

**UTILIZATION OF POTASSIUM CARBONATE-BASED DEEP EUTECTIC SOLVENTS  
AS CATALYST IN TRANSESTERIFICATION REACTION OF *JATROPHA CURCAS*  
OIL**

**BY**

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**MARCH, 2018**

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*CURCASOIL***

**BY**

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ZARIA, NIGERIA**

**MARCH, 2018**

## DECLARATION

I hereby declare that this dissertation titled “Utilization of Potassium carbonate-based Deep Eutectic Solvents as Catalyst in Transesterification Reaction of *Jatropha curcas* Oil” was carried out by me under the supervision of Dr. S.M. Waziri and Dr. O. A. Ajayi and it is a product of my work and all literature cited are duly acknowledged. This work has not been published or presented for the award of any diploma or degree at any institution.

Abdulwasiiu **ABDURRAHMAN**

(P16EGCE8081)

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Signature

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Date



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No dissertation is a complete work of just one or two people. It is always the result of many people working together. So, it is always hard to single out a few people for recognition when there are so many to thank. Those I must specially recognize include: Prof. B. J. El-Yakub, Prof. I. A. Mohammed-Dabo, Dr. M.T. Isa, Dr. NurudeenSalahudeen, Dr. ZaharadeenGano, Engr. Nuhu Muhammad, Halima Hamza, MalamaAsma'u Umar, Abubakar Habib Adebisi, GazaliTanimu, Salisu Muhammad, JamiluSalihu, Malam Musa lab., Salihu Adam Kahinde, Engr. Hassan, OladipoSulaimanAdewale, Abdullahi class rep.,Mas'udAlao,and many others, I said thank and God bless you all.

## ABSTRACT

Deep eutectic solvents (DES) were synthesized from different mole ratios of  $K_2CO_3$ /glycerol at 400 rpm and 353 K for a period of 2 hours to form a homogenous transparent colorless liquid. ThreeDES were successfully formed at the ratio 1:20, 1:30 and 1:40. The DES synthesized were used as catalyst in transesterification reaction of *Jatropha curcas* oil with time varied from 30 to 120 minutes, concentration of DES varied from 8 to 10% w/w, stirred at 300 rpm with a magnetic stirrer hot plate and at a temperature of 60°C. Response surface methodology (RSM) based on Box–Behnken Design (BBD) was employed to examine the major reaction parameters (such as  $K_2CO_3$ /Glycerol ratio, catalyst (DES) concentration and reaction time), and to optimize the reaction conditions for achieving the maximum yield of fatty acid methyl ester (FAME). Design Expert 6.06 software was used in the regression and graphical analyses of data. The statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). Maximum FAME yield of 98.2845% was achieved at optimum conditions of 1:32.58 mole ratio of  $K_2CO_3$ /glycerol, 8.96% w/w concentration of DES and 69.58min. GC-MS analysis revealed that the biodiesel contains 98.87% ester content and 1.13% non-ester composition. The properties of *Jatropha curcas* oil biodiesel produced were characterized and found to agree with the ASTM D6751-12 standard.

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## **ABBREVIATIONS, DEFINITIONS, GLOSSARY AND SYMBOLS**

ASTM American Society for Testing and Material

AOCS American Oil Chemist Society

BBD Box-Behnken Design

ChClCholine chloride

DESDeep Eutectic Solvent

EN European

FAME Fatty Acid Methyl Ester

FFAFree Fatty Acid

FTIR Fourier-transform Infra-red

GC-MSGas Chromatography/Mass Spectrometry

HBD Hydrogen Bond Donor

IL Ionic Liquid

IV Iodine Value

LGPO Low grade crude palm oil

MTPB Methyl triphenylphosphonium bromide

P-DES Phosphonium-baesd deep eutectic solvent

PTSA Ptoluenesolphonic acid monohydrate

SV Saponification Value

TBD1,5,7-triazabicyclodec-5-ene

rpm revolution per minute

RSM Response Surface Methodology

RTIL Room Temperature Ionic Liquid

VOS Volatile Organic Solvent

## CHAPTER ONE

### 1.0 INTRODUCTION

#### 1.1 Preamble

The general term used to describe the important class of organic reactions where vegetable oils, animal fats, or microalgae oil (triglyceride) reacts with an alcohol (methanol or ethanol) to produce fatty acid alkyl esters and glycerol is called transesterification. Transesterification is the most common method for synthesizing biodiesel. Generally, transesterification reaction can be catalyzed by alkalis, acids, and enzymes (Ma and Hanna, 1999).

Recently, enzyme catalysts have attracted more scientists' attention because these catalysts prevent soap formation and the purification process is effortless to complete. Nevertheless, they have not been utilized commercially due to their long reaction times and high cost (Fukuda *et al.*, 2001; Leung *et al.*, 2010).

The alkali and acid catalysts are more used in the production of biodiesel compared to enzyme catalysts because of their inexpensive raw material chemicals. The acid-catalyzed transesterification reaction requires a high molar ratio of methanol to oil; moreover, its reaction time is very long as compared with alkali catalysts and the acidic catalysts are corrosive and non-environmentally friendly (Marchetti and Errazu 2008; Rashtizadeh *et al.*, 2010).

The most common catalysts for the transesterification reaction are the alkali catalysts (homogeneous base catalysts) such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) which are being used commercially in biodiesel production (Demirbas 2008; Dias *et al.*, 2008; Rashid *et al.*, 2008).

While homogeneous catalyst cause difficulties in separation of catalyst from liquid mixtures, severe operating conditions (i.e. reaction time, reaction temperature) are required for producing biodiesel using heterogeneous catalyst. The prospect of ionic liquids (IL) as a catalyst in biodiesel synthesis is promising. IL is considered as homogeneous catalyst because they are in the same phase with reactants, and thus possesses the advantage of homogeneous catalyst over heterogeneous catalyst.

In addition, the ability to recycle IL at the end of reaction and easing the separation of products are benefits obtained if heterogeneous catalyst is used. Hence, by combining these two advantages of homogeneous and heterogeneous catalysts, application of IL as catalyst in biodiesel synthesis have started to gain popularity. On top of that, advantages in terms of high catalytic activity, excellent stability, easy product isolation and environmental benefits are the reason why ionic liquids are better compared to conventional liquid and solid catalysts (Wu, 2007)

Due to ionic liquids (IL) unusual favorable properties, they have attracted more attention and became a focus point for many applications. However, there is still a challenge for the large-scale applications of ionic liquids in industry, because of complicated synthesis processes and the expensive raw material chemicals (Robin, 2003). Hence, deep eutectic solvents (DESs) can be utilized as a low cost alternative of ILs (Houet *al.*, 2008). DES is formed from mixtures of organic halide salts with an organic compound which is a hydrogen bond donor (HBD) and able to form a hydrogen bond with the halide ion (Shahbazet *al.*, 2011).

Deep eutectic solvents have properties similar to ionic liquids, especially, their potential as tuneable solvents that can be customized to a particular type of chemistry (Nkuku and LeSuer, 2007).

Currently, DES are being used in research as well as industry because of their potential as an alternative environment friendly solvents and advantages over traditional ionic liquids such as ease of preparation in high purity at low cost, non-toxicity, non-reactivity with water and being biodegradable (Abbott *et al.*, 2004). In addition, DES is being studied comprehensively in many research areas as media for organic and inorganic reactions and separations. In addition, the advantages of the DESs have the best answer for the industrial requirements for large-scale applications.

Conventionally, deep eutectic solvents have been synthesized from ammonium or phosphonium based salts. These salts were combined in different ratios with varieties of hydrogen bond donors such as: alcohols, carboxylic acids, esters, ethers, amides, and hydrated metal salts of chlorides, nitrates and acetates (Abbott *et al.*, 2007).

Furthermore, metal halides based DESs were also reported later (Abbott *et al.*, 2007). However, potassium based salts were not used as an ingredient for DES synthesis. Potassium carbonate ( $K_2CO_3$ ) known as pearl ash is a white salt having a melting point of 1164.15 K. It is highly soluble in water (112 g/100 mL at 293.15 K) forming a strong alkaline solution. In its aqueous form, potassium carbonate is utilized for the removal of carbon dioxide from the ammonia production synthesis gas in the fertilizers industry (Leonard *et al.*, 1998).

Potassium carbonate, used in a concentration of 2 and 3mol% gives high yields of fatty acid alkyl esters (90.3 and 92.4% respectively) and reduces the soap formation. This can be explained

by the formation of bicarbonate instead of water, which does not hydrolyze the esters. (Schuchard *et al.*, 1998). However, excess methanol is used to drive the equilibrium of the reversible reaction to the product side (Granados *et al.*, 2007) while co-solvent (such as THF) is added to overcome the limit associated with mass transport in a heterogeneous system (Gryglewicz, 1999). But these common organic solvents (including methanol and THF) are typically volatile, flammable, toxic and harmful to the environment (Tang *et al.*, 2013). Also the little soap formed lowers the yield and increases formation of emulsions in the product making it difficult to separate biodiesel from glycerine.

In deep eutectic solvents, glycerol has been successfully used as a hydrogen bond donor with Choline Chloride to form DES by several research groups (Qamar and Leo, 2010). Potassium carbonate and glycerol were used in different molar ratios to make a new DES system and some physical properties like density, viscosity, surface tension, refractive index, and pH at different temperatures were investigated (Naser *et al.*, 2013).

This research focused on the utilization of these eutectic solvents prepared from potassium carbonate and glycerol as catalyst in transesterification reaction.

## **1.2 Problem Statement**

Reusable homogeneous catalyst like ionic liquids have been used in transesterification reaction, however, they are complicated to synthesize, raw materials are expensive, and non-environmentally friendly.

### 1.3 Aim and Objectives

The aim of this work was to synthesize and study the application of potassium carbonate-based deep eutectic solvents as catalyst in transesterification reaction of *Jatropha curcas* oil.

The specific objectives of the work were:

- i. To synthesize DES using  $K_2CO_3$  as salts and glycerol as hydrogen bond donor (HBD)
- ii. To characterize the *Jatropha Curcas* oil and the DES synthesized
- iii. To optimize the transesterification process conditions using Box-Behnken Design (BBD)
- iv. To reuse the biodiesel by-product containing the DES as a catalyst
- v. To characterize the biodiesel produced and compare it with the ASTM D 6751-12 standard.

### 1.4 Justification

One of the major factors that determine the feasibility of transesterification reaction is the performance and the type of catalyst used. Hence, the following justify the work:

- i. DES can serve as good alternative to ionic liquid and are environmentally friendly.
- ii. The by-product (glycerol) is one of the ingredients for the synthesis of the catalyst (DES).
- iii. Fatty acid methyl ester is not soluble in the DES/methanol mixture; hence saponification side-reaction, separation and purification can be minimized.

## 1.5 Scope

The scope of this research includes:

- i. Utilization of deep eutectic solvents synthesized from  $K_2CO_3$  and glycerol in transesterification reaction.
- ii. Optimization of the transesterification process conditions.
- iii. Characterization of the optimized catalyst and optimally produced biodiesel was limited to FTIR and GCMS.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Biodiesel

The plant oils usually contain free fatty acids, phospholipids, sterols, water, odourants and other impurities, because of these, the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification mainly transesterification, pyrolysis and emulsification. Among these, the transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel from vegetable oils (Meheret *al.*, 2006).

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. It is considered as a possible substitute to the conventional diesel fuel, and it commonly composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics (Meheret *al.*, 2006).

The quickly growing demand for energy which has led to higher depletion rate of fossil fuels reserve, coupled with the increasing global warming threat due to increase in greenhouse gasses emission have drawn significant attention globally. This has led to the impeccable need of finding renewable energy sources to ensure future sustainability. Biodiesel fuel i.e., fatty acid methyl esters (FAMEs), is a renewable and environmentally friendly fuel (Nawshadet *al.*, 2015).

There are different varieties of processes and feedstock's from which the biodiesel can be synthesized such as castor beans, palm, palm kernel, olive, sesame, corn, linseed, soybean, canola, sunflower, peanuts, coconut, oilseed radish, cotton, sunflower, babassu, algae, jatropha,

sea mango, polanga, pongamia, animal fat (butter, lard, tallow, grease and fish oil, etc.) and waste cooking oil.

## **2.2 Factors Affecting Yield of Biodiesel**

Some of the major factors affecting yield, cost and quality of biodiesel are listed and explained below:

### **2.2.1. Alcohol quantity**

Ma and Hanna, (1999), Zhang *et al.*, (2003) and Leung and Guo, (2006) recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol triglyceride ratio is raised beyond 3 and reaches a maximum. Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase the cost for alcohol recovery (Leung *et al.*, 2006).

In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of alcohol to triglycerides in most investigations is 6:1, with the use of an alkali catalyst (Zhang *et al.*, 2003). When the percentage of free fatty acids in the oils or fats is high, such as in the case of waste cooking oil, a molar ratio as high as 15:1 is needed when using acid-catalyzed transesterification (Leung *et al.*, 2010).

### **2.2.2. Reaction time**

Conversion rate of fatty acid esters increases with reaction time (Freedman *et al.*, 1984). At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of <90 min, and then remains relatively constant with a further increase in the reaction time (Leung and Guo, 2006). Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps (Leunget *al.*, 2010).

### **2.2.3. Reaction temperature**

Rate of reaction and yield of the biodiesel product are clearly influenced by temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides (Leung and Guo, 2006; Eeveraet *al.*, 2009). The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization. Depending on the oil used, the optimal temperature ranges from 50°C to 60°C (Leung *et al.*, 2010).

### **2.2.4. Catalyst concentration**

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, the most commonly used catalyst for the reaction is sodium hydroxide. Catalyst concentration can affect the yield of the biodiesel product. However, Freedman *et al.*, 1984 found that sodium methoxide was more effective than sodium hydroxide because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will

affect the product yield because of the hydrolysis reaction. This is the reason why the catalyst should be added into the methanol first and then mixed with the oil. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters. Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt.% and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Leung *et al.*, 2010).

### **2.3. Yields of biodiesel produced from different catalysts**

Schuchardt *et al.* (1998) compared the catalytic activity of 1,5,7-triazabicyclodec-5-ene (TBD) to that observed for typical industrial catalysts (*e.g.* NaOH and  $K_2CO_3$ ). The experiments were performed when 8.00 g (27.2 mmol) of rapeseed oil reacted with 2.00 g (62.5 mmol) of methanol for 1 hour, at temperature of 70 °C and the results of their study are shown in Table 2.1. The reaction yields obtained with TBD were close to those observed with NaOH and no undesirable by-products such as soaps (easily formed when alkaline metal hydroxides are used) were observed. When compared to potassium carbonate, TBD was always more active, even at low molar concentrations. Although TBD is less active than sodium methoxide (at only 0.5%,  $CH_3ONa$  produces more than 98% of methyl esters after 30 min) but its use does not require any special condition.

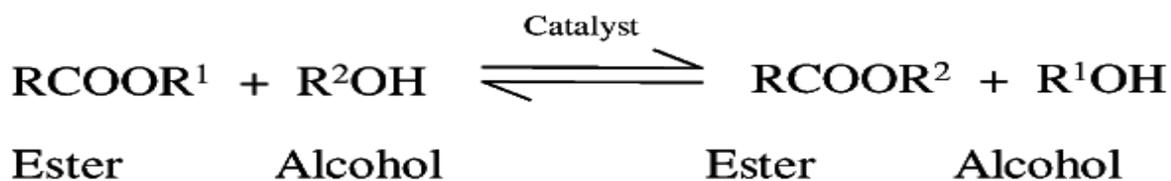
Table 2.1: Comparison between TBD and the conventional inorganic catalysts.

Catalyst	Yield (%) after 1 h
NaOH (1 mol%)	98.7
K <sub>2</sub> CO <sub>3</sub> (1 mol%)	84.0
K <sub>2</sub> CO <sub>3</sub> (2 mol%)	90.3
K <sub>2</sub> CO <sub>3</sub> (3 mol%)	92.4
TBD (1 mol%)	89.0
TBD (2 mol%)	91.4
TBD (3 mol%)	93.0

a: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 h, 70 °C.

## 2.4. Transesterification

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Meheret *al*, 2006). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation shown in scheme 2.1.

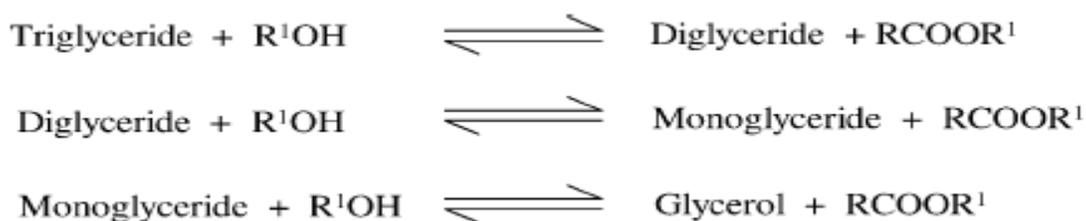


Scheme 2.1: General equation for transesterification

Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) accelerates the conversion.

### 2.4.1 Mechanism of base-catalyzed transesterification reaction

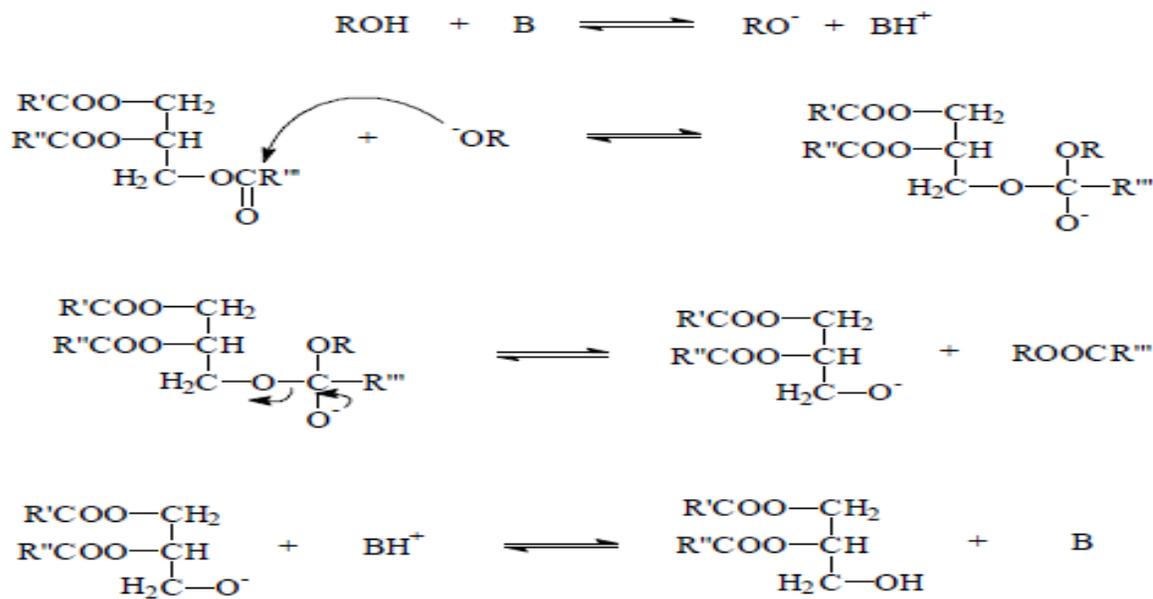
Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in scheme 2.2.



Scheme 2.2: General equation for transesterification of triglycerides

The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali (Meher *et al*, 2006).

The mechanism of alkali-catalyzed transesterification is described in scheme 2.3. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride (Meher *et al*, 2006).



Scheme 2.3: Mechanism of a based catalyzed transesterification reaction.

where

R' = carbon chain of the fatty acid and

R = alkyl group of the alcohol

## 2.5 Ionic Liquids

The term ionic liquids (IL) has been used to describe salts that melt below 100 °C. Whereas, the term room temperature ionic liquids (RTIL) is usually reserved for ILs melts with melting points below room temperature. IL is an electrolyte forming liquids that consist only of cations and anions. IL has extremely low vapour pressure being non-volatile, highly polar, miscible with certain organic solvents and/or water and good solubility of organic and inorganic materials, chemically inert. They are reusable (residual reagents, reaction products and catalysts are separated by suitable procedures e.g., removal under reduced pressure or extraction), and can be

designed, non-inflammable and thermally stable as well (high thermal stability and liquid range up to about 300 °C)(Ahmad and Dzulkefly, 2010).

IL is usually characterized by a wide electrochemical window of stability, a reasonable ionic conductivity (similar to most non-aqueous electrolytes). IL typically consists of organic nitrogen-containing heterocyclic cations and inorganic anions. IL has promising environmentally benign, numerous of reaction media which are expected to provide an attractive alternative to conventional volatile organic solvents (VOS) in current synthetic organic chemistry since their growing use does not lead to air pollution. Nevertheless, in the last few years they have become more attractive in other fields such as catalysis, in basic electrochemical studies of organic compounds and inorganic compounds, formation of metal nanostructures, analytical chemistry including sensors, bio-analytical chemistry, and for electrochemical biosensors(Ahmad and Dzulkefly, 2010).

ILs have been hailed as the green alternative to VOSs in chemistry due to their novel properties, while maintaining the ability to dissolve a wide range of organic and inorganic compounds for example, 1-allyl-3-methylimidazolium chloride could be dissolved cellulose up to 39% without derivatization and 1-butyl-3- methylimidazolium chloride have been shown to stabilize proteins. Since VOSs nature consists of relatively small molecules, they have weak intermolecular forces between them and making them highly volatile. They are also flammable and often toxic, consequently there has been much interest in finding non-volatile solvents as replacements. Therefore, unlike VOSs, ILs do not vaporize into the air, effectively eliminating one of the major routes of environmental contamination, making its operations safer and environmentally acceptable.

Among these, IL have recently been classified to three types namely traditional ionic liquid, protic ionic liquid and deep eutectic solvent (Ahmad and Dzulkefly,2010).

### **2.5.1 How ILs affect the catalytic reactions pathway**

ILs proved to be very complex solvents, they can solvate polar and non-polar species, they can behave as polar or non-polar solvents. Besides their “chemical” characteristics, their physical properties such as an elevated viscosity can affect the diffusion and reduce reaction rates. The solubility of gas or the selective solubilization of reactants relative to the products can also change the reaction selectivity. The formation of primary reaction products can be favoured by their selective extraction from the IL catalytic phase in an organic upper phase. It is then difficult to rationalize the IL effects on chemical and catalytic reactions. Nevertheless, it would be of primary importance to understand how their physico-chemical properties can affect the outcome of catalytic reactions in order to be able to choose the best ILs for a given reaction. Solvation properties, interactions with solutes, substrates, transition states, metal complexes, reactants, their cohesive pressure, their degree of organization and their viscosity are all to be considered when ILs are used as solvents. To date, the ILs’ effects have been best described and rationalized on chemical reactions rather than on catalytic reactions involving transition metal complexes. We will see below that some effects of ILs are not expected and then not under control. In some cases, the generation of the active catalyst has been dependent on the nature of the ILs. ILs can inhibit or promote the formation of the active species. They can also dramatically affect the outcome of reactions (Olivier-Bourbigouet *al.*, 2010)

### 2.5.2 Ionic liquids in biodiesel synthesis

The conversion of renewable feed stocks takes place through chemical reaction to produce biodiesel. Conventional organic and inorganic solvents are used in biodiesel synthesis. Although they are usually used due to their wide availability and inexpensiveness, these types of solvents can pose threats on environment especially regarding their toxicity and flammability. Furthermore, inappropriate disposal of waste containing these solvents can also lead to contamination of the environment. Ionic liquids offer several advantages over conventional solvents. Their perspective and usefulness in biodiesel synthesis have made their utilization become more prominent. Figure 2.4 represents several applications of ionic liquids in biodiesel production (Ahmad and Nor, 2012)

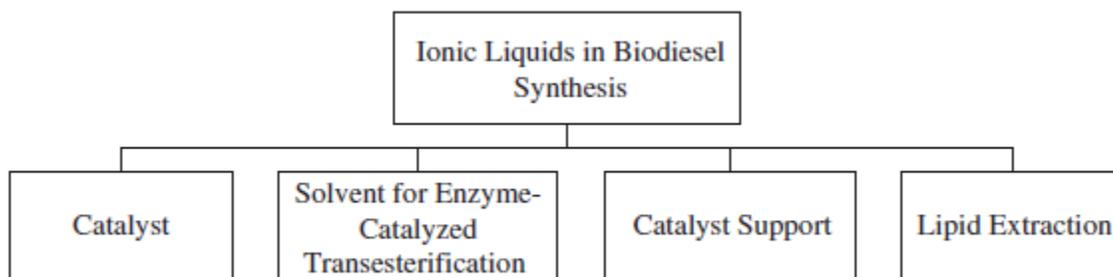


Figure 2.1: Applications of ionic liquids in biodiesel synthesis (Ahmad and Nor, 2012)

Ionic liquids are used as an extracting solvent in the biodiesel production for extracting lipids from microalgae and oil seeds (Young *et al.*, 2010; Kim *et al.*, 2012), free fatty acids from the oily feedstock (Manic *et al.*, 2011), glycerol from the biodiesel product (Abbott *et al.*, 2007), as well as glycerol (Hayyan *et al.*, 2010) and unsaturated fatty acid esters (Li *et al.*, 2009) from crude biodiesel.

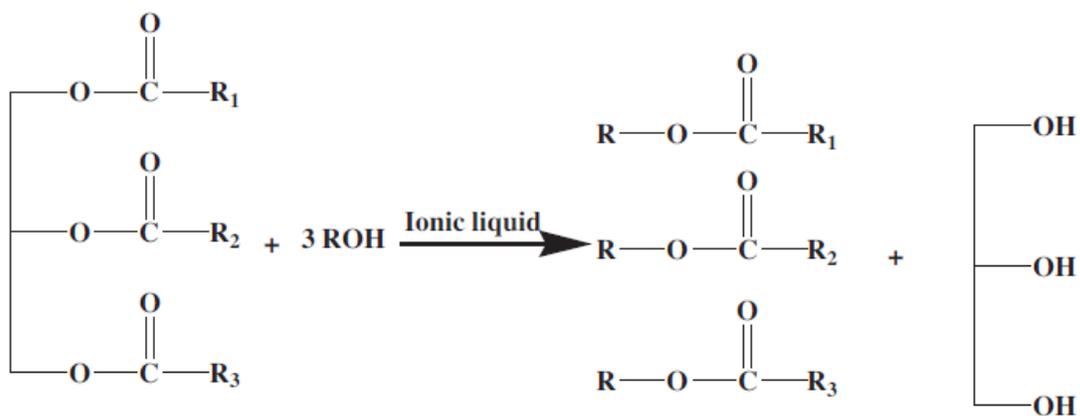
### **2.5.3 Role of ionic liquid as a catalyst for preparation of biodiesel**

Ionic liquids have been widely accepted as a new green chemical that is capable of revolutionizing chemical processes due to their interesting properties. The subject has created tremendous interest within both the academia and the chemical industries. ILs is basically a molten salt which exist in liquid state at temperature below 100 °C. Often they are also called room temperature ionic liquids (RTIL). For a start, the ionic liquids possessed greener properties such as very low relative volatility i.e., close to zero, wide liquids temperature and significantly less toxic compared to the organic solvent. More important is their ability to selectively dissolve various organic, inorganic, and organometallic materials due to their tuneable polarity which can be designed for specific purposes. They can also be made miscible or immiscible with organic solvents and water. Both could be achieved by simply varying their anion–cation combinations. Because of these, IL possesses numerous advantages over the conventional organic solvents, besides being more environmentally compatible (Nawshadet *al.*, 2015).

In industrial practice, IL has also been proven through few chemical manufacturing processes to give significant advantage such as in the production of alkoxyphenolphospines which is a generic precursor for photo-initiator by BASF (BASIL process) where the reaction time was reduced considerably resulting in tremendous increase in capacity. In addition, the separation of the product from the catalyst and ionic liquids was also easily attained compared to the earlier process. Generally for industrial applications, considerable efforts have been made on designing acidic ionic liquids to replace homogeneous and heterogeneous acids in a variety of chemical applications, such as catalysis in supporting enzyme catalyzed reactions, homogeneous and heterogeneous catalysis, purification, photo-isomerization and electrochemistry. In view of the

environmentally friendly nature of IL, the catalyst developed was also dubbed as green catalyst (Nawshadet *al.*, 2015).

Among the major impetus in reaction catalysis developments involved, is the development of processes in which easy separation of products and reuse of catalyst is made viable along with high reactivity and selectivity. In this context, IL are viewed as prospective catalysts for biodiesel production where the technical, economic and environmental aspects were addressed through their inherent characteristics of being less corrosive, ease of separation, recyclable, applicable for continuous process and less production of waste water. Applying ILs based catalyst could reduce the number of reactions and purification steps required in the biodiesel preparation and separation hence rendering the process to be more economically competitive. A typical path way for biodiesel preparation while using ionic liquid as a catalyst has been depicted in scheme 2.4 (Nawshadet *al.*, 2015)



Scheme 2.4: Mechanism of biodiesel preparation via ionic liquid catalyzed process.

In the recent past few years, deep eutectic solvents (DESs) were developed sharing similar characteristics to ionic liquids but with more advantageous features related to preparation cost, environmental impact, and efficiency for gas separation processes (Rima and Abdulkarem, 2018).

## 2.6 Deep Eutectic Solvents (DES)

Another ILs that is receiving interest is deep eutectic solvents (DES) which is a type of ILs. DES is a simple mixture of salt (like zinc(II)chloride,trimethylehanolamine (cholin) chloride, methyl triphenylphosphonium bromide, etc) and hydrogen bond donor compound such as alcohol (like glycerol, ethylene glycol and triethylene glycol), acid, halide, amine, amide (like 2,2,2-trifluoroacetamide), amino acid etc. They are easy to make simply take the two solids, mix them together with gentle heating, until they melt, and when they cool they remain liquid. When these two components are mixed in a proper ratio, a eutectic point is observed. The liquid state of the DES is produced through freezing point depression, whereby hydrogen-bonding interactions between an anion and an HBD are more energetically favored relative to the lattice energies of the pure constituents (Nkuku and LeSuer, 2007). Considering that deep eutectic solvents contain a significant molecular component, the researchers show ambivalence on whether they could be formally classified as ion liquids. However, their properties as tunable solvents are comparable to those of ionic liquids. Furthermore, they have several advantages over ionic liquids, such as easy preparation in high purity at low cost, non-toxicity, no reactivity with water and biodegradability (Abbott *et al.*, 2004).

### 2.6.1 Use of glycerol in deep eutectic solvents synthesis

Abbott *et al.* (2011) reported an effective method for decreasing the viscosity of glycerol phase by adding choline chloride (ChCl) into the system. It is impressive that addition of 33 mol% ChCl decreases the viscosity of glycerol by a factor of 3. While this is higher than most molecular solvents it is similar to many ionic liquids and deep eutectic solvents (DES). It is assumed that this is due to the 3D intermolecular hydrogen bond interactions in glycerol that are broken up on addition of ChCl resulting in a less ordered system. This strategy can be a sustainable way of

preparing non-toxic, tunable solvent systems, complimenting thus the insufficient capacity of glycerol in fitting the current requirements of green solvent on its diversity and structural tunability. Besides the excellent fluidity, these glycerolDES systems display also a good thermal stability to nearly 200°C, which allows their applications in moderately high temperature. Performing esterification of glycerol and lauric acid in these glycerol eutectic solvents at 150°C demonstrated that, at low fatty acid concentrations and high ChCl concentrations, the monoester can be selectively produced at a significantly higher rate than in pure glycerol. The low viscosity of the glycerol eutectic solvent might play a key role in enhancing the reaction rate because the esterification has long been affected by a notorious insufficient mass transfer in pure glycerol system. Furthermore, the addition of ChCl into glycerol phase leads also to a considerably higher proportion of product in the form of the diester whereas pure glycerol results in predominantly the monoester. All these observations demonstrated that glycerol eutectic solvents possess a great potential to act as a new type of green media, with which some results that cannot be attained in conventional systems might be obtained.

Gorkeet *al.*, (2008) found that a eutectic solvent composed of ChCl and glycerol exhibited comparable activity with toluene in *i*CALB-catalyzed transesterification of ethyl valerate and 1-butanol. Surprisingly, the reaction selectivity was not detrimentally affected by glyceryl ester formation because glycerol was > 600-fold less reactive in transesterification when it was presented as a component of DES. The glycerol eutectic solvents have also been applied as potential media in the enzymatic production of biodiesel through transesterification of Miglyoloil 812 with methanol. Under optimal conditions, conversion of the triglyceride reached to 97 % within 3 h by using Novozym435 as catalyst in choline acetate/glycerol (1:1.5 molar ratio)(Zhao, *et al.*, 2011). Protease activation in glycerol-based deep eutectic solvents have also be evaluated

recently. In the 1:2 molar ratio mixture of ChCl/glycerol containing 3% (v/v) water, a cross-linked subtilisin, immobilized on chitosan, exhibited an excellent activity ( $2.9 \mu\text{mol min}^{-1} \text{g}^{-1}$ ) in the transesterification reaction of N-acetyl-L-phenylalanine ethyl ester with 1-propanol. An aqueous solution of ChCl/glycerol has been selected as a model DES solution for checking the performance a fluorescence-based high throughput screening method for directed evolution of cellulases, which aims at cost-effective hydrolysis of cellulose. All these results demonstrated that the glycerol eutectic solvents warrant further exploration as potential media in the synthesis with the aid of enzymatic catalysis(Gu, 2013).

### **2.6.2 Deep Eutectic Solvents synthesized from Potassium carbonate and glycerol**

Naseret *al* (2013) used potassium carbonate as salt ingredient in an attempt to prepare a DES with glycerol as a hydrogen bond donor. The DES was not successfully formed at molar ratio 1:1, 1:2 and 1:3 but successfully formed at molar ratio 1:3.5 and above. The DESs didn't show freezing points, instead glass transition temperatures were observed. The physical properties including density, viscosity, surface tension, refractive index, conductivity and pH were measured and reported as a function of temperature for three different molar ratios of salt to HBD. The maximum conductivity of the DESs was about 3.5 mS/cm for DES7 at 80°C. The conductivity for all DESs was very small (7.89  $\mu\text{S/cm}$ ) at 20°C. The effect of temperature is also manifested on the value of conductivity. All studied molar ratios have close conductivities at low temperatures; on the other hand, these ratios attain considerably large differences in conductivity at higher temperatures. The refractive index and surface tension values for this system are strong function of salt: HBD molar ratio and temperature. This important behavior can be used to tune the composition and temperature to be in favor of the application sought.

The DES needs to be used at relatively moderate temperatures to improve its fluidity and transport properties, because of its high viscosity, density and surface tension at room temperature, The pH values of the DESs varied with temperature in the range of 11.5-13.5 and the studied DESs ratios pH values were basic with little decreasing basicity with temperature increase. This makes it suitable for certain applications than involve basic media. It was also found that the molar composition of the DES has a pronounced effect on the physical properties.

### **2.6.3 Deep eutectic solvents (DESs) in biodiesel production**

Recently, a special class of ILs known as the deep eutectic solvents (DES) was introduced and they are believed to be a new generation of ionic liquids. The DES has received increasing interest due to their potential to be even more environmentally benign compared to the earlier traditional ILs besides also possessing equally good if not better solvation properties (Nawshad *et al.*, 2015). Deep eutectic solvents (DES) have recently attracted attention in the biodiesel production, where they can act as a catalyst, cosolvent or extracting solvent (Ivan *et al.*, 2014). DESs provide an ideal medium for the separation of the biodiesel and for the removal of the glycerol by-product (Nawshad *et al.*, 2015).

Abott *et al.*, (2007) showed that a glycerol-based deep eutectic solvent is efficient in the separation of glycerol and biodiesel from the final reaction mixture obtained from rape seed and soybean oils by ethanolsis in the presence of KOH. The most effective solvents contained quaternary ammonium salt and glycerol at a molar ratio of 1:1. The best glycerol removal was achieved using choline chloride, [ClEtMe<sub>3</sub>N]Cl, and [EtNH<sub>3</sub>]Cl. The amounts of glycerol remaining in the soya bean and rape seed biodiesels after separation using the 1:1 glycerol:cholinechloride mixture were 0.06% and 0.02%, respectively.

Hayyanet *al.* (2010) successfully used a quaternary ammonium– salt –glycerol-based deep eutectic solvent for the extraction of glycerol from crude biodiesel based on palm oil. The crude biodiesel contained 0.28% of total glycerol, which was higher than the standard limit. The best glycerol removal (51%) was achieved with the molar ratio of biodiesel to deep eutectic solvent of 1:1. In this case, the optimum composition of the deep eutectic solvent was 1:1 (salt:glycerol).

Shabazet *al.* (2010) have confirmed that deep eutectic solvents are effective in the removal of glycerol, mono– and diacylglycerols, as well as an alkali catalyst from crude biodiesel obtained from palm oil. The deep eutectic solvents were synthesized from choline chloride and methyl triphenylphosphonium bromide (MTPB) as a salt component and various hydrogen-bond donors. The mixtures of choline chloride with ethylene glycol (molar ratio of 1:2.5) or 2,2,2-trifluoroacetamide (molar ratio of 1:1.75) efficiently removed glycerol from crude biodiesel at the optimum molar ratio of deep eutectic solvent to biodiesel of 1:1 (Shahbaz, *et al.*, 2010). The deep eutectic solvents based on MTPB and ethylene glycol or triethylene glycol removed all free glycerol from crude biodiesel, while the total glycerol content was reduced below the standard limit (Shahbaz, *et al.*, 2011). Moreover, triethylene–glycol-based deep eutectic solvent (molar ratio of 1:4) removed mono- and diacylglycerols for 37.9% and 53.4% at the solvent-to-biodiesel molar ratio of 3:1 and 0.75:1, respectively. The same research group developed an artificial neural network model to predict the removal of glycerol from crude biodiesel using choline chloride- and MTPB- based deep eutectic solvents (Shahbaz, *et al.*, 2012).

The deep eutectic solvents synthesized with glycerol as a hydrogen bond donor had lower removal efficiencies than those synthesized with ethylene glycol, triethylene glycol or 2,2,2-trifluoroacetamide, and the phosphonium- based deep eutectic solvents were more efficient in removing total glycerol than the ammonium-based deep eutectic solvents. The choline

chloride:glycerol and MTPB:glycerol deep eutectic solvents were also shown to reduce KOH (around 98%) and water contents in the crude biodiesel based on palm oil below the standard limits (Shahbaz, *et al.*, 2011).

Zhao and Baker (2013) critically addressed the possibility of combining the conventional ILs with deep eutectic solvents for biodiesel production. In another study, Huang *et al.*, (2013) identified a straightforward and energy efficient method to activate commercial CaO for biodiesel production without any pretreatment by the addition of a novel DES which could easily remove the inactive layers of calcium carbonate and calcium hydroxide on the surface of the commercial CaO during the reaction to achieve a high FAME yield, while the reaction resulted in an extremely low yield without the addition of DES.

Hayyan *et al.*, (2013) used a phosphonium-based deep eutectic solvent (P-DES) followed by alkali treatment for esterification of low grade crude palm oil (LGCPO). The P-DES was added in the range from 0.25 to 3.5% (wt/wt) of reaction mixture and high catalytic activity in the pretreatment of LGCPO was noted. Hayyan *et al.*, (2013) also evaluated the ammonium-based deep eutectic solvent which consisted of hydrogen bond donor (i.e., p-toluenesulfonic acid monohydrate, PTSA) and salt (i.e., N,N-diethylenethanol ammonium chloride) as a novel recyclable catalyst (DEAC-DES) for esterification of LGCPO. The free fatty acid content of LGCPO was reduced from 9.5% to 1% using optimum conditions, could be efficiently converted to biodiesel after alkali treatment.

Ling *et al.*, (2015) introduced a novel deep eutectic solvent consisting of choline chloride (ChCl) and glycerol as the cosolvent for a base-catalyzed transesterification of rapeseed oil to produce biodiesel. The actual FAME yield of 98% was achieved under the optimized conditions. Due to

its ionic nature, the addition of DES to the transesterification reaction improved the effective dissolution of NaOH in DES/methanol mixture, enabled the capture of glycerol byproduct and other impurities, allowing FAME settled as a separate phase from the reaction mixture, which not only improve the FAME yield but also simplify the separation and purification process. This study exemplifies a cost-effective and environmental benign approach to biodiesel production by using a DES as the co-solvent in the transesterification reaction.

This work focused on the synthesis of potassium carbonate-based deep eutectic solvent and using it as catalyst in transesterification reaction of *Jatropha curcas* oil, as no work has been published on the use of deep eutectic solvent as a catalyst in transesterification reaction.

## CHAPTER THREE

### 3.0 EXPERIMENTAL PROCEDURE

#### 3.1 Materials

The *Jatropha curcas* oil was obtained from the National Research Institute for Chemical Technology NARICT, Zaria. Glycerol, methanol, and  $K_2CO_3$  were obtained from Stevemore Chemical Company, Zaria. Another  $K_2CO_3$  was obtained from Romtech Scientific Supplies Company Limited, Tukur-tukur layout, opposite Gaskiya junction, Zaria, all were of analytical grade. Apparatus used include thermometer, retort stand, pipette, measuring cylinder, separating funnel, magnetic stirrer hot plate, oven, water bath, hydrometer, conical flask, digital weighing balance, stop watch, distilled water.

#### 3.2. Characterization of the *Jatropha curcas* Oil

Viscosity, density, free fatty acid (FFA), iodine value, saponification value, acid value and saponification value were determined at National Research Institute for Chemical Technology NARICT, Zaria.

##### 3.2.1. Determination of viscosity

The viscosity of the oil was measured using brookfield rotary digital viscometer NDJ-8S at 40°C. 200 ml of the oil was poured into a beaker and spindle No 2 was attached to the viscometer, set at 60rpm, then lowered into the beaker and allow to attain same temperature with the sample. The reading at 25% shear rate was taken.

### 3.2.2. Determination of specific gravity

Density bottle was used to determine the density of the oil. A clean dry bottle of 50 mL was weighed and then filled with the oil; give  $w_0$ . The oil substituted with water after washing and drying and weighed to give  $w_1$ . The specific gravity was calculated using the formula:

$$\text{Specific gravity} = \frac{\text{mass of substance}}{\text{mass of equal volume of water}} = \frac{w_1 - w_0}{50} \dots\dots\dots(3.1)$$

### 3.2.3 Determination of free fatty acid

Free fatty acid is the percentage by weight of specified fatty acid in oil. American Oil Chemist Society (AOCS) method 5a-40 was used.

1 g of the *Jatropha*oil was dissolved in 25 mL of isopropyl alcohol in 250 mL conical flask, 3 to 4 drops of phenolphthalein indicator was then added and titrated against 0.1 M KOH. The content was constantly stirred until a pink colour which persisted for fifteen seconds was obtained. The percentage oil was then calculated using the formula:

$$\% \text{ FFA} = \frac{\text{Titre value} \times \text{Molarity of standard KOH} \times 28.2}{\text{weight of Oil}} \times 100 \dots\dots\dots(3.2)$$

### 3.2.4 Determination of acid value

This is the number of milligram of KOH required to neutralize the free fatty acid in 1g of the sample. One gram (1g) of the sample was weighed and poured into conical flask, 25ml of methanol was added with thorough stirring followed by 2 drops of phenolphthalein indicator and a drop of 0.1M KOH solution. The contents were then titrated with 0.1M KOH solution until a light pink color, which persist for 1minute was seen. The end point was recorded and used to calculate acid value as follows:

$$\text{Acid value} = \frac{\text{Titre value} \times \text{Molarity of standard KOH} \times 56.1}{\text{weight of Oil}} \times 100 \dots\dots\dots (3.3)$$

**3.2.5 Determination of iodine values**

This is measure of degree of unsaturation in relation to the amount of oil.

1 g of the oil was placed in a 250ml conical flask followed by 30ml Hanus solution and flask stoppered. The contents were mixed and placed in the dark and allowed to stay for 30 minutes, it was then titrated against a standard 0.1 N sodium thiosulphate solution until the solution became light yellow. 2 cm<sup>3</sup> of 1% starch indicator was added and titration continued until the blue colour just disappeared. A blank determination was carried out under the same conditions and the iodine value was calculated using the formula:

$$\text{Iodine value} = \frac{(\text{sample titre} - \text{blank titre}) \times \text{Normality} \times 12.69}{\text{weight of Oil}} \dots\dots\dots (3.4)$$

**3.2.6 Determination of saponification value**

Saponification value is the milligram of KOH required to saponify 1g of oil. It is a measure of the molecular weight of the fatty acid. AOCS method Cd 3-25 was the method employed. 2g of the oil was placed in 250ml conical flask and 25ml of 0.5N ethanolic potassium hydroxide solution (that has stayed overnight) was added. The mixture was then heated to saponify the oil. The unreacted KOH was back titrated against 0.5N HCl using phenolphthalein indicator. The computation of the saponification value was done using:

$$\text{Saponification value} = \frac{\text{Titre value} \times \text{Normality of HCl} \times 36.5}{\text{weight of Oil}} \text{ (Mohammed-Dabo } et al., 2012)\dots\dots(3.5)$$

### **3.3. Synthesis of the DES**

DES samples were synthesized in different molar ratios of potassium carbonate to glycerol. A magnetic stirrer hot plate (Searchtech Instrument) was used to mix the salt and the hydrogen bond donor. Each DES mixture was shaken at 400 rpm and 353 K for a period of 2 hours until a homogenous transparent colorless liquid was formed. DES samples were synthesized at atmospheric pressure and under tight control of moisture content.

### **3.4 Characterization of DES**

Viscosity and density were determined as described in 3.2.1 and 3.2.2 above. FTIR analysis was carried out in Multi-user laboratory, Department of Chemistry, Ahmadu Bello University, Zaria.

#### **3.4.1 Fourier transform infrared (FTIR) spectroscopy analysis**

FT-IR is used to determine the different functional group such as alcohol, alkane, alkynes, alkenes and other such groups present in the sample. Basically, it was applied to check the formation of hydrogen bond which indicates the formation of DES.

FTIR is a computer based program which is launched by double clicking the OMNIC icon. Number of scans, resolution and apodization (Absorbance) are selected from setup the Collect pull down menu. From the Edit pull down menu, select Options. Click on the Collect tab at the top. Click the "Collect to New Window" box to deselect it. Click OK to close window. From the Collect pull down menu, select Background (Repeat background collection every 30 min-1 hr, if the humidity is high). Also, from the Collect pull down menu, select Collect Sample Place the sample in the holder in the IR, then select Yes Add to window. Finally, from the Process pull down menu, select-Automatic Baseline Correct old spectrum shown in red and new spectrum shown in blue Click on the red one.

The FTIR spectroscopy experiments were recorded on a microlab PC software of Fourier-transform infrared spectrometer (model 630, Agilent Technology), all samples were scanned over a wavenumber range of 400-4000  $\text{cm}^{-1}$ . The spectra of the samples were recorded in 16 scans at 4  $\text{cm}^{-1}$  resolution and plotted in the transmittance mode. Prior to each measurement, the quality of the background signal was evaluated and a background spectrum was recorded using the same settings as for the sample measurement if necessary (residual peaks after cleaning > 0.2 % transmittance). The spectra presented in ESI8 were submitted to an automatic baseline correction performed with microlab PC software.

### **3.5. Reduction of the Free Fatty Acid (Esterification)**

As obtained in the test carried out on the jatropha oil, it was discovered that the free fatty acid (FFA) contents of the oil are high (6.68%). Hence, it became necessary to reduce it as follows: crude jatropha oil was poured into a conical flask and heated to a temperature of 60°C. A mixture of concentrated  $\text{H}_2\text{SO}_4$  (1% w/w) with methanol (30% v/v) was heated separately at (60°C) and then added to the heated oil in the flask. The mixture was stirred for 1 hour and allowed to settle for 2 hours.

### **3.6 Transesterification**

Forty grams (40g) of the esterified Jatropha oil was transesterified in conformity with the provision in the design layout matrix. The mole ratio of  $\text{K}_2\text{CO}_3$ /glycerol was varied from 1:20 to 1:40, time varied from 30 to 120 minutes and concentration of DES varied from 8 to 10% w/w. The mixture was stirred at 300 rpm with a magnetic stirrer hot plate (Searchtech Instrument) at a temperature of 60°C. At the completion of reaction, the reaction mixture settled into a biphasic system. Due to differences in the viscosity and density of the two products, two layers were

formed in the separating funnel. The upper layer was the biodiesel (FAME) while the lower layer consisted of crude glycerol. The separation was allowed overnight in order to purify the FAME layer from the free glycerol and other impurities which can negatively affect the final quality of biodiesel. The yield was calculated using Godlisten *et al.* (2010) formula as follows:

$$\text{Yield} = \frac{\text{weight of biodiesel produced}}{\text{weight of oil}} \times 100\% \dots\dots\dots(3.6)$$

The final product was then analyzed according to the official standard analysis methods as described under the characterization of the crude oil.

### 3.7. Experimental Design

Following the experiments described in section 3.5 and 3.6, the reaction temperature was fixed at 60°C and the agitation rate was maintained at 300 rpm in the following experiments. Response surface methodology (RSM) and Box–Behnken Design (BBD) were employed to examine the major reaction parameters (such as K<sub>2</sub>CO<sub>3</sub>/Glycerol ratio, catalyst (DES) concentration and reaction time), and to optimize the reaction conditions for achieving the maximum yield of fatty acid methyl ester (FAME). The range and levels of the parameters are listed in table 3.1 and Design Expert 6.06 software was used in the regression and graphical analyses of data. The statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA).

Table 3.1: Experimental range and level of independent variables

<b>Name</b>	<b>Unit</b>	<b>Low</b>	<b>High</b>
Mole ratio of K <sub>2</sub> CO <sub>3</sub> /glycerol (A)	-----	20.00	40.00
Concentration of the DES (B)	% w/w	8.00	10.00
Time (C)	minute	30.00	120.00

### **3.8 Characterization of Biodiesel**

The properties of the biodiesel produced such as acid value, FFA, iodine value, viscosity, density and saponification value were determined as described in 3.2 above. Then, pour point, cloud point and cetane number were also determined. GCMS analysis was carried out in multi-user laboratory, Department of Chemistry, Ahmadu Bello University, Zaria.

#### **3.8.1 Cloud point test**

The temperature at which biodiesel begins to solidify is the cloud point of the biodiesel. 10ml of biodiesel was put in a test tube and into an ice bath, a thermometer was used to note the temperature at which solidification begins.

#### **3.8.2 Pour point test**

A cylindrical test tube was filled with the biodiesel to a specific level (10ml) and clamped with a clamp bearing thermometer. The sample was then allowed to cool below 0°C in an ice bath, after which it was removed and tilted on the clamp and the set up was observed at intervals. The lowest temperature at which the biodiesel was observed to flow was recorded as the pour point.

#### **3.8.3 Cetanenumber**

Cetane number (CN) was calculated from the model reported by Demirbas (2009) using iodine value (IV) and saponification value (SV):

$$CN = 46.3 + \frac{5458}{SV} - 0.225 IV \dots\dots\dots(3.7)$$

#### **3.8.4 Gas chromatography and mass spectrometry (GC-MS)analysis:**

GC-MS was carried out to determine the percentage of methyl esters present in the biodiesel obtained from the *Jatropha curcas* oil. Two drops of the oils were converted to methyl ester using 0.5ml 2N KOH in methyl alcohol, in 1.5ml n-hexane. After each addition of solution the sample was mixed by using vortexed for 2min. Then the supernatant of the top layer containing methyl ester was extracted for GC injection.

The prepared sample was subjected to GC-MS analysis using a Gas Chromatograph (Model: 7890B, Agilent Technologies) attached with quadruple Mass Spectrometer (Model: 5977A) with a capillary column of length = 30 m, inner diameter = 0.25 mm and film thickness = 0.25  $\mu$ m. The injector column temperature was maintained at 250 °C and the oven temperature was programmed linearly. Injection mode was split type at 250 °C; total and column flow were 40.8 ml/min and 1.80 ml/min respectively at a linear velocity of 46.3 cm/sec., purge flow of 3.0 ml/min, ion source temperature 200 °C and split ratio of 1:20. The identification of the peaks was achieved by retention times by means of comparing them with authentic standards analyzed under the same conditions. Computer matching was done with the mass spectral libraries (NIST05s.LIB) provided with the computer controlling the GC-MS System.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

#### 4.1 Properties of Raw *Jatropha Curcas* Seed Oil

The properties of the *Jatropha curcas* oil, such as: iodine value, saponification value, acid value and density were all shown in the Table 4.1 and were all found to be within the specified limit. However, the viscosity (31.11 mm<sup>2</sup>/s) and free fatty acid, FFA, (6.808%) were higher than the specified limit for biodiesel production.

Viscosity is a resistance of a substance to flow or measure of the resistance of a fluid to deformation under shear stress. Kinematic viscosity is the measure of the rate at which momentum is transferred through a fluid (Fazal, 2015). According to EN 14214 Standard, kinematic viscosity of diesel fuel is the range 3.5-5.0 mm<sup>2</sup>/s at 40 °C. This value is much lower than that of *Jatropha curcas* oil. Direct usage of jatropha oil in diesel engines can cause problems in injection pump and combustion chamber, hence, the need for esterification and transesterification.

High FFA content (>1% w/w) will lead to soap formation which reduces catalyst efficiency, cause an increase in viscosity, lead to gel formation and make separation of glycerol difficult (Mohammed-Daboet *et al.*, 2012), therefore, the need for the oil to be neutralized via esterification reaction.

Table 4.1: Properties of raw *Jatropha curcas* seed oil

Property	Unit	Value	Literature Value
Free fatty acid (FFA)	%	6.808	14.8 <sup>*</sup>
Iodine value	g of Iodine/ 100g of oil	101.496	102 <sup>**</sup>
Acid value	%	13.6	28 <sup>***</sup>
Saponification value	mg KOH/ g oil	193.545	190 <sup>**</sup>
Viscosity @ 40 <sup>0</sup> C	mm <sup>2</sup> /s	31.11	29.4 <sup>***</sup>
Density	g/cm <sup>3</sup>	0.90	0.912 <sup>**</sup>

Sources ( <sup>\*</sup> Mohammed-Dabo *et al.*, 2012, <sup>\*\*</sup> Joshua2013, <sup>\*\*\*</sup> Dennis *et al.*, 2010)

#### 4.2 Synthesis and Characterization of DES

Different molar ratios of glycerol to potassium carbonate were used to prepare the DESs. Table 4.2 shows these ratios along with their abbreviations and observations during the preparation process.

DES1 to DES8 were not successful as the two components did not form DES as the products were in either turbid white liquid or a mixture of colorless liquid and solid throughout the process and after cooling to room temperature. Although, Naseer *et al.*, (2013), reported formation of successful DESs at those mole ratios, the presence of solid particles in the mixture might be attributed to some impurities present in the salt which cannot build hydrogen bonds with the hydrogen bond donor.

During the synthesis stage, DESs samples were formed in a white viscous gel within the first 30 min. After 60 min of mixing, a liquid phase started to appear with some precipitation. Therefore, the period of mixing was extended to 120 min in order to get a homogenous liquid phase DES.

Adding more glycerol achieved the necessary balance between the two DES constituents and guaranteed complete miscibility.

DES9, DES 10 and DES11 remained in colorless liquid phase at room temperature, and the unsuccessful DESs were not considered for further investigation.

Table 4.2: Mole ratio and abbreviations of DES synthesized

<b>Mole Ratio</b>	<b>Abbreviation</b>	<b>Appearance</b>
1:3.5	DES 1	turbid white liquid
1:4	DES 2	turbid white liquid
1:5	DES 3	turbid white liquid
1:6	DES 4	turbid white liquid
1:7	DES 5	colorless liquid with solids
1:8	DES 6	colorless liquid with solids
1:9	DES 7	colorless liquid with solids
1:10	DES 8	colorless liquid with solids
1:20	DES 9	colorless liquid
1:30	DES 10	colorless liquid
1:40	DES 11	colorless liquid

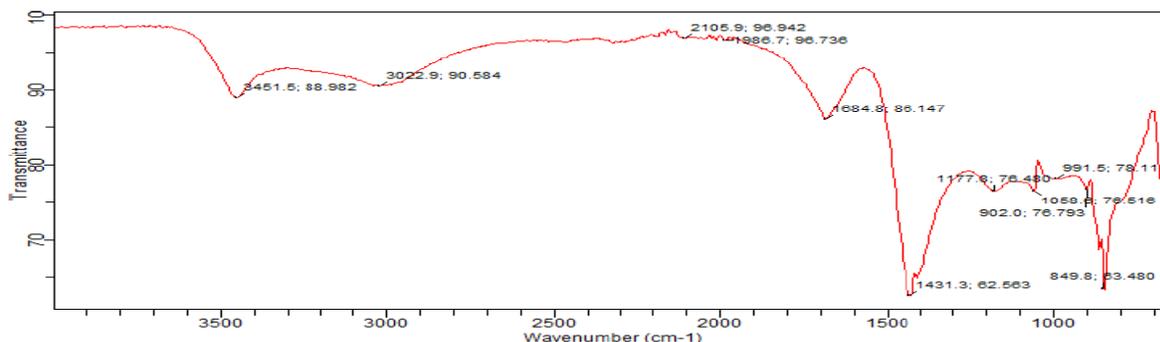
Viscosity, density and pH of the synthesized DES were displayed Table 4.3. The pH is important in applications related to catalytic reactions. pH of 10.53 was obtained, which dictates the basicity of the mixture. Hence, when the DES is used as catalyst, the reaction will follow nucleophilic transesterification mechanism. The density and viscosity found, conform with those reported by Naseer *et al.* (2013)

Table 4.3: Properties of DES synthesized.

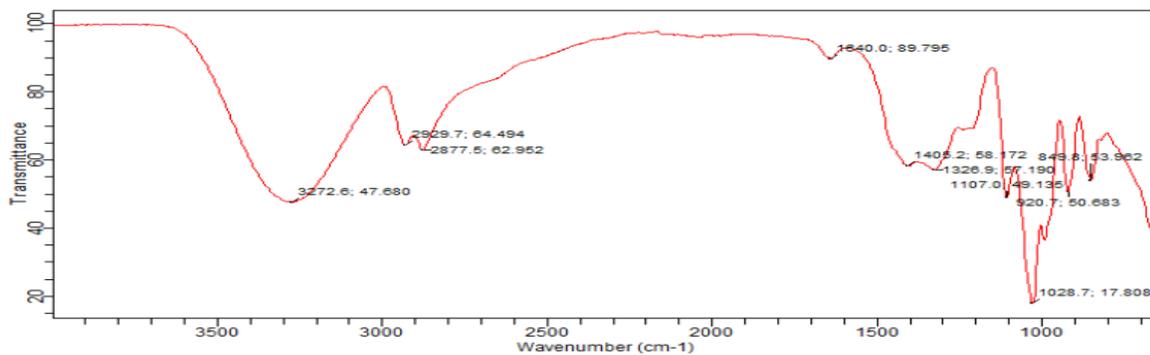
Property	DES synthesized	Literature value
Viscosity @ 40 <sup>0</sup> C	0.428 Pa.s	0.4 Pa.s*
Density	1.322g/mL	1.36 g/mL*
pH	10.53	10.64*

Source (\*Naseeret *al.*,2013)

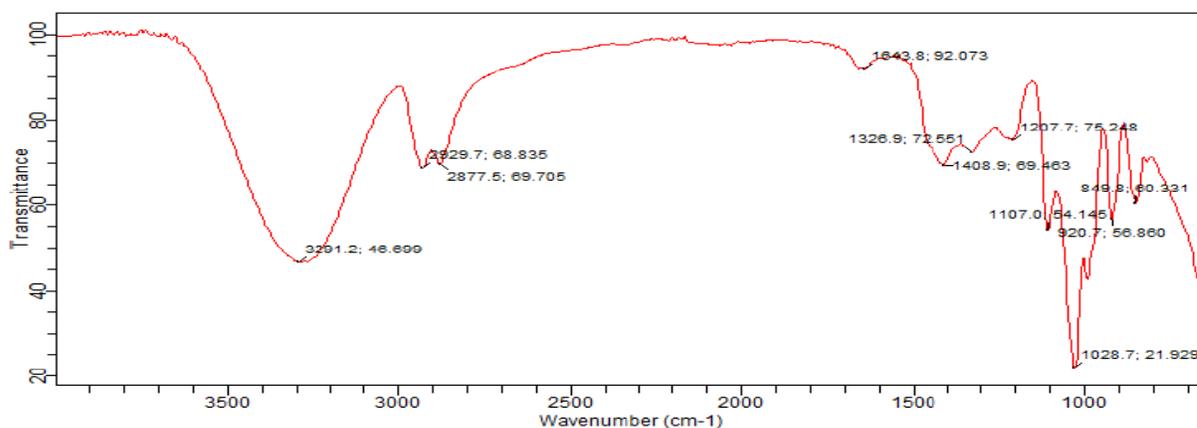
The formation of proton transfer salts was revealed by the observed FT-IR spectra. The presence of O–H stretching bands between 3200 and 3500 cm<sup>-1</sup> in the spectrum figures was attributed to hydroxyl group. Figure 4.1 reveals that a shift in the OH stretching vibration of glycerol occurred when the DES was formed (3291.2 cm<sup>-1</sup>). This in agreement with the observation reported in the literature. The FT-IR spectra of the glycerol in the DES indicate that the change in vibrational state occurred because a portion of the cloud of electrons of the oxygen atom was transferred to the hydrogen bond, reducing the force constant. Thus, the shift of the OH stretching vibration indicated the existence of a hydrogen bond between the glycerol and K<sub>2</sub>CO<sub>3</sub> when the DES was formed. The region between 3000 and 2800 cm<sup>-1</sup> shows the existence of C–H stretching bands of the alkanes CH<sub>3</sub> and CH<sub>2</sub> for the DES as shown in the table 4.4.



(a)



(b)



(c)

Figure 4.1: FT-IR result of (a)  $K_2CO_3$ , (b) Glycerol, and (c) DES

Table 4.4: Functional groups coming from DES

Functional group	Wave band	$K_2CO_3$ Wave number ( $cm^{-1}$ )	Glycerol Wave number ( $cm^{-1}$ )	DES Wave number ( $cm^{-1}$ )
O-H (stretching)	3200-3400	3451.5	3272.6	3291.2
$sp^3$ hybridized C-H (stretching)	2850-3000	3022.9	2877.0	2877.5
C-O (stretching) in 2° alcohol	1085-1125	1177.8	1106.8	1107.0

### 4.3 Reduction of FFA

Table 4.5 shows how the FFA were reduced after the first 3 hours to 2.427%, after 4 hours to 1.112% and after 6 hours to 0.409% which is within the range (0 – 0.5%) of standard oil for the production of biodiesel.

Table 4.5: Reduction of FFA (esterification)

S/No	Time (min)	FFA (%)
1	0	6.808
2	180	2.427
3	240	1.122
4	360	0.409

1% w/w conc. H<sub>2</sub>SO<sub>4</sub> and 30% v/v methanol at 60<sup>0</sup>C and 400rpm.

### 4.4 Production of Biodiesel Using the DES as Catalyst

The transesterification of *Jatropha curcas* oil with methanol was carried out at ratio 1:6 oil/methanol molar ratio using K<sub>2</sub>CO<sub>3</sub>/glycerol DES as the catalyst. The reaction temperature was fixed at 60<sup>0</sup>C and the agitation rate was maintained at 300 rpm. The ranges of key reaction parameters (i.e., K<sub>2</sub>CO<sub>3</sub>/glycerol molar ratio, catalyst concentration and reaction time) are listed in Table 4.6. As shown in Table 4.6, FAME yields in the range of 88.97–98.15% could be achieved at different reaction conditions.

Table 4.6: Design layout for the transesterification reaction

Std	Run	Mole ratio of K <sub>2</sub> CO <sub>3</sub> /glycerol	Conc. Of DES (%w/w)	Time (min)	Yield of Biodiesel (%)
1	1	20.00	8.00	75.00	88.98
4	2	40.00	10.00	75.00	95.80
15	3	30.00	9.00	75.00	97.67
17	4	30.00	9.00	75.00	98.15
12	5	30.00	10.00	120.00	96.35
2	6	40.00	8.00	75.00	95.45
5	7	20.00	9.00	30.00	88.97
10	8	30.00	10.00	30.00	96.45
14	9	30.00	9.00	75.00	98.15
7	10	20.00	9.00	120.00	89.65
8	11	40.00	9.00	120.00	96.39
11	12	30.00	8.00	120.00	95.90
6	13	40.00	9.00	30.00	94.90
9	14	30.00	8.00	30.00	94.475
13	15	30.00	9.00	75.00	97.93
16	16	30.00	9.00	75.00	98.10
3	17	20.00	10.00	75.00	91.32

#### 4.4.1 Modified quadratic model for transesterification process

A quadratic polynomial equation in terms of actual factors was generated to fit the experimental data using response surface methodology as shown below.

$$\% \text{ Biodiesel Yield} = +98.00 + 2.95A + 0.64B + 0.44C - 4.21A^2 - 0.90B^2 - 1.31C^2 - 0.50AB + 0.20AC - 0.38BC \dots\dots\dots 4.1$$

Where:

A is the mole ratio of potassium carbonate/glycerol,

B is the conc. of DES and

C is the reaction time

The analysis of variance (ANOVA) in Table 4.7 suggests that a second-order polynomial model (Equation 1) appears to better represent the correlation between the response and the significant variables. A very high F value (204.13) and a small p-value (<0.0001) indicate significance of the regression model (A, B, C, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup> are significant model terms). A satisfactory determination coefficient (R<sup>2</sup> = 0.9962) suggests that the sample variation of 99.62% for biodiesel production can be attributed to the independent variables (i.e., K<sub>2</sub>CO<sub>3</sub>/glycerol molar ratio, catalyst concentration and reaction time) and only 0.38% of the total variations are not explained by the model (Ling *et al.*, 2015).

To confirm the model validity, the model prediction was compared with experimental data as shown in Figure 4.2. It was found that the model was successful in capturing the correlation between the process parameters to the response with a correlation coefficient. The high value of adjusted determination coefficient (Adj.R<sup>2</sup> = 0.9913) further confirms the significance of the model, and a relatively low value of variation coefficient (CV = 0.32%) indicates a high precision and reliability of our experimental data. The adequate precision higher than 4 confirms the adequacy of model by measuring the signal to noise ratio.

Table4.7: ANOVA for selected factorial model

Source	Sum of squares	DF	Mean squares	F Value	Prob > F
Model	167.03	9	18.57	204.13	< 0.0001 significant
A	69.74	1	69.74	766.80	< 0.0001
B	3.27	1	3.27	35.96	0.0005
C	1.53	1	1.53	16.79	0.0046
A <sup>2</sup>	74.78	1	74.78	822.27	< 0.0001
B <sup>2</sup>	3.40	1	3.40	37.34	0.0005
C <sup>2</sup>	7.21	1	7.21	79.22	<0.0001
AB	0.99	1	0.99	10.89	0.0131
AC	0.16	1	0.16	1.80	0.2212
BC	0.58	1	0.58	6.39	0.0393
Residual	0.64	7	0.091		
Lack of Fit	0.47	3	0.16	3.70	0.1195 not significant

Table 4.8: Predicted and adjusted R-squared

Std. Dev.	0.30	R-Squared	0.9962
Mean	94.98	Adj R-Squared	0.9913
C.V.	0.32	Pred R-Squared	0.9538
PRESS	7.75	Adeq Precision	39.784

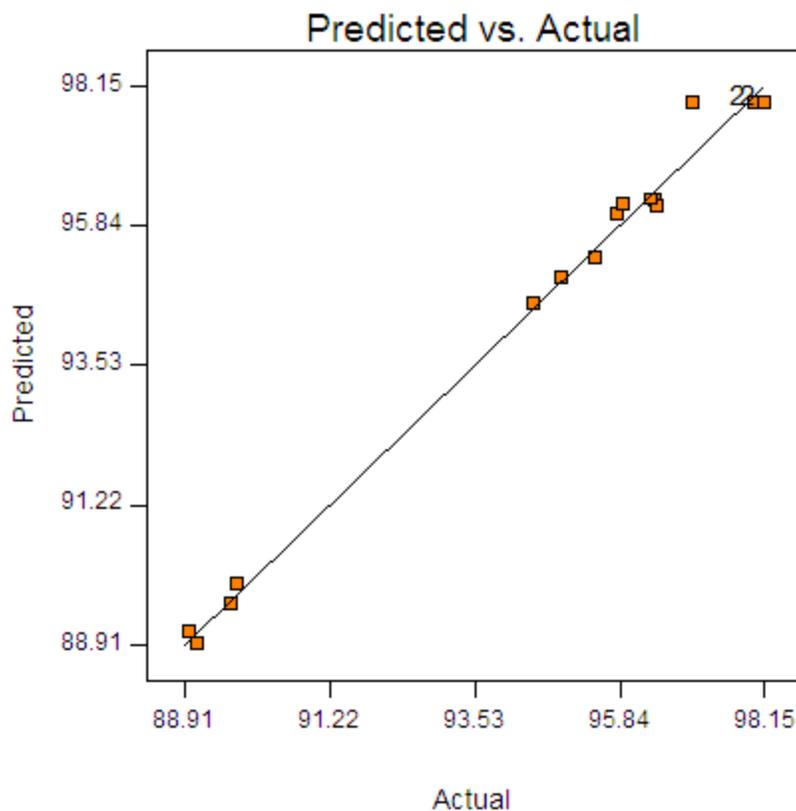


Figure 4.2: Plot of predicted yield against experimental yield

Figures 4.3, 4.4 and 4.5 present the three-dimensional graphs of a second-order prediction model for the FAME yield response. As seen from Figures 4.3 and 4.4, the FAME yield sharply increased when the mole ratio of  $K_2CO_3$ /glycerol increased to its mid-range. This is in line with our results in Table 4.7 (mole ratio of  $K_2CO_3$ /glycerol has the largest determined F-value and the smallest p-value). This is attributed to the fact that the amount of salt added to the glycerol plays a significant role in the formation of hydrogen bonding which can lead to better activity of the DES as catalyst in the transesterification reaction. When excess mole ratio is used, it indicates that the amount of salt is in excess to the corresponding hydrogen bond donor which results in

the precipitation of the extra amount of salt which cannot build hydrogen bonds with the hydrogen bond donor (Naseret *al*, 2013).

Reaction time is also an important operating parameter due to its direct effect on the cost and quality of biodiesel. Sufficient but not excessive reaction time must be provided to achieve a complete and perfect reaction. The transesterification reaction time was optimized in the range of 30–120min as shown in Figures 4.4 and 4.5. There is no significant effect on the yield after 75min of reaction time.

Figures 4.3 and 4.5 also show that FAME yield increases as the concentration of the catalyst (DES) increases. A low catalyst dosage does not produce sufficient methoxide to afford a high FAME yield. An excess catalyst dosage does not lead to a high yield due to possible side reactions such as saponification (Ling *et al.*, 2015). Hence, the region of the optimum concentration was shown in the Figures 4.3 and 4.5.

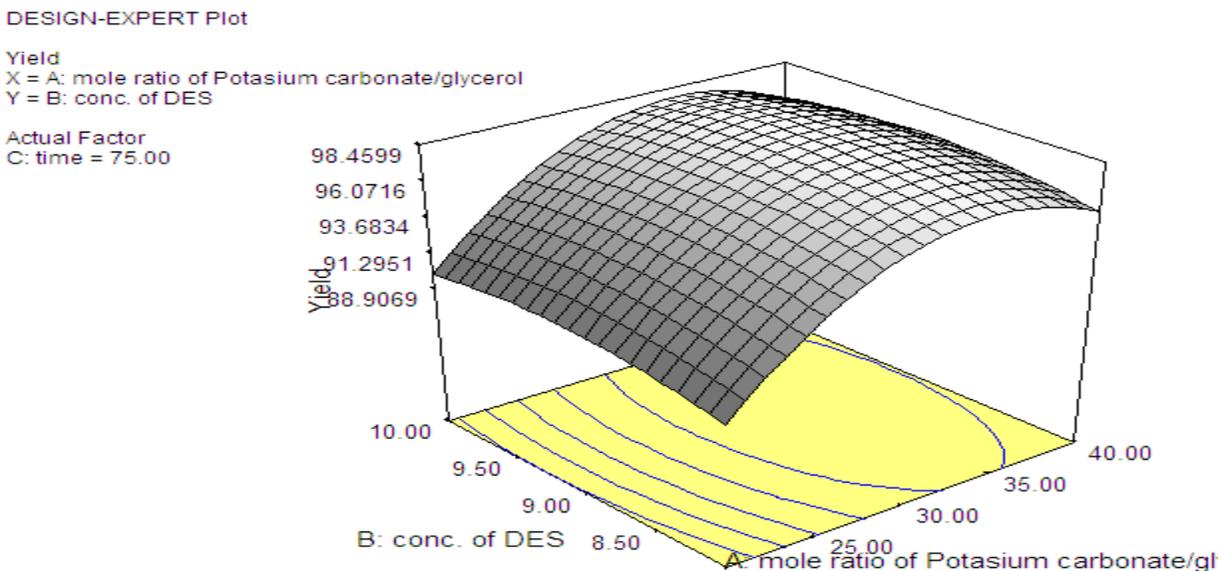


Figure 4.3: 3D response surface plot between  $K_2CO_3$ -glycerol mole ratio and conc. of DES interaction

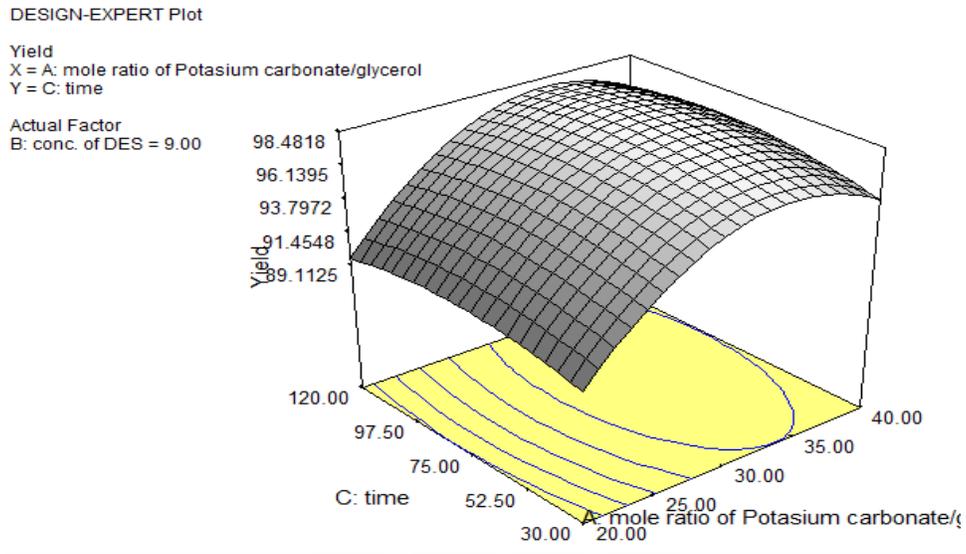


Figure 4.4: 3D response surface plot between  $K_2CO_3$ -glycerol mole ratio and time interaction

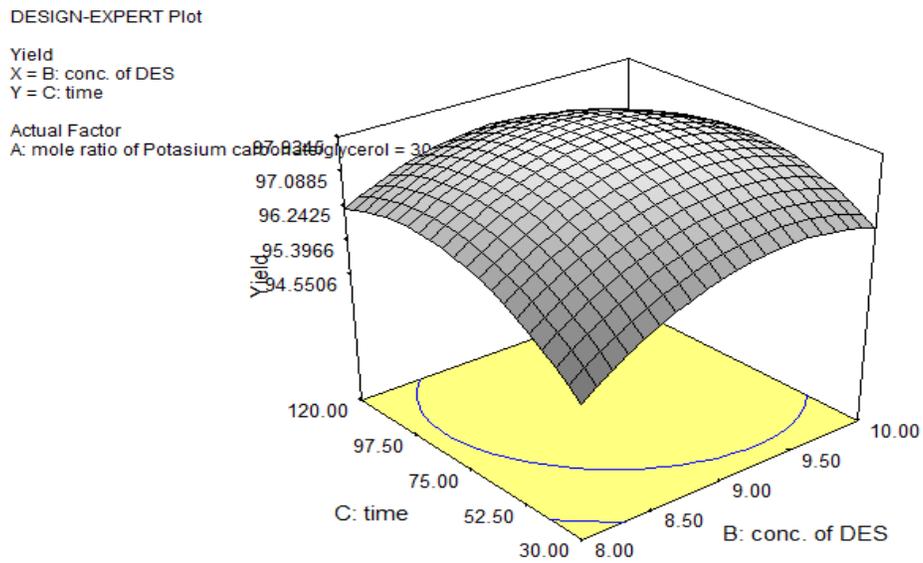


Figure 4.5: 3D response surface plot between time and conc. of DES interaction

#### 4.5 Optimization Solution

Maximizing the yield is one of the major goal of optimization process. Table 4.9 shows various solutions of optimization. As mentioned earlier, time and concentration of catalyst have direct effect on the cost and quality of biodiesel. In this case, the mole ratio of  $K_2CO_3$ /glycerol also has a great effect on yield of the biodiesel, therefore, mole ratio of  $K_2CO_3$ /glycerol of 1:32.58, concentration of DES of 8.96% w/w and time of 69.58min were selected as the optimum conditions.

Table 4.9: Solutions for optimization

<b>mole ratio of Potasium carbonate/glycerol</b>	<b>conc. of DES (%w/w)</b>	<b>Time (min)</b>	<b>Yield of Biodiesel</b>	<b>Desirability</b>	
34.96	8.63	84.67	98.1643	1.000	
32.13	8.84	74.77	98.2353	1.000	
33.79	9.20	103.67	98.3144	1.000	
35.31	9.41	65.35	98.1606	1.000	
34.22	8.69	103.56	98.1709	1.000	
33.69	8.77	99.53	98.2959	1.000	
34.69	8.84	80.65	98.3464	1.000	
32.58	8.96	69.58	98.2845	1.000	<u>Selected</u>
35.66	8.81	95.63	98.2006	1.000	
34.34	8.76	85.51	98.3365	1.000	

The numerical optimization predicts that the maximum FAME yield of 98.2845% could be achieved at 1:32.58 mole ratio of  $K_2CO_3$ /glycerol, 8.96% w/w concentration of DES and 69.58minutes. Further experimental examinations at the suggested optimum conditions were carried out and obtained the FAME yield of 98.20%, 98.20%, 98.22% and average of 98.207%, which was in a good agreement with the predicted value based on RSM. The relative error between the predicted and actual data was 0.0789%, suggesting the optimization of DES-catalyzed preparation of biodiesel from jatropha oil was successfully developed by BBD and RSM.

Table 4.10: Optimized conditions and validation for transesterification process

Predicted optimal conditions and yield			
A(mole ratio)	B (wt.%)	C(min)	Yield (%)
32.58	8.96	69.58	98.2845
Actual experiments (validations)			
Yield 1 (%)	Yield 2 (%)	Yield 3 (%)	Average yield (%)
98.20	98.20	98.22	98.207
Predicted yield (%)		Actual yield (%)	Deviation
98.2845		98.207	± 0.1%

#### 4.6 Reuse of the Catalyst (DES)

Table 4.11 shows the various yields obtained from DES (98.22%), K<sub>2</sub>CO<sub>3</sub> (84.0%), DES from the first run (71.98%), DES from the second run (53.24%) and there was no conversion when crude glycerol was used. The amount of the DES added is shown in the appendix A.

The ability to reuse the DES is a positive improvement towards reducing the production cost of a process. Catalytic activity is an important parameter for the DES that is used as catalyst. Table 4.11 summarized the performance of reused DES in transesterification process. There was significant change in catalytic activity of DESs after they have been reused for the second and third times. The decline in the DES catalytic activity may be caused by deactivation of hydrogen bond in the DES, inability to separate the DES from the reaction by-product especially the glycerol, and the presence of unreacted components in DES. There was a decrease in the yield of FAME after the DES was used twice from 98.22 to 53.24%.

Table 4.11: Comparison of the catalytic activity of DES, reused DES and other catalysts at optimized conditions.

S/No	Catalyst	Yield (%)
1	DES	98.22
2	K <sub>2</sub> CO <sub>3</sub>	84.0
3	DES from run 1	71.98
4	DES from run 2	53.24
5	Glycerol	0.00

Other DESs were attempted to be synthesized from the first and second transesterification by-products at the optimized conditions. The by-product was assumed to contain only glycerol and a calculated amount of  $K_2CO_3$  was added to make another DES, but Table 4.12 showed that DESs were not successfully formed. This may be attributed to unreacted methanol and other impurity in the by-product.

Table 4.12: DES from the by-product at optimized condition

Component	Initial Weight of glycerol (g)	Final Weight of glycerol (g)	Abbreviation	Appearance
DES from run 1 + $K_2CO_3$	1.713	6.333	DES 12	turbid brown liquid
DES from run 2 + $K_2CO_3$	1.713	6.654	DES 13	turbid dark brown liquid

#### 4.7 Properties of the Biodiesel Produced

Some properties of the jatropha oil biodiesel produced are presented in Table 4.13 and are placed with the corresponding limit set for (ASTM D6751) biodiesel standard.

Viscosity is of utmost importance in fuels because it affects the atomization of the fuel being injected into the engine combustion chamber (Joshua, 2012). The viscosity ( $4.27 \text{ mm}^2/\text{s}$ ) of the biodiesel produced is within the range as given by ASTM standards for biodiesels.

The density of a fuel is another important factor for good engine performance; the higher the density, the more difficult it becomes to pump the fuel. The density of the biodiesel produced was  $0.882 \text{ g/cm}^3$ ; this falls within the range of the standard.

Cetane number is another important property of fuels; this is a measure of the combustion quality of a diesel during compression ignition. The ignition quality, as a result of the cetane number, affects engine performance, cold starting, warm up, and engine combustion roughness. Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion (Joshua, 2012). The biodiesel produced has a value of 51.18, which is well within range; it is hence suitable to run in diesel engines.

Acid value is the number of milligram of KOH required to neutralize the free fatty acid in 1g of the oil. 0.74mg KOH/g of oil was obtained and it conforms to the ASTM standard.

Pour point is the temperature below which the fuel will not flow. The pour point obtained for the jatropha oil biodiesel was  $-2^{\circ}\text{C}$  which is in agreement with ASTM D6751 standard of  $-15 - 16^{\circ}\text{C}$ .

Cloud point is the temperature at which the biodiesel began to solidify.  $10^{\circ}\text{C}$  was obtained as the cloud point for the jatropha oil biodiesel which is in agreement with ASTM D6751 standard of  $-3 - 16^{\circ}\text{C}$ .

Although ASTM does not give limitation for saponification value and iodine value of biodiesel, these properties of the biodiesel produced were very close to those reported by Mohammad-Daboet *al.* (2012).

GC-MS analysis reveals that the biodiesel produced contains 98.87% ester content and 1.13% non-ester composition. This further confirms the quality of the jatropha oil biodiesel produced. The GC-MS result is also shown in appendix B.

Table 4.13: Physical properties of *Jatropha* oil biodiesel

Property	Produced Biodiesel	ASTM D6751 STANDARD
Density at 40 <sup>0</sup> C (g/cm <sup>3</sup> )	0.882	0.86–0.90
Viscosity at 40 <sup>0</sup> C (mm <sup>2</sup> /s)	4.27	1.6 –6.0
Acid value (mg KOH/g)	0.74	≤ 0.8
Cetane number	51.18	≥ 47
Pour point <sup>0</sup> C	-2	-15 to 16
Cloud point <sup>0</sup> C	10	-3.0 to 12
Iodine value (mg I/100g oil)	104.133	-----
Saponification value (mg KOH/g oil)	192.8	-----

Table 4.14: GC-MS of *Jatropha* oil biodiesel

Peak No	Name of the compound	Molecular formula	Retention time (min)	Peak Area (%)
1	Dodecanoic acid, methyl ester	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	24.408	0.03
2	Methyl tetradecanoate	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	29.271	0.09
4	Hexadecanoic acid, methyl ester	C <sub>17</sub> H <sub>32</sub> O <sub>2</sub>	33.791	16.38
5	Heptadecanoic acid, methyl ester	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	35.717	0.22
6	8,11-Octadecadienoic acid, methyl	C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	37.332	30.43
7	9-Octadecenoic acid, methyl ester	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	37.479	22.44
8	Methyl stearate	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	37.797	8.96
9	9,12-Octadecadienoic acid, ethyl ester	C <sub>20</sub> H <sub>36</sub> O <sub>2</sub>	38.392	0.08
10	Oleic Acid*	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	39.908	0.30
11	Glycidylpalmitate	C <sub>19</sub> H <sub>36</sub> O <sub>3</sub>	40.857	4.94
12	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	C <sub>21</sub> H <sub>40</sub> O <sub>4</sub>	43.125	2.72
13	Glycidyloleate	C <sub>21</sub> H <sub>38</sub> O <sub>3</sub>	43.987	9.99
14	Adipic acid, butyl 3-heptyl ester	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	44.154	0.85
15	6-Octadecenoic acid, (Z)-*	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	44.571	0.50
16	Docosanoic acid, methyl ester	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	44.721	0.21
17	Tetracosanoic acid, methyl ester	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	47.856	1.52
22	2,2-Dimethyl-3-(3,7,16,20-tetramethyl-heneicosa-3,7,11,15,19-pentaenyl)-oxirane*	C <sub>29</sub> H <sub>48</sub> O	49.525	0.34
<b>Total composition</b>				<b>100</b>
<b>Total Non-ester content (*)</b>				<b>1.13</b>
<b>Total ester content</b>				<b>98.87</b>

\* indicates non-ester compounds

## CHAPTER FIVE

### 5.0 CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

From the results of this investigation, the following conclusions were made:

1.  $K_2CO_3$  was used as the salt ingredient in an attempt to prepare a DES with glycerol as a HBD, and it was found that the DES can serve as a promising catalyst in the transesterification reaction of *Jatropha curcas* oil with yield of 98.22%.
2. Mole ratio of  $K_2CO_3$ /glycerol of 1:32.58, concentration of DES of 8.96% w/w and time of 69.58 minutes were selected as the optimum conditions for the transesterification reaction.
3. There is increase in yield of biodiesel by 16.93% when compared with use of only  $K_2CO_3$ .
4. The catalyst (DES) was utilized in a reusability studies, the catalyst produced 53.24% yield of the biodiesel after the third run.
5. GC-MS analysis revealed that the biodiesel contains 98.87% ester content and 1.13% non-ester composition.
6. The fuel properties of *Jatropha* oil biodiesel produced agreed with the ASTM D6751-12 standard.

## 5.2 Recommendations

The following recommendations are made with respect to this work:

1. The kinetics of transesterification of *jatropha curcas* oil using DES as catalyst should be looked into.
2. Since using deep eutectic solvents (synthesized from  $K_2CO_3$ ) as catalyst is found to be effective in transesterification reaction, it should be further studied for extension and scale-up of the process.
3. Full characterization should be carried out on the used catalyst to establish how much of its properties changed during the reaction.

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## APPENDIX A

### Synthesis of DES

Molar mass of  $K_2CO_3 = 138\text{g/mol}$ ,

Melting point of  $K_2CO_3 = 1164.15\text{K}$ ,

Freezing point of  $K_2CO_3 = 891^{\circ}\text{C}$

Molar mass of glycerol =  $92.09\text{g/mol}$ ,

Specific gravity of glycerol = 1.261,

Freezing point of glycerol =  $18^{\circ}\text{C}$

$K_2CO_3$  : Glycerol

138g    92.02g

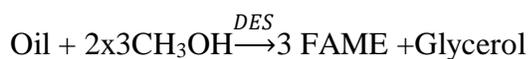
$$\frac{138}{138} \frac{92.02}{138}$$

1mol    0.667mol

1g         $3.5 \times 0.667 = 2.3345\text{g}$

From the literature, molar mass of jatropha oil =  $874\text{g}$ , molar mass of FAME =  $295.833\text{g}$

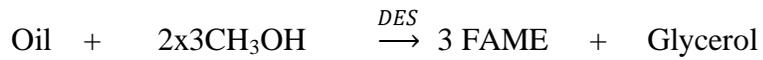
Theoretically,



874g                   $2 \times 3 \times 32.04$                    $3 \times 295.833\text{g}$                   92.1g

874g	192.24g	887.5g	92.1g
1	0.10998	1.015	0.105

From the experiment, at 1: 6 oil/methanol ratio



1	0.10998	1.015	0.105
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20g	4.399g	weight of DES = 1.8g	9.64g	4.62g
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Assuming the weight of the DES at end of the reaction does not change

Weight of the glycerol produced =  $4.62 - 1.8 = 2.82\text{g}$

1g of  $\text{K}_2\text{CO}_3$  was mixed with 21.731g of glycerol, at optimized conditions

xg of  $\text{K}_2\text{CO}_3$  will be mixed with 2.82g of glycerol

$$x = \frac{2.82 \times 1}{21.731} = 0.13\text{g}$$

Mass of  $\text{K}_2\text{CO}_3$  to be added to the by-product to produce another DES = 0.13g

## APPENDIX B

### GC-MS ANALYSIS OF BIODIESEL PRODUCED

MULTI-USER SC. RES. LAB. ABUZ Library Search Report

Data Path : D:\MassHunter\GCMS\1\data\28220178\

Data File : 28220171.D

Acq On : 28 Feb 2017 23:37

Operator : Multi-User Science Research Laboratory

Sample : Biodiesel

Misc :

ALS Vial : 8 Sample Multiplier: 1

Search Libraries: D:\MassHunter\Library\NIST14.L Minimum Quality: 0

Unknown Spectrum: Apex

Integration Events: ChemStation Integrator - autoint1.e

Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	24.408	0.03	D:\MassHunter\Library\NIST14.L			
			Dodecanoic acid, methyl ester	78067	000111-82-0	98
			Undecanoic acid, 10-methyl-, methyl ester	78103	005129-56-6	95
			Dodecanoic acid, methyl ester	78066	000111-82-0	95
2	29.271	0.07	D:\MassHunter\Library\NIST14.L			
			Methyl tetradecanoate	104286	000124-10-7	98
			Methyl tetradecanoate	104287	000124-10-7	98
			Methyl tetradecanoate	104289	000124-10-7	97
3	31.369	0.02	D:\MassHunter\Library\NIST14.L			
			Hexadecanal	102561	000629-80-1	95
			Pentadecanal-	89765	002765-11-9	95
			Tetradecanal	76509	000124-25-4	94
4	31.521	0.02	D:\MassHunter\Library\NIST14.L			
			Methyl 13-methyltetradecanoate	117456	1000336-31-4	95
			Pentadecanoic acid, methyl ester	117468	007132-64-1	95
			Methyl 9-methyltetradecanoate	117450	213617-69-7	94
5	32.934	0.07	D:\MassHunter\Library\NIST14.L			
			Dodecanoyl chloride	81373	000112-16-3	35
			Undecanoyl chloride	68093	017746-05-3	35
			Tetradecanedioic acid	118874	000821-38-5	35

6 33.156 0.05 D:\MassHunter\Library\NIST14.L  
Methyl hexadec-9-enoate 128645 010030-74-7 99  
9-Hexadecenoic acid, methyl ester, 128693 001120-25-8 99  
(Z)-  
7-Hexadecenoic acid, methyl ester, 128697 056875-67-3 99  
(Z)-

7 33.253 0.87 D:\MassHunter\Library\NIST14.L  
9-Hexadecenoic acid, methyl ester, 128693 001120-25-8 99  
(Z)-  
9-Hexadecenoic acid, methyl ester, 128700 001120-25-8 99  
(Z)-  
7-Hexadecenoic acid, methyl ester, 128697 056875-67-3 99  
(Z)-

8 33.791 15.46 D:\MassHunter\Library\NIST14.L  
Hexadecanoic acid, methyl ester 130813 000112-39-0 99  
Hexadecanoic acid, methyl ester 130821 000112-39-0 99  
Hexadecanoic acid, methyl ester 130820 000112-39-0 98

9 35.063 0.08 D:\MassHunter\Library\NIST14.L  
9,17-Octadecadienal, (Z)- 125003 056554-35-9 92  
9,12-Octadecadienoic acid (Z,Z)- 140138 000060-33-3 76  
1,5,9,13-Tetradecatetraene 56133 051487-38-8 72

10 35.175 0.08 D:\MassHunter\Library\NIST14.L  
13-Octadecenal, (Z)- 126830 058594-45-9 98  
E,E-2,13-Octadecadien-1-ol 126835 1000131-09-8 92  
cis-11-Hexadecenal 100562 053939-28-9 91

11 35.258 0.08 D:\MassHunter\Library\NIST14.L  
cis-10-Heptadecenoic acid, methyl ester 142127 1000333-62-1 99  
(Z)-Methyl heptadec-9-enoate 142098 014101-91-8 98  
Methyl 8-heptadecenoate 142082 1000336-36-4 95

12 35.717 0.14 D:\MassHunter\Library\NIST14.L  
Hexadecanoic acid, 14-methyl-, methyl ester 144335 002490-49-5 99  
Heptadecanoic acid, methyl ester 144319 001731-92-6 98  
Heptadecanoic acid, methyl ester 144315 001731-92-6 98

13 37.332 30.32 D:\MassHunter\Library\NIST14.L  
9,12-Octadecadienoic acid (Z,Z)-, 153889 000112-63-0 99  
methyl ester  
8,11-Octadecadienoic acid, methyl 153872 056599-58-7 99  
ester  
10,13-Octadecadienoic acid, methyl 153881 056554-62-2 99  
ester

14 37.479 22.44 D:\MassHunter\Library\NIST14.L  
9-Octadecenoic acid, methyl ester, 155754 001937-62-8 99  
(E)-  
9-Octadecenoic acid, methyl ester, 155758 001937-62-8 99  
(E)-  
8-Octadecenoic acid, methyl ester, 155753 026528-50-7 99  
(E)-

15 37.797 8.96 D:\MassHunter\Library\NIST14.L  
Methyl stearate 157885 000112-61-8 99  
Methyl stearate 157884 000112-61-8 99  
Methyl stearate 157883 000112-61-8 99

16 38.071 0.03 D:\MassHunter\Library\NIST14.L  
9,17-Octadecadienal, (Z)- 125003 056554-35-9 97  
10,13-Octadecadienoic acid, methyl 153881 056554-62-2 93  
ester  
9,12-Octadecadienoic acid, methyl 153894 002566-97-4 90  
ester, (E,E)-

17 38.392 0.03 D:\MassHunter\Library\NIST14.L  
10,13-Octadecadienoic acid, methyl 153881 056554-62-2 97  
ester  
9,12-Octadecadienoic acid, ethyl e 167389 007619-08-1 96  
ster  
9,12-Octadecadienoic acid (Z,Z)-, 153891 000112-63-0 96  
methyl ester

18 38.480 0.05 D:\MassHunter\Library\NIST14.L  
(E)-9-Octadecenoic acid ethyl este 169327 006114-18-7 90  
Ethyl Oleate 169275 000111-62-6 83  
9-Octadecenoic acid, (E)- 142089 000112-79-8 83

19 38.875 0.08 D:\MassHunter\Library\NIST14.L  
Methyl 9-cis,11-trans-octadecadien 153865 1000336-44-0 99  
oate  
Methyl 10-trans,12-cis-octadecadie 153874 1000336-44-2 99

noate

9,12-Octadecadienoic acid, methyl ester, (E,E)- 153894 002566-97-4 97

20 39.277 0.03 D:\MassHunter\Library\NIST14.L  
Palmitoleic acid 115311 000373-49-9 74  
cis-Vaccenic acid 142073 000506-17-2 62  
cis-10-Nonadecenoic acid 155709 073033-09-7 62

21 39.908 0.07 D:\MassHunter\Library\NIST14.L  
9-Octadecenoic acid, (E)- 142089 000112-79-8 55  
16-Hexadecanoyl hydrazide 130649 002619-88-7 50  
Oleic Acid 142072 000112-80-1 50

22 40.022 0.16 D:\MassHunter\Library\NIST14.L  
Hexatriacontyl pentafluoropropionate 274663 1000351-89-0 25  
Octatriacontyl pentafluoropropionate 275090 1000351-89-1 25  
Tetratriacontylheptafluorobutyrate 274999 1000351-84-1 25

23 40.502 0.18 D:\MassHunter\Library\NIST14.L  
cis-11-Hexadecenal 100562 053939-28-9 94  
9-Eicosenoic acid, (Z)- 169286 029204-02-2 91  
9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester 210570 003443-84-3 81

24 40.587 0.08 D:\MassHunter\Library\NIST14.L  
Methyl 9.cis.,11.trans,t,13.trans.-octadecatrienoate 152039 1000336-42-6 97  
Methyl 6-cis,9-cis,11-trans-octadecatrienoate 152023 1000336-37-7 78  
9,12,15-Octadecatrienoic acid, methyl ester 152022 007361-80-0 58

25 40.660 0.09 D:\MassHunter\Library\NIST14.L  
Methyl 9.cis.,11.trans,t,13.trans.-octadecatrienoate 152039 1000336-42-6 83  
9,12,15-Octadecatrienoic acid, methyl ester 152022 007361-80-0 58  
9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)- 152042 000301-00-8 58

26 40.857 2.74 D:\MassHunter\Library\NIST14.L  
Glycidylpalmitate 171251 1000383-37-8 91  
Palmitoyl chloride 134687 000112-67-4 38

1H-Tetrazole-1-ethanol, 5-amino- 13048 015284-29-4 38

27 41.037 0.38 D:\MassHunter\Library\NIST14.L  
 Glycidylpalmitate 171251 1000383-37-8 47  
 Adipic acid, isobutyl 3-methylpent 146028 1000353-68-8 27  
 yl ester  
 4-(Trifluoromethyl)phenylacetoneitr 52442 002338-75-2 25  
 ile

28 41.346 0.45 D:\MassHunter\Library\NIST14.L  
 Methyl 18-methylnonadecanoate 184595 1000352-20-6 99  
 Eicosanoic acid, methyl ester 184599 001120-28-1 98  
 Eicosanoic acid, methyl ester 184598 001120-28-1 97

29 42.603 0.03 D:\MassHunter\Library\NIST14.L  
 trans-13-Octadecenoic acid 142094 000693-71-0 59  
 cis-13-Octadecenoic acid 142083 013126-39-1 59  
 cis-Vaccenic acid 142073 000506-17-2 56

30 42.932 0.07 D:\MassHunter\Library\NIST14.L  
 Cyclopropanoethanal, 2-octyl- 140252 056196-06-6 90  
 9,17-Octadecadienal, (Z)- 125003 056554-35-9 90  
 9,12-Octadecadienoic acid, methyl 153894 002566-97-4 87  
 ester, (E,E)-

31 43.059 0.23 D:\MassHunter\Library\NIST14.L  
 9,12-Octadecadienoic acid (Z,Z)-, 208895 003443-82-1 93  
 2-hydroxy-1-(hydroxymethyl)ethyl e  
 ster  
 9,12-Octadecadienoic acid (Z,Z)-, 208883 002277-28-3 91  
 2,3-dihydroxypropyl ester  
 9,12-Octadecadienoic acid (Z,Z)-, 208894 003443-82-1 91  
 2-hydroxy-1-(hydroxymethyl)ethyl e  
 ster

32 43.125 0.31 D:\MassHunter\Library\NIST14.L  
 9,17-Octadecadienal, (Z)- 125003 056554-35-9 96  
 9-Octadecenal, (Z)- 126829 002423-10-1 96  
 9-Octadecenoic acid (Z)-, 2,3-dihy 210562 000111-03-5 87  
 droxypropyl ester

33 43.543 0.06 D:\MassHunter\Library\NIST14.L  
 9-Octadecenoic acid, (E)- 142089 000112-79-8 83  
 cis-13-Octadecenoic acid 142083 013126-39-1 60  
 9-Octadecenoic acid 142074 002027-47-6 53

34 43.987 9.99 D:\MassHunter\Library\NIST14.L  
     9-Octadecenal, (Z)- 126829 002423-10-1 94  
 Glycidyleolate 195537 1000383-37-7 91  
     9,17-Octadecadienal, (Z)- 125003 056554-35-9 86

35 44.154 0.66 D:\MassHunter\Library\NIST14.L  
 Adipic acid, butyl 2-hexyl ester 145906 1000353-71-0 38  
 Adipic acid, butyl 3-heptyl ester 159530 1000353-64-9 35  
 Cyclohexanecarboxylic acid, pentyl ester 63330 006553-83-9 30

36 44.316 1.65 D:\MassHunter\Library\NIST14.L  
 Glycidylpalmitate 171251 1000383-37-8 86  
 Diethylmalonic acid, monochloride, 250811 1000369-75-2 43  
 octadecyl ester  
 ,Myristoyl chloride 107807 000112-64-1 30

37 44.571 0.29 D:\MassHunter\Library\NIST14.L  
 Cyclopropanoic acid, 2-octyl- 140252 056196-06-6 55  
     6-Octadecenoic acid, (Z)- 142084 000593-39-5 53  
 Cyclohexanecarboxylic acid, nonyl ester 115391 070289-37-1 46

38 44.721 0.18 D:\MassHunter\Library\NIST14.L  
 Docosanoic acid, methyl ester 209118 000929-77-1 97  
     Methyl 20-methyl-heneicosanoate 209123 1000336-47-4 97  
 Docosanoic acid, methyl ester 209117 000929-77-1 91

39 46.323 0.10 D:\MassHunter\Library\NIST14.L  
 Tricosanoic acid, methyl ester 219422 002433-97-8 76  
     9-Hexadecenoic acid, methyl ester, 128698 001120-25-8 41  
     (Z)-  
     Methyl 20-methyl-docosanoate 219410 1000336-49-8 38

40 46.651 0.03 D:\MassHunter\Library\NIST14.L  
 Eicosanoic acid, TMS 229810 1000414-25-2 12  
 Decanoic acid, octyl ester 144289 002306-92-5 10  
 n-Capric acid n-heptyl ester 130800 060160-17-0 9

41 46.780 0.12 D:\MassHunter\Library\NIST14.L  
     9,17-Octadecadienal, (Z)- 125003 056554-35-9 90  
     9,12-Octadecadienal 124999 026537-70-2 56  
 cis-9-Hexadecenal 100560 056219-04-6 45

42 47.086 0.60 D:\MassHunter\Library\NIST14.L  
 Cinnamylcinnamate 124958 000122-69-0 25  
 2-Ethylbutyric acid, hexadecylest 197606 1000369-72-6 18  
 er  
 Silane, dimethyl(dimethyl(3-phenyl 237440 1000347-99-1 15  
 pro-2-enyloxy)silyloxy)(3-phenylpr  
 o-2-enyloxy)-

43 47.474 1.35 D:\MassHunter\Library\NIST14.L  
 9-Octadecenoic acid (Z)-, 2-hydrox 210570 003443-84-3 89  
 y-1-(hydroxymethyl)ethyl ester  
 9-Octadecenoic acid (Z)-, 2,3-dihy 210562 000111-03-5 78  
 droxypropyl ester  
 13-Tetradecenal 74476 085896-31-7 64

44 47.856 0.57 D:\MassHunter\Library\NIST14.L  
 Tetracosanoic acid, methyl ester 228681 002442-49-1 99  
 Tetracosanoic acid, methyl ester 228680 002442-49-1 99  
 Tetracosanoic acid, methyl ester 228678 002442-49-1 93

45 48.546 0.12 D:\MassHunter\Library\NIST14.L  
 10-(1-Methylallyl)tricyclo[6.3.1.0 91613 1000191-90-0 14  
 (2,7)]dodeca-2(7),3,5-trien-10-ol  
 Carbonic acid, but-3-en-1-yl penta 184481 1000383-23-6 11  
 decyl ester  
 Carbonic acid, but-3-en-1-yl hepta 209052 1000383-23-8 10  
 decyl ester

46 48.670 0.06 D:\MassHunter\Library\NIST14.L  
 N-Methoxy-N-methylamonodifluoropho 13035 1000306-18-9 35  
 sphine  
 6-Octadecenoic acid 142075 1000336-66-8 30  
 9,19-Cyclolanost-24-en-3-ol, (3.be 249569 000469-38-5 30  
 ta.)-

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 13-Octadecenal, (Z)- 126830 058594-45-9 60  
 9-Octadecenoic acid, (E)- 142085 000112-79-8 58  
 Cyclopentadecanone, 2-hydroxy- 102369 004727-18-8 56

48 48.873 0.07 D:\MassHunter\Library\NIST14.L  
 Citronellal 27476 000106-23-0 49  
 2,6,10,14-Hexadecatetraen-1-ol, 3, 190443 061691-98-3 44  
 7,11,15-tetramethyl-, acetate, (E,  
 E,E)-

9-Octadecenoic acid, (E)- 142085 000112-79-8 43

49 48.908 0.07 D:\MassHunter\Library\NIST14.L  
 Cyclohexene, 4-(4-ethylcyclohexyl) 123186 301643-32-3 96  
 -1-pentyl-  
 p-Menth-8(10)-en-9-ol, cis- 27588 015714-13-3 55  
 Citronellal 27476 000106-23-0 47

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 3,7,11-Tridecatrienoic acid, 4,8,1 124937 036237-70-4 35  
 2-trimethyl-, methyl ester, (Z,E)-  
 Octadec-9-enoic acid 142076 1000190-13-7 35  
 Benzonitrile, 2-fluoro-4-(4'-propy 185402 093743-04-5 25  
 l[1,1'-bicyclohexyl]-4-yl)-

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 Methyl 22-methyl-tetracosanoate 236720 1000336-26-9 92  
 Pentacosanoic acid, methyl ester 236725 055373-89-2 91  
 Methyl 18-methyl-tetracosanoate 236717 1000336-26-6 62

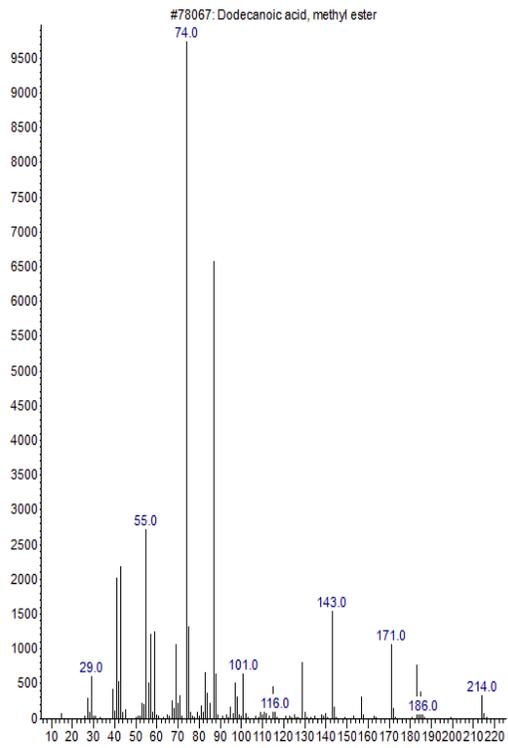
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 methyl-heptadeca-3,7,11,15-tetraen  
 yl)-cyclohexanol  
 2,2-Dimethyl-3-(3,7,16,20-tetramet 244184 1000194-78-6 35  
 hyl-heneicosa-3,7,11,15,19-pentaen  
 yl)-oxirane

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 11,14-Eicosadienoic acid, (Z)-, TM 227372 1000333-62-0 60  
 S derivative  
 9-Octadecenoic acid (Z)-, 2,3-dihy 210562 000111-03-5 58  
 droxypropyl ester  
 cis-13-Octadecenoic acid, methyl e 155747 1000333-58-3 45  
 ster

54 50.764 0.16 D:\MassHunter\Library\NIST14.L  
 Hexacosanoic acid, methyl ester 243163 005802-82-4 99  
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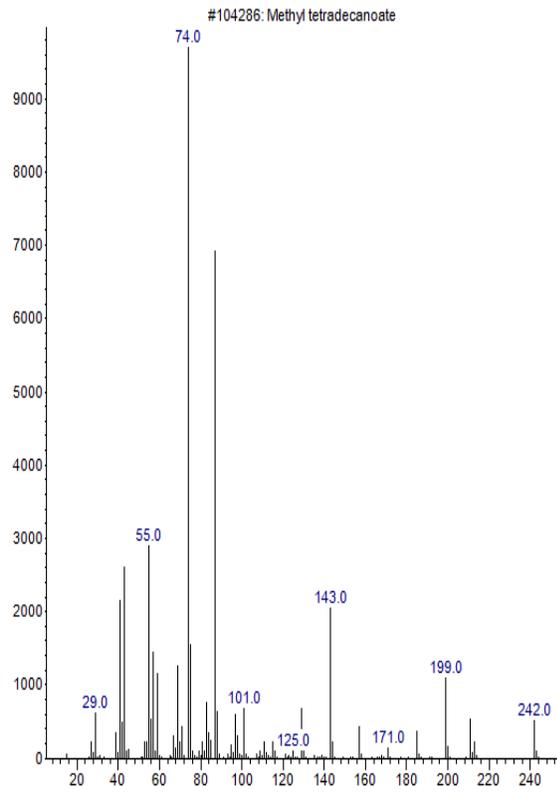
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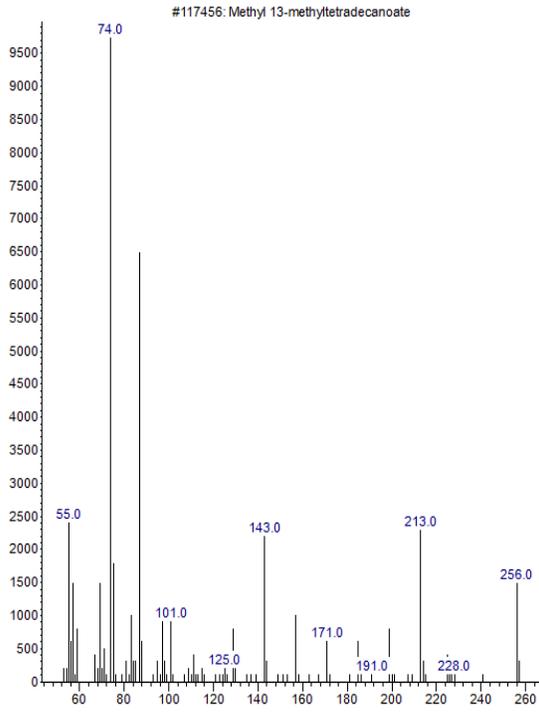
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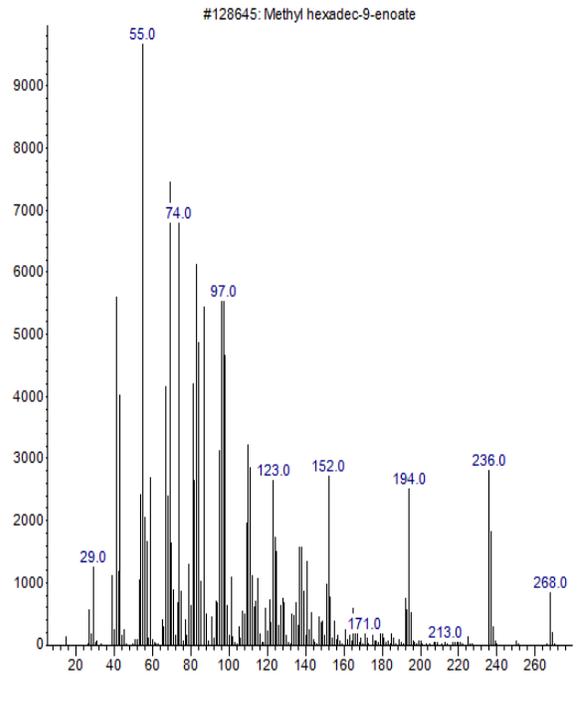


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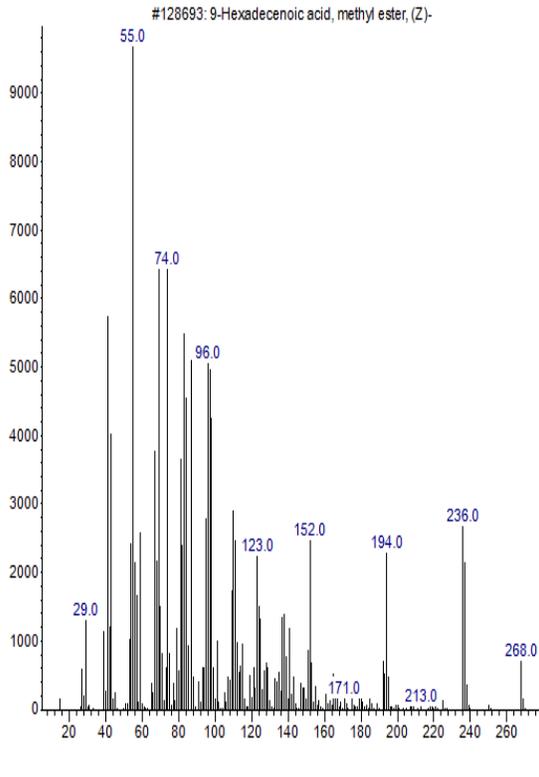
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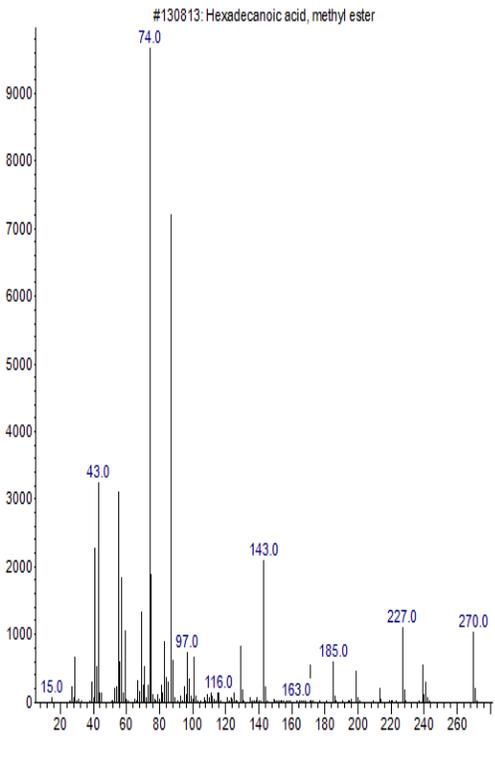
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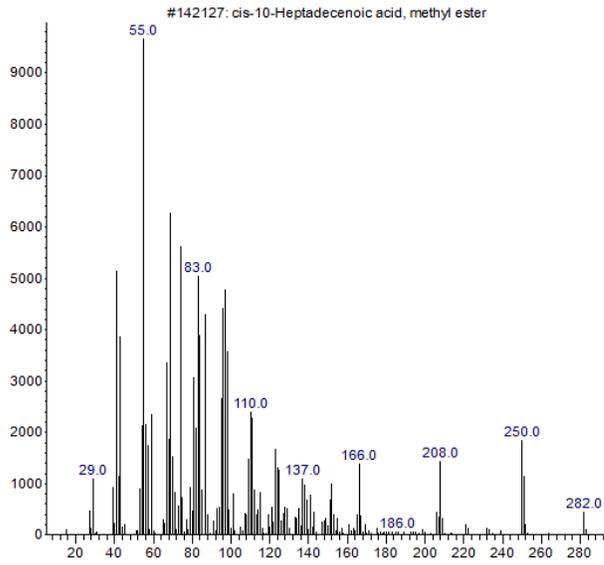
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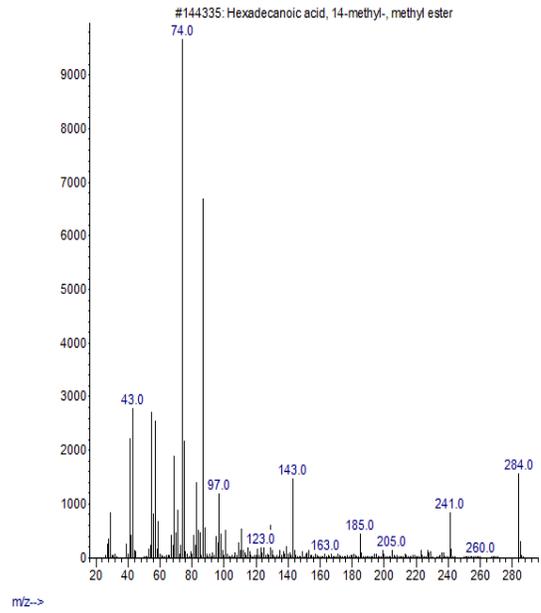


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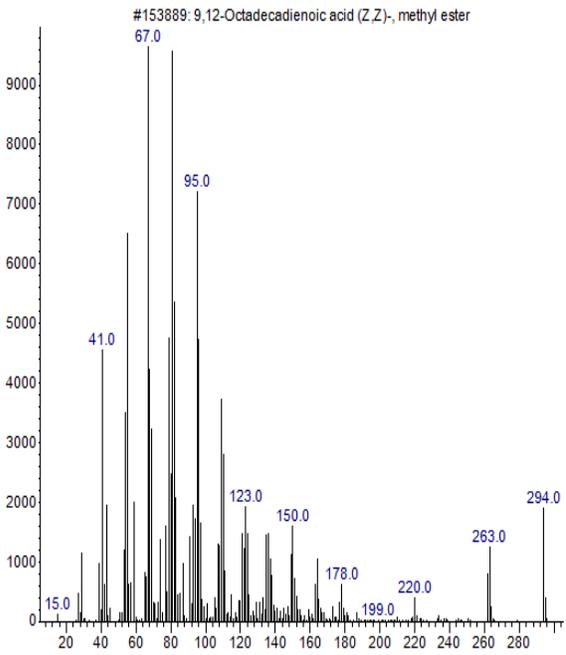
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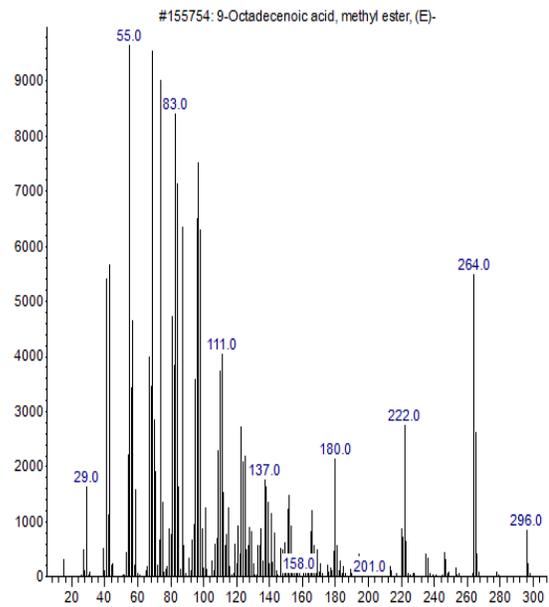
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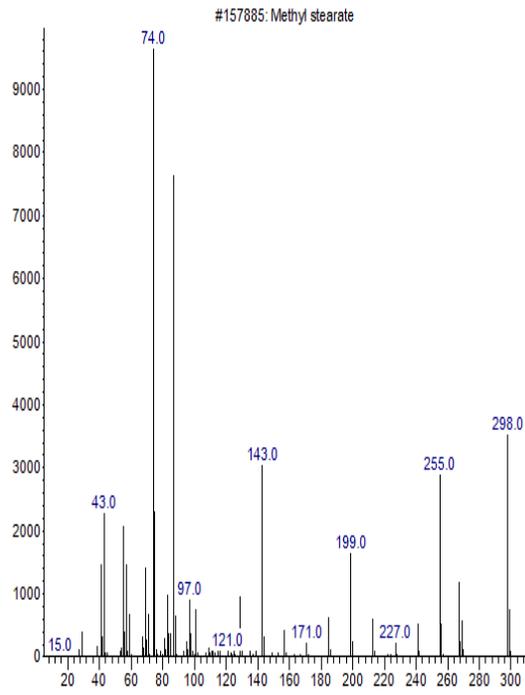
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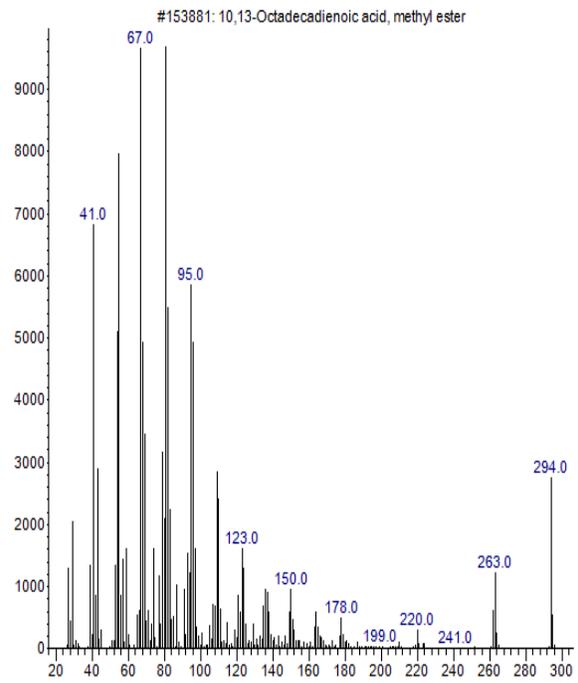
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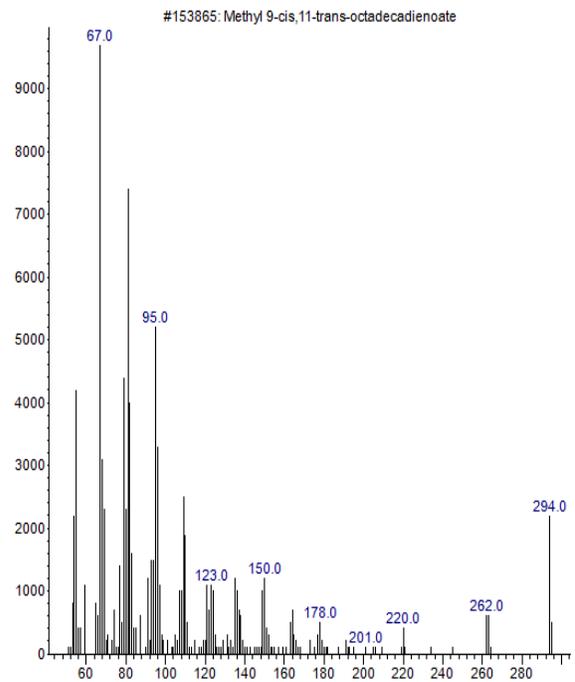
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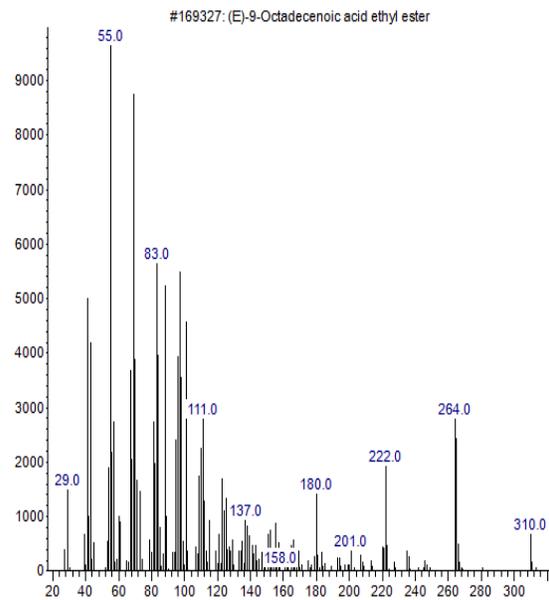
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