



Institute of Water and Energy Sciences (Incl. Climate Change)

CEMENT KILN DUST CATALYZED TRANSESTERIFICATION OF PALM AND WASTE COOKING OILS TO BIODIESEL AND GLYCEROL: PROCESS OPTIMIZATION AND CHARACTERIZATION STUDIES

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DECLARATION

I, **Mahmoud Sayed Hefney** do hereby declare that this thesis is my original work and to the best of my knowledge, it has not been submitted to any award in any University or Institution.

Signed _____ Date _____

ABSTRACT

Conventional fossil fuels such as natural gas, oil, and coal have been the main sources of energy utilized to satisfy the unceasing growth of energy needs of the world. However, the environmental issues of fossil fuels and the depletion of their reserves have directed many researchers to search for sustainable alternatives that can compete with conventional fuels economically and technically while conserving the environment. Liquid biofuels such as biodiesel have been of interest to many researchers due to the associated benefits. Availability and sustainability of feedstock, as well as catalyst cost-effectiveness and activity, are the top research interests in the research area of biodiesel for improving its mass production. In this regard, designing a transesterification process to valorize waste, used materials and materials of low value could be one of the best solutions not only to overcome the energy and environmental problems mentioned above but also to ensure better management of used materials and waste reuse. This research introduces a study of different input variables influencing the designed single step transesterification process through which biodiesel is produced from a characteristically enhanced vegetable oil blend of 60 wt % waste cooking oil and 40 wt % low to moderate grade palm oil (which is not suitable for cooking) using cement kiln dust (CKD), as a heterogeneous catalyst. In addition, it aims at determining the optimum reaction conditions in the range of the study to achieve the highest oil to biodiesel conversions (complete conversion). This was done through following the statistical and the experimental procedures of factorial design concept and response surface methodology (RSM). The studied reaction conditions were reaction time 1, 3.5, 6 hours, methanol to oil molar ratio (12:1, 15:1, 18:1), reaction temperature (45, 55, 65 °C) and lastly, catalyst loading (1, 2, 3 % of blend weight). 850 rpm was the stirring speed used in all the CKD catalyzed transesterification reactions of the study. Both quadratic and linear models were developed based on the experimental results obtained. The quadratic model was preferred to the linear one as the optimum conditions can be more accurately obtained from its response surfaces and it proved more validity in explaining the range of experimentally obtained results. The optimum conditions obtained statistically from the quadratic model based response surfaces were catalyst loading of 2.7% of feedstock weight, 4.5 hours reaction time, 17:1 methanol to oil molar ratio and 59-60 °C. Whereas correlating the data from the quadratic model regression equation and the response surfaces plots, plus checking experimentally the validity of conversion values obtained have led to identifying the following conditions at which complete conversion can be achieved: 3 % catalyst loading, 65 °C, 15:1 methanol to oil molar ratio and 3.5 hours reaction time. These conditions were

considered to be optimum as they include lower methanol to oil molar ratio and shorter time which can better enhance biodiesel production process economically. Characterization of the produced biodiesel showed that its properties meet the ASTM standards.

A suggested model of a lab to industry scaling-up and design of an agitated batch reactor for biodiesel and glycerol production was introduced. An amount of 30 tons of 60 wt % waste cooking oil and 40 wt % palm oil blend per day is the daily rate proposed to feed in the industrial scale biodiesel and glycerol production plant demonstrated. Transesterification reaction conditions of the suggested process are adjusted in order to give a 100 % conversion which means production of about 30 tons biodiesel and 3 tons glycerol per day.

Key Words:

Palm oil, Waste cooking oil (WCO), Valorizing, Transesterification, Biodiesel, Cement kiln dust (CKD), Factorial design of experiments, Response surface methodology (RSM), Optimum conditions and Characterization.

ABSTRAIT

Les combustibles fossiles classiques tels que le gaz naturel, le pétrole et le charbon ont été les principales sources d'énergie utilisées pour satisfaire la croissance incessante des besoins énergétiques du monde. Cependant, les problèmes environnementaux des combustibles fossiles et l'épuisement de leurs réserves ont conduit de nombreux chercheurs à chercher des solutions de rechange durables qui peuvent concurrencer les carburants classiques économiquement et techniquement tout en conservant l'environnement. Les biocarburants liquides tels que le biodiesel ont intéressé de nombreux chercheurs en raison des avantages associés. La viabilité des matières premières ainsi que la rentabilité et l'activité du catalyseur sont les principaux intérêts de recherche dans le domaine de recherche du biodiesel pour l'amélioration de sa production de masse. À cet égard, la conception d'un processus de transestérification pour valoriser les déchets, les matériaux utilisés et les matériaux de faible valeur pourrait être l'une des meilleures solutions non seulement pour surmonter les problèmes d'énergie et d'environnement mentionnés ci-dessus, mais aussi pour assurer une meilleure gestion des matériaux usés et la réutilisation des déchets. Cette recherche introduit une étude de différentes variables d'entrée influençant le processus de transestérification à une étape conçu à travers lequel le biodiesel est produit à partir d'un mélange d'huile végétale caractéristique amélioré de 60% en poids d'huile de cuisson et d'huile de palme de qualité inférieure à modérée à 40% en poids (ce qui n'est pas approprié pour la cuisson) à l'aide de poussière de four à ciment (CKD), en tant que catalyseur hétérogène. En outre, il vise à déterminer les conditions de réaction optimales dans la gamme de l'étude pour obtenir les conversions les plus élevées en carburant au biodiesel (conversion complète). Cela a été fait en suivant les méthodes statistiques et expérimentales du concept de conception factorielle et de la méthodologie de la surface de réponse (RSM). Les conditions de réaction étudiées étaient le temps de réaction 1, 3,5, 6 heures, le rapport molaire méthanol / huile (12: 1, 15: 1, 18: 1), la température de réaction (45, 55, 65 ° C) et enfin le chargement du catalyseur (1,2, 3% du poids du mélange). 850 tr / min était la vitesse d'agitation utilisée dans toutes les réactions de transestérification catalysées par la CKD de l'étude. Les modèles quadratiques et linéaires ont été développés sur la base des résultats expérimentaux obtenus. Le modèle quadratique a été préféré à l'élément linéaire car les conditions optimales peuvent être obtenues plus précisément à partir de ses surfaces de réponse et il s'est avéré plus valable pour expliquer la gamme des résultats obtenus expérimentalement. Les conditions optimales obtenues statistiquement à partir des surfaces de réponse basées sur le modèle quadratique étaient le chargement du catalyseur de 2,7% de poids de charge, 4,5 heure de temps de

réaction, rapport molaire méthanol / huile de 17: 1 et 59-60 ° C. Alors que la corrélation entre les données de l'équation de régression du modèle quadratique et les surfaces des surfaces de réponse, plus la vérification expérimentale de la validité des valeurs de conversion obtenues a permis d'identifier les conditions suivantes auxquelles la conversion complète peut être obtenue: 3% de chargement du catalyseur, 65 °C, 15: 1 le rapport molaire méthanol / huile et 3,5 heures de temps de réaction. Ces conditions ont été considérées comme optimales car elles incluent un rapport molaire de méthanol à huile inférieur et un temps plus court qui peut améliorer le biodiesel processus de production économiquement. La caractérisation du biodiesel produit montre que ses propriétés répondent aux normes (ASTM).

Un modèle suggéré d'un laboratoire à l'échelle de l'industrie et la conception d'un réacteur discontinu agité pour la production de biodiesel et de glycérol a été introduit. Une quantité de 30 tonnes d'huile de cuisson à déchets de 60% en poids et 40% en poids de mélange d'huile de palme par jour est le taux quotidien proposé pour alimenter à l'échelle industrielle la production de biodiesel et de glycerol démontrée. Les conditions de réaction de la transestérification du procédé suggéré sont ajustées pour donner une conversion à 100%, ce qui signifie une production d'environ 30 tonnes de biodiesel et 3 tonnes de glycérol par jour.

Mots clés:

Huile de palme, Huile de cuisson des déchets (WCO), Valorisation, Transestérification, Biodiesel, Poudre de ciment (CKD), Conception factorielle des expériences, Méthode de surface de réponse (RSM), Conditions optimales et Caractérisation.

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LIST OF ABBREVIATIONS

ASTM:	American Society for Testing and Materials
BET:	Braunauer, Emmett, and Teller
BTU:	British Thermal Unit
CFD:	Computational Fluid Dynamics
CN:	Cetane Number
cSt:	Centi Stock
EDAX:	Energy Dispersive Analysis X-ray
EIA:	Energy Information Administration
FAME:	Fatty Acid Methyl Esters
FFA:	Free Fatty Acid
HHV:	High Heating Value
GHG:	Green House Gases
LHV:	Low Heating Value
OVAT:	One Value at Time
PV:	Photovoltaic
RPM:	Revolutions per Minute
RSM:	Response Surface Methodology
SEM:	Scanning Electron Microscopy
SSA:	Specific Surface Area
TGA:	Thermo-gravimetric Analysis
THF:	Tetrahydrofuran
WCO:	Waste Cooking Oil
Wt %:	Weight Percent
XRF:	X-ray Fluorescence

CHAPTER 1: INTRODUCTION

- **OUTLINE:**

- 1.1. General introduction.....
- 1.2. Problem Statement
- 1.3. Thesis objectives
- 1.4. Scope of the study
- 1.5. Relevance of the study

1.1. General introduction

The rise of loading of abhorrent gases such as carbon dioxide, carbon monoxide, nitrogen oxides, sulfur oxides and methane in the atmosphere as a result of burning conventional fossil fuels as well as other anthropogenic factors have led to serious environmental hazards. Hazards such as acid rain and climate change with its related consequences of flooding, drought, desertification, etc. which are caused by polluting gases and emissions, threaten human health and life. On the other hand, there has been an incredibly increasing energy demand as a result of the huge population growth in almost all parts of the world. Based on the world's energy-related information that (IEA) monitors and records, a significant increase in energy products consumption (e.g. fossil oil and natural gas) from 2009 to 2014 is observed. Also, it is expected that at the current rate of energy use and demand, the conventional fossil fuel reserves will be depleted in the following few decades which may not exceed 2050 (Demirbas, 2009). Therefore, the environmental and the energy security concerns in addition to some economic issues resulted from the burden of importing fossil fuels (like the situation in Egypt), have increased the importance of renewable and sustainable energy research and made many countries adopt renewable energy utilization strategies (Ölz, 2011).

Nowadays, there are numerous renewable energy technologies adopted by many countries that look forward to satisfying a big portion of their energy needs from sustainable energy resources. However, the immaturity of some renewable energy technologies and intermittency of their green resources have a negative impact on implementing more renewable energy projects. Although the huge trend towards improving renewable energy technologies namely solar PV, solar thermal and wind turbines as well as utilization of a variety of renewable energy resources, fuels of liquid nature are preferred by transport, industrial sectors and individuals as well. Liquid fuels are utilized through well-established technologies and they can be easily handled and stored. Therefore, adoption of sustainable alternatives to fossil liquid fuels can have the advantages of both renewable energy resources and liquid fuels. In this manner, biodiesel is a liquid biofuel that has similar characteristics to petrodiesel, is used by conventional diesel engines without any modifications, decreases GHG, and is considered to be the perfect alternative to it as a substitute or an additive (Babulal, K. S. et al., 2015), (Hill, J. et al., 2006). Based on common definitions of biodiesel, fatty acid alkyl (methyl or ethyl) esters are the main constituents of bio-based diesel made

from vegetable oils or fats (Hill, J. et al., 2006). Different techniques namely transesterification, direct blending, pyrolysis, and micro-emulsification have been in use for biodiesel fuel synthesis from vegetable oils and fats (Yusuf, N. et al., 2011). Transesterification is the most preferred and common method among the above-mentioned methods for producing biodiesel due to economic and technical considerations.

Biodiesel as a sustainable resource of energy can contribute significantly to environmental, economic and energy security in any nation adopting its production on an industrial scale. And it has already been in use by individuals and organizations in the USA and some European countries, mainly as an additive to make blends with petrodiesel. Nevertheless, the main obstacles to biodiesel mass production are feedstock cost and yield of transesterification reaction (conversion of feedstock to biodiesel). Whereas using waste and used materials as well as other low-value materials (e.g. WCO and low to moderate-grade palm oil) could be the best solutions for reducing the feedstock costs plus offering the advantage of recycling waste materials. As for conversion of feedstock to biodiesel, choosing a cost-effective catalyst and identifying the optimum conditions influencing the production process is necessary to achieve the highest conversion at the lowest production costs. In transesterification, the reactants are triglycerides (oil) and alcohol whereas the products are biodiesel as the main product of the reaction and glycerol formed as the by-product. Catalyst is a crucial component in the process of producing biodiesel and the feedstock nature has to be considered in its selection. Heterogeneous catalysts are different from homogeneous ones in the following: (1) they are not intensely affected by the acidity and water content of feedstock used in transesterification, (2) there is no need for sophisticated separation techniques for by-product separation, (3) they can be reused (Atadashi et al., 2012). Nevertheless, most commercial biodiesel and glycerol plants have not been run employing heterogeneous catalysts due to economic considerations. Therefore, commercialization of transesterification process in which waste materials as heterogeneous catalyst are used can effectively contribute to dissemination and enhancement of mass production of biodiesel and glycerol.

1.2. Problem Statement

Energy is the engine of life which is fueled mainly using environmentally unfriendly energy products such as (fossil fuels). Environmental and energy security plus fossil fuels prices fluctuations (like the situation in Egypt), have been the main factors that have led to searching for sustainable alternative fuels. Sustainable energy alternatives to fossil fuels can be part of the energy mix until the reserves of fossil fuels are completely finished and after that, they shall be the main sources that will secure the future world's energy needs. Biodiesel is considered as a sustainable alternative to petrodiesel but the main challenge which its industrial-scale production is facing in many parts of the world is commercializing the process. Process commercialization of biodiesel production depends majorly on feedstock cost-effectiveness and yield of transesterification reaction plus activity and price of the catalyst introduced to the process. Thus, a combination of cost-effective feedstock, 100 % transesterification reaction yield as well as viable and active catalyst, can overcome the challenge of commercialization above plus offer environmental, energy and economic security.

1.3. Thesis objectives

The research objectives are divided into an overall objective and specific objective as follows:

Overall objective:

This research generally aims at valorizing and unlocking the potential of WCO and low-cost palm oil through a designed single step transesterification process using a selected cost-effective CKD to catalyze the reaction for achieving complete conversion (from feedstock to clean burning bio-based diesel). This green fuel produced results in no net increase in the proportion of greenhouse gases (CO₂) in the atmosphere and can contribute to energy, economic and environmental security affected negatively by the dependence on fossil fuels.

Specific Objectives:

- Treating and characterizing CKD used as a catalyst and then investigating its catalytic activity during the reaction.
- Optimizing the single step transesterification process by recognizing the optimum conditions influencing the reaction yield (reaction time, methanol to oil, reaction temperature, and catalyst loading) in order for the process to be proposed for an industrial scale production.
- Checking the usability of CKD for more than once for catalyzing the transesterification reaction.
- Characterizing the produced biodiesel.

1.4. Scope of the study

The research scope was limited to the following:

- Determining the best (palm oil : WCO) wt % ratio needed for the blend technically and economically, to be then used as feedstock for biodiesel and glycerol production.
- Developing CKD to be the catalyst for the biodiesel production and investigating its performance during the process.
- Optimizing and investigating the effect of the factors (reaction conditions) influencing the yield of the produced biodiesel using statistical means (factorial design of experiments and response surface methodology).
- Performing reusability tests on CKD.
- Producing good quality biodiesel.

1.5. Relevance of the study

The purpose of the work is to design a single step transesterification process in which cost-effective catalyst (CKD) and feedstock (palm oil-WCO blend) are introduced in order to produce biodiesel in a more economical way. In this manner, achieving the goal of the research brings one of the best solutions to not only overcome the energy and environmental problems resulted from the intense dependence on fossil fuels but also contribute to recycling of used materials and waste management due to using the waste materials in the study to produce valuable products. The example of Egypt can illustrate the potential of CKD production and shows the economic importance of

unlocking that potential for industrial scale biodiesel production. Three million tons per year is the average rate of cement kiln dust (CKD) production from cement industry in Egypt. This high amount of waste can offer an active and a cost-effective catalyst for biodiesel and glycerol production (El-Mahallawy, 2013). Also, using waste cooking oil and low to moderate grade palm oil as feedstock may affect the economic feasibility of the process positively. It is worth mentioning that the conception of (Waste to sustainable energy) may be used to describe the process of biodiesel production from majorly waste materials mentioned above.

CHAPTER 2: LITERATURE REVIEW

- **OUTLINE:**

<u>2.1. Biodiesel</u>	
<u>2.1.1. Background</u>	
<u>2.1.2. Standard specifications and properties of biodiesel</u>	
<u>2.1.3. Biodiesel benefits</u>	
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<u>2.1.5. Raw materials for biodiesel production</u>	
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<u>2.2.2. Microemulsion</u>	
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<u>2.3. Heterogeneous solid catalysts for transesterification in biodiesel production</u>	
<u>2.3.1 Solid base catalysts</u>	
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<u>2.4. Theoretical and statistical considerations</u>	
<u>2.4.1. Factorial Design of experiments</u>	
<u>2.4.2. Response Surface Methodology (RSM)</u>	
<u>2.4.3. Statistical optimization of Controlling Factors of transesterification process</u>	

- **Overview**

This chapter introduces an overview of biodiesel as one of the best sustainable energy alternatives to fossil fuels, and some of its raw materials plus different techniques through which it can be produced. More emphasis is placed on transesterification as the most widely production method studied and followed to valorize diverse vegetable oils and animal fats by producing biodiesel (main product) plus glycerol (valuable by-product).

2.1. Biodiesel

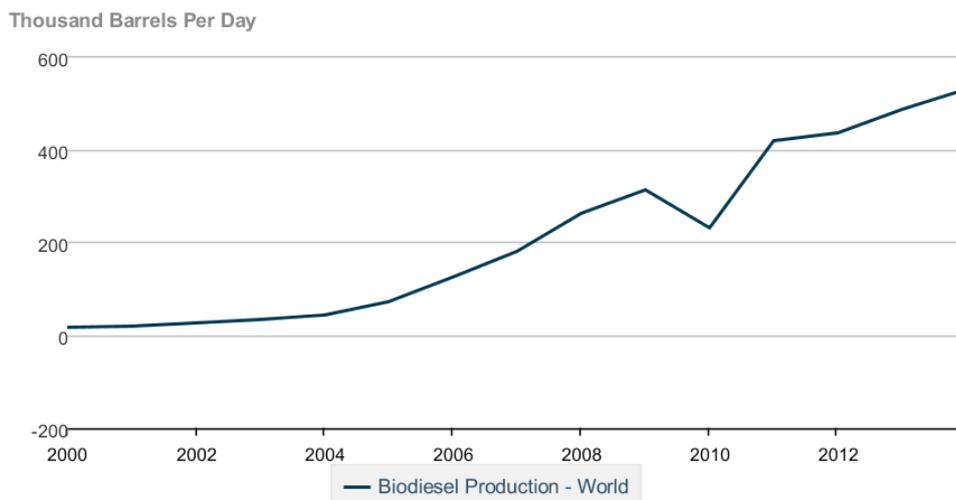
2.1.1. Background

Biodiesel is commonly known as a non-petroleum diesel fuel and it is considered as a diesel substitute in some developed and developing countries that adopt biodiesel production to achieve more energy and environmental security. Biodiesel also works as an additive to petroleum diesel for some industrial activities, agriculture, and transportation. Recently, the main reasons for biodiesel and other biofuels importance are insufficiency of fossil fuels, instability of fossil fuels prices and the need for environmentally friendly fuels. It was also stated that generally in many nations and particularly in developed nations which are looking forward to environmental security, substituting petroleum diesel with biodiesel (the green fuel) has been widely assessed (Choo, Y. M., and Cheah, K. Y., 2000). Biodiesel is a green sustainable energy resource as it is synthesized from the triglycerides present in plant and animal-based lipids. It is worth mentioning that in 1895, Dr. Rudolf Diesel was the first person who came up with the idea of using vegetable oil as fuel in his diesel engine without making any modifications to it (Gupta, A. K., et al, 2004). Figure (2-1) illustrates the rate of biodiesel production in the world. From the figure, it is observed that there was a significant increase in the production rate from 2000 to 2013 and it is expected that there the production rate is still increasing year after year. Country environment sensitivity, government encouragement and available technology and feedstock, can be the drivers of including biodiesel in countries' energy mix and producing a huge amount of it, which is the case in developed countries.

The USA and the western countries in Europe have fortified working with biodiesel as a sustainable energy resource and have made a substantial headway in biodiesel production on the large industrial scale. By 2014, the amount of biodiesel produced in the USA was

estimated to be 1279 million gallons. Africa is still far as regards utilizing the huge potential it has to produce biodiesel. However, Egypt as an example from the African context is encouraging the transition to renewable and sustainable energy resources, while as regards biodiesel production, it is growing a bit slowly and some small commercial plants have been established.

Biodiesel Production - World



 Source: U.S. Energy Information Administration

Figure (2-1): The trend of world production of Biodiesel from 2000 to 2013 (EIA, 2014)

According to American Society for Testing and Materials (ASTM), biodiesel fuel can be defined as long chain fatty acids monoalkyl esters whose origin is lipid feedstock such as animal fats or vegetable oils. Biodiesel can be used in compression-ignition engines directly without modifications to the engine due to the similarity of properties and specifications between it and conventional petrodiesel. Moreover, biodiesel and petrodiesel can be used together in a blend for many industrial and agricultural purposes, which is being applied currently. For example, blends of biodiesel and petrodiesel can be expressed as Bx, where x is the biodiesel amount percentage present in the blend (i.e. a B50 blend has 50% biodiesel and 50 % petrodiesel whereas B100 is pure biodiesel without petrodiesel).

2.1.2. Standard specifications and properties of biodiesel

Based on (ASTM) standard methods in determining specs of diesel and biodiesel fuels, Table (2-1) compare between biodiesel and petrodiesel in terms of their fuel properties.

Table (2-1): ASTM standard fuel properties of biodiesel and petro-diesel (Tyson, 2009)

Property	Petro-diesel (ASTM D975)	Pure biodiesel (ASTM D6751)
Kinematic Viscosity at 40 °C (cSt)	1.3 – 4.1	4 - 6
Specific gravity at 15 °C (kg/l)	0.85	Around 0.88
HHV Btu/gal	137640	127042
LHV Btu/gal	129050	118170
Flash Point °C	60 – 80	100 – 170
Cloud Point °C	(-35) - 5	(-3) - 15
Pour Point °C	(-35) - 15	(-5) - 10
Cetane index	40 - 55	48 - 65
Carbon wt%	87	77
Hydrogen wt%	13	12
Oxygen wt%	0	11
Sulfur wt%	Maximum 0.0015	0 - 0024

2.1.3. Biodiesel benefits

Generally, there are many advantages of substituting fossil fuels with biodiesel or even blending both of them together such as decreasing harmful emissions which makes it environmentally friendly, enhancing combustion quality, and using a non-toxic liquid fuel produced from available and sustainable green sources (Zhang, Y. et al., 2003). A simple description of some biodiesel benefits is introduced as follows:

2.1.3.1. Human health and safety

Biodiesel does not cause health risks and it is non-toxic to human skin. It is safer for human health than petrodiesel because aromatic compounds are by far less concentrated in it than in petrodiesel. Aromatic compounds such as polycyclic aromatic hydrocarbons

(PAH) and nitrated PAH are considered as cancer-causing compounds. Therefore, using biodiesel instead of petrodiesel or with it in a blend can reduce the mentioned carcinogenic aromatic compounds concentration significantly. Biodiesel has a higher flash point compared to petrodiesel which means that it is not hazardous and safer to be stored.

2.1.3.2. Lower emissions and high combustion efficiency

In several studies of performance evaluation of diesel engines operating on pure biodiesel, many tests were done on the emissions generated when biodiesel (B100) burns in a diesel engine to study the environmental impact of using biodiesel. After analyzing the exhaust emissions it was found pure biodiesel reduces carbon monoxide, particulate matter (PM) and total hydrocarbon (THC) emissions while nitrogen oxides (NO_x) emissions experienced a slight increase (Lin, Y. C., et al, 2006). Increase in NO_x emissions may be attributed to the high oxygen content of biodiesel compared to petrodiesel, and that gives an indication of a very important advantage, which is that biodiesel has higher combustion efficiency than petrodiesel (Labeckas, G., and Slavinskas, S., 2006). As for sulfur oxides emissions (SO_x), pure biodiesel generates no (SO_x) as it does not have sulfur in its constituents. Biodiesel has a major contribution to decreasing greenhouse gases emissions and it is considered to produce zero net CO₂ emissions as it is mainly produced from sustainable plant-based materials (vegetable oils). It is worth mentioning that biodiesel and petrodiesel blends generate lower emissions than petrodiesel alone. For example, B20 can decrease the generated emissions of hydrocarbon by approximately 30 %.

2.1.3.3. Biodegradability

Biodegradability one of the important advantages of biodiesel. Several studies conducted by many scientists demonstrated that biodiesel is biologically degradable by microorganisms and can decompose back to natural components and this means that it is an environmentally friendly energy product (Demirbas, 2009).

2.1.3.4. Rural economy and domestic energy

Biodiesel production and use can contribute significantly to energy security in rural areas for doing diverse activities (e.g. agriculture), which refreshes by its turn their economy and decreases the poverty level of rural people. Also, biodiesel can be produced domestically as its production is not energy intensive and it can be used for transportation and electrification as well.

2.1.4. Biodiesel drawbacks

Despite all the benefits of using biodiesel mentioned above, there are some weaknesses and drawbacks of using biodiesel which require solutions to be avoided or at least minimized. These drawbacks are high viscosity compared to petrodiesel, low volatility, high reactivity which causes polymerization as well as some undesirable effects on engines operating on pure biodiesel. Low volatility of some components of biodiesel and high viscosity cause deposits formation inside engines (Meher, L. C., Sagar, D. V., and Naik, S. N., 2006). Moreover, using either pure biodiesel or higher blends of it in diesel engines may also cause thermal efficiency and power reduction plus a relative increase in NO_x emissions. Cold flow properties of biodiesel are main limitations for biodiesel to be used in cold weather countries as biodiesel of the best cold flow properties starts to crystallize and then freeze at around -3 °C. Figure (2-2) shows some characteristics of biodiesel and how they can affect ignition- compression engine's performance.

2.1.5. Raw materials for biodiesel production

Since biodiesel is produced from plant and animal-based lipids, materials such as animal fats, vegetable oils (i.e. virgin oils and WCO) and non-edible oils are valuable assets for biodiesel production. The mentioned raw materials are mainly composed of triglycerides. Following is a brief introduction and explanation of different categories of biodiesel feedstock.

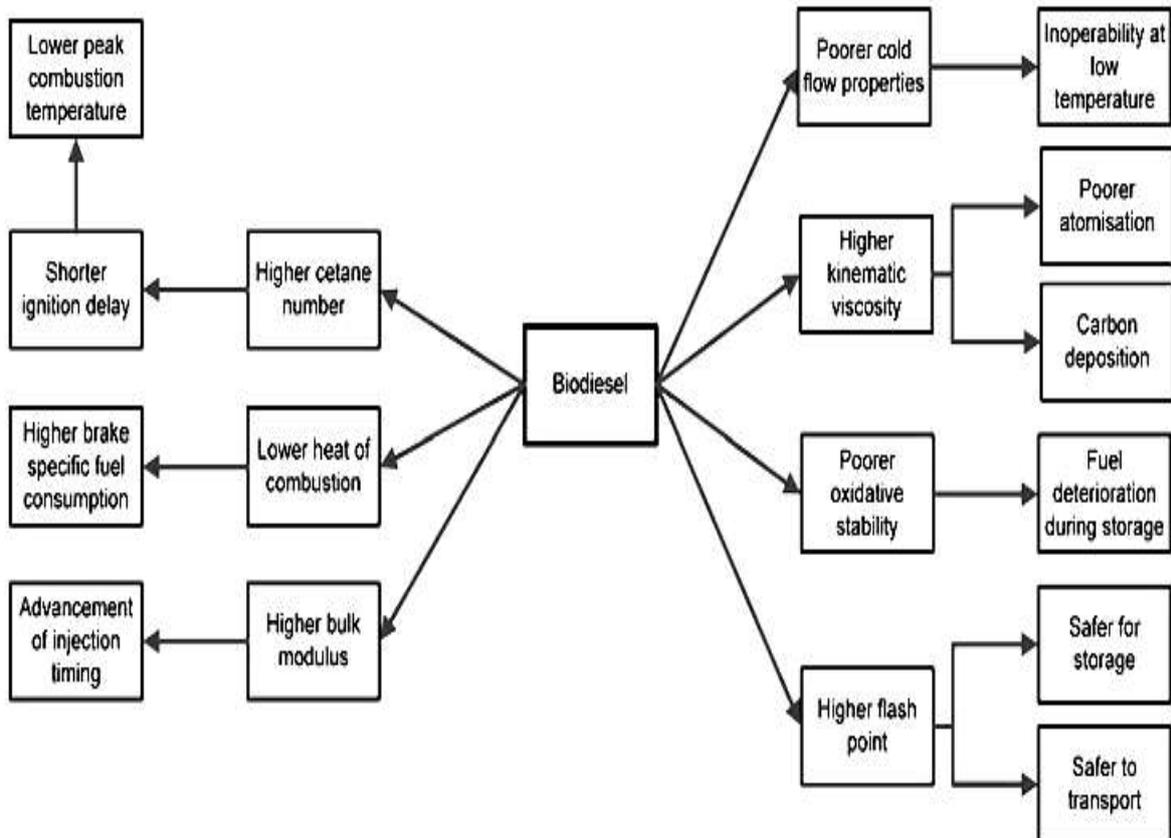


Figure (2-2) Properties of biodiesel and their positive and negative effects on engine's performance (Ng, J. H. et al., 2010)

2.1.5.1. Animal fats

Animal fats or lipids are composed of triglycerides but they have different chemical and physical properties from those of plant-based oils. It was found that animal fats have more saturated fatty acids than plant-based biodiesel raw materials, which can cause formation of deposits inside engines as well as affect engine performance and durability (Ma, F., and Hanna, M. A. , 1999). Animal fats in its original form cannot be used as an alternative fuel due to their solid and semi-solid nature. Sheep and beef tallow, poultry oil as well as yellow grease are the most known examples of animal-based lipids and may be used for biodiesel production (Demirbas, 2008).

2.1.5.2. Virgin oil

Virgin oil is a pure vegetable oil such as palm oil, canola oil, soybean oil and rapeseed oil. The use of virgin oils for biodiesel production may be closely related to their availability. For example, palm oil is used broadly for biodiesel production in tropical countries which are endowed with high potential of palm fruits. It is worth to mention that many countries import palm oil to use it for industrial activities and cooking purposes as it is one of the cheapest virgin oils as well as there is a variety of its quality grades which makes it economically and technically suitable for many industrial and domestic activities. Rapeseed oil and soybean oil are the most virgin oils used for biodiesel production in Europe and USA respectively. Although there are very many types of virgin oil, only limited number of them (e.g. sunflower, palm, cottonseed, etc.) were classified as potential fuels for ignition-compression engines (Demirbas, 2007), (Shahid, E. M., and Jamal, Y.) stated that palm and rapeseed oils are the best virgin oil raw materials for biodiesel production. Table (2-2) shows the estimated biodiesel amount could be produced from each hectare of different virgin oil sources.

Table (2-2): Estimated biodiesel amount which may be produced from some vegetable oil sources (Beerens, 2007)

Oil source	Liters per hectare
Palm	3800
Rapeseed	800
Soybean	320
Sunflower	850
Cotton	160
Castor bean	2000
Coconut	1750

2.1.5.3. Waste cooking oil (WCO)

Waste cooking oil, spent cooking oil, used cooking oil and waste vegetable oil are alternative names of any vegetable oil collected after being used for cooking and/or frying. It is worth mentioning that WCO has less preferred characteristics than its original virgin oil for biodiesel production. Therefore, it is better to start with neat virgin oil than starting with WCO due to the high conversion of the triglycerides to biodiesel without side reactions and the relatively short transesterification reaction time compared to that of WCO (Leung, D. Y. C., and Guo, Y. , 2006). However, WCO can be considered as the

most cost-effective raw material for producing biodiesel because it can be either obtained for free or at very low prices. Disposing WCO either into drainage systems or to the environment will cause serious environmental problems such as water and soil contamination plus wastewater treatment difficulties. The current huge human population growth can play an important role in generating much more WCO as its generation is closely related to increasing food demand and consumption. It can be concluded that using WCO for biodiesel production could contribute positively to waste management, food, environmental and energy securities.

2.1.5.4. Non-edible oil

Using non-edible oils for biodiesel production has been widely studied in order to find alternative raw materials which are not used for cooking purposes not to affect food security. *Jatropha*, *Pongamia*, rubber seeds as well as algae are examples of non-edible oils sources (Demirbas, 2008), (Karmakar, A. et al., 2010). The main advantages of using non-edible oils such as *jatropha* oil and oil from algae are relatively the high biodiesel yield, availability, and ease of growing their sources and improvement of biodiesel production economics.

2.2. Main techniques of biodiesel production

The main four techniques for biodiesel production from vegetable oil (i.e. WCO and virgin oil) are direct use and blending, microemulsions, pyrolysis (thermal cracking) and lastly transesterification. The four techniques have been widely studied using different feedstock oils in order to optimize the production processes and biodiesel yield. Among the four techniques, transesterification has been the most studied and undertaken on a commercial scale for producing biodiesel.

2.2.1. Direct use and blending

The concept of using vegetable oil as an alternative fuel in a diesel engine was developed for the first time by Dr. Rudolf Diesel when he tested the performance of the engine operating on peanut oil. The main issue with the direct use of vegetable oil is the high viscosity which makes its atomization poor. However, there are some benefits of using vegetable oil as a petrodiesel alternative such as sustainability, high calorific value, and availability. On the other hand, direct use of vegetable oils as a fuel or blending them at high percentages with petrodiesel and then used in engines, affect negatively the engine durability on the long term due to problems such as gelling, carbon deposits formation and coking of injectors (Gupta, A. K., et al, 2004). In 1980, a pre-combustion chamber engine was used by Caterpillar Brazil Company and provided with a blend of 10 % vegetable oil and 90 % petrodiesel without doing any modifications to the engine. The total power generated by the engine was same as the power generated when 100 % petrodiesel was used (Ma, F., and Hanna, M. A. , 1999).

2.2.2. Micro-emulsion

Microemulsion is defined as colloidal equilibrium dispersion of fluid microstructures with dimensions range of (1 ± 150) nm in a solvent to form two liquid immiscible phases (Ma, F., and Hanna, M. A. , 1999), (Gupta, A. K., et al, 2004). This process can be applied in order to overcome the problem of the high viscosity of vegetable oils and use them as alternative fuels in diesel engines. Solvents such as methanol, ethanol, and 1-butanol have been used in micro-emulsion studies and the results proved that atomization characteristics and vegetable oil viscosity can be improved by dispersing the oil microstructures with the solvents mentioned above (Ma, F., and Hanna, M. A. , 1999).

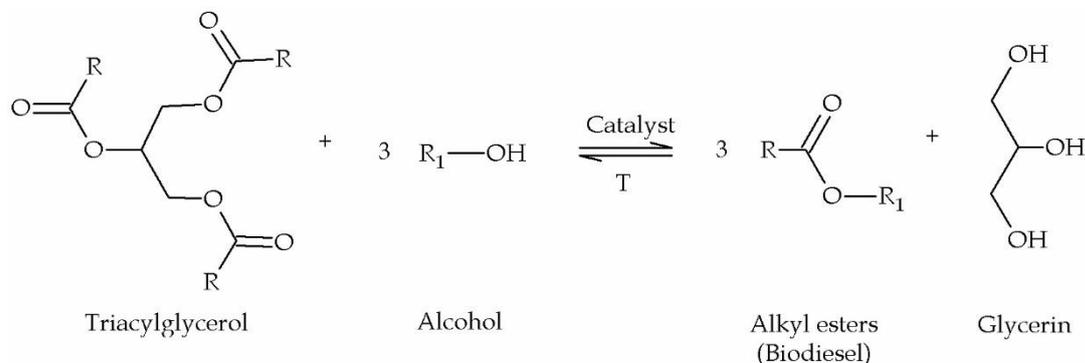
2.2.3. Pyrolysis (thermal cracking)

Pyrolysis (thermal cracking) is applying either heat only or heat with adding a catalyst in absence of oxygen to break the chemical bonds of a substance and produce another substance(s) of smaller molecules (Gupta, A. K., et al, 2004). Catalysts are used sometimes in pyrolysis in order to complete the reaction faster. Different products can be produced from one substance when pyrolysis is applied because the reaction may have variety of paths which makes pyrolytic chemistry is somehow more complicated (Gupta, A. K., et al, 2004). Materials such as animal fats, natural fatty acids and methyl esters of fatty acids and vegetable oils can be feedstock for pyrolysis in order to be converted to products chemically similar to conventional energy resources (e.g. diesel and gasoline). Many studies on pyrolysis of fats have been conducted for very many years, especially in countries which do not have conventional resources of energy (Ma, F., and Hanna, M. A. , 1999). Thermal cracking of vegetable oils occurs at elevated temperatures and may give light hydrocarbons as products. The main difficulty of using pyrolysis as a method for biodiesel and gasoline production from vegetable oils and animal fats is that its equipment is very costly and the process may not be economically feasible.

2.2.4. Transesterification

Transesterification is a reaction in which alcoholysis of triglycerides of plant or animal based lipids occurs producing less viscous alkyl esters than triglycerides as a main product and glycerol as a by-product. In most cases, transesterification occurs by reacting triglycerides with an alcohol in presence of a catalytic material to speed up the reaction and enhance its yield (Gupta, A. K., et al, 2004). Since transesterification is a reversible reaction of one mole of triglycerides and three moles of alcohol, adding excess alcohol is highly recommended in order to accelerate and drive the reaction in the direction of producing three moles of fatty acids alkyl esters and one mole of glycerol (Ma, F., and Hanna, M. A. , 1999). Figure (2-3) illustrates the transesterification reaction of triglycerides. Methanol is the most used alcohol in transesterification process to produce methyl esters (i.e. biodiesel). Other alcohols of longer chain alkyl group than methanol (e.g. ethanol) can also be used but their cost is high compared to methanol. Many studies conducted on using methanol and ethanol in transesterification reaction, recommended that methanol is better because the reactivity of triglycerides with ethanol is low compared

to methanol and this reflects on biodiesel yield. Low reactivity of triglycerides may result from the hindrance of the (-OH) of long chain alkyl group of an alcohol to react effectively with triglycerides to produce high alkyl esters yield (Hawash, S. et al., 2014)



R, R₁: alkyl chain with different lengths and/or saturation degrees

Figure (2-3) Transesterification reaction of triglycerides (Feltes, M. M. C. et al., 2011)

Glycerol (i.e. the by-product of the reaction) can be a very important commodity for many applications and activities, and it should be well utilized, especially at a commercial scale biodiesel production through transesterification. High qualities and grades of glycerol have been used as feedstock for many industrial applications such as food, cosmetics, pharmaceuticals, animal feed, tobacco industry, plasticizers, and emulsifiers industry (Pachauri, N., and He, B., 2006). The glycerol produced through transesterification process has impurities and this mandates refining the glycerol before using it commercially via removal of solid residues, fractional vacuum distillation, and some chemical additions. Recovery of the methanol present in glycerol phase may make the purity of glycerol close to 80 or 90 %. Alternative more cost-effective technologies than refining of glycerol, have been proposed for biodiesel production plants which lack refining facilities, to utilize the crude glycerol by converting it into useful products such as 1,3-propanediol, 1,2-propanediol, hydrogen, succinic acid and polyesters (Pachauri, N., and He, B., 2006).

The biodiesel produced through transesterification may have some impurities such as catalyst residues, excess methanol, and monoglycerides which can be removed by either water washing or dry washing (Roman K., 2003). In general, transesterification as a technique of producing biodiesel and crude glycerol can be classified into different

categories based on the catalyst used or the process conditions. Following are different categories of transesterification for biodiesel production.

2.2.4.1. Base-catalyzed homogeneous transesterification for biodiesel production

Base-catalyzed transesterification is a reaction in which reaction of triglycerides and alcohol occurs in presence of a base catalytic material such as KOH or NaOH in order to produce fatty acids alkyl esters (i.e. biodiesel) and 1,2,3-propanetriol (i.e. glycerol) as a by-product. Figure (2-4) illustrates the reaction mechanism of base-catalyzed transesterification technique. Among all methods of biodiesel production, base-catalyzed transesterification is the most widely used as it is an inexpensive process and gives high or almost complete conversion from oil to biodiesel, which is achieved only if the process limitations of sensitivity to moisture and FFA contents of triglycerides source, are overcome (Singh, A. et al., 2006). FFA content higher than 1 % of the feedstock oil weight, can stimulate soap formation, decrease the activity of the catalyst and increase the viscosity of the reaction medium. Whereas moisture or water in reaction medium stimulates hydrolysis of produced esters and formation of soap.

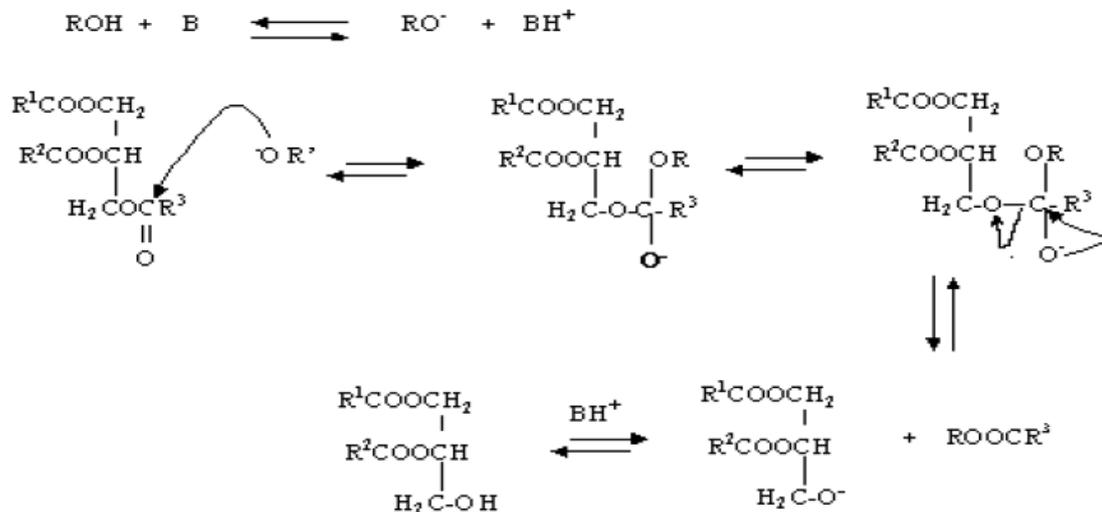


Figure (2-4) Mechanism of base-catalyzed transesterification reaction (Gupta, A. K., et al, 2004)

2.2.4.2. Acid-catalyzed homogeneous transesterification for biodiesel production

Contrary to catalysts for base-catalyzed transesterification, acid catalysts' activity is not affected by FFA content higher than 1 % present in oils (Pathak S., 2015). Acid catalysts can be used to catalyze transesterification of feedstock oils and esterification of FFA in

feedstock oils as well. This makes acid catalysts suitable for catalyzing biodiesel production from feedstock oils with high FFA contents such as WCO and low-grade vegetable oils through one step transesterification reaction or at least catalyzing esterification of high FFA in oils as a pretreatment process prior to transesterification. Practically, homogeneous acid catalyzed transesterification is not widely used at mass production scale of biodiesel because it requires very long reaction time compared with that of homogeneous base-catalyzed (Lotero, E. et al., 2005) to give high biodiesel yields, high methanol to oil molar ratio as well as costly setups (Pathak S., 2015). Inorganic acids such as phosphoric and sulfuric acids are the most common catalyst for the process. Figure (2-5) illustrates the mechanism of acid catalyzed transesterification reaction.

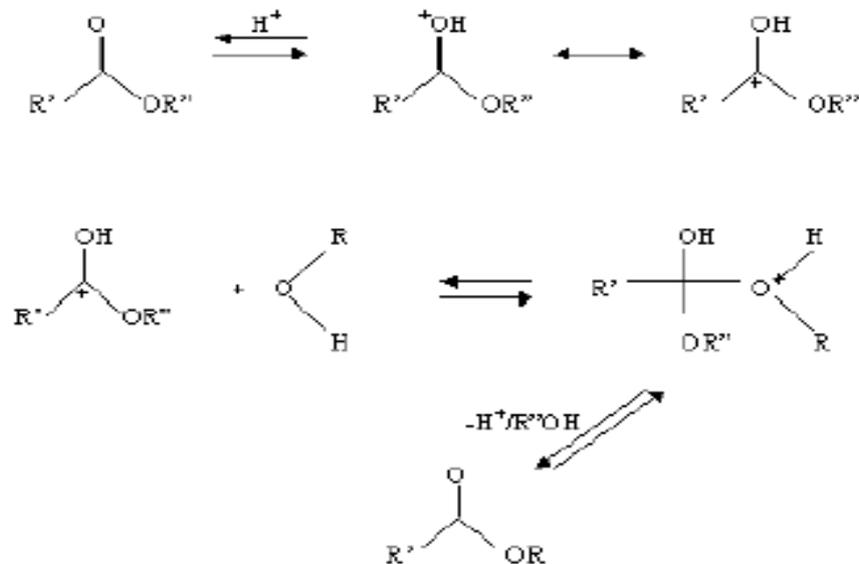


Figure (2-5) Mechanism of acid catalyzed transesterification reaction (Gupta, A. K., et al, 2004)

2.2.4.3. Two-step transesterification for biodiesel production

This process is a combination of both acid catalyzed transesterification and base catalyzed transesterification techniques. The first step of the process is pretreatment of feedstock oil through esterification of its FFAs in order to produce a new feedstock for the next step with FFA content lower than 1 % of its weight. The second step involves using a base catalyst to catalyze the esterified feedstock transesterification. Figure (2-6) shows the two steps of the process.

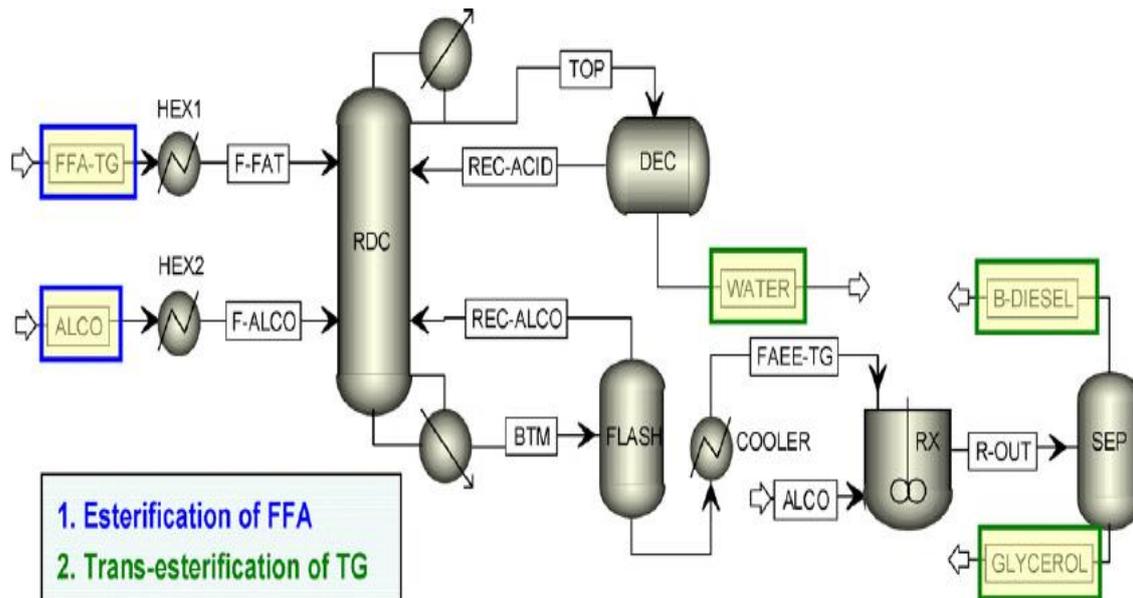


Figure (2-6) Two-step transesterification process (Kiss, 2010)

2.2.4.4. Enzymatic or biocatalyst-based transesterification for biodiesel production

The catalyzing materials in this technique of transesterification are biocatalysts which by its turn catalyze the hydrolysis of triglycerides of feedstock oils in presence of an alcohol such as methanol. The reaction yield alkyl esters (i.e. biodiesel) and glycerol. This technique for biodiesel production has many technical advantages over conventional chemical catalysts based transesterification. Some of these advantages are higher selectivity and efficiency, fewer energy requirements (i.e. lower temperature and pressure needed for carrying out the reaction), possibility to improve their catalytic activity and catalyst reusability (Akoh, C.C. et al., 2007). However, there are challenges this method is facing in order to be commercial such as its high cost of operation, its sophisticated production process and biocatalyst deactivation by alcohol (Meher, L. C. et al., 2006). Carrying out hydrolysis of triglycerides using enzymes as catalysts requires paying attention to some important influences of reaction conditions which can affect the entire process. These influences which should be taken into account are the required water content for the catalyst to start working, reaction temperature, feedstock selection and alcohol type used in the reaction (Ranganathan, S.V. et al., 2008).

2.2.4.5. Non-catalytic transesterification techniques for biodiesel production

Non-catalytic transesterification is a process in which there is no need for a catalyst to speed up the reaction and obtain products. It has two major techniques which are co-solvent technique and supercritical methanol technique. A co-solvent such as tetrahydrofuran (THF) is to be used in the first technique in order to convert the two different phases of methanol and vegetable oil into only one phase medium in which methanol and oil are miscible. Transesterification using the first non-catalytic technique may be done in five to ten minutes without agitation in presence of THF and at ambient conditions of temperature and pressure. THF and methanol have close boiling points to each other so that excess methanol and THF can be distilled to be reused. This method can produce alkyl esters (biodiesel) and glycerol free of catalyst residues (Meher, L. C. et al., 2006). In the second technique, methanol is used at supercritical conditions, which are temperature of about 350 °C, and pressure of about 35 MPa. It was reported that transesterification reaction time can be 4 minutes only if the reaction is performed at the supercritical conditions mentioned earlier and with methanol to oil molar ratio of (42:1) (Kusdiana, D., and Saka, S., 2001). Apart from short reaction time, supercritical methanol technique offers other advantages such as high oil to biodiesel conversion and dealing with feedstock oils which have high water and FFAs contents (Hawash, S. et al., 2014). But the main drawback of the technique is the high operation and equipment costs and this makes the entire process economically unfeasible. Table (2-3) illustrates the differences between using supercritical technique and the common techniques for biodiesel production.

Table (2-3) Comparison between (base and acid catalyzed transesterification), and supercritical methanol technique (Kusdiana, D., and Saka, S., 2001)

Factor	Base or acid catalyzed transesterification	Supercritical methanol technique
Pressure	Atmospheric	35 MPa
Temperature	30 to 65 °C	350 °C
Reaction time	1 to 6 hours	4 minutes
Catalyst	Acid or base	No catalyst
Yield	97 to 98 %	98.5 %

2.2.4.6. Heterogeneously catalyzed transesterification for biodiesel production

Another technique for biodiesel production is catalyzing transesterification using heterogeneous catalysts. Heterogeneous solid catalysts can be divided into two main groups of catalytic materials, namely acidic and basic solid catalysts (Chouhan, A.S. and Sarma, A.K, 2011). There are many examples of solid basic catalysts which are used in heterogeneous catalytic reactions such as metal oxides, mixed metal oxides, and basic metal salts. As for acidic solid catalysts, the most known examples are tungstated and sulfated zirconia, ion-exchange resins and zeolites (Chouhan, A.S. and Sarma, A.K, 2011). Basic solid catalysts have higher catalytic activity than solid acid catalysts, but they are less stable (Lotero, E. et al., 2005). This method of transesterification offers many important benefits, namely catalyst reusability, fewer purification requirements, easiness of separation, ability to deal with oils with high FFA and water contents, and production of almost pure products (Veljković, V.B. et al., 2015). Heterogeneous catalysts have active components which may catalyze both esterification and transesterification (e.g. CaO as an active metal oxide) (Yan S., Salley S. O. and Simon Ng K.Y. , 2009). Despite all the advantages mentioned, there are some drawbacks of using this method such as high operating conditions (i.e. agitation speed, temperature, etc.) and lower catalytic activity of some heterogeneous catalysts compared with homogeneous catalysts. Furthermore, there are some other disadvantages, namely losing the activity of catalyst with time due to leaching, viscous reaction medium which may limit mass transfer during the reaction (MacLeod, 2008) and low reaction rate (Veljković, V. B. et al., 2015). The drawbacks can be effectively decreased and overcome by optimizing reaction conditions and other parameters influencing transesterification process. Economic feasibility of the process has been a big research interest to many researchers and this has led to revealing new generation of more cost-effective heterogeneous catalysts from wastes such as cement kiln dust, fish bones and eggshells (Al-Sakkari, E.G. et al., 2017)

Generally, heterogeneous catalytic reactions include major seven steps which explain the operation and the transition from reactants to products. Almost all heterogeneous catalytic reaction steps are mass transfer steps except the reaction step in which products are formed. The first three steps are diffusion of reactants from the bulk to the external catalytic surface, diffusion from the external surface to the internal catalytic surface and finally the reactants get adsorbed on the catalyst surface. Step 4 is the reaction step (i.e. product(s) formation). The last three steps include desorption of product(s) from the

catalyst surface, then their diffusion to the external surface of the catalyst and finally their diffusion to the bulk. Figure (2-7) illustrates the mentioned main steps of a heterogeneous catalytic reaction.

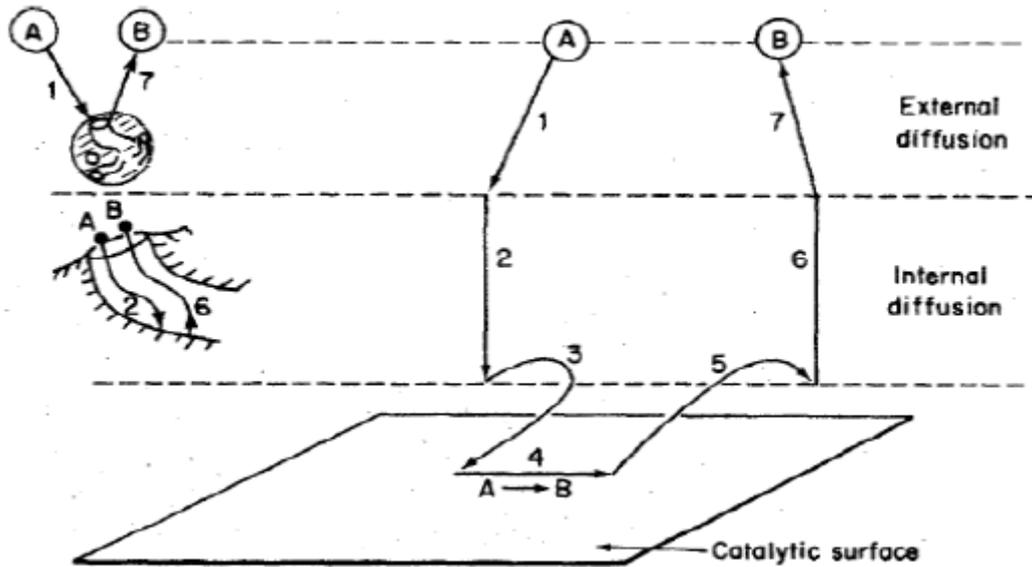


Figure (2-7) Main steps of a heterogeneous catalytic reaction (Fogler, 2005)

2.3. Heterogeneous solid catalysts for transesterification in biodiesel production

There are parameters and characteristics which heterogeneous solid catalysts should have in order to be used for biodiesel mass production. Some of these parameters required to be taken into account for choosing heterogeneous solid catalysts are:

- Low energy requirement for its preparation or treatment if it is derived from waste.
- High catalytic activity and selectivity.
- Cost-effectiveness and availability.
- High stability.

Following is a summary of the major categories of heterogeneous solid catalysts and some of their examples which have been studied for biodiesel and glycerol production.

2.3.1 Solid base catalysts

This group of catalysts is characterized by its catalysts' basic active sites such as alkali metals and metal oxides, mixed alkaline metal oxides, and alkali metal salts supported on other substances such as alumina and other metal oxides to enhance the catalyst's basicity. Diverse solid base catalytic materials have been studied for enhancing the process of transesterification. Two examples of using this group of catalysts for biodiesel production are introduced.

2.3.1.1 Metal oxides for biodiesel production

The oxides of metals such as magnesium, strontium, and calcium can be used as active solid base catalysts for biodiesel production and they are partially soluble in alcohols. One of the advantages of these catalysts is that they are available and not very expensive, especially CaO and MgO. This has made these materials promising alternative catalysts to conventional base catalysts in biodiesel industry. Calcium oxide is considered as the most used metal oxide catalyst for biodiesel synthesis, because of its cost-effectiveness, relatively high basicity, and less environmental effects.

In a study of transesterification of rapeseed oil conducted by (Gryglewicz, 1999), calcium oxide was used as a catalyst under conditions of 2.5 hours reaction time, 65 °C reaction time, 9:1 methanol to oil molar ratio and 1 % catalyst loading of the feedstock oil mass. The study resulted in 90 % conversion of rapeseed oil to methyl esters. (Venkat Reddy et al., 2006) conducted a study of transesterification of soybean oil using nanoparticles of CaO instead of conventional CaO at room temperature. Complete conversion was obtained in the mentioned study after 24 hours reaction, 1 % catalyst loading and 25 fold excess of methanol. High Surface area of CaO nanoparticles have turned out to play an important role in the catalyst's catalytic activity as conventional CaO was used at the same conditions mentioned above and the conversion obtained was 2 %. (Granados, M.L. et al., 2007) focused on preparation conditions of calcium oxide and their effect on its catalytic activity. They found that conditions of preparing and treating calcium oxide have an important influence on the catalyst performance. Also, hydration and carbonation were observed to occur quickly and lead to reducing significantly the catalytic activity of CaO. According to the catalysts' stability studies conducted, improving CaO stability is recommended because studies and experiments showed that CaO leaches into reaction medium which will normally require a washing step to remove the residues from the

products. Although magnesium oxide as an alkaline earth oxide catalyst is less active and basic strength than calcium oxide, it also can give high reaction conversions at elevated reaction temperature (Di Serio, M et al., 2006). As previously mentioned, being inexpensive as well as having high catalytic activity, CaO and MgO can be considered promising heterogeneous catalysts for biodiesel mass production.

2.3.1.2 Mixed metal oxides for biodiesel production

Developing mixed metal oxides as heterogeneous solid base catalysts can increase the basicity of a single metal oxide and improve conversion of triglycerides of plant or animal based lipids to biodiesel. It was found that using synthesized mixed calcium oxide and magnesium oxide for transesterification of rapeseed oil to biodiesel, showed higher catalytic activity and basicity than that of CaO powders (Guo, F. and Fang, Z., 2011). (Kawashima et al) studied the catalytic activities of the following mixed oxides: CaO-MnO₂, (CaO)₂-Fe₂O₃, CaO-TiO₂, CaO-ZrO₂, and CaO-CeO₂. The conversions of triglycerides to biodiesel obtained were averagely at a percentage of 90 % (Guo, F. and Fang, Z., 2011). These results may play a role in adopting such solid base catalysts for biodiesel production.

2.3.2 Solid acid catalysts

Studying and using heterogeneous acid catalysis has a longer history than that of heterogeneous base catalysis. Many developed solid materials with acidic characteristics have been investigated to assess their performance as acid catalysts. As mentioned earlier, most of the heterogeneous acidic catalysts can catalyze both transesterification of triglycerides and esterification of FFA content of triglycerides. This has made them a promising choice for dealing with feedstock oils with high FFA content. One of the most important advantages of these catalysts is that they are stable and have almost constant catalytic activity with time during transesterification. There are many examples of this group of catalysts such as ion exchange resins, sulfated and tungstated zirconia, and zeolites (Guo, F. and Fang, Z., 2011). Following are two detailed examples of heterogeneous solid acid catalysts which have been studied for biodiesel production.

2.3.2.1 Sulfated and tungstated zirconia solid acid catalysts (supported acid catalysts)

Based on the experimental study done by (Lopez, D.E. et al., 2005) on the catalytic activities of sulfated and tungstated zirconia for conversion of triacetin to biodiesel, the results showed that SO_4/ZrO_2 is nearly as active and acidic as sulfuric acid, while WO_3/ZrO_2 showed much lower activity. However, tungstated zirconia showed greater stability with time during the reaction. Also, it was found that tungstated zirconia treated at 800 °C before the reaction has the highest acidic strength and activity during the reaction compared to the other activities and values of acidity of the catalyst at different calcination temperatures (Lopez, D.E. et al., 2007). Other study performed by (Jitputti, J. et al., 2006) on transesterification of palm kernel oil and coconut oil found that sulfated zirconia and zinc oxide showed the highest catalytic activity among many solid base and acid catalysts used in the study. The achieved conversion was 95 % from palm kernel oil to biodiesel at 200 °C and reaction time of 4 hours using sulfated zirconia.

2.3.2.2. Ion-exchange resins

Ion exchange resins (polymers) are broadly involved in many industrial applications and uses such as metal separation, catalysis, pharmaceuticals, etc. Ion exchange polymers in the acid form can be used as solid catalysts for biodiesel production. They are relatively expensive compared with the catalytic materials used biodiesel mass production, however, they are more cost-effective than biocatalysts and supercritical methanol (Guo, F. and Fang, Z., 2011). The acidic active sites are fixed in the organic matrix. As for catalytic activities of this type of heterogeneous catalysts, acidic resins with larger pores are more active than those of smaller pores. The catalytic activity of acidic resins at reaction temperatures of lower than 100 °C does not experience significant changes for long time reactions. A fixed bed reactor was used and supplied with materials for continuous biodiesel synthesis using ion exchange acidic resins as catalysts. The results showed that resins still kept their activity after very long reaction time (about 500 h) with almost constant conversion of more than 98 % (Guo, F. and Fang, Z., 2011). It was found that the catalytic activity of NKC-9 acidic resin catalyst a bit improved during performing the first 10 experiments, which may be attributed to resin breakdown as a result of agitation during the reactions (Feng, Y. et al., 2010)

Catalytic deactivation of acidic resins may occur as a result of salt ions present in oil which cause contamination. This contamination may lead to exchanging acidic active sites of resins with salt ions in oil as well as catalytic activity loss with time. Recovery of deactivated acidic resins is possible by applying acid washing technique (Guo, F. and Fang, Z., 2011).

2.3.3. Waste based heterogeneous solid catalysts

This category of catalysts is very promising in biodiesel production as the sources of the catalysts or the catalytic components are available waste materials. Cement kiln dust, marble dust, fish bones and egg shells are examples of wastes which have active and important constituents. Therefore, unlocking the potential of such wastes may offer many important benefits such as enhancing the economic feasibility of biodiesel mass production and managing such waste materials by using them in industry. Treatment and preparation methods are supposed to be used in order to treat, prepare and activate waste materials to active components such as CaO. There are many preparation methods followed for that purpose such as drying, calcination, reducing particle size and homogenization of waste materials. Following are some important examples of waste based active catalysts for transesterification of plant and animal based lipids.

2.3.3.1. Eggshells based CaO

Many researchers have studied the catalytic performance of different kinds of waste eggshells for transesterification of diverse feedstock oils as they are mainly composed of CaCO₃. (Sharma, Y.C., Singh, B. and Korstad, J., 2010) performed experiments using chicken eggshells as a catalyst for transesterification of high FFA content Karanja oil. Calcination of the waste material was done at 900 °C prepare it before the reaction. Prior to the step of heterogeneous catalysis using eggshells for the transesterification, esterification of the high FFA content of Karanja oil was performed using sulfuric acid. Conditions of 8:1 methanol to oil molar ratio, 2.5 % of oil mass catalyst loading, 2.5 hours reaction time and 65 °C reaction temperature yielded biodiesel as a conversion rate of 97.34 %. Another study was done by (Buasri, A. et al., 2013) on transesterification of palm oil using chicken and duck shells as catalytic materials. The waste materials were calcined for 4 hours at 900 °C. The conditions of the process were optimized based on the maximum conversion obtained. The optimum conditions were 9:1 methanol to molar

ratio, 65 °C reaction temperature, 20 % catalyst loading and four hours reaction time. The achieved conversions at the mentioned conditions were 92.92 % for the duck shell and 94.49 % for the chicken shell. It was also found out that there is a possibility of reusing the catalysts but the conversion will decrease after four cycles.

2.3.3.2. Fish bones

Fish bones are natural materials of which the skeleton of the fish is mainly made. These materials have high content of calcium as a main component of the bones. Therefore, fish bones can contribute to biodiesel production through using them as solid catalyst after preparation (El-Sheltawy, S.T. and Al-Sakkari, E.G., 2016). It is worth mentioning that some researchers proposed fish scales to be also used as a catalyst (source of CaO) for biodiesel synthesis (Chakraborty, R et al., 2011). In a study of transesterification of palm oil for biodiesel production, it was reported that calcined fish bones catalyst at °C 900 was used at constant loading of 10 % of oil mass in all the transesterification experiments to optimize the conditions and assess the catalyst's activity. A conversion of 77.2 % was obtained at 65 °C, reaction temperature, 4 hours reaction time, 3 hours calcination time, and 12:1 methanol to oil molar ratio, which were considered to be the optimum conditions of the process (El-Sheltawy, S.T. and Al-Sakkari, E.G., 2016).

2.3.3.3. Cement kiln dust

Cement kiln dust (CKD) is a waste material generated from cement industry and it has important constituents such as high CaO content in its composition which make it a valuable resource for producing economically important products. The rate of production of (CKD) in Egypt is about 3 million tons a year and this makes unlocking its potential in Egypt very necessary from both environmental and economic points of view (El-Mahallawy, 2013). The industrial importance of different types of (CKD) has been studied by many researchers and it was reported that CKD can be used for enhancing cement properties, slag activation, glass manufacturing and producing environmentally friendly products such as biodiesel and wollastonite (El-Sheltawy, S.T. and Al-Sakkari, E.G., 2016). CKD is characterized by a wide range of specific surface areas. (Samidi, 2012) developed two CKD based catalysts to be used for transesterification of WCO. The first one was prepared by impregnating CKD with KOH and the second one with water and methanol. The two catalysts were treated by calcination at 650 °C for 3 hours before

performing the transesterification. The study outcomes showed that (CKD-KOH) catalyst is higher in catalytic activity than (CKD-CH₃OH, H₂O). Synthesis of biodiesel through soybean oil transesterification catalyzed by CKD was studied by (Lin, V.S. et al., 2011). The reaction temperature for all reactions was kept constant at 40 °C, while a wide range of both catalyst loading (0.1 % to 25 % of oil mass) and methanol to oil molar ratio was used to carry out the experiments. They observed that complete conversion of soybean oil to biodiesel was obtained using catalyst loading of 1.7 % of oil mass, 561:1 methanol to oil molar ratio in a reaction lasted for 20 minutes. It was also noticed by them that conditions of 4.3 % catalyst loading, 37:1 methanol to oil molar ratio and 30 minutes reaction time gave 100 % conversion. On the possibility of reusing (CKD) for many cycles, many parameters may play an important role in that such as type of CKD, its stability and leach-ability, reaction conditions and the extent of losing catalytic activity during reusing the catalyst (El-Sheltawy, S.T. and Al-Sakkari, E.G., 2016).

2.3.3.4. Waste catalysts treatment

Parameters such as specific surface area, size of particles, moisture content and active components concentration can influence and identify the catalyst's quality. Treatment and preparation of waste materials before using them as catalysts are mandatory to avoid side reactions and produce catalysts with active components for good catalytic performance. Generally, treatment of waste catalysts includes washing, drying, grinding, homogenization, and calcination. Based on a review study done by (El-Sheltawy, S.T. and Al-Sakkari, E.G., 2016), table (2-4) is introduced to show treatment steps and calcination conditions of some examples of waste materials to produce CaO as an active component for biodiesel synthesis. Treatment techniques and cost of catalysts have a significant effect on transesterification economic feasibility. (CKD, eggshells, marble dust, etc.) are examples of catalysts whose main active catalytic component is (CaO). In this manner, figure (2-8) shows the mechanism of how transesterification reaction occurs using pure CaO or waste based CaO as a catalyst for producing methyl esters (biodiesel).

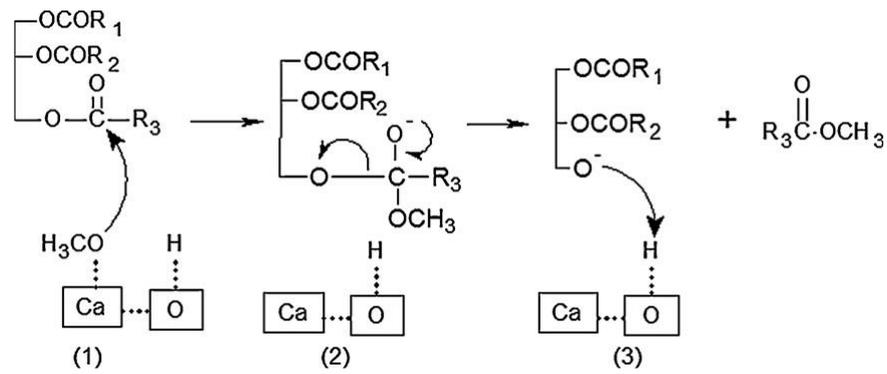


Figure (2-8) Transesterification reaction mechanism using CaO catalyst (Boey Peng-Lim et al., 2011)

Table (2-4) Treatment steps and conditions of some waste catalysts to produce CaO
(El-Sheltawy, S.T. and Al-Sakkari, E.G., 2016).

Waste material	CaO %	Treatment Steps before use	Calcination conditions
Chicken eggshell	>98 %	washing, drying, grinding, homogenization, and calcination	Optimum (800 °C – 4 hours)
Mud crab shell	>98 %	washing, drying, grinding, homogenization, and calcination	(900 °C – 2 hours)
Animal bones	>98 %	washing, drying, grinding, homogenization, and calcination	Optimum (800 °C – 4 hours)
Fish scales	>98 %	washing, drying, grinding, homogenization, and calcination	(Optimum 1000 °C – 2 hours)
Fish bones	>98 %	washing, drying, grinding, homogenization, and calcination	(900 °C – optimum 2 hours)
Shrimp shell	>98 %	shrimp shell was calcined after incomplete carbonization at 300-500 °C, and dipping in a solution of KF	(200 to 500 °C – 2 hours)
CKD	19-60%	CKD was generated from a cement Kiln in which the operating temperature is 1100 °C	In a cement kiln at 1100 °C

2.4. Theoretical and statistical considerations

In this section, a brief explanation of some statistical techniques and theoretical considerations used in the research is presented. The overall goal of using statistical techniques such as factorial design of experiments and response surface methodology is enhancing industrial scale mass production of biodiesel and glycerol through identifying the optimum controlling factors of the production process.

2.4.1. Factorial Design of experiments

The method has been in use by many researchers and it helps them better understand how different input variables influence a distinct dependent variable. Conventional research methods which are also called one variable at a time (OVAT) investigate separately the influence of each variable of the input variables chosen on a certain dependent variable. Such methods were preferred before due to the simplicity of handling them statistically. Nevertheless, dealing with codependent variables the same way as in the conventional method could be unpractical and the method is considered a time-consuming one. For illustration, if the relation between five input variables and a certain response is to be investigated with including six variation levels, the number of experiments that should be performed is (7776) experiments (Lazic, 2004). The simplest full factorial design has two controlling variables and two variation levels. On contrary to the conventional technique of performing experiments, there are many advantages of adopting the method of factorial design of experiments instead, some of which are saving time, contributing to making the process simpler and cheaper, carrying out the least number of runs plus getting a big amount of results and data. Although all these advantages, the main challenge of this method is involving more than two factors and levels in the experimental design which by its turn adds more statistical complexity.

The conception of factorial design of experiments can be applied in the researches that investigate the controlling variables of biodiesel and glycerol production. In this method, central point experiments should be carried out to estimate the error and the standard deviation of the design. This and some other statistical analyses can help in evaluating the significance of the generated regression equation and its factors and coefficients that shows the relation between the response variable and the other input variables.

2.4.2. Response Surface Methodology (RSM)

As a tool of optimization in many research fields, response surface methodology (RSM) is an assembly of statistical and mathematical techniques used for building a statistical model in which a functional relationship between an output dependent variable (response) x , and certain input variables or factors: $(y_1, y_2 \dots y_n)$, is developed. This relationship is represented by the following equation:

$$x = f(y_1, y_2 \dots y_n) + E$$

Where $y = (y_1, y_2 \dots y_n)$, $f(y)$ is the response surface and a function of levels of the factors $(y_1, y_2 \dots y_n)$, while (E) is a random experimental noise (Khuri, André I., and Siuli Mukhopadhyay, 2010). The mathematical equations in this method can be translated into a graphical demonstration for better picturing of the response surface. The two ways of graphically representing the response are 3D plots and contour curves as the examples shown in Figure (2-9) and Figure (2-10). One of the most important advantages of using RSM for optimization design is cutting down the cost of expensive mathematical modeling techniques such as CFD and minimizing their related numerical errors.

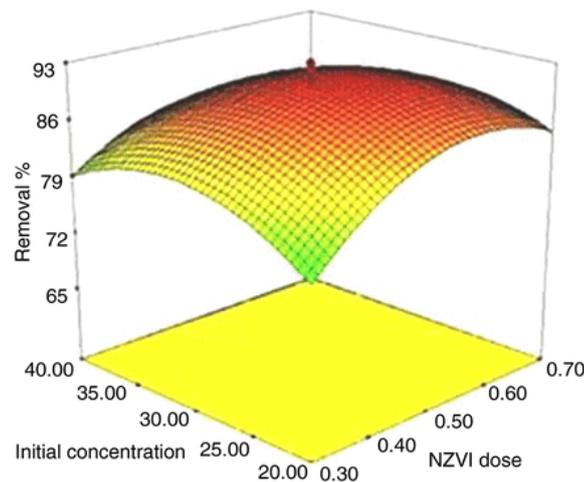


Figure (2-9): Response surface of the joint effect of initial concentration and NZVI dose on removal of MB dye (Khosravi, M., and Arabi, S., 2016)

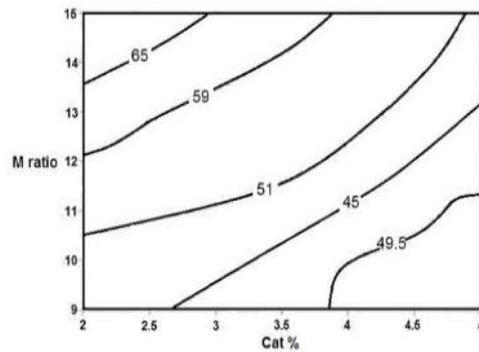


Figure (2-10): Contour curves of the joint effect of Cat. % and M ratio on conversion of soybean oil (Al-Sakkari, E.G., et al, 2017)

2.4.3. Statistical optimization of Controlling Factors of transesterification process

Transesterification reaction conditions such as (reaction time, methanol to oil molar ratio and catalyst loading, etc.), are the controlling factors influencing biodiesel and glycerol production process. In this research area, process optimization has been of great interest to many scientists in order for making substantial headway in mass production of glycerol and biodiesel. The following step after the statistical considerations and the factorial design introduced earlier should be factors optimization. So, response surface is the main tool from which optimum conditions are obtained and then the values of optimum factors are substituted into the regression equation (the model) to ensure that both will give almost the same value for the output variable. And in case optimization of input variables could not be obtained precisely from the response surface, there are other means such as steepest ascent method and partial differentiation of generated regression equations, can assist in identifying the optimum input variables. In the method of partial differentiation of the produced regression equation with respect to the input variables or factors, equating each resultant equation to zero after differentiation has to be done. After that, the maximum values of variables are obtained by solving the equations equated to zero and from that, the maximum value of the response (output variable) should be obtained. Nevertheless, this method may not be preferable in all cases because the values of the input variables identified through solving the equations, may correspond to values other than the maximum ones (Thomas, G. B., and Finney, R. L., 1995). For the method of steepest ascent, optimum conditions can be obtained through a pathway of the steepest ascent created on the response surface (Rodrigues, L. et al, 2006).

CHAPTER 3: EXPERIMENTAL WORK

- **OUTLINE:**

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- **Overview**

In this chapter, materials and tools as main aspects of the experimental setup are introduced and characterized. In addition, all methodological techniques and considerations adopted for the present study are described.

3.1. Materials

3.1.1. Feedstock (oils)

The feedstock used in the present study is a mixture of low to moderate grade palm oil and waste cooking oil at an optimized ratio for more desirable products properties. The low-quality palm oil used has poor cold flow properties and also high acid value compared to virgin refined palm oil which is mostly used for cooking purposes. It was kindly provided by (Zewail City of Science and Technology) as it has been stored to be used for different research purposes. As for the other fraction of the mixture, waste cooking oil as described on the product cover was a mixture of 50 % soybean oil and 50 % sunflower oil used for frying and cooking purposes and it was obtained from a number of households and the university's restaurant. The following tables present some properties of palm oil and (WCO) used as raw materials in the study.

Table (3-1) Physical and chemical properties determined for palm oil used in the study:

Property (unit)	Value
Density at 20 °C (g/mL)	0.89
Dynamic viscosity at 30 °C (cP)	57.8
Acid value (mg KOH/g Oil)	2.8
Saponification value (mg KOH/g)	198
Color	Pale yellow
Odor	Odorless
Slip melting point (°C)	34

Table (3-2) Fatty acid composition of palm oil used in the study:

Fatty acid (carbon number)	Percentage %
Myristic acid (14:0)	1
Palmitic acid (16:0)	44
Stearic acid (18:0)	4.5
Oleic acid (18:1)	39
Linoleic acid (18:2)	9.5
Linolenic acid (18:3)	0.4
Free fatty acids	1.4

Table (3-3) Some Properties of (WCO) used in the study:

Property	Value
Density (room temp) (g/mL)	0.902
Acid value mg KOH/g oil	18.35
Saponification value mg KOH/g	200
Viscosity $\text{mm}^2 \text{s}^{-1}$ at 20 °C	50
Water content wt %	< 0.01%

3.1.2. Methanol

Methanol was the main reactant used with the blend of palm oil and WCO in order to perform oil transesterification reaction. It was obtained from Sigma- Aldrich Egypt Company for Chemicals. The following table (3-4) presents some properties of methanol used.

Table (3-4) Some Properties of methanol used:

Property	Value
Molecular weight (g / mol)	32.042
Assay or purity	≥ 99.8
Molecular formula	CH ₄ O or CH ₃ OH
Grade	Analytical
Form	Liquid
Boiling point (°C)	64.7
Density (g/mL at 25 °C)	0.791

3.1.3. Cement kiln dust (CKD)

The catalyst used in the study is a waste based catalyst, which is cement kiln dust (CKD). It was kindly provided by (Tura Cement Factory) as one of the biggest cement production plants in Egypt located in Helwan in south Cairo. The CKD obtained from the factory, was not prepared through collecting it at the operation temperature of the kiln and then keeping it away from water and humidity in air. Therefore, treatment by calcination for the CKD obtained, was mandatory to ensure absence of (moisture content and CO₂) in CKD that may affect its catalytic activity negatively. Characterization of CKD was done via using some testing methods to determine some characteristics of the heterogeneous catalyst used. Those characteristics determined were particle size distribution, specific surface area and chemical constituents of CKD used.

3.1.4. Analytical gases for characterization

In the conducted research, helium (99.99 %) and nitrogen (99.99 %) are the gases required for the devices of characterizing some of the materials used. Nitrogen as an unreactive gas was used for the gas sorption device (Nova 2000 Quanta chrome) for determining specific surface area of CKD, while helium was used as a carrier gas (mobile phase) in a gas chromatograph that identifies different components of materials tested and tests their purity as well.

3.1.5. Other chemicals

The following materials were obtained from Sigma Aldrich Company as well for some purposes such as carrying out two-step transesterification reaction using homogeneous acid and base catalysts, and biodiesel purification:

Potassium hydroxide (KOH): purity of 99%, sulfuric acid (H₂SO₄) and calcium chloride (CaCl₂): purity of 99%.

3.2. Methodology

3.2.1. Catalyst treatment and preparation

Calcination as a preparation and treatment method for cement kiln dust is needed to guarantee that the catalyst used for catalyzing the process of producing biodiesel and glycerol, is free of moisture content. Calcination of CKD was performed at 850 °C for 2 h to ensure not only absence of moisture content but also, release of carbon dioxide (CO₂). Conditions of calcination were chosen based on a study conducted by (Al-Sakkari, E. G. et al., 2017) in which thermal analysis (TGA) for CKD was done to monitor its chemical decomposition as a function of increasing temperature. CO₂ gas release is a result of converting all calcium carbonate (CaCO₃) in the catalyst to calcium oxide (CaO) as the active component needed for an effective catalysis of the reaction.

3.2.2. Characterization of CKD

After catalyst preparation, samples of the CKD were collected to carry out characterization studies on them. Characterization was commenced by studying the particle size distribution of the CKD samples. Sieves of (90, 75, 63 and 50µm) hole diameter, were used for that purpose. Axios Sequential WD- XRF Spectrometer, was also used for determining the chemical composition of CKD. BET gas sorption (adsorption-desorption isotherm) method was the technique of (Nova 2000 Quanta chrome device) used in order to measure the specific surface area of CKD (total surface area per unit mass of the material). This technique is based on (BET) theory of generating results of specific surface area through evaluation of gas adsorption-desorption data of materials. For accurate determination of (SSA), CKD samples were heated up to a high temperature prior to the adsorption-desorption process to get free of any adsorbed gases on the surface of the CKD samples. Worth mentioning, Nitrogen was the gas used for the process and its adsorption on CKD was at - 196.15 °C, whereas desorption was at 25 °C (ambient temperature). Some other characteristics were also used to better know more about the catalyst from a previous study (Al-Sakkari, E. G. et al., 2017) in which the CKD used was obtained from the same production plant that CKD was obtained from, for the present study. These characteristics obtained were the morphology of the catalyst (CKD) and its elemental composition and this was done

using a Scanning Electron Microscope (FEI QUANTA) equipped with EDAX unit as a material characterization system provider.

3.2.3. Determination of the optimum palm oil to WCO ratio for their blend preparation

The purpose of using WCO and mixing it with palm oil was to achieve the best enhanced properties for the blend. In the present study, the determined optimum ratio of palm oil and WCO for their blend preparation should ensure good feedstock blend characteristics, cost-effectiveness of the blend (especially for the industrial scale utilization) as well as good specs for the products produced from the blend through transesterification. The main considerations taken into account for the blend fractions wt % determination and optimization were the feedstock cost, its acid value and its oxidative stability plus cold flow properties and combustion quality of biodiesel (main product) produced from it.

Synthesis of biodiesel and glycerol from different mass fractions of a blend of palm and waste cooking oils was done through a two-step transesterification process. Seven samples of different palm oil to WCO weight percentage ratios (100:0, 80:20, 60:40, 50:50, 40:60, 20:80 and 0:100) were prepared by blending to be homogeneously transesterified. Then the seven blends with different palm oil to WCO ratios mentioned were involved in a comparative study to come up with the best blend could be used for carrying out transesterification process optimization using CKD as a catalyst. The reason for using homogeneous acid and base catalysts was to ensure that the produced biodiesel samples from all the seven blends were of nearly complete conversion. Cold flow properties (cloud and pour points) and acid values for biodiesel produced from each blend, were determined and compared.

3.2.4. Experimental procedure for the two-step homogeneously catalyzed transesterification

In the first step, acid catalyzed esterification of the high FFA content in the collected WCO was done to decrease the acidity present in the oil to less than 1% of FFAs. As for the procedure, in a 250 ml glass spherical bottom flask, a sufficient amount (100

grams) of the WCO collected, was placed and a hot plate was used to heat the oil to 65°C. A solution of mixed methanol and sulfuric acid was added to the flask. The catalyst loading of sulfuric acid was 3.5 % of the 100 grams WCO introduced to the reaction. Whereas the methanol poured into the flask was at a methanol to oil ratio of 52:1 (bout 185 ml methanol). The mixture in the flask was stirred at a moderate stirring speed by a magnetic stirrer for a reaction time of one hour at a fixed temperature of 65 °C. Other tools were used such as thermometer and water condenser that was used to prevent evaporation of methanol as well as ensure that the system was closed. When the reaction was finished, the unreacted methanol was separated from the esterified WCO and then excess methanol in the oil was removed through heating the oil at 100 °C for an hour. Acid value was determined to ensure the reduction of FFA content.

In the base catalyzed-transesterification step, 20 grams of a blend of palm oil and esterified WCO were introduced for the reaction at different palm oil to WCO weight percentage ratios (100:0, 80:20, 60:40, 50:50, 40:60, 20:80 and 0:100). The reaction was performed at 65 °C for one hour with stirring at a moderate stirring speed not to stimulate soap formation. Potassium hydroxide as the homogeneous base catalyst used and methanol were mixed together and added in all the seven experiments after adding the feedstock. KOH was loaded at a 1 % of the 20 grams of feedstock introduced. Also, the methanol to oil ratio at which methanol was loaded, was 6:1 (4.5 grams of KOH). After one hour of reaction, biodiesel and glycerol produced were heated to remove excess methanol and then separated in a separating funnel. After separating the biodiesel, water washing was done to remove all catalyst residues, methanol, and other impurities. Biodiesel samples were then dried using anhydrous calcium chloride (CaCl₂), and ready for the comparative study to choose the best (palm oil to waste cooking oil) weight percentage ratio.

3.2.5. Experimental procedure for the CKD catalyzed transesterification

250 ml and 500 ml spherical bottom flasks were used to contain the reactants of the single step transesterification process (feedstock oil, methanol, and CKD) during the reactions. Hot plate was used in the setup to heat the flask and control the reaction temperature. Other tools were added to complete the experimental setup such as thermometer, water condensers, magnetic stirrers and 2000 ml beakers. Figure (3-1)

illustrates the tools used together to set up the experiments for transesterification process. As for performing the reaction, Thirty grams of a mixture of palm and waste cooking oils at a ratio of 2:3 respectively (the decided ratio), were heated in a round bottom flask to the required temperature (45, 55, 65 °C) based on the experimental design. CKD was then introduced to the flask at diverse catalyst loadings of (1, 2 and 3% of the feedstock oil weight), and got stirred with the heated feedstock by a magnetic stirrer. Methanol as the selected alcohol for the reaction and its last element for it to start, was added at different (methanol to oil) ratios (12:1, 15:1 and 18:1) and got mixed and stirred with the other reaction components at an adjusted stirring speed of 850 rpm. Reactions were performed for (1, 3.5 and 6 hours). After each reaction performed, CKD in the mixture and all suspended solid impurities were removed by filtration. After filtration, the mixture composed of biodiesel phase, glycerol phase, and excess or unreacted methanol in both phases, was heated at 100 °C for an hour in an oven to get rid of methanol in the mixture and separate the two phases easily. Afterwards, the mixture was poured into a separating funnel in order for glycerol to settle down and biodiesel (methyl esters) remains on top. Glycerol was separated from biodiesel and weighted in order to calculate the reaction conversion percentage (yield). In transesterification process, reaction of one mole of fatty lipids or oil with three moles of an alcohol (methanol), gives one mole of glycerol plus three moles methyl esters. This means that a complete reaction yields 92 grams/mole of glycerol from roughly 900 grams/mole of oil. So it can be concluded that glycerol accounts for about 10 % of the oil it is synthesized from via transesterification, at complete conversion. The following equation describes the way by which the yield of each reaction conducted, was estimated.

$$\text{Yield (conversion \%)} = \frac{\text{Wt(p)}}{\text{Wt(c)}} * 100$$

Where: Wt(p) is the weight of produced glycerol and Wt(c) is the weight of glycerol at a 100 % conversion. So for the thirty grams of feedstock used in each experiment, the yield was considered 100 % if the weight of glycerol produced was three grams.

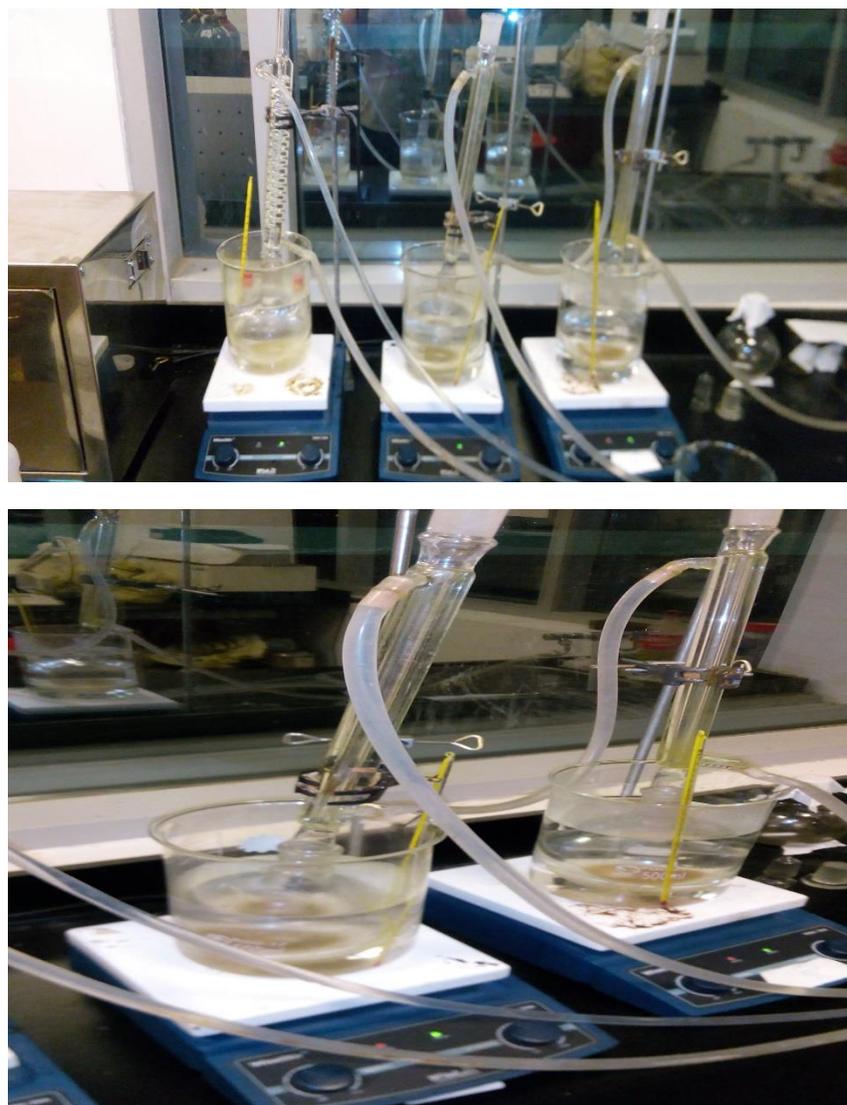


Figure (3-1): The experimental setup for the transesterification reaction carried out

3.2.6. Factorial design of experiments for the CKD catalyzed transesterification

Biodiesel production was developed and optimized using full factorial 2^n design in which all possible combinations of the input variables (or factors) involved in the experiment are used. Four chosen input factors are x_1 : time (1, 3.5, 6 h), x_2 : methanol to oil molar ratio (12, 15, 18), x_3 : catalyst amount (1, 2, 3 wt. %) and x_4 : temperature (45, 55, 65 °C). The response is the percentage conversion of mixed oils to biodiesel and glycerol, which is obtained by calculation of glycerol weight produced from the reaction. Each parameter was coded to two levels low (-1) and high (+1), center points were given the code of (0). 16 factorial points, 8 star or axial points, and 6 center points were the factorial design of experiments in this study. The center points were repeated

six times to calculate the standard deviation of the conversion values in the design of experiments.

3.2.7. Statistical analysis

After carrying out factorial design set of experiments, a regression equation that relates percentage conversion with the chosen input variables was obtained then its coefficients were tested to identify the significance of each one using the t-test. The validity of regression equation was examined using determination coefficient (R^2). Optimum conditions of reaction were obtained through applying response surface methodology. Excel software was used to develop a linear model of the data of factorial design of experiments. Expert Design software was used to develop a quadratic model for the same data obtained and plot the response surfaces and the contour plots of the joint effects of the input variables on the conversion percentage.

3.2.8. Catalyst Reusability

CKD reusability tests were done to assess its recyclability and applicability for the industrial scale use. CKD was used twice for performing two different transesterification reactions at their reaction conditions. In the first reaction, 10 grams of a 40 % palm oil to a 60% WCO blend was used, and 0.3 g of CKD was loaded at a catalyst loading of 3 %. Whereas methanol to oil ratio, reaction temperature and reaction time, were 18:1, 65 °C and 3.5 hours respectively. On the other hand, another transesterification reaction was performed at different conditions to test CKD reusability. The conditions were almost same as the conditions of the first reaction except reaction time was adjusted to one hour. The stirring speed was constant (850 rpm) for both reactions. After each reaction, CKD used was filtered and washed carefully using methanol to remove any residues associated with it. After that, CKD washed was then heated until it g dried. The two reactions were conducted again using the used CKD. Reaction conversions were determined for the four reactions performed to assess the reusability of CKD.

3.2.9. Gas Chromatography analysis for purity determination of FAMES

Gas chromatography analysis was used to determine the fatty acids profiles for 3 biodiesel samples produced via transesterification and the calculated conversion for each one was 100 %. Sample (1) was produced using at the following conditions: 65 °C, 3.5 h, 15:1 methanol to oil ratio and 3 % CKD loading. And the conditions under which sample (2) was obtained, were 60 °C, 4.5 h, 17:1 methanol to oil ratio and 2.7 % CKD loading. Worth mentioning, the conditions of producing sample no.2 were obtained from the response surface and the regression equation as optimum conditions for the reaction. For sample (3), 1 % KOH loading was used to homogenously catalyze the reaction at the following conditions: 65 °C, 1 h and 6:1 methanol to oil ratio. Silica capillary column (DB-5) of 0.32 mm internal diameter and 60 m length was used for the FAME composition identification. The column was maintained at 150 °C for one minute and then the temperature increased to 240 °C for thirty minutes. Helium was used as a carrier gas for the product samples tested at a flow rate of 1 ml per minute. Internal standards were used to translate the peaks created into fractions of the fatty acid composition.

3.2.10. Biodiesel properties (the main product of the feedstock valorization)

Some physical and chemical properties of the produced biodiesel that identify its quality, were determined under standard testing methods (ASTM). Following are the methods followed for determining specifications of the produced biodiesel:

- ASTM (D1298-12b, 2017): it is a standard testing method used to determine the density of biodiesel at a reference temperature of 15 °C. Measuring the density is essential for giving an idea about storage required for the fuel as well as fuel combustion. The standard unit for density is kg/m^3 .
- ASTM (D445-17a, 2017): The method is for measuring the kinematic viscosity of liquid fuel products. It was used to measure the kinematic viscosity of the produced biodiesel by calculating the time in order for the introduced volume of biodiesel to flow through a standard capillary viscometer. The SI unit for the property is $\text{mm}^2/\text{s} = 1 \text{ cSt}$.

- ASTM (D947-14e2, 2014): the method was used to determine the acid value of the produced biodiesel. It uses color indicator titration to estimate the acidity present in the sample. The standard unit of acid value is (mg KOH/g).
- ASTM (D93-16a, 2016): It is a standard test to identify the flash point of a specimen of fuel through Pensky-Martens closed cup tester. Flash point determination is very important for safety regulations as it is the lowest temperature at which the vapors of the fuel is stimulated to form flames with air when an ignition source is present.
- ASTM (D240-17, 2017): the method was followed to measure the mass heat of combustion of the produced biodiesel. The units are either MJ per Kg or KJ per g.
- ASTM (D7346-15, 2015) and (D2500-17, 2017) methods were followed to perform pour point and cloud point respectively (cold flow properties). The measurements were done for the seven different weight percentage (palm oil - WCO) blends based biodiesel produced using KOH as a homogeneous catalyst to choose a blend for the CKD catalyzed transesterification process. Also, the properties were determined for the produced biodiesel using CKD as a catalyst.
- Cetane number (CN):

Cetane number, cetane index, and cetane rating are different terms of the same property which is the most important indicator of diesel combustion quality and the delay time of ignition in diesel engines. In the present study, two studies conducted by (Hawash, S. et al., 2014) and (Clements, 1996) were used to identify the correlation between CN and mass fractions of the different fatty acids present in biodiesel. The correlation could be used to predict the cetane number of the produced biodiesel via the following equation:

$$CN = \sum ME_{(Wt\%)} * ME_{(CN)}$$

Where:

CN is the cetane number of the produced biodiesel.

$ME_{(Wt\%)}$, is the weight percentage of each methyl ester.

$ME_{(CN)}$, is the cetane number of each methyl ester

CHAPTER 4: RESULTS AND DISCUSSION

- **OUTLINE:**

- 4.1. Characterization of CKD.....
- 4.2. Determination of the optimum palm oil to WCO ratio for their blend preparation
- 4.3. Modelling and studying the input variables influencing biodiesel production
- 4.4. Optimization of the reaction conditions of the process.....
- 4.5. CKD Reusability
- 4.6. Characterization of the produced biodiesel.....

4.1. Characterization of CKD

After conducting the particle size analysis, it was observed that approximately 58 % of the particles remained on the sieve of 75 μm diameter while almost the rest of CKD particles remained on the 63 μm diameter sieve. CKD particles that crossed through the 50 μm diameter sieve, were neglected because their percentage was insignificant. Figure (4-1) shows the morphology of CKD obtained from (Tura Cement Factory) after calcination. Also, table (4-1) introduces the chemical formula of the CKD constituents obtained XRF analysis. Calcium oxide as a targeted catalyzing component for the reaction is the major component of CKD and accounts for approximately 46 %. Worth mentioning, the 9 % content of other alkali components such as (K_2O , Na_2O , and MgO) may also play an important role in catalyzing the reaction. Elemental analysis results reviewed in other studies, indicate that there are acidic sites present in CKD. This can be useful for esterification of FFA if the feedstock for transesterification, is of high acid content. Specific surface area was measured to be $18.1 \text{ m}^2 / \text{g}$ using a gas sorption device "Nova 2000 Quanta chrome". This low specific surface area may give an indication that transesterification using CKD occurs on the external part of the catalyst particles.

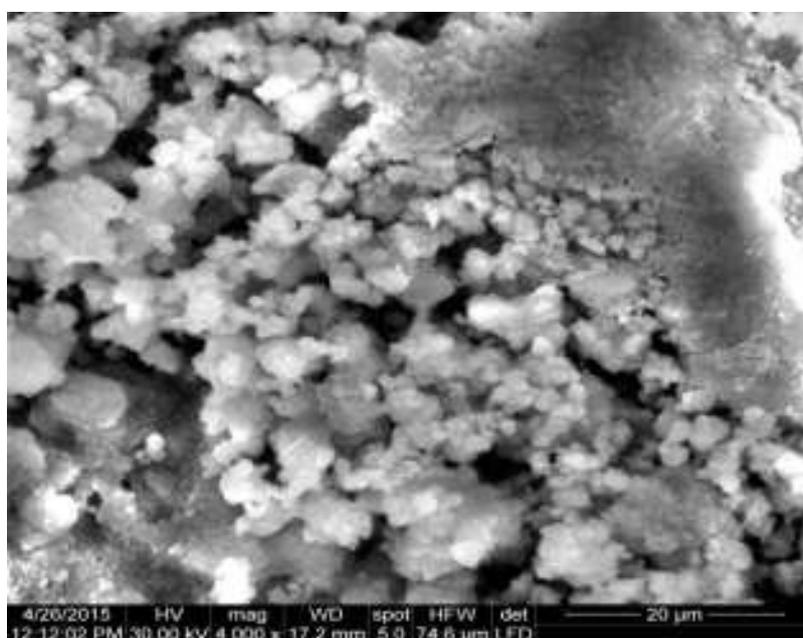


Figure (4-1): A morphological image of CKD used by SEM (4000 \times) (Al-Sakkari, E.G. et al., 2017)

Table (4-1) Chemical constituents of CKD:

Chemical formula for core constituents	Weight percent (wt %)
CaO	45.9
LOI (loss on ignition)	23.7
SiO ₂	7.01
Cl	6.61
K ₂ O	5.60
Na ₂ O	2.49
SO ₃	2.43
Fe ₂ O ₃	2.31
Al ₂ O ₃	1.90
MgO	1.14
TiO ₂	0.27
P ₂ O ₅	0.06
MnO	0.05

4.2. Determination of the optimum palm oil to WCO ratio for their blend preparation

Oxidation stability, cold flow properties, and acid value are of the most important properties of biodiesel and the feedstock oil from which biodiesel is derived. If the mentioned biodiesel properties are poor, this may cause impairment to diesel engine performance and biodiesel quality (Pullen, James, and Khizer Saeed, 2012), (Verma P. et al., 2016). Therefore acid value and oxidation stability enhancement of WCO based plus improving the poor cold flow properties of palm biodiesel were the reasons behind blending WCO with palm oil at an optimum ratio. Optimization of the blend fractions (%) was done by correlating the experimentally obtained results of cold flow properties of biodiesel produced from each blend prepared and acid value of each blend. From an economic point of view as the most important parameter of the blend optimization, it was decided that the WCO should represent $\geq 50\%$ of the blend to make the feedstock more cost effective particularly for use on the industrial scale. This means that although the blends of $\geq 50\%$ palm oil have low acid content and high oxidation stability which are needed for good quality biodiesel, the blends of $\geq 50\%$ palm oil were discarded. Hence the (50% palm: 50% WCO) and (40% palm: 60% WCO) blends were considered the best in terms of free fatty acid content of the blends before and after transesterification. Their acid values before transesterification were (7.8 and 8.4 mg

KOH/g oil) whereas after transesterification were (0.68 and 0.7 mg KOH/g FAME). Table (4-2) illustrates the cloud and pour points of the seven blends based biodiesel. Blends based biodiesel of wt % ratios of (100:0, 80:20 and 60:40) palm oil to WCO, showed relatively high PPs and CPs compared to the cold flow properties of the other blends. These high PPs and CPs are considered poor cold flow properties of biodiesel which can be used in areas of constant warm to hot climate throughout the year. Lastly, the (40% palm: 60% WCO) blend was selected to be the optimum blend because it has good cold flow properties, low acid value, good oxidation stability as result of presence of a moderately high percentage palm oil in the blend and above all of that, the blend is cost effective.

Table (4-2) Cloud and pour points of biodiesel produced through homogenously catalyzed transesterification from palm-WCO blends at different ratios:

(Palm oil wt%: WCO wt%)	CP	PP
100 % : 0 %	17	12
80 % : 20 %	13	8
60 % : 40 %	10	4.5
50 % : 50 %	6	2.5
40 % : 60 %	2.5	1
20 % : 80 %	1.5	0
0 % : 100 %	- 2	- 3.5

4.3. Modelling the effects of the input variables on biodiesel yield

As previously mentioned the factorial design for biodiesel production was performed using four variables. Thirty transesterification Reactions were performed to study the effect of time (1, 3.5, 6 hours), methanol to oil molar ratio (12:1, 15:1, 18:1), catalyst (CKD) loading (1% , 2%, 3% of oil weight) and temperature (45,55, 65 °C). The stirring rate was fixed at 850 rpm to have a turbulent radial flow inside the reactor and avoid mass transfer limitations. The results obtained from applying the previously stated methodology and operating conditions are illustrated in table (4-3) which represents the matrix of the input variables and the response of each point (conversion %).

Table (4-3): Matrix of the input variables and the response of each value.

Point type	x ₁ (h)	x ₂ (ratio)	x ₃ (%)	x ₄ (°C)	y %
Factorial	6	18	3	65	100
Factorial	6	18	3	45	100
Factorial	6	18	1	65	60
Factorial	6	18	1	45	54
Factorial	6	12	3	65	88
Factorial	6	12	3	45	64
Factorial	6	12	1	65	58
Factorial	6	12	1	45	45
Factorial	1	18	3	65	90
Factorial	1	18	3	45	87
Factorial	1	18	1	65	46
Factorial	1	18	1	45	38
Factorial	1	12	3	65	73
Factorial	1	12	3	45	49
Factorial	1	12	1	65	39
Factorial	1	12	1	45	32
Star	6	15	2	55	96
Star	1	15	2	55	65
Star	3.5	15	3	55	91
Star	3.5	15	1	55	76.5
Star	3.5	18	2	55	100
Star	3.5	12	2	55	43
Star	3.5	15	2	65	90
Star	3.5	15	2	45	74
Center	3.5	15	2	55	100
Center	3.5	15	2	55	95
Center	3.5	15	2	55	96
Center	3.5	15	2	55	98
Center	3.5	15	2	55	93
Center	3.5	15	2	55	90

The data were fitted to both linear including factors interaction and quadratic models. In the case of linear model, the coded data (-1, 1) were put in a matrix called design matrix shown in table (4-4) then the inverse of that matrix was multiplied by a matrix whose elements are the responses which are the percentages of conversion of each run to obtain a matrix of coefficients. The data codes of (0) are the center points (the repeated 6 experiments) and they were used to calculate the standard deviation for the 16 factorial points. Based on that, T-test and the significance of the model coefficients were then determined. The result was the matrix of coefficients of the following dimensionless equation:

$$y = a_0 + \sum a_i z_i + \sum a_{ij} z_i z_j + \sum a_{ijk} z_i z_j z_k + a_{ijkl} z_i z_j z_k z_l$$

Where

$$z_i = \frac{x_i - x_{0i}}{\Delta x_i}$$

$$x_{0i} = \frac{x_{imax} + x_{imin}}{2}$$

and

$$\Delta x_i = \frac{x_{imax} - x_{imin}}{2}$$

While on developing the quadratic model, the result was the following equation:

$$y = a_0 + \sum a_i z_i + \sum a_{ij} z_i z_j + \sum a_{ii} z_i^2$$

Table (4-4): Design Matrix of full 2⁴ Factorial Design (linear model)

	Z ₀	Z ₁	Z ₂	Z ₃	Z ₄	Z ₁₂	Z ₁₃	Z ₁₄	Z ₂₃	Z ₂₄	Z ₃₄	Z ₁₂₃	Z ₁₂₄	Z ₁₃₄	Z ₂₃₄	Z ₁₂₃₄	Y
1	1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-1	1	32
2	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	45
3	1	-1	1	-1	-1	-1	1	1	-1	-1	1	1	1	-1	1	-1	38
4	1	1	1	-1	-1	1	-1	-1	-1	-1	1	-1	-1	1	1	1	54
5	1	-1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	1	-1	49
6	1	1	-1	1	-1	-1	1	-1	-1	1	-1	-1	1	-1	1	1	64
7	1	-1	1	1	-1	-1	-1	1	1	-1	-1	-1	1	1	-1	1	87
8	1	1	1	1	-1	1	1	-1	1	-1	-1	1	-1	-1	-1	-1	100
9	1	-1	-1	-1	1	1	1	-1	1	-1	-1	-1	1	1	1	-1	39
10	1	1	-1	-1	1	-1	-1	1	1	-1	-1	1	-1	-1	1	1	58
11	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	46
12	1	1	1	-1	1	1	-1	1	-1	1	-1	-1	1	-1	-1	-1	60
13	1	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	-1	-1	1	73
14	1	1	-1	1	1	-1	1	1	-1	-1	1	-1	-1	1	-1	-1	88
15	1	-1	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1	-1	90
16	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100

The values of the coefficients of the dimensionless regression equation are shown in table (4-5) together with the results of t-test used to eliminate statistically insignificant values at a significance level of 0.05 where the critical t-value equals 2.57.

Table (4-5): Results of (t-test) (Significance Test)

Coeff.	Value	T-test	P value	Result
a₀	63.9375	71.85955	8.86E -09	S
a₁	7.1875	8.078053	0.000406	S
a₂	7.9375	8.92098	0.000256	S
a₃	17.4375	19.59806	5.68E -06	S
a₄	5.3125	5.970735	0.00158	S
a₁₂	-0.5625	0.632195	0.299029	I
a₁₃	-0.5625	0.632195	0.299029	I
a₁₄	0.0625	0.070244	0.476293	I
a₂₃	4.9375	5.549271	0.002166	S
a₂₄	-3.1875	3.582441	0.012166	S
a₃₄	1.0625	1.194147	0.168305	I
a₁₂₃	-0.3125	0.35122	0.383637	I
a₁₂₄	-0.6875	0.772683	0.261176	I
a₁₃₄	-0.4375	0.491708	0.34	I
a₂₃₄	-2.4375	2.739513	0.029417	S
a₁₂₃₄	0.3125	0.35122	0.383637	I

Where (S) indicates that the coefficient is significant while (A) indicates that the coefficient is not significant. This leads to the following regression dimensionless equation:

$$y = 63.9375 + 7.1875z_1 + 7.9375z_2 + 17.4375z_3 + 5.3125z_4 + 4.9375z_2z_3 - 3.1875z_2z_4 - 2.4375z_2z_3z_4$$

Then the dimensionless variables (z) can be then replaced by the original ones (x) to translate the regression equation from the dimensionless form into the dimension form.

The validity of resultant equation was tested by calculating determination coefficient (R^2). This test showed that the regression equation is valid for the range of experiments done as $R^2 = 0.90$. Figure (4-2) shows the graph of calculated conversion versus observed values

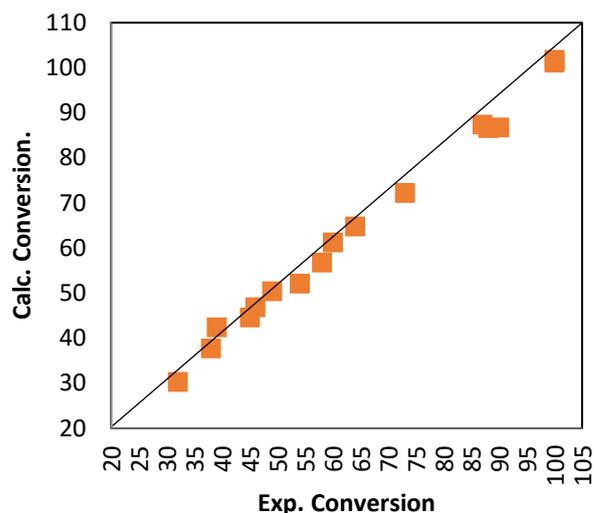


Figure (4-2): Calculated vs. Experimental conversion

The developed quadratic model has a determination coefficient of 0.95 and the values of its significant coefficients are illustrated in table (4-6). From these results, it may be concluded that both models can be used to predict reaction conversions but the quadratic one is preferred as the effects of the conditions can be observed easily on the response surfaces plots.

Table (4-6): The significant coefficients of the quadratic model obtained using (Expert Design software)

Coefficient	Value
Constant a_0	-199.536
a_1	10.4653
a_2	6.6155
a_3	39.3396
a_4	4.2482
a_1*a_1	- 0.8167
a_2*a_2	- 0.0394
a_3*a_3	-12.6042
a_4*a_4	- 0.021
a_1*a_2	- 0.075
a_1*a_3	- 0.225
a_1*a_4	0.0025
a_2*a_3	1.6458
a_2*a_4	- 0.1063
a_3*a_4	0.1062

And the regression equation of the quadratic model would be:

$$\begin{aligned}
 y = & -199.536 + 10.4653 x_1 + 6.6155 x_2 + 39.3396 x_3 + 4.2482 x_4 \\
 & - 0.8167x_1^2 - 0.0394 x_2^2 - 12.6042 x_3^2 - 0.021 x_4^2 \\
 & - 0.075 x_1x_2 - 0.225 x_1x_3 + 0.0025 x_1x_4 + 1.6458 x_2x_3 \\
 & - 0.1063 x_2x_4 + 0.1062 x_3x_4
 \end{aligned}$$

4.4. Optimization of the reaction conditions of the process

In order to obtain the optimum conditions of the reaction two methods were applied, the first one is to differentiate the regression equation obtained partially with respect to its variable (reaction time, catalyst loading %, temperature and methanol to oil molar ratio) then make each resultant equation equal to zero and then these set of equations solved to obtain the values of variables that give the maximum conversion. However, this method was not very useful as the values obtained did not correspond to a maximum conversion. The conditions obtained could point out to a minimum conversion or a critical point that is neither maximum nor minimum.

The second method is plotting the response surfaces. By correlating the data on the four response surfaces and the contour plots that represent the joint effect of the factors on the conversion percentage, it was observed that the optimum conditions that could give a complete conversion were 4.5 h time, 17:1 molar ratio, 2.7 % wt catalyst loading and temperature of 60 °C. An experiment was carried out at these conditions to check the validity of the proposed model, and the experimental value obtained for conversion was 100% (complete conversion) which is in good agreement with the calculated figure of 102% obtained from the quadratic model. Response surfaces of conversion percentage versus the joint effect of (methanol to oil molar ratio and reaction time), (catalyst loading and time), (methanol to oil molar ratio and catalyst loading) and (temperature and methanol to oil molar ratio) as well as their contour plots are shown in figures (4-3), (4-4), (4-5) and (4-6). Based on the regression equation and the response surfaces plots, it can be concluded that high values of the four individual studied factors (in the range of the study) correspond to maximum values of conversion percentage. On the other hand, the minus signs in the equation such as (- 0.8167 x_1^2 , - 0.0394 x_2^2 , - 0.075 x_1x_2 and others) can be a justification of why the response (conversion) decreases with continuing to increase the values of the input variables after reaching the maximum values on some of the response surface plots and contour lines. As for the effect of methanol to molar ratio on reaction conversion observed on the response surfaces, it is observed that the values ranging from 15:1 to 18:1,

correspond to high conversion values which are close to each other with insignificant differences. Whereas the response surfaces and the contour plots show that there is an insignificant increase in conversion starting from reaction time values of 3 or 3.5 hours to 6 hours. So it can be concluded that a correlation between the quadratic model data and the response surfaces, plus checking the validity of data obtained experimentally, can come up with more optimum factors which may offer both high conversion % and economic feasibility. Based on what discussed, the conditions of 3 % catalyst loading (maximum value), 65 °C (maximum value), 3.5 hours reaction time (where conversion % started increasing insignificantly) and 15:1 methanol to molar ratio, were chosen from the response surface to test their effect on conversion % experimentally as well as check the value of conversion % statistically from the regression equation of the quadratic model. The calculated value of conversion percentage obtained from the regression equation of the quadratic model was 95 %. A transesterification reaction was performed at the same conditions chosen, to check whether both conversions have the same value. Almost a complete conversion was achieved, which means that there is an error of 4-5 % between the two values. So it may be concluded that the conditions of 3%, 3.5 h, 15:1 and 65 °C, can be considered also to be optimum conditions since the reaction time and methanol to oil ratio values are the lowest among the other values which can give a complete conversion experimentally. It is worth mentioning that the amount of methanol used and reaction time of transesterification process play a crucial role in the economic feasibility of biodiesel mass production.

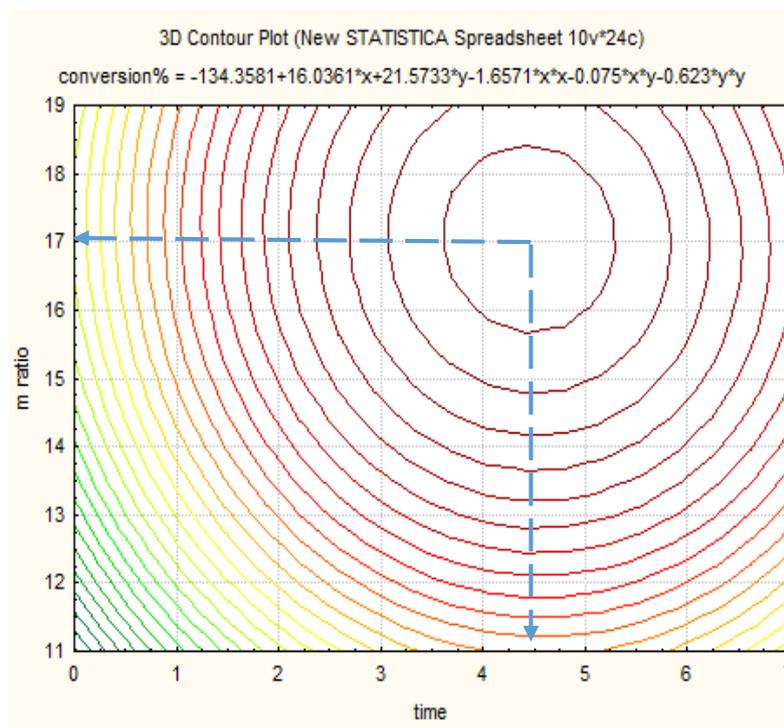
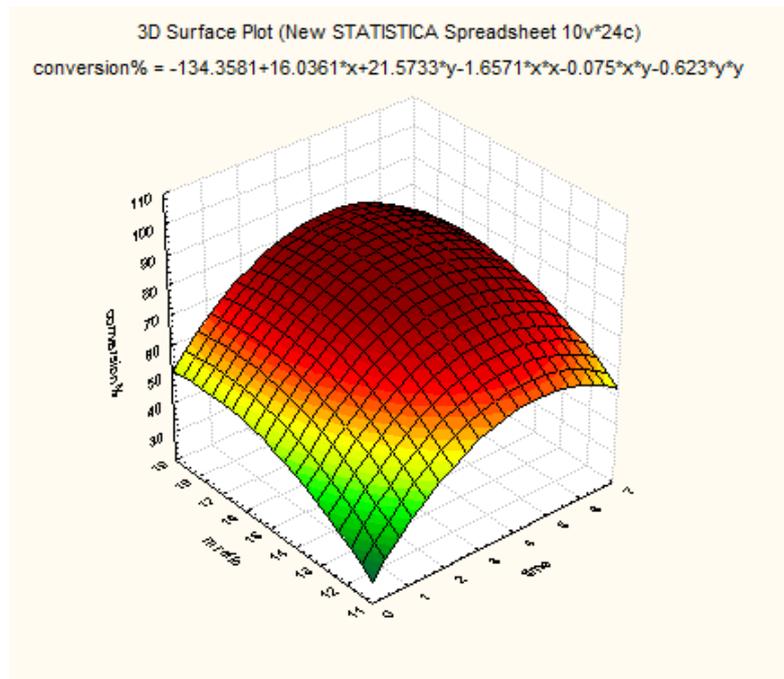


Figure (4-3) Response surface and contour plot of the effect of methanol to oil molar ratio and time (h) on conversion of mixed feedstock oil (palm oil-WCO)

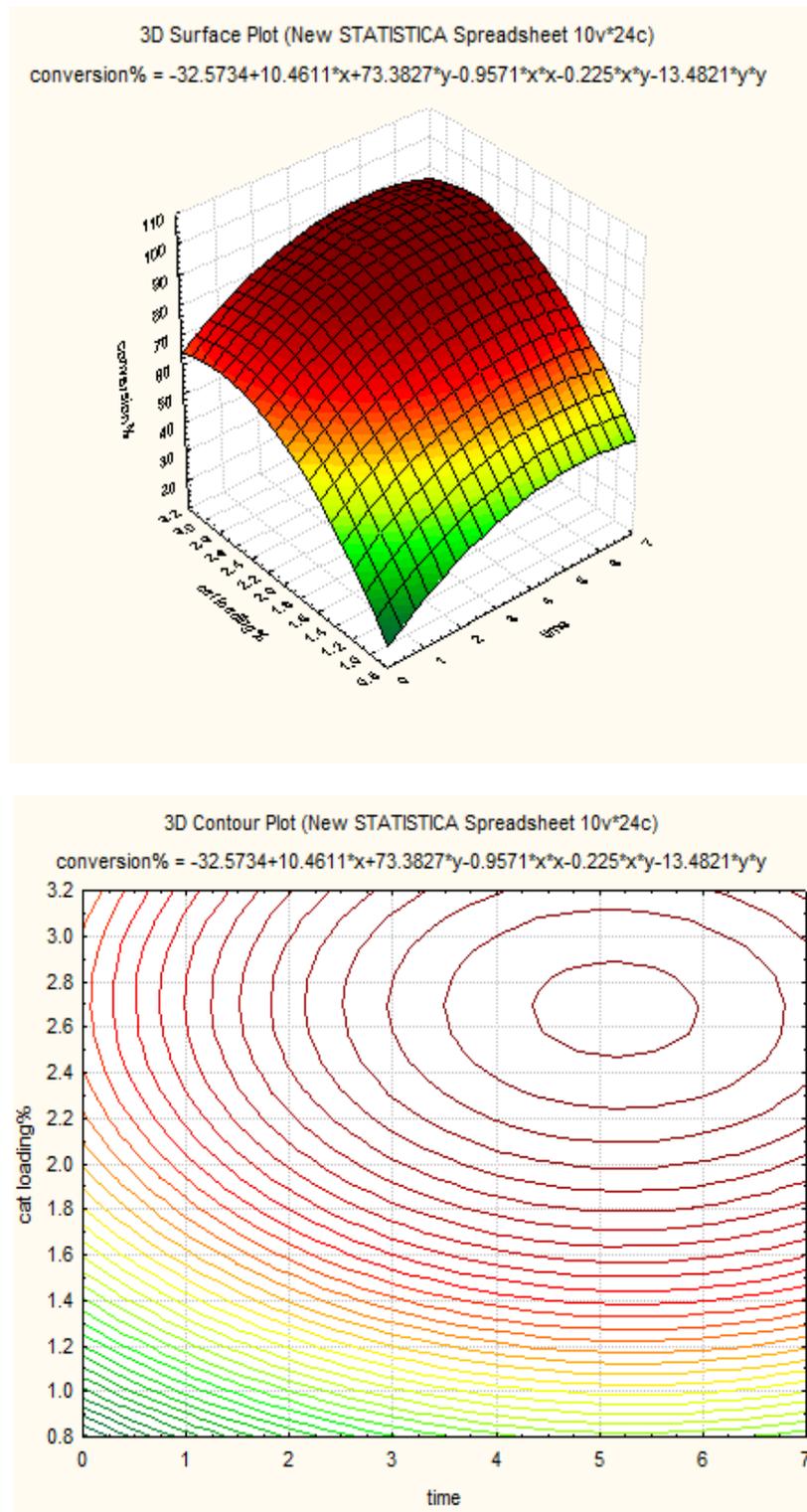


Figure (4-4) Response surface and contour plot of the effect of catalyst loading % of oil mass and time (h) on conversion of mixed feedstock oil

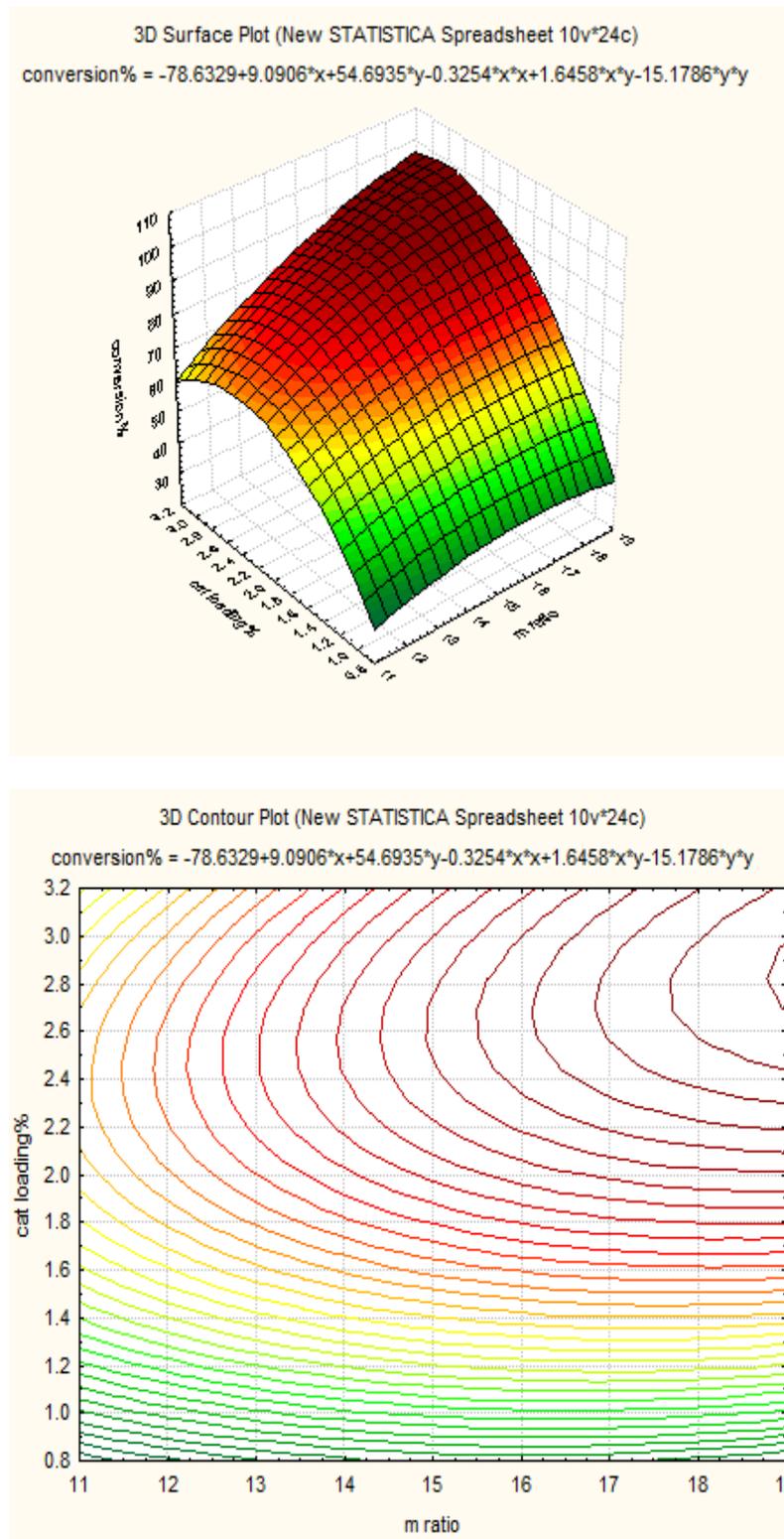


Figure (4-5) Response surface and contour plot of the effect of catalyst loading % of oil mass and methanol to oil molar ratio on conversion of mixed feedstock oil

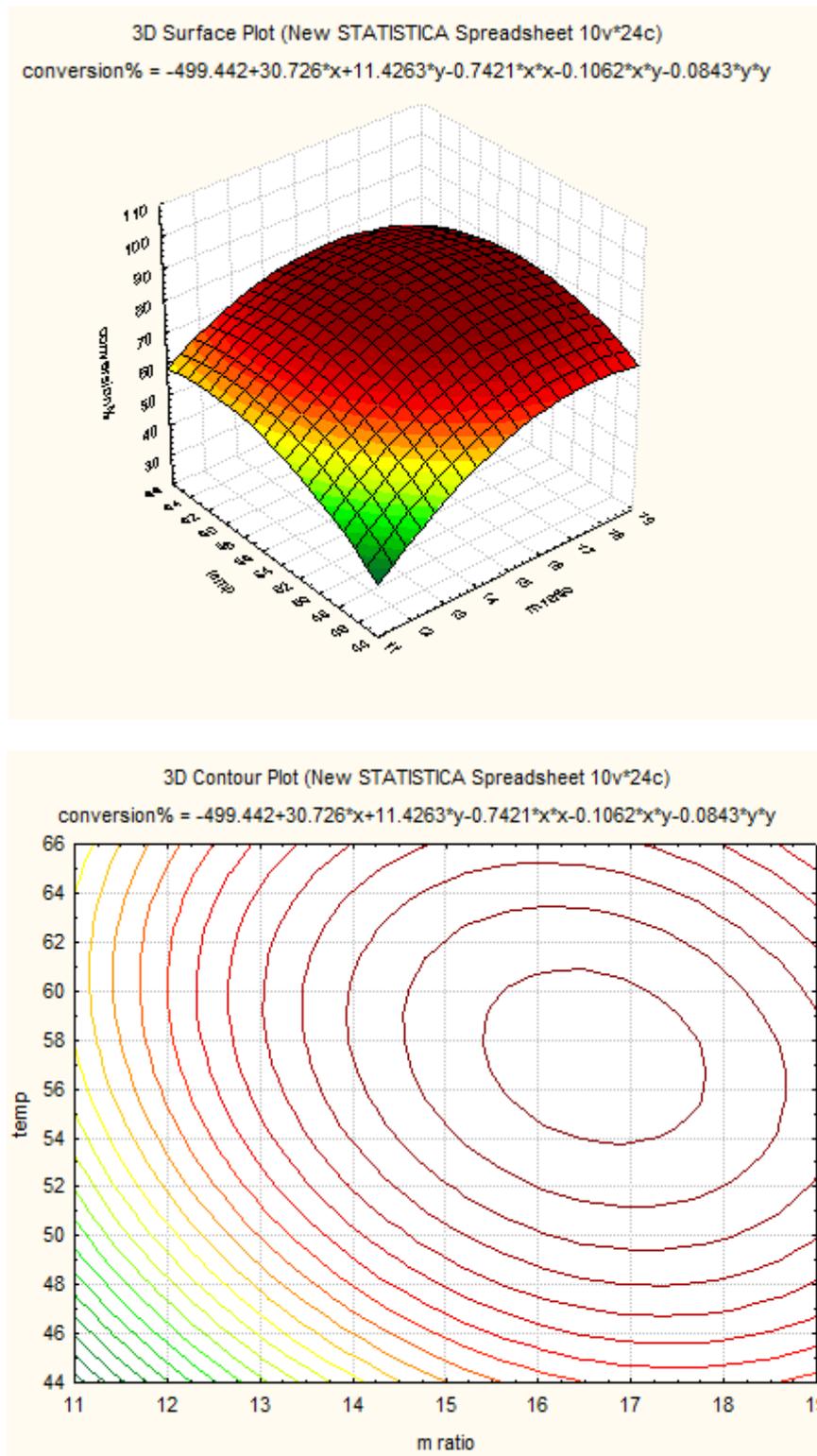


Figure (4-6) Response surface and contour plot of the effect of temperature °C and methanol to oil molar ratio on conversion of mixed feedstock oil

4.5. CKD Reusability

Figure (4-7) illustrates the results of reusability tests of CKD. After performing the first CKD reusability test and calculating the percentage of conversion, it was found that conversion % dropped by 21% from complete conversion in the first run to 79 % conversion in the second run using the used CKD. While as for the second reusability test, it was observed that the conversion % decreased from 90 % to 72.9 % conversion. In conclusion, the transesterification reaction conversion percentage dropped by averagely 20 % when CKD was reused. The reduction of conversion percentage may be attributed to the catalytic activity decline of CKD as a result of its leaching as well as the surface area reduction of CKD which may be due to contamination and covering parts of the catalyst's surface by glycerol formed. Some other cause may justify the reduction of conversion and the drop in catalytic activity of the reused CKD, which is the back-conversion of some active components such as (CaO) present in the catalyst to lesser active components such as (CaCO₃). From the results of reusability tests, it can be concluded that CKD reuse for biodiesel production, is not economically feasible for the industrial scale (mass production scale) compared with using it once. This is attributed to factors affecting the feasibility of transesterification such as the more sophisticated purification systems that would be required for incomplete transesterification reaction conversion obtained when CKD is reused.



Figure (4-7): Reusability tests of CKD

4.6. Characterization of the produced biodiesel

Table (4-7) presents the results of characterization tests done to determine the characteristics of the produced biodiesel. Table (4-8) summarizes the GC analysis results of fatty acids composition of the three biodiesel samples produced through transesterification as well as the reaction conditions and considerations for producing the samples. It is observed that the properties of the produced biodiesel meet the standard specs of biodiesel. These good properties of biodiesel such as heat of combustion, cold flow properties, and viscosity lead to desirable diesel engine performance. The high flash point of biodiesel produced adds an important safety factor for using it. Also, the enhancement of cold flow properties achieved by mixing palm oil and WCO assures the possibility of using the produced biodiesel in cold weather (minimum 3 °C). Whereas the low acid content of the produced biodiesel can play an important role in avoiding corrosion of engine's internal parts when used in engines. It is worth mentioning that CKD catalyzed transesterification decreased the acid value from 8.4 mg KOH per one gram of (40 wt% palm-60 wt% WCO) blend to 0.7 mg KOH per one gram FAMES produced.

Table (4-7) Characteristics of the produced biodiesel

Property	Value	Standard
Viscosity 40 °C cSt.	4.7	4.0-6.0
Density g/ml	0.86	0.86-0.9
Heat of combustion KJ/Kg	38140	35000- 42000
Flash Point °C	165	≥ 130
Cloud Point °C	3	-3 to 12
Pour Point °C	1	-15 to 10
Acid Value mg KOH/g FAMES	0.7	≤ 0.8

From the GC analysis results, it is noticed that sample (1) has a higher saturated fatty acid content than that in sample (2) and (3) while it is lower in polyunsaturated fatty acid composition. This gives a strong indication that sample (1) has higher oxidation Stability than the other two samples (Pullen, James, and Khizer Saeed, 2012), (Yun, Jung-Mi, and Jeonghee Surh., 2012). Therefore, it can be concluded that sample (1) could be the optimum on quality and stability basis compared even with biodiesel produced through homogeneously catalyzed transesterification plus being produced at the optimum conditions on technical and economic feasibility basis.

Table (4-8): Fatty acids composition of some produced biodiesel samples

Fatty Acids	Mass Fraction % of Sample (1)	Mass Fraction % of Sample (2)	Mass Fraction % of Sample (3)
Myristic Acid C14	1.48	0.62	0.60
Palmitic Acid C16	33.41	23.47	23.48
Stearic Acid C18	2.30	3.62	4.07
Oleic Acid C18:1	45.63	38.26	37.91
Linoleic A. C18:2	15.35	32.60	32.07
Linolenic A. C18:3	1.48	1.40	1.40
Saturated Fatty A. SFA	37.19	27.71	28.15
Un-Saturated F.A. USFA	62.46	72.26	71.38
Mono-Un-Saturated F.A. MUSFA	45.63	38.26	37.91
Poly-Un-Saturated F.A. PUSFA	16.83	34.00	33.47
Total F.A. TFA	99.65	99.97	99.53
Transesterification considerations and conditions			
Catalyst(s)	Hetero (CKD)	Hetero (CKD)	Homo (H ₂ SO ₄ , KOH)
Catalyst(s) loading	3 %	2.7 %	3.5 % and 1%
Methanol to feedstock oil molar ratio	15:1	17:1	6:1
Reaction time (h)	3.5	4.5	2
Reaction temperature (°C)	65	60	65
Conversion percentage calculated on molar basis	100 %	100 %	100 %

- **Cetane number determination**

As mentioned in chapter (4), CN was calculated using the following equation:

$$CN = \sum ME_{(Wt\%)} * ME_{(CN)}$$

Therefore, the values of ME_(CN) obtained from literature and the mass fractions of fatty acids obtained for the 3 samples of biodiesel analyzed, were used to substitute in the equation. Linolenic acid (C18:3) was not included in the samples CN calculation because it accounts only for a small fraction of the composition of biodiesel samples and also there

was no standard CN for it in the literature reviewed. The cetane numbers calculated for samples 1, 2 and 3 were 61, 57.5 and 57 respectively. This indicates that the three biodiesel samples produced from the optimum weight percentage ratio of (40 % palm: 60 % WCO) using CKD ensure good quality of combustion and ignition properties which can reflect positively on diesel engine performance (MaríaJesús Ramos et al., 2009). The high cetane number of sample (1) which is slightly higher than the CNs of the other two samples, indicate that there is a direct relation between high cetane numbers for biodiesel fuels and high mass fractions (%) of their esters with saturated fatty acids such as palmitic acid (Knothe, G. et al., 2003).

CHAPTER 5: MODEL OF (LAB TO INDUSTRY) SCALING-UP FOR BIODIESEL AND GLYCEROL PRODUCTION

- **OUTLINE:**

<u>5.1. Model description</u>	
<u>5.1.1. Biodiesel production and purification unit</u>	
<u>5.1.2. Glycerol production and purification</u>	
<u>5.2. Materials and products quality</u>	
<u>5.3. Reactor design and sizing</u>	
<u>5.4. Catalyst reusability</u>	
<u>5.5. Economic viability of the process</u>	

- **Overview**

In this chapter, a process simulation of an industrial plant for biodiesel and glycerol synthesis is introduced. The feedstock used is a blend of low-grade palm oil and WCO at a mass fraction ratio (40 wt%:60 wt%) respectively and the catalyst used is cement kiln dust (CKD) treated by calcination. For better economic feasibility for the process and for cutting down costs, it is highly recommended that such industrial-scale plants for biodiesel and glycerol production to be close or in the surrounding area of a cement production plant where CKD can be calcined at the operation temperature up to 1100 °C of cement kiln (Lin, 2011). Therefore, there will be no need for further energy intensive catalyst preparation or treatment.

5.1. Model description

The proposed model for the plant involves a process of two main units; biodiesel production and purification unit as well as glycerol production and purification unit. Figure (6-1) illustrates the proposed process flow-sheet whereas Table (5-1) introduces the instruments proposed for the process. A brief description of how the entire system operates is introduced.

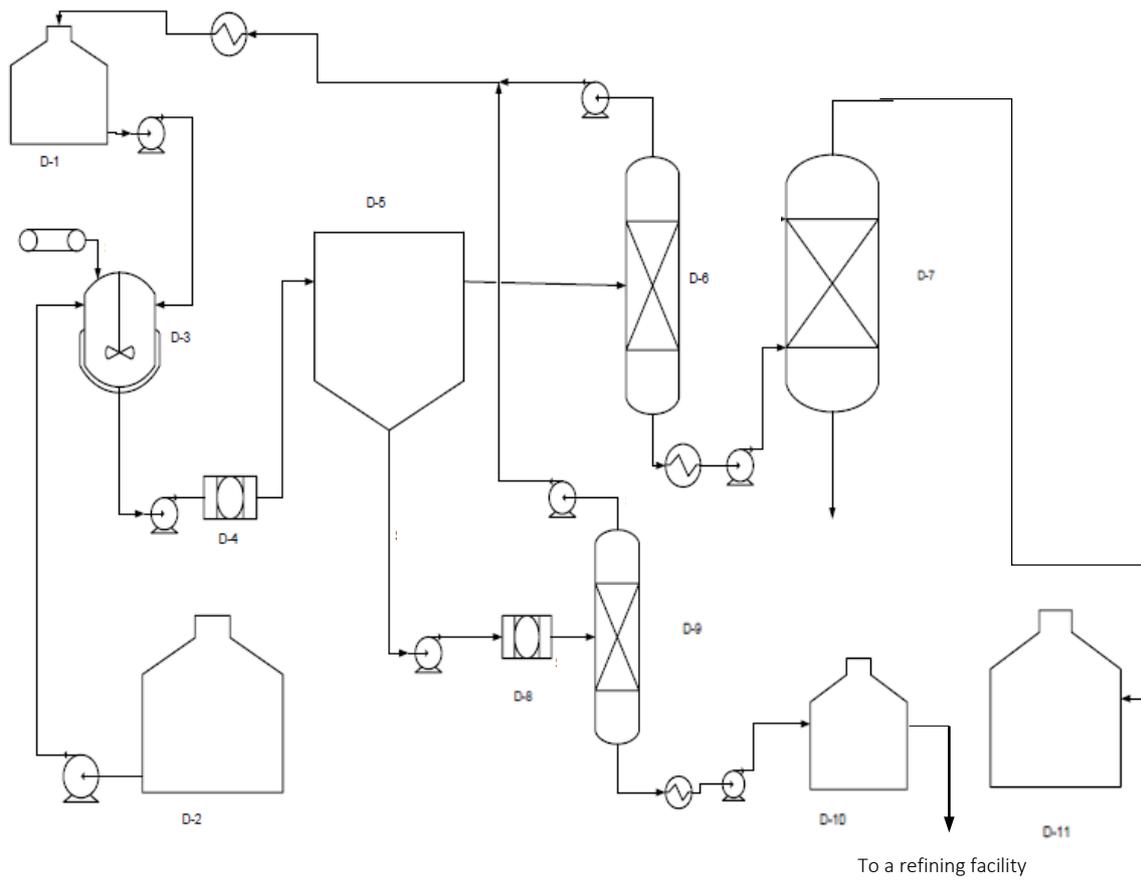


Figure 5-1: Flow sheet of Single step transesterification for biodiesel and glycerol production using CKD as a heterogeneous catalyst

Table (5-1): The proposed biodiesel production process instruments

Symbol	Instruments
D-1	Methanol Storage Container
D-2	Blended Oils Storage Container
D-3	Transesterification Reactor
D-4	Filter Press Machine 1
D-5	Separation Container
D-6	Methanol Distillation Column 1
D-7	Washing Tank
D-8	Filter Press Machine 2
D-9	Methanol Distillation Column 2
D-10	Glycerol Storage Container
D-11	Biodiesel Storage Container

5.1.1. Biodiesel production and purification unit

The unit includes two stages; the first one is synthesis of oil-based diesel through transesterification of a mixture of low-cost palm oil and waste cooking oil, and the second one is getting the product purified and suitable for direct use in diesel engines. The process is a single step transesterification in a batch reactor catalyzed by CKD as a solid base heterogeneous catalyst. The process of biodiesel production is adjusted to certain conditions for achieving complete conversion; temperature, methanol to oil ratio, catalyst loading and reaction time are the controlling factors. The reaction temperature for the process is fixed at 65 C°. CKD as the catalyst is introduced into the reactor at a loading of 3% of oil weight. The methanol to oil molar ratio proposed is 15:1. Reaction time of three hours and a half is needed to ensure high purity ($\geq 99\%$) of (FAME) produced through complete conversion of oil to biodiesel in a single step batch transesterification reaction. Filtration of CKD from the mixture of biodiesel and glycerol is required via a filter press machine and then introduced to separation tank. The separation process occurs on cold for better separation of the two phases. Pumping system is needed for driving the liquids to

the different sections throughout the operation such as separation and purification sections in order for obtaining a standardized good quality end-products.

There is no need for sophisticated purification system techniques and biodiesel distillation column as the targeted yield of the reaction is almost 100%, which means there is no unreacted oil. The main role of the purification stage in the unit is to ensure that the product is free of catalyst residues as well as methanol. According to the experiments carried out earlier for optimizing the reaction conditions, the maximum percentage of soap might account for 1% of biodiesel weight. Worth mentioning, soap formation could be avoided by ensuring that feedstock is not of high acid value and also ensuring that there is no moisture content affecting the catalyst activity. Since the non-polar esters of biodiesel do not mix with the polar molecules of glycerol as well as the density of glycerol is higher than the density biodiesel that has a standard density range of (0.86 – 0.9 g/ml) (ASTM D1298), a separation container is used to have glycerol settled down at the bottom of the container. In the purification stage, the separated biodiesel phase passes through two main steps. The first one is in order to eliminate the excess amount of methanol present in the biodiesel layer, which accounts for approximately 3-4% of total weight. In this step, excess methanol is recovered and recycled via a distillation column. Biodiesel is then oriented to a washing container in which the phase gets rid of all associated residues and impurities by washing it with a warm fresh water. It is worth pointing out that the wastewater loaded with impurities and residues after washing has no economic value and has to be managed carefully (Roman, 2003). After washing, biodiesel gets dried to remove water and then it is pumped as end-product into a storage container. Dry washing could be introduced instead of water washing for better washing and more time-saving.

5.1.2. Glycerol production and purification

The production stage is same as the one of biodiesel synthesis. As mentioned earlier, due to the difference in density, glycerol settles down while biodiesel is on top. In the purification stage, the glycerol layer is oriented to a filter press machine and then to a distillation column for having a product free of dissolved solids, impurities, and excess methanol. The excess methanol is then recycled for reuse. After purification, the purified product is directed to a storage container before sending it to a refining facility where a commercial grade of glycerol for diverse industrial purposes is produced. It is worth to mention that there is another alternative way to benefit from the produced crude glycerol

in case of unavailability of refining facility in the proposed plant. This alternative way is converting crude glycerol to valuable derivatives and compounds such as 1,3-propanediol, 1,2-propanediol, hydrogen, succinic acid and polyesters through diverse more economic processes (Pachauri, N., and He, B., 2006).

5.2. Materials and products quality

Based on the experimental work conducted, there is a possibility of obtaining a yield of 100% under different adjusted certain reaction conditions. For producing 30 tons of biodiesel per day, 30 tons of palm and spent oils are needed as a daily feedstock at a ratio of 2:3 respectively. The produced glycerol will be about 3 tons/day. According to the reaction conditions proposed for the industrial scale plant, the amount of methanol delivered to the production plant is at a rate of about 16 tons per day, representing a methanol to oil feedstock molar ratio of 15:1. In addition, the needed amount of CKD is 3% of the feedstock oil weight used which is equivalent to 0.9 tons.

Heat recovery and integration between different process streams are suggested in order to increase the profitability of the process and cut down costs of some heating intensive operations. Biodiesel and glycerol produced at the plant should be under a monitoring program for assuring their quality constantly as well as guaranteeing that they meet the standard specifications.

5.3. Reactor design and sizing

The design and the sizing of a batch reactor suggested by (El-Sheltawy S. T. et al., 2016) were used as a guide for proposing dimensions for an agitated batch reactor needed for scaling up the lab-scale operation. In the proposed operation, it is suggested that there will be two agitated reactors. The needed agitator type for agitation is a radial flow impeller in order to impose shear stress to the mixture of the reactants and the catalyst inside the reactor as well as to cause high turbulence. Therefore, Rushton turbine as a radial flow impeller is highly recommended for the process. Table (5-2) introduces the parameters of designing an agitated batch reactor. The following Law was used to scaling up the stirring speed from 850 rpm used at the lab scale to an industrial scale that can keep mass transfer rate the same.

$$N1/N2 = (D2/D1)^2/3 \text{ (Coker, 2011)}$$

Where D1 and N1 are the lab reactor diameter and the magnetic stirrer speed respectively and they equal 850 rpm and 0.15 m, whereas D2 is the suggested industrial reactor diameter which equals 4.2 m.

Table (5-2): Agitated batch reactor design

Parameter	Value
Agitated batch reactor	
Working volume	27 m ³
Diameter	3.2 m
Height	3.9 m
Agitator type	Rushton turbine (radial flow)
Agitator diameter	1.4 m
Agitator speed	106 rpm

5.4. Catalyst reusability

In accordance with the experiments carried out for testing reusability of CKD, transesterification reaction yield dropped by averagely 20% in the second use of CKD for the two reusability tests conducted. The possible reason for that conversion percentage reduction as mentioned in (chapter 4) might have been the negative impact on the catalyst's catalytic activity due to CKD leaching and catalyst's surface area decrease. For the proposed industrial scale model, CKD could not be reusable because the proposed plant is designed for nearly a complete oil to biodiesel conversion through a single step batch reactor. However, CKD could be reused if a vacuum distillation column introduced to the process design for extracting the unreacted feedstock and sending it back to the reactor. For such a case, additional costs are required and the process profitability may be affected.

5.5. Economic viability of the process

Many controlling factors could influence the economic aspect of the transesterification process. Feedstock availability and affordability have turned out to be the most important factors as the cost of feedstock accounts for more than 70% of the entire process costs (Sam, Behzadi and Farid, M. M., 2007). For the case of the present process, since low-cost palm oil and spent cooking oil are suggested to be used, this could strongly promote cutting down a big part of the total process costs. Also, other parameters such as a simple purification system, availability of CKD, low cost of its preparation, heat integration between processes streams, optimized reaction conditions are advised to contribute to the process feasibility. Therefore, the suggested process model could compete with conventional homogeneously catalyzed transesterification in terms of economic profitability.

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

The study outcomes ensure the applicability and the significance of integrating the experimental work done on producing biodiesel and glycerol from (no to low) cost feedstock (i.e. WCO and low to moderate grade palm oil) using waste as a catalyst (i.e. CKD), with the statistical based conceptions of factorial design and response surface methodology. Factorial design of experiments and response surface methodology can effectively be used for the following objectives: Generating the biggest amount of data from the least number of transesterification reactions performed, studying the effect of the chosen factors on biodiesel yield, and to predict the optimum conditions for CKD catalyzed transesterification. The factors studied in the present study are methanol to feedstock oil molar ratio, reaction time, catalyst loading and reaction temperature. The stirring speed was adjusted to 850 rpm in all experiments and it may be concluded that this high speed can contribute successfully to avoiding mass transfer problems associated with the viscous reaction medium. Both quadratic and linear models were developed using the experimental data. The quadratic model was found to be better than the linear one as the optimum conditions can be more accurately obtained from its response surfaces and it is more valid to explain the range of experimentally obtained results. The optimum conditions obtained were 4.5 hours reaction time, 17:1 methanol to oil molar ratio, 60 °C reaction temperature, and 2.7% catalyst loading of feedstock mass. Conditions of 3 % catalyst loading, 65 °C reaction temperature, 15:1 methanol to oil molar ratio and 3.5 hours reaction time obtained by correlating some data on the response surfaces and the experimental results, may also be optimum as they include lower methanol to oil molar ratio and reaction time which reflect on the process feasibility as well as give complete conversion experimentally.

Biodiesel produced from the blend of palm oil and WCO at the determined ratio of 2:3 (i.e. 40 wt %: 60 wt %), shows good fuel specs which make it suitable for diverse uses. Treated CKD showed a good catalytic performance and yielded a complete conversion at a high catalyst loading (in the range of the study). Also, it may be recommended that CKD should be utilized as a catalyst for a commercial wide scale biodiesel production due to the following reasons which can contribute to lowering the total production costs: CKD is an available

waste in cement-producing countries, its preparation and treatment processes may occur in cement production plants kilns where it is generated, it can be reused based on its type and characteristics, using it for biodiesel production does neither require special equipment nor sophisticated purification system. Other recommendations for future work may contribute to the present proposed process economic and technical feasibility if taken into account. For example, performing studies on the reaction kinetics as well as substituting low to moderate grade palm oil with waste cooking palm oil to lower the cost of feedstock without compromising the enhanced properties of the products which palm oil gives such as oxidation stability and combustion quality. Moreover, Heat integration could be very important to more conserve energy during the operation and this may reflect positively on the process economy. Studies of assessing the performance of diesel engines operating on (Palm-WCO) based diesel are highly recommended to evaluate the technical effect of using it on different parameters (i.e. thermal efficiency, knocking, torque, etc.) of diesel engines' performance.

A scaling up model to turn the lab-scale biodiesel production from palm oil and WCO over CKD as a catalyst into a large-scale mass production, is proposed in the present study. The proposed reaction conditions for achieving complete conversion of oil to biodiesel are 3 % catalyst loading, 65 °C reaction temperature, 15:1 methanol to oil molar ratio and 3.5 hours reaction time. Two units of purification and production are included to produce pure products. The process can be recommended to be applied on an industrial scale due to its technical and economic feasibility.

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APPENDIX

- **Work Plan**

Activities	Feb	Mar	April	May	June	July	Aug	Sep
Proposal writing								
Literature review								
Midterm report								
Experimental work								
Thesis writing								
Internship report								
Thesis defence								