow and as in ASTM D974 the colors of waste frying oils range from light yellow to brown depending on the frying temperature and frying time. Light-colored oils have low acid value and the dark yellow and brown one have high acid value.

Figure 4.1. The color of collected (WFO).

The results obtained from the acid value (0.92 mg kOH/g), and the observed color are evidence of the low FFA present in the waste frying oil from chips frying (0.46%). As many researchers recommend when the FFA content in the oils is less than 1 wt. %, only an alkaline-catalyst assisted process should be applied (Yaakob et al., 2013).Therefore, this finding makes the process economically significant by the possibility of producing biodiesel from WFO through only one step of the transesterification reaction method. As mentioned in chapter one, this study set out with the aim of assessing the efficiency of using waste frying oil used for potato frying as high grade oil, these results confirm that hypothesis. The FFA% was calculated using Equation 4.2 below(Mansir et al., 2018).

$$FFA\% = Acid\ Value\ /2$$

Equation 4.2. Calculation formula of the free fatty acid %

4.2. GC-MS analysis of the WFO (Fatty acid profile):

All the main component of the oil were identified and they were completely separated and eluted from each other. For the purpose of clarity, the solvents peaks (n- hexane and methanol) are not shown. Figure 4.2 and Table 4.3 show the chromatogram and the list of constituents of the WFO from GC-MS analysis.
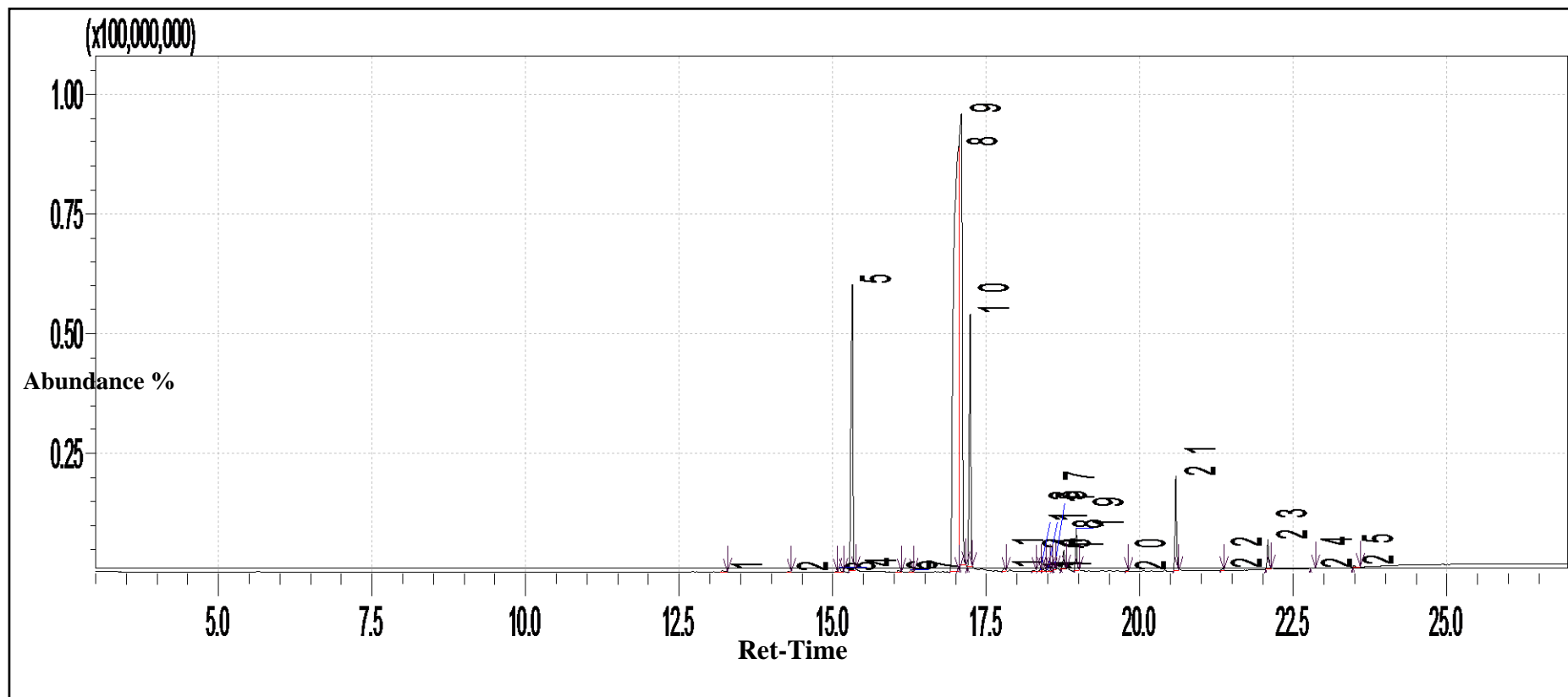
Figure 4.2. GC-MS chromatogram of the WFO

Table 4.2. The constituents of WFO from GC-MS analysis.

No	Name	Ret.Time	Area	Area%
1.	Methyl tetradecanoate	13.204	1083519	0.10
2.	Pentadecanoic acid, methyl ester	14.277	246998	0.02
3.	7-Hexadecenoic acid, methyl ester, (Z)-	15.058	340762	0.03
4.	9-Hexadecenoic acid, methyl ester, (Z)-	15.102	2027394	0.18
5.	Hexadecanoic acid, methyl ester	15.317	130927142	11.51
6.	cis-10-Heptadecenoic acid, methyl ester	16.067	724292	0.06
7.	Heptadecanoic acid, methyl ester	16.276	969457	0.09
8.	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	17.045	525216804	46.15
9.	9-Octadecenoic acid (Z)-, methyl ester	17.093	303388161	26.66
10	Methyl stearate	17.238	96156300	8.45
11	Methyl 10-trans,12-cis-octadecadienoate	17.787	1410850	0.12
12	.gamma.-Linolenic acid, methyl ester	18.270	422628	0.04
13	Methyl 9.cis.,11.trans.t,13.trans.-octadecatrienoate	18.378	654238	0.06
14	13-Tetradecenal	18.427	697740	0.06
15	9,12-Octadecadienoyl chloride, (Z,Z)-	18.497	567418	0.05
16	Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester	18.573	308945	0.03
17	8,11,14-Eicosatrienoic acid, methyl ester	18.613	1235504	0.11
18	cis-11-Eicosenoic acid, methyl ester	18.761	7345708	0.65
19	Eicosanoic acid, methyl ester	18.962	15279097	1.34
20	Heneicosanoic acid, methyl ester	19.786	236103	0.02
21	Docosanoic acid, methyl ester	20.584	35005313	3.08
22	Tricosanoic acid, methyl ester	21.345	845061	0.07
23	Tetracosanoic acid, methyl ester	22.084	11715443	1.03
24	Squalene	22.805	477168	0.04
25	Hexacosanoic acid, methyl ester	23.487	620005	0.05

The results obtained from GC-MS are informative, chemically significant and provide further progress in identifying the fatty acid profile, calculating the fatty acid content % and estimating the average molecular weight of the WFO as shown below:

Table 4.3. Fatty Acid Profile, Content % and Average molecular weight of the WFO

No	Name	Abbreviation * (CX:Y)	Area %
1.	Myristic acid	C14:0	0.10
2.	Pentadecanoic acid	C15:0	0.02
3.	Palmitoleic acid	C16:1	0.21
4.	Palimitic acid	C16:0	11.51
5.	Heptadecanoic acid, (Margaric acid)	C17:0	0.15
6.	Linoleic Acid	C18:2	46.27
7.	Oleic Acid	C18:1	26.66
8.	Stearaic Acid	C18:0	8.45
9.	Linolenic acid	C18:3	0.10
10	8,11,14-Eicosatrienoic acid,	C20:3	0.11
11	Eicosanoic acid, methyl ester	C20:1	0.67
12	Arachidic Acid	C20:0	1.34
13	Heneicosanoic acid	C21:0	0.02
14	Lignoceric acid	C23:0	0.07
15	Behenic Acid	C22:0	3.08
16	Tetracosanoic acid	C24:0	1.03
17	Hexacosanoic acid,	C26:0	0.05
Fatty Acid Content %			99.84%
Average Molecular Weight			877.78/mole

* (CX: Y) represents: (X: Number of carbon atom. Y: Number of double bond)

Table 4.3 summarizes the fatty acids composition (Fatty acid profile) of the WFO. Overall, the fatty acids range from (C:14 to C:26), and the most abundant fatty acids are Linoleic Acid (46.27 %,), Oleic Acid (26.66%),Palimitic, acid (11.51%), Stearaic Acid (8.45%), Behenic acid (also docosanoic acid) (3.08%), Tetracosanoic acid (1.03%) and the rest the other fatty acids represent (3%).These findings may help to understand the influence of individual FAs on fuel properties, the scientific literature has given much attention to this issue (Moser and Vaughn, 2012). Therefore, in general, it seems that here, the amount of saturated fatty acids is (25.77%), monounsaturated fatty acid (27.58%) and the polyunsaturated fatty acid (46.55%). Biodiesel is mainly formed by transesterification of saturated and monounsaturated fatty acids. The polyunsaturated and some bulky saturated fatty acids are responsible for the high viscosity of biodiesel. (Murugesan et al., 2015). Hence, the FA profile is an efficient predictor and recommended as a screening tool for investigation of alternative feedstock.

Continue to Table 4.3, the fatty acid content % was calculated by dividing the sum of all individual area under peak of the fatty acids (Table 4.3) by area under peak of all the scanned component by GC-MS (Table 4.2). The fatty acid content was equal to 99.84% .This high percentage increases the possibilities of formation the desert product of the transesterification reaction, yet, during the transesterification reaction the fatty acids have different possibilities to interact with alcohol (Some fatty acids are not found in free form i.e. polymerization, they have higher stability and they have higher efficiency in reacting in the transesterification process giving a higher conversion rate to esters). As for the average molecular weight, an online calculator was used to determine the average molecular weight using fatty acid profile (Table 4.3).The calculated molecular weight was 877.78 g/mole which is consistent with the reference molecular weights of vegetable oils (From 600 to 900) (Balat, 2008). This high molecular weight is due to the presence of long chain fatty acid (C14:C26) as shown in the fatty acid profile. Furthermore, the calculated molecular weight was used to calculate methanol to oil ratio in transesterification reaction.

4.3. Estimation of the prospective biodiesel fuel properties of the WFO:

Experimental determination of the quality parameters of a biodiesel sample requires considerable amount of time and consumes chemicals. Therefore, the fatty acid profile including chain length and the presence of unsaturation are an important factors in determining the physiochemical characteristics of biodiesel. In this study, a biodiesel analyzer software was used for prediction of the prospective biodiesel fuel properties, here the only input data required by the Biodiesel Analyzer is the weight percent of the individual fatty acids present the feedstock oil as determined by GC-MS. This evaluation would provide a good guideline to the biodiesel producer to improve the feedstock general characteristic before the production process. Table 4.4 shows the estimated values of the prospective biodiesel fuel properties.

Table 4.4. The estimated values of the prospective biodiesel fuel properties using Biodiesel Analyzer software.

No		Property	Estimated values	Standard range	References
1	SFA	Saturated Fatty Acid %	25.680	12	(Mansir et al., 2018)
2	MUFA	Monounsaturated Fatty Acid %	27.540	27	(Mansir et al., 2018)
3	PUFA	Polyunsaturated Fatty Acid %	46.340	61	(Mansir et al., 2018)
4	DU	Degree of Unsaturation	120.280	-	-
5	SV	Saponification Value (mg/g)	198.586	185-200	(Alok Patel et al., 2017)
6	IV	Iodine Value (mg/g)	108.818	*Max 120	EN 14214
7	CN	Cetane number	49.30	*Min 47	ASTM D6751
8	LCSF	Long Chain Saturated Factor	13.396	10-15	(Alok Patel et al., 2017)
9	CFPP:	Cold Filter Plugging Point (°C)	25.609	-10 -30	(Alok Patel et al., 2017)
10	CP	Cloud Point (°C)	1.062	-3 -12	ASTM2500
11	PP	Pour Point (°C)	-5.668	−15 to 5	ASTM D6751
12	APE	Allylic Position Equivalent	119.400	-	-
13	BAPE	Bis-Allylic Position Equivalent	49.150	-	-
14	HHV	Higher Heating Value MJ/kg	39.386	(39 to 43.33)	(Sivaramakrishnan and Ravikumar, 2011)
15	OS	Oxidation Stability (h)	5.1340	*Min 3	ASTM D6751
16	υ	Kinematic Viscosity (mm^2/s)	3.865	1.9 - 6.0	ASTM D6751
17	ρ	Density (g/cm^3).	0.874	0.86-0.90	EN ISO 3675

(-): Not reported   *(Max): Maximum   *(Min): Minimum

As biodiesel must meet the criteria set up by international standards, it can be seen that from Table 4.4, almost all the estimated properties meet the standard specification of biodiesel ASTM, EN and biodiesel literature for not reported specifications. the most important specifications were selected and discussed below:

Wt. % of the individual components of FAME: No, exactly, reference standard available for the wt. % of the individual component of FAME of biodiesel, yet, Mansir.et al. (2018), reported that, basically, the biodiesel comprised of five major fatty acids components, namely, palmitic (16:0): 7.3%, stearic (18:0): 4%, oleic (18:1): 26.9%, linoleic (18:2): 60.05% and linolenic (18:3): 0.5%. Accordingly, the estimated wt. % of saturated (25.680%), monounsaturated (27.540%) and polyunsaturated (46.340%) fatty acids are consistent with the wt. % of literature qualitatively and quantitatively.

The estimated value of **Degree of unsaturation** is (120.280) which is calculated using the amounts of monounsaturated (27.540 %) and polyunsaturated fatty acids (46.340 %). Mainly, the high amount of polyunsaturated fatty acids indicates high degree of unsaturation. No reference value available for degree of unsaturation. Thought, higher degree of unsaturation of biodiesel fuels led to a longer ignition delay and, consequently, more retarded start of combustion. This explanation is supported by Benjumea et al. (2011), they reported that the degree of unsaturation of biodiesel fuels did not significantly affect engine performance, but it had a noticeable influence on combustion characteristics, emissions and generally, via its effect on the cetane number.

Further, the predicted value of **Cetane number** is (49) meets the reference standard (Min 47), high cetane number can be obtained with long chain saturated fatty acids in feedstock. It's apparent that the estimated value is still closer to the minimum value of the standard. This is due to the presence of polyunsaturated fatty acid (46.3%). (The term cetane number is generally understood as a measure of ignition quality of diesel fuels, the high cetane number implies short ignition delay).

With regard to the **Higher Heating Value (**HHV) (The thermal energy released per unit quantity of fuel). Both ASTM D6751 and EN 14214 standards do not have any reference values. In literature the HHVs of biodiesel is (39 to 43.33 MJ/kg).The estimated value (39.386 MJ/kg) is consistent with the HHVs of biodiesel literature.

Furthermore, **Oxidation Stability** is an important characteristic to determine its shelf-life. Unsaturation and double bond in fatty acid chains are responsible for their interaction with oxygen when being exposed to air. From Table 4.4, although the high percentage of mono and poly unsaturated constituents in the oil, the estimated value of oxidation stability (5.1340 hour) meets the reference standard (Min 3 hours). This is due to the oxidation process is severely affected by the position, number of double bond and other reaction parameters. Beside that the oxygen content of biodiesel improves the combustion process and decreases its oxidation potential(Sivaramakrishnan and Ravikumar, 2011).

As for **Kinematic viscosity** (The ability of biodiesel to flow), it increases with chain length of fatty acid or saturation of fatty acid, however, the viscosity of unsaturated fatty acid depends on number and nature of double bonds but less affected by position. Consequently, due to the possibility of blending the biodiesel produced from both saturated and unsaturated fatty acid, the estimated viscosity (3.865 mm^2/s) meets the standard reference range of biodiesel (1.9 – 6 mm^2/s).

Finally, the **density** of biodiesel is important because it gives an indication of the delay between the injection and combustion of the fuel in a diesel engine (ignition quality) and the energy per unit mass (specific energy).This can influences the efficiency of the fuel atomization for airless combustion systems. The estimated density (0.875 g/cm^3) meets the reference value (0.86-0.90 g/cm^3).

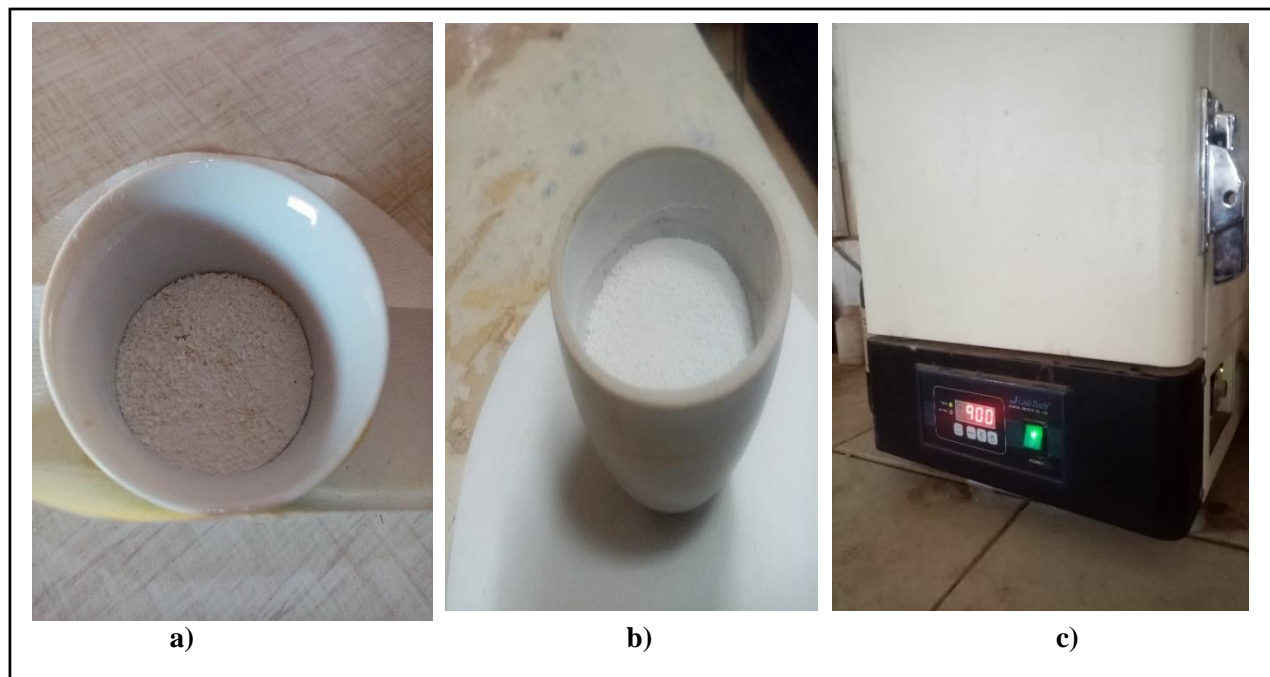**4.4 Physical observation of eggshells before and after calcination:**

a)	b)	c)

Figure 4.3. a) The raw eggshell   **b)** Calcined eggshells **c)** A furnace adjusted at 900°C**.**

It can be seen that from Figure 4.3, powder a) is the raw eggshells which is contain calcium carbonate ($CaCO_3$) as the main elements (about 94%).The calcium carbonate ($CaCO_3$) was converted into b) calcined eggshells (CaO) via c) calcination process at 900°C for 2 hours according to thermal gravimetric analysis (TGA) for eggshell studied by Ahmad et al. (2015). It's apparent that the color of b) became more clear white than a) and also the weight was decreased after calcination, a possible explanation for this is the high temperature exposes the catalytic sites by eliminating the loosely bound carbon dioxide, water molecules and other impurities. Additionally the calcination temperature plays enormous role in catalyst synthesis, through the development of the major catalytic properties such as surface area, pore volume as well as molecular and crystalline structure, and also rearranges the bulk atoms on surface of the catalyst(Mansir et al., 2018).

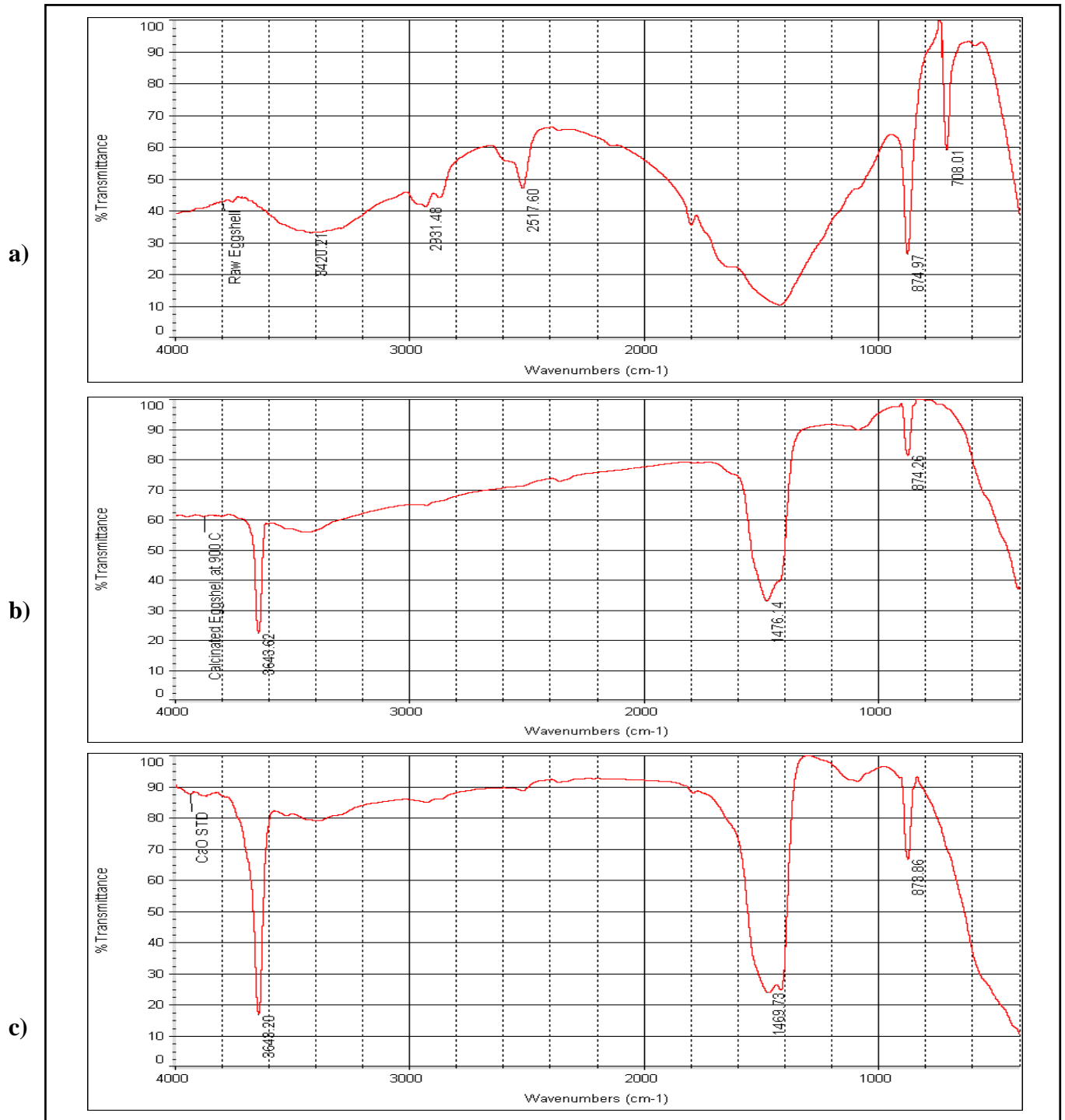## 4.5 FT-IR analysis of the raw eggshells, calcined eggshells and standard Calcium Oxide:

Figure 4.4. IR spectrums of **a)** Raw Eggshell. **b)** Calinated eggshell at 900 ºC. **c)** Standard CaO

From Figure 4.4 it can be seen that:

a) IR spectra for raw eggshell showed wide stretching peaks at 1409 cm^{-1} attributing to C-H bonding. Sharp and intense peak observed at 708.01 cm^{-1} represent C-O stretching and bending modes of $CaCO_3$ .Meanwhile, the sharp band at 874.97 cm^{-1} represent Ca-O bonds.

b) The spectrum of calcined eggshells showed the general decrease in the intensity of the peaks in the raw eggshells denoted that most of the functional groups were destroyed during heat treatment. The spectrum showed three specific vibrations unique for calcium oxide detected in wavenumber at 874.26 cm^{-1} for stretching vibration of Ca-O, a band at 3643 cm^{-1} associated with -OH mode of water physical-adsorbed on the surface of the CaO and 1476.4 Cm^{-1} assigned as a bending vibration of -OH (Mohadi et al., 2018).

c) The spectrum of standard calcium oxide showed the same wavenumbers found in the spectrum of calcined eggshells, denoted that the calcium oxide catalyst is successfully prepared. The wavenumbers appeared at 878.86 cm^{-1}, 1469.73 cm^{-1} and 3643.20 cm^{-1}.

4.6. A proposed mechanism and reaction condition of the transesterification reaction using calcium oxide in heterogeneous system:
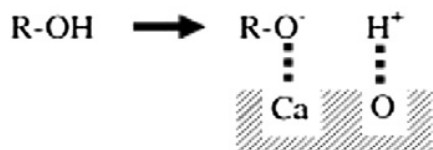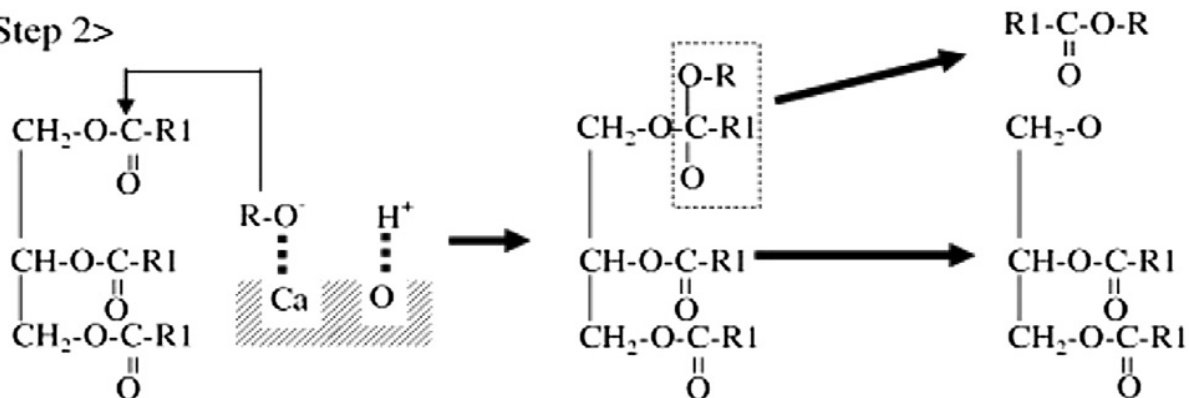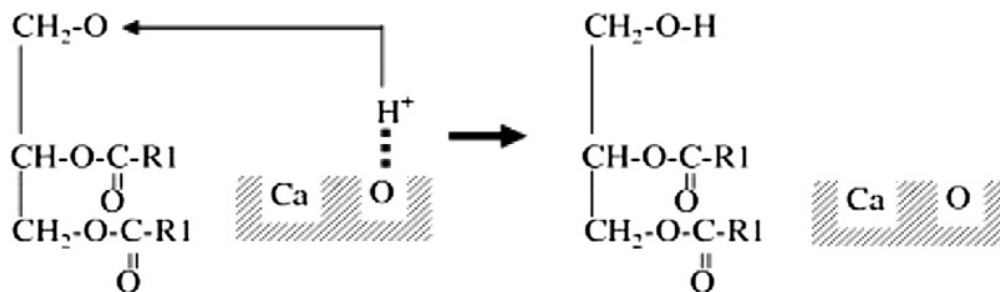
Equation 4.3. A purposed mechanism for the transesterification reaction using Calcium oxide in heterogeneous system (Solis et al., 2016, Mohadi et al., 2018).

It can be seen from Equation 4.3, the transesterification reaction involved three steps reaction mechanism i.e. methoxide ion from methanol reacts with the catalyst (CaO) (Step 1), reaction of carbonyl carbon of triglyceride with step 1 to form a tetrahedral intermediate (Step 2), and the intermediate forms a mole of methyl ester and di-glyceride anion (Step 3). The reaction was repeated to form three moles of methyl ester (Biodiesel) and one mole of Glycerol (Byproduct).

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Numerous studies have attempted to explain the effect of the reaction parameter to biodiesel purity. It was decided that the best condition to adapt the reaction in the case of study was: Methanol: Oil: (1:15), Contact Time: (3 hours), Catalyst loading: (3%) and Temperature: (55-60°C). according to following debates.

Although, theoretically three mole of methanol is required for one mole of triglyceride, as showed in the proposed mechanism (Equation 4.3), the ratio of (Methanol: Oil) was adopted at (15:1), this is due to the excess amount of methanol enhances FAME conversion. This view is supported by Mansir et al. (2018) who reported that 90% of biodiesel yield was achieved at the maximum of (15:1) methanol to oil molar ratio, no significant increase in biodiesel yield was observed from (15:1 to 18:1) another reason for that (15:1) was adopted in view of economics and methanol recovery after the reaction. Similarly, Prasertsit et al., (2014) reported that the FAME purity in the product increases from (35 to 88%wt) as the methanol to oil molar ratio increases from (3:1 to 15:1), in contrast, a ratio higher than (15:1) without increasing the catalyst decreases FAME purity i.e. (Increases methanol content in the product). Therefore, a mass ratio of (3%wt) CaO was adapted to provide higher amount of the intermediate (Methoxide - CaO) as illustrated in the proposed mechanism in Equation 4.3. This point was emphasized by Prasertsit et al. (2014), they reported that a mass ratio of CaO up to (2%wt) can improve the purity of methyl ester, However, for a higher value than 2%wt of alkaline base (CaO) without increasing methanol supports the side reactions (saponification) which increases soap content in the product. Regarding to the reaction temperature, it was adopted at (55-60°C) as it is known the temperature speeds up the reaction rate and to maintain the reaction temperature lower than the boiling point of methanol (65°C).

The reaction was rigorously kept in anhydrous condition for several reason: a) Water deactivates the calcium oxide catalyst by converting it to calcium hydroxide. b) Water increases the possibility of hydrolysis of triglyceride and that produces fatty acids. c) The liberated fatty acids increase the acidity and soap formation.

4.7 Physical observation of the transesterification reaction products:
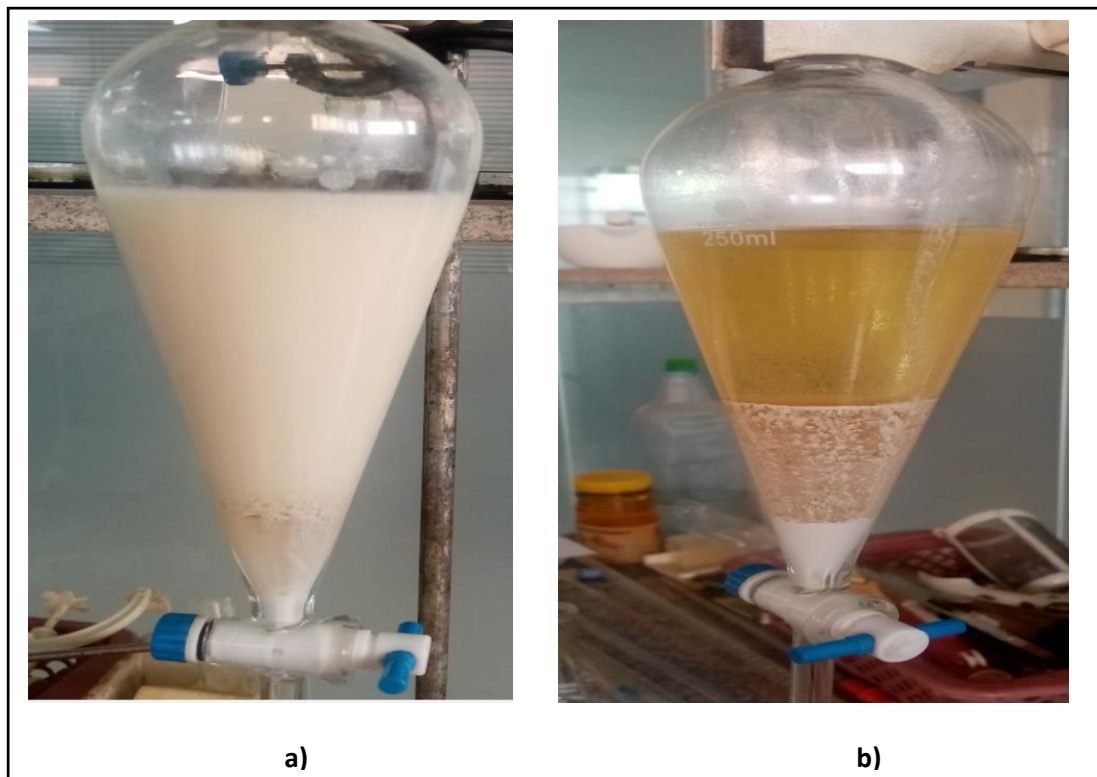

Figure 4.5. Transesterification reaction products a) before and b) after settling down.

It can be seen that from Figure 4.5 the mixture of the products (a) was left overnight to enable the products to settle down (b) to separate the top (methyl ester) and bottom (glycerol) layers. The top layer is mainly composed of methyl esters and the bottom layer is mostly made up of glycerol, salts, soap, other impurities and excess methanol. It's apparent that, there are some CaO particles suspended in the glycerol layer. This is due to the capability of CaO to dissolve in glycerol (PubChem, 2004). The top methyl ester layer was separated and removed from every impurity using silica gel as dry washing technology (waterless) which is the most regularly used method in the dynamics of biodiesel purification process. It can easily attract polar substances (glycerol and methanol, etc) through its basic and acidic adsorption sites. The dry washing procedure improves fuel quality. Silica gel was experimented in the adsorption of glycerol and monoglycerides and the values obtained indicated efficiency of adsorption of glycerol and monoglycerides (Atadashi, 2015).Then the purity of the product (Biodiesel) was analyzed by GC-MS.

4.8 Physiochemical properties of biodiesel (Density, Acid value, Color and Yield):

Table 4.5. Physiochemical properties of biodiesel (Density, Acid value, Color and Yield)

Assay	Result	Reference	Test Method
Density (g/cm^3)	0.85	0.86-0.90	EN ISO 3675
Acid value mg KOH/g	0.30	0.50 max.	ASTM D6751
Color	Golden Yellow	Yellow or Brown	ASTM D974
Yield%	85%	-	-

Table 4.5 shows some of the main characteristics of the biodiesel, it is apparent that, no limits had been assigned for the density by ASTM. Though, the measured value (0.85 g/cm^3) is in agreement with European standard (0.86-0.90) and the estimated density by biodiesel analyzer (0.874) as showed in Table 4.4. Additionally, the density was decreased from (0.91) of WFO to (0.85) of the product this is due to the formation of FAME. Further, the measured acid value (0.30) meets the standard specification of biodiesel (0.50 max). It's obviously, the acid value decreased from (0.92) of WFO to (0.3) of biodiesel. Mainly the acidity of biodiesel and WFO comes from the FFA, so a possible explanation for decreasing the acidity might be to esterification reaction of FFA by methanol and CaO, and occurring of another undesired reaction (Saponification). Regarding to the observed color (Golden yellow), it supports the result of acid value because the color of biodiesel range from light yellow (Low acidity) to dark yellow depend on the acidity of used feedstock. Finally, the obtained yield was 85% calculated by (Weight of biodiesel / Weight WFO)*100.

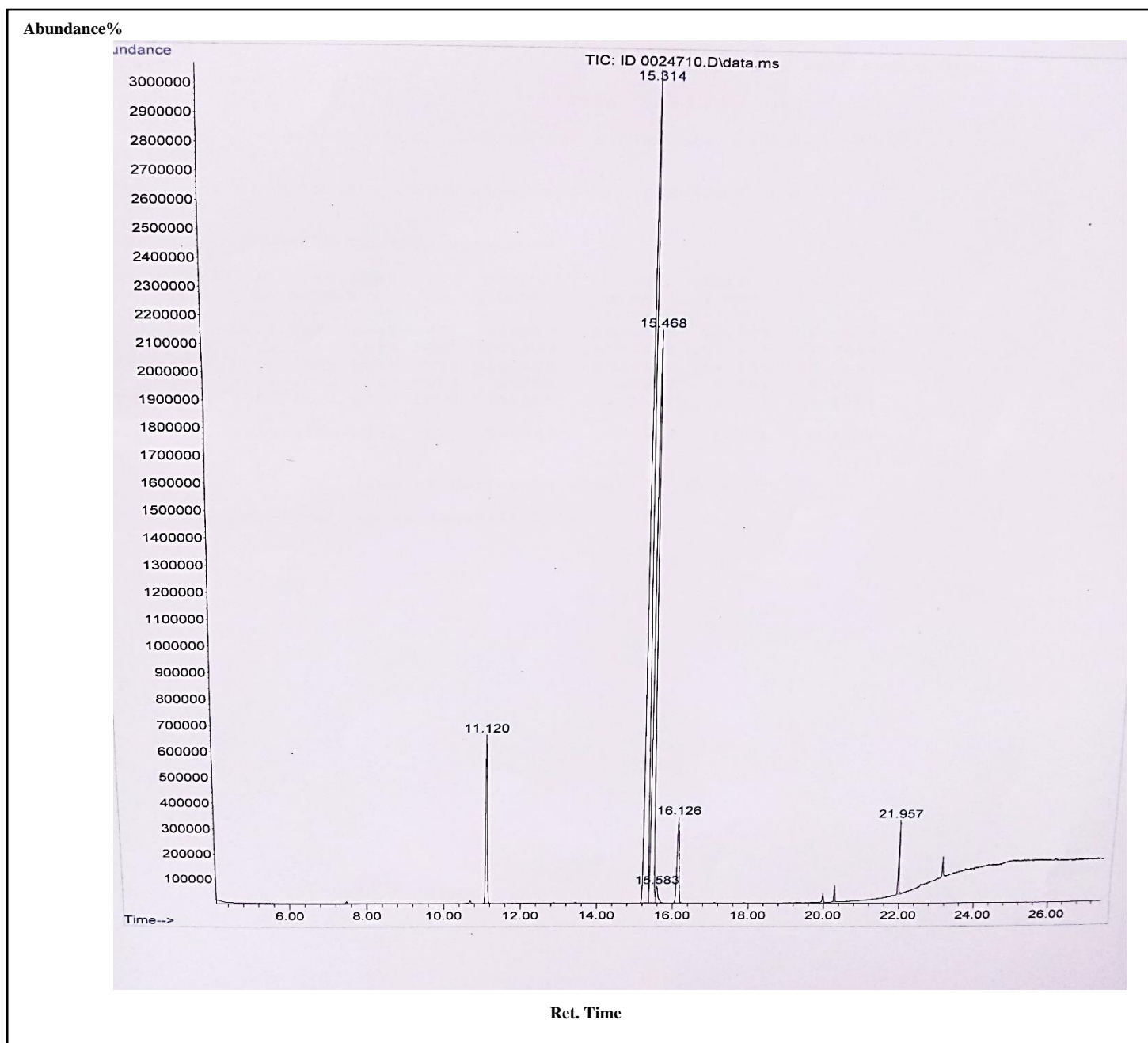## 4.9 GS-MS analysis of biodiesel (FAME profile):

Figure 4.6. GC-MS chromatogram of the biodiesel.

Table 4.6. The constituents of biodiesel from GC.MS

No	Name	Ret.Time	Area	Area%
1.	Hexadecanoic acid, methyl ester	11.120	1875268	6.667 %
2.	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	15.314	15374645	54.660 %
3.	9-Octadecenoic acid (Z)-, methyl ester	15.468	8929459	31.746 %
4.	Methyl stearate	15.583	282033	1.003 %
5.	Cis 13 octadecanoic acid, methyl ester	16.126	1245978	4.430 %
6.	Docosanoic acid, methyl ester	21.957	420569	1.495 %

From Table 4.6 The majority of methyl esters (biodiesel) are found in highly pure form and in large quantities, the compounds found in high quantities are shown in peaks No. 2 (linoleic methyl ester 54.660 %) and 3(oleic methyl ester 31.746 %), which they produced from the same most abundant fatty acids of the WFO. This finding confirmed by Mansir, et al. (2018), they reported that, basically, the biodiesel comprised of five major fatty acids components, namely, palmitic (16:0): 7.3%, stearic (18:0): 4%, oleic (18:1): 26.9%, linoleic (18:2): 60.05% and linolenic (18:3): 0.5%. Overall, these results indicate that the FAME (biodiesel) mainly produced from monounsaturated fatty acids and polyunsaturated fatty acids, the later are relatively responsible for the high viscosity of biodiesel. Obviously, of the total 17 fatty acids of the WFO only 6 fatty acids contributed to produce the biodiesel (FAME).

Chapter Five

(CONCLUSION AND RECOMMENDATIONS)

5.1 Conclusion

In summary, this work shows that waste frying oil taken from chips frying has an acid value of 0.92 mg KOH/g oil. This value has a significant impact on the direct transesterification of WFO using CaO as a solid base catalyst without any pretreatment. In addition, the use CaO bio-derived catalyst from waste eggshell makes the process valuable economically. Finally, the use of fatty acid profile and biodiesel analyzer software provides good guideline to improve the general characteristics of the raw oil before scaling up the production process.

5.2 Recommendations:

- When WFO would be suggested as feedstock it's required to check the free fatty acid and water content as major problems correlated with utilizing of WFO in biodiesel production. Additionally it's recommended to consider the chemical composition of the raw oil specifically the presence of the polyunsaturated fatty acids due to it is notable impact on the quality of biodiesel.
- When low grade oil is used as feedstock it's recommended to use the new modified catalytic system (Bi-functional catalyst) as it could perform both transesterification and esterification of TGs and FFA simultaneously under moderate reaction conditions. This is because the, bi-functional catalysts are having both basic and acidic sites. Hence, modified waste egg shell derived bi-functional heterogeneous catalysts could be promising alternative catalysts to overcome the problems associated with the low grade feedstock.
- Another possible area of future research would be to optimize the condition to separate and purify the valuable bi-product (Glycerol) together with the main product (biodiesel) of the transesterification reaction. This makes the whole process possess more economically feasible.

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Biodiesel Analyzer Software

The Biodiesel Analyzer is a software used for predicting the properties of a prospective biodiesel. Biodiesel Analyzer can estimate 16 different quality parameters of biodiesel. The current version of the Biodiesel Analyzer is intended for the Windows platform and is publically available at http://www.brteam.ir/biodieselanalyzer. This software is based on the previously published highly-reliable modeling data.

Input data

The only input data required by the Biodiesel Analyzer is the fatty acid profile of the feedstock oil as determined by gas-chromatography (GC). Once the weight percent of the individual fatty acids present in the oil has been entered, pressing 'continue' leads the user to a new page where the various calculated properties of the prospective biodiesel are given under different tabs.

Analysis

 Biodiesel Analyzer provides the estimated properties under the following tabs: Unsaturation Level, including the amount of the saturated and the unsaturated fatty acids and the degree of unsaturation (DU); the Cetane Number; the Cold Flow Properties including the cloud point (CP) and the cold filter plugging point (CFPP); the Oxidation Stability including the allylic (APE) and the bis-allylic position equivalents (BAPE); the Higher Heating Value (HHV); the kinematic viscosity; and the Density. The Equations 1–12 provided below are used in estimating the various properties from the fatty acid methyl ester profile (FAME) and the structure of the relevant fatty acids.

The cetane number (CN) is calculated as follows

$$CN = 46.3 + (5.458/SV) - (0.225 \times IV) \quad \textbf{(Eq. 1)}$$

The saponification value (SV) and iodine value (IV) for use in the above equation are calculated using the following equations:

$$SV = \Sigma(560 \times N)/M \quad \textbf{(Eq. 2)}$$

$$IV = \Sigma(254 \times D\ N)/M \quad \textbf{(Eq. 3)}$$

In the above equations D is the number of double bonds in the fatty ester, M is the molecular mass of the fatty ester, and N is the percentage of the particular fatty ester in the oil sample.

The degree of unsaturation (DU) is calculated using the amounts of the monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) present in the oil; thus:

$$DU = MUFA + (2 \times PUFA) \quad \textbf{(Eq. 4)}$$

The allylic position equivalents (APE) and bis-allylic position equivalents (BAPE) are calculated using the equations previously developed by Knothe, (2002):

$$APE = \Sigma(ap_n \times A_{cn}) \quad \textbf{(Eq. 5)}$$

$$BAPE = \Sigma(bp_n \times A_{cn}) \quad \textbf{(Eq. 6)}$$

where ap_n and bp_n are the numbers of allylic and bis-allylic positions in a specific fatty acid, respectively, and A_{cn} is the amount (mass percent) of each fatty acid in the mixture.

The long-chain saturated factor (LCSF) and the cold filter plugging point (CFPP) are estimated:

$$LCSF = (0.1 \times C_{16}) + (0.5 \times C_{18}) + (1 \times C_{20}) + (1.5 \times C_{22}) + (2 \times C_{24}) \quad \textbf{(Eq. 7)}$$

$$CFPP = (3.1417 \times LCSF) - 16.477 \quad \textbf{(Eq. 8)}$$

The accuracy of the above empirical equations in estimating the quality of a biodiesel have been previously proven Ramos et al., (2009).

The cloud point (CP) is calculated using the following equation:

$$CP = (0.526 \times C16) - 4.992 \qquad \textbf{(Eq. 9)}$$

Eq. 9 is used to estimate the CP value based the C16:0 content (wt %) in the FA profile.

The kinematic viscosity (υ, mm^2/s) at 40 °C is estimated as follows:

$$\ln(\upsilon) = \Sigma N_i(-12.503 + (2.496 \times \ln Mw_i) - 0.178 \times D_i) \qquad \textbf{(Eq. 10)}$$

Here Mw_i is the molecular weight of a fatty acid, N_i is the percentage of the given fatty acid in the biodiesel and D_i is the number of double bonds in the given fatty acid.

The density (ϱ, g/cm^3) of the biodiesel at 20°C is estimated using the following equation

$$\rho = \Sigma N_i(0.8463 + (4.9/Mw_i) + 0.0118 \times D_i) \qquad \textbf{(Eq. 11)}$$

The higher heating value (HHV) of the biodiesel is estimated as follows

$$HHV = \Sigma N_i(46.19 - (1794/Mw_i) - 0.21 \times D_i) \qquad \textbf{(Eq. 12)}$$

<div align="center">**Appendix-B**</div>

Average molecular online calculator

The average molecular is calculated using an online calculator available in (https://www.biodieseleducation.org/Production/MolecularweightCalculator.html).

Input:

The only input data required by the Average molecular calculator is the fatty acid profile of the feedstock oil as determined by gas-chromatography (GC). Once the fatty acid profile of the oil is known, it is easy to calculate the average molecular weight of the oil.

Calculation:

The molecular weight of a particular oil depends on its fatty acid profile. A saturated fatty acid chain with 'n' number of carbons will have a chemical structure of CH_3- (CH_2) $_{n-2}$ -COOH. The molecular weight of a single fatty acid 'i' can be calculated as:

$$MW_i = 14.027C - 2.016d + 31.9988 \qquad \textbf{(Eq.1)}$$

Where 'C' is the number of carbons and 'd' is the number of double bonds.

The average molecular weight of fatty acid mixture is calculated by dividing the sum of all reported fatty acid weights by total moles in the mixture.

Numerically, Average molecular weight of fatty acids $= \sum f_i / \sum (f_i/MW_i)$ **(Eq.2)**

Where, f_i are the weight fraction of a reported fatty acid.