SYNTHESIS OF TRIACETIN FROM GLYCEROL

HENG WEPOH

A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical Engineering

Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature :

Name : HENG WEPOH

ID No. : 10AGB04286

Date : 10th SEPTEMBER 2015

APPROVAL FOR SUBMISSION

I certify that this project report entitled **"SYNTHESIS OF TRIACETIN FROM GLYCEROL"** was prepared by **HENG WEPOH** has met the required standard for submission in partial fulfillment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical at Universiti Tunku Abdul Rahman.

Approved by,

Signature :

Supervisor : Dr. Tan Kok Tat

Date : 10th SEPTEMBER 2015

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ABSTRACT

Glycerol is the by-product of biodiesel with about 10 wt% of its production. The excessive amount of glycerol is a very promising feedstock for converting into more valuable product. One of the prospective glycerol's derivatives is triacetin which produce by glycerol acetylation. Synthesis of triacetin from glycerol with acetic acid using homogeneous acid catalyst has been carried out in a batch reaction and was analyzed by gas chromatography. The parameters that were manipulated are glycerol to acetic molar ratio of 1:3, 1:6, and 1:9 mol/mol and the reaction times are 30, 60 and 120 minutes. Besides, the catalyst amount used were glycerol to sulphuric acid molar ratio of 1:0.00, 1:0.02 and 1:0.04 mol/mol and the temperatures being manipulated were between 90 to 120 ^{o}C. After manipulating among the parameters, a set of parameter that produce highest yield of triacetin will be obtained and studied. In the study, the triacetin production efficiency was further improved by determining the optimum operating condition for the process. The optimum conditions for triacetin production were molar ratio of glycerol to sulphuric acid 1:0.02 mol/mol, 1:9 mol/mol molar ratio of glycerol to acetic acid, 60 minutes of reaction time and 105 ^{o}C of reaction temperature. The highest yield for the triacetin synthesis through the research is 31.89% with the help of full factorial design.

TABLE OF CONTENTS

CHAPTER

4 RESULT AND DISCUSSION

LIST OF FIGURE

LIST OF TABLE

LIST OF SYMBOLS / ABBREVIATIONS

FAME	Fatty acid methyl esters
FTIR	Fourier transforms infrared spectroscopy
GC	Gas chromatography
A_i	peak area, i = component
A_{is}	peak area of internal standard (methyl heptadecanoate)
C_i	content of components, %

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, biodiesel has increased greatly as a renewable transportation fuel. There is noticeable concern in growing biodiesel as a substitute fuel because it is environmental friendly compare to petrol-diesel fuel that is extracted from the fossil fuels. It is also a biodegradable fuel which has a higher octane number and superior ignition properties compare to petroleum-diesel fuel. Biodiesel is also known as fatty acid methyl esters (FAME). FAME's are normally produced from renewable sources such as animal fats or vegetable. Biodiesel production involves transesterification of triglycerides with ethanol or methanol in the presence of alkali-based catalyst (Corma et al., 2007). The reaction occurs with the production of three methyl esters of fatty acid molecules (biodiesel) and glycerol as by product.

Glycerol is a by-product of biodiesel production as mentioned earlier. Glycerol commonly formed with 10wt% mass balance from the reaction (C.H. Zhou, 2008). The global glycerol production in the biodiesel market is estimated to reach 36.9 million metric tons in 2020 and this means that there will be around 3.7 million metrics tons of crude glycerol produced as a by-product of biodiesel (B. Katryniok, S. Paul, F. Dumeignil, ACS Catal, 2013). The fast increase in the biodiesel production has resulted in a large surplus of crude glycerol. However, the use of glycerol is restricted because of the contaminant of poisonous methanol and fatty acid (soaps) (Yuan et al., 2010). Hence, researchers have paid more consideration and attention to the utilization of glycerol from the biodiesel production in order to overcome the production cost and encourage the biodiesel production in a wide range. In other words, there is an advantage of the glycerol co-product as it is a promising option for lowering the production cost. Besides, researchers have been putting in effort to seek out different ways for disposal and utilization of this crude glycerol including compositing, combustion anaerobic digestion and thermochemical/biological conversion to value added products.

One of the chemical transformations of glycerol can be achieved by acetylation (Ferreira et al., 2009). Acetylation is an acid catalyzed reaction. The glycerol produced from the biodiesel process can be greatly utilized in acetylation processes. The products produce via acetylation of glycerol are mono-acetyl glycerides, di-acetyl glycerides and tri-acetyl glycerides. The tri-acetylated glycerides derivative is also known as triacetin which can be formed from the glycerol acetylation reaction with solvent named acetic acid. Triacetin has applications such as cosmetics, pharmaceutical and fuel additive. Besides, biodiesel also uses triacetin as an additive in lowering the emission of nitrogen oxide to an acceptable amount. The fuel mixed with triacetin can reduce the engine exhaust smoke because it lowers down the carbon molecules in the fuel.

1.2 Glycerol

Glycerol is an organic compound with a molecular formula $C_3H_8O_3$. It is colorless, clear, sweet tasting, and a viscous liquid. The boiling point, melting point and flash point of glycerol are 290 ^oC, 18 ^oC and 177 ^oC respectively (Speight, 2002). Glycerol is also known as glycerine, propane-1, 2, 3-triol. It is mainly produced during biodiesel transesterification, saponification and hydrolysis reaction. Glycerol is a valuable by-product of biodiesel produced from animal, vegetable fats and oils as feed stock. Crude glycerol produced during the transesterification in biodiesel production would consist of impurities such as soap, ash, water, methanol and other organic materials （Tan HW et al., 2013）. Glycerol has multiple functions in food, cosmetic and pharmaceutical industries.

The improvement of transformation of glycerol to other value-added products is being intensively studied. Lately, researches have been done on the catalytic of glycerol to produce usefulness chemicals such as glyceric acid and ester glycerol (Climent et al., 2010). Among all the glycerol conversion reactions, acetylation reaction is one the most promising process that transforms the glycerol into applicable biodiesel additives by enhancing the fuel properties. The intended result by converting of glycerol into desired chemicals such as triacetin has successfully reduced both economic losses and environment pollutions.

1.3 Triacetin

Triacetin is also known as 1,2,3-triacetoypropane or glycerin triacetate. It is the ester of glycerol that forms with acetic acid. Triacetin can be produced through the acid catalyzed reaction of acetic acid or acetic anhydride with glycerol. Triacetin is greatly used in industrial application such as pharmaceutical, cosmetic and fuel additives. In biodiesel, triacetin is used as an additive which can improve the cetane number in order to decrease the nitrogen oxide emission to an acceptable emission level. Addition of 10% of triacetin in biodiesel can lead to the enhancement of the engine in performance as compared to the pure biodiesel (P. V. Rao et al., 2011).

Besides, triacetin can also be applied as a fuel additives as an anti-knocking agent to minimize the engine knocking in the gasoline engine. Researchers found that triacetin can be used to enhance cold and viscosity properties in final fuel produced (Melero et al., 2007).

1.4 Problem Statements

Biomass is a renewable and clean energy to replace diesel fuel. Due to the emission of greenhouse gases, researchers had been working more on rectifying these problems caused in the environment. There are problems arising from production of biodiesel, which is glycerol. The rapid increase in biodiesel production has resulted in an increase of low value crude glycerol in the world market.

In order to overcome the problem of excessive glycerol, it is recommended to convert the glycerol into useful and valuable products such as mono-, di- and tri-acetin. Utilization of glycerol can reduce both of the environment and economic losses (A. Yuksel, 2010). Triacetin is the most desired product produced from acetylation of glycerol with acetic acid. Most scientists are now drawing attention towards the triacetin production with different types of processes and different type catalysts used.

In previous studies by Mufrodi et al. (2014), it is shown that the optimum condition to achieve highest conversion of glycerol acetylation is at 373-393K in the presence of catalyst with a mole ratio of sulfuric acid to glycerol at 2.5, with 30 minute of reaction time

In this study, the optimum conditions for acetylation of glycerol and acetic acid will be investigated using batch reactor, where sulfuric acid homogenous catalyst and amberlyst-35 heterogeneous were used.

1.5 Aims and Objectives

The aims and objectives for this thesis are listed below:

I. To determine the optimum conditions for conversion of glycerol to triacetin.
II. To set up an experiment of batch reaction for glycerol acetylation.
III. To characterize the product using various characterization tests.

CHAPTER 2

LITERATURE REVIEW

2.1 Acetylation

Glycerol produced as a by-product from biodiesel is an extremely low cost feedstock. Variables chemical reactions of low value glycerol to other valuable chemicals can be done by using several catalytic processes, such as the selective oxidation to glyceric acid or hydrox-yacetone(S. Sato et al., 2012), dehydration to acrolein (H. Atiaet et. al., 2008), hydrogenation to 1,2- or1,3-propanediol (I. Gandarias et al., 2012), etherification to alkyl ethers (N. Ozbay et al., 2013), condensation to dimers or oligomers and the acetylation to ester of glycerol.

Acetylation of glycerol is one of the most common ways to produce mono-acetin, diacetin and triacetin. Acetylation is also known as ethanoylation in the IUPAC nomenclature. It is a reaction that initiates an acetyl functional group into a chemical compound. Acetylation including the substitution of the hydrogen atom of a hydroxyl group with an acetyl group resulting in an acetoxy group. The chemical compounds used are glycerol which has a hydroxyl group and acetic acid which has an acetyl functional group.

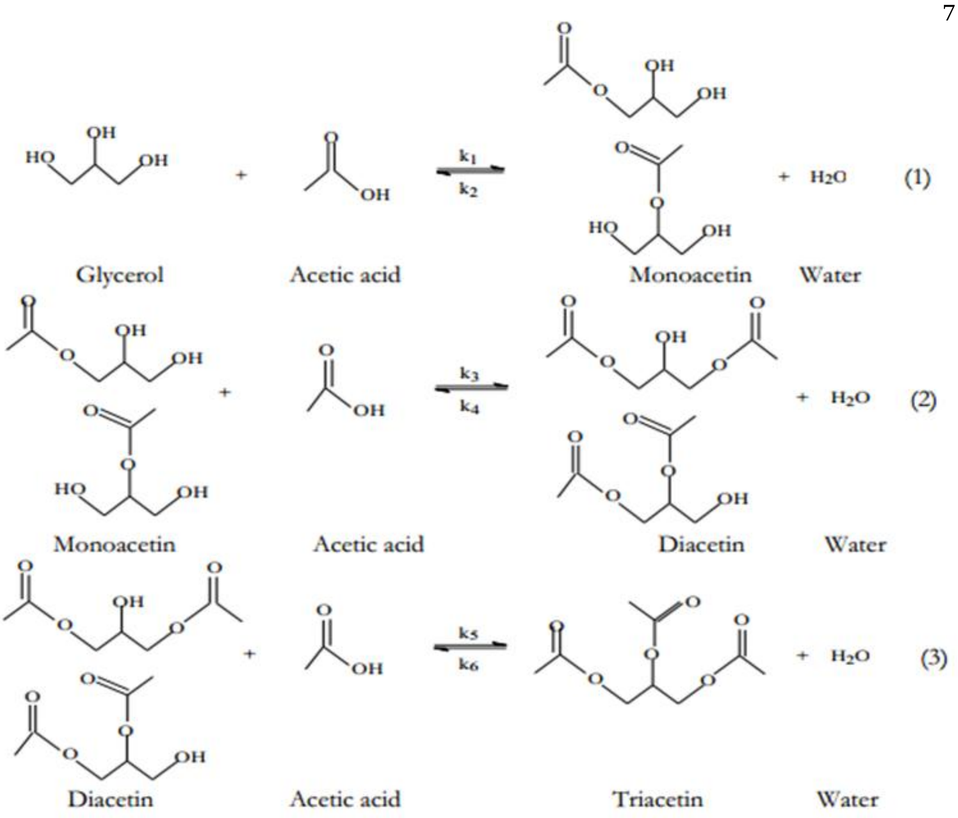


Figure 2.1: The Steps of Acetylation of Glycerol Reaction Mechanism (Zahrul,Mufrodi, Rochmandi, Sutijan & Arief Budiman, 2014)

Basically, acetylation can be synthesized by two different types of reaction, which are the batch reactor reaction and the continuous reactive distillation column reaction. Acetylation can be carried out with or without the uses of catalyst. However, the presence of catalyst can highly increase the rate of reaction and the product selectivity. There are many researches and experiments had been done on the glycerol acetylation process. From most researches, it is proven that acetylation can used either heterogeneous catalyst or homogenous catalyst.

2.2 Trans-esterification

Production of glycerol can’t be avoided during the trans-esterification of biodiesel fuel production. Therefore, many studies have been carried out to investigate the decrease in production of glycerol from vegetable oil during the biodiesel production. Triacetin can be produced via trans-esterification reaction between triglycerides and methyl acetate via supercritical conditions. In this reaction, the triacetin produced as side product with is targeted for resolving the issues of high glycerol yield in biodiesel production in conventional processes.

Saka and Isayama studied supercritical methyl acetate by transforming the rapeseed oil into triacetin and fatty acid methyl ester (FAME). They found that the trans-esterification by supercritical conditions can be processed in the absence of catalyst which produces FAME and triacetin. Besides, they also found that high yield of FAME and triacetin can be produced by supercritical process (Saka and Isayama, 2009). The reaction formula for the trans-esterification of triglycerides and methyl acetate is shown below.

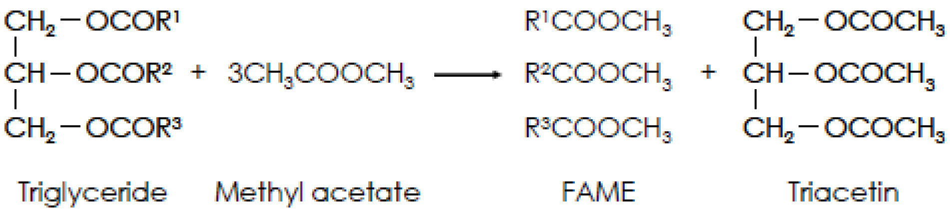


Figure 2.2: Trans-esterification of Triglycerides and Methyl Acetate (Tan, Lee and Mohamed, 2011)

2.3 Interesterification

Another research had been done by Casas, Ramos and Pérez. Methyl acetate and triglycerides were used to produce triacetin and biodiesel. They proposed a study on chemical reaction of sun flower oil with methyl acetate by using different catalyst such as potassium hydroxide, methoxide, and polyethylene. This chemical reaction is known as interesterification. However this reaction has only been studied using vegetable oils. Interesterification has been mostly studied in the presence of enzymes (Du et al., 2004) (Ognjanovic, Bezbradica and Knezevic-Jugovic, 2009) or under supercritical condition (Casas, Ramos and Pérez, 2011). The Figure 2.3 shows the reaction formula for interesterification.

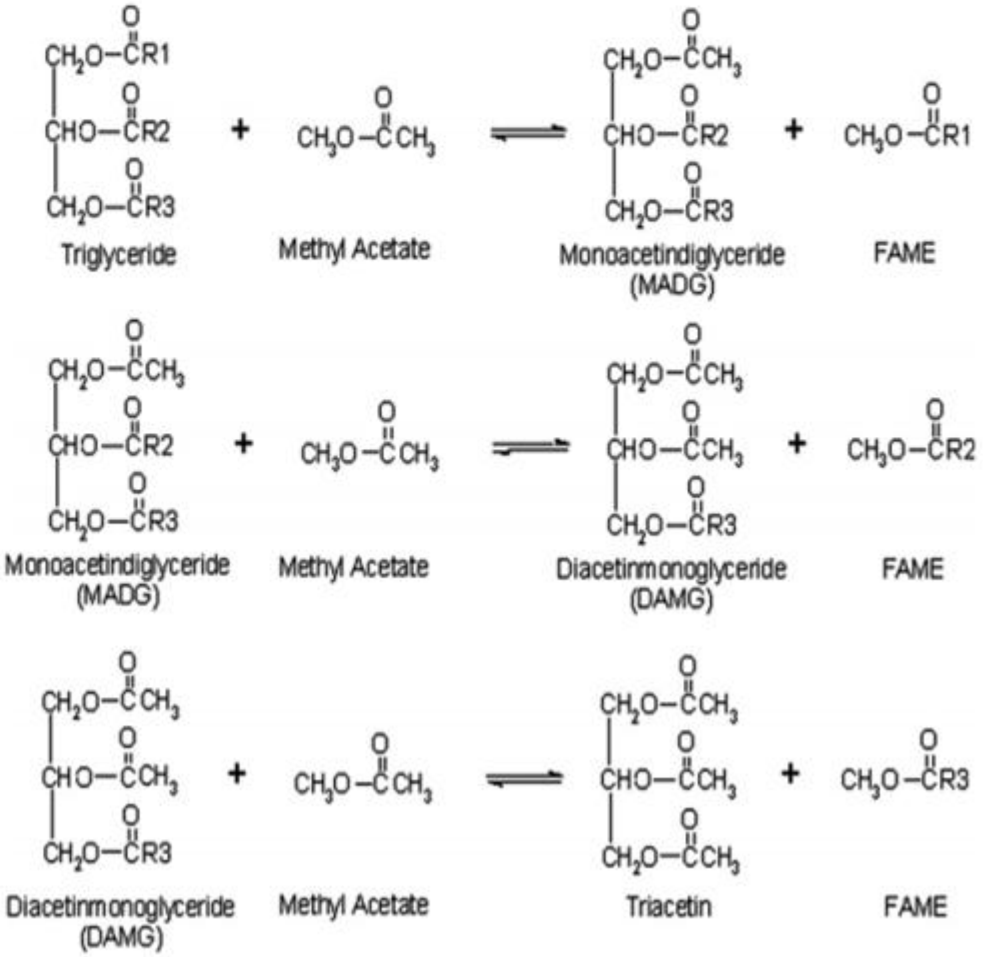


Figure 2.3: Inter-Esterification Reaction of Triglycerides with Methyl Acetate (Casas, Ramos and Pérez, 2011)

2.4 Method

2.4.1 Batch Reaction

Batch reactor is commonly used in the process industries. The catalyst and reactants are put in a closed reactor and the reaction is let to run for a specific time. This is the mechanism of a batch reactor. Batch reactors are a simple and need some supporting equipment to carry out the process. It is used for small amount of material and produces high-value products. Synthesis of triacetin from glycerol is carry out in a batch reactor and the research was done by (Mufrodi et al., 2014). The aim of this study is to identify by two different processes for glycerol acetylation.

In this research, the conversion of glycerol from continuous distillation column is 98.51% and batch reactor is 96.30%. Both of the reactions use sulfuric acid as the catalyst. Sulphuric acid is a homogenous catalyst and it achieved the best performance during the acetylation of glycerol amongst the various type of heterogeneous catalyst used. Although the conversion of glycerol in a batch reactor is lower than the continuous distillation column, but the selectivity of triacetin produced in a batch reactor is higher. The selectivity of triacetin in a batch reactor is 13.96% and the reactive distillation column is only 8.98%.

Besides, temperature is also one of parameters that need to be considered during the batch reaction in order to increase the selectivity of triacetin. From the research, monoacetin, diacetin and triacetin selectivity can be increased by increasing temperature in the batch reactor. The highest yield of triacetin is 13.69% at temperature of 388K (Mufrodi et al., 2014). However, the boiling point of acetic acid is 391K, if the temperature increase to this temperature, the acetic acid will start to evaporate and thus decreasing the selectivity of triacetin.

2.4.2 Continuous Acetylation Reaction

Continuous acetylation processes was studied as early as the 1960s by morrissette (1964). Continuous acetylation reaction is a process for the continuous production of triacetin consisting essentially of continuously charging liquid glycerol into liquid reaction area through which acetic acid vapors and water vapors flows.

Normally the triacetin are produce using batch reactor tank. However, batch reactor is very versatile for small production. For the large scale production of triacetin, batch reactor is labor intensive and low in productivity. Therefore, continuous acetylation process is more suitable in commercial production compare to the batch process.

There are several parameters that will affect the selectivity of production of triacetin in the continuous acetylation reaction. In other researches, the parameters include the effect of height packing and the effect ratio of glycerol to acetic acid. In the continuous acetylation, the height of packing can affect the yields of triacetin due to contacting time between acetic acid and glycerol. For example, by increasing height packing of the distillation column, more time is given to the reactants to contact each other and thus higher selectivity of triacetin can be formed. Next, from the stoichiometric calculation, 1 mole of glycerol needs 3 mole of acetic acid to produce one mole of triacetin. Therefore, by increasing the ratio of acetic acid to glycerol, there will be an increase in triacetin production.

2.5 Type of Catalyst

Acetylation of glycerol with acetic acids produces fuel additives like triacetin. Acetylation of glycerol can be carried out using different types of suitable mineral acid catalyst. Catalysts are classified into two categories, which are homogenous catalyst and heterogeneous catalyst.

Table 2.1: Comparison of Main Advantages and Disadvantages of Homogenous and Heterogeneous Catalyst (Erica Farnetti, Roberta Di Monte and Jan kaspar, n.d.)

Property	Homogeneous	Heterogeneous
Catalyst recovery	Difficult and expensive	Easy and cheap
Thermal stability	Poor	Good
Selectivity	Excellent/good- single active site	Good/poor-multiple active sites

2.5.1 Homogeneous Catalyst

The homogenous catalyst operates respectively in the same phase where the reaction involves a liquid catalyst with the reactants as in either liquid or gases. Strong acid must be used in order perform well the glycerol acetylation. This reaction is performed using the homogeneous catalyst such as sulphuric acid, hydrofluoric or p-toluene sulfonic acid (Kale et al., 2015). Khayoon et al. (2011) studied the performance of H_3PO_4, HCl, HNO_3 and H_2SO_4 as homogeneous catalysts for glycerol esterification. Among these H_2SO_4 showed the highest glycerol conversion. Synthesis of triacetin from glycerol and acetic acid acid required 72 hours in the existents of homogeneous catalyst (Lu & Ma, 1991).

However, these strong acids are not beneficial because they are hazardous, corrosive and difficult to remove from the glycerol acetylation (Kale et al., 2015). Besides, homogeneous catalyst also suffers from the inherent problems in terms of catalyst separation, reactor corrosions and environment protections as well as economical inconveniences (Zhu et al., 2013). Therefore, quite a number of researchers did their research by changing the catalyst and developing the heterogeneous solid acid catalyst system for the glycerol acetylation.

2.5.2 Heterogeneous Catalyst

The heterogeneous catalyst includes the use of catalyst in a different phase where the reaction involves a solid catalyst with the reactants as either liquid or gases. Different types of solids are used in heterogeneous catalysis. For example metals, metal oxides, metal sulphides and these materials may be used in their pure form or in the form of their mixtures. Besides, catalyst can be both in acidic and alkaline based. Generally, acetylation of glycerol is using solid acid catalyst.

In order to overcome the environment problems and economical inconvenience, a huge number of heterogeneous solid acid catalyst has been developed in recent works. Studies had been made using solid acid catalyst such as Amberlyst-15, K-10 montmorillnite, HUSY, niobic acid, and HZSM-5 (Gonçalves et al., 2008). All the reaction times are carried out within 30 minutes and temperature used is 150^{o}C to monitor the initial products. The results display the selectivity of mono-, di- and tri- acetin are different for each different catalyst used and conversion degree. Amberlyst-15 is more active compare to niobic acid, HUSY, HZSM-5 and catalysts (T.A Peters et al., 2006). After reaction time of 30 minutes, the conversion of glycerol was as high as 97% with a selectivity of 31% to monoacetin, 54% to diacetin and 13% to triacetin. However, they find out the conversion and selectively can be increased by increasing the reaction time.(Gonçalves et al., 2008). Zeolite HZSM-5 and HUSY showed the bad achievement among all the catalyst as their glycerol conversion are only 30% and 14 % respectively, probably due to the acid site deactivation and diffusion problem.

Liao et al. (2009) did glycerol acetylation with two-step method in order to get a higher selectivity and conversion. The esterification of glycerol with acetic acid was performed using resins and zeolites. Amberlyst-35 was discovered to be an outstanding catalyst among the catalyst used in this research. The reaction parameters were enhanced by using catalysts at different temperatures, feedstock ratios and catalyst loading. Optimum conditions have been found where the molar ratio of acetic acid to glycerol is 9:1 at the temperature of 105 ℃ with 0.5g of catalyst and a reaction time of 4 hours. Acetic anhydride was then added there to increase the selectivity of triacetin. Besides, the result shows that the reaction needed to increase the amount of acetic acid used in order to push equilibrium toward the improvement of the conversion of glycerol and triacetin.

Zhu et al. 2009 proposed silver-exchanged phosphotungstic acid (AgPW) catalysts for glycerol acetylation with acetic acid. Among the catalysts partially silver-exchanged phosphotungstic acid (Ag1PW) showed high activity and good performance in the reaction. The conversion of glycerol is 96.8% at 120 ^{o}C within 15 min of reaction time. The reason is because Ag1PW shows remarkable stability, unique kegging structure, high acidity as well as excellent water-tolerance property. The selectivity of acetylated products is 5.2% for triacetin, 46.4% for diacetin and 48.4% for monoacetin. Compare with others exploited mixed metal oxides such as MoO_3/ZrO_2, WO_3/ZrO_2, and Nb_2O_5/ZrO_2, their reactivity were very low, which might be due to their low acidity.

Rodriguez et al.(2007) researched glycerol acetylation by using sulfated zirconia with acetic acid. The catalyst is also named as AC-SA5. This catalyst is produced from activated carbon (AC) at 85 ^{o}C for 4 hours with the help of sulphuric acid in order to initial the functionalities of the catalyst surfaces. The surface interaction between the acyl group and the glycerol molecules can be enhanced due to the presence of sulphur that consist functional group on the AC surface.

The conversion of glycerol by using this catalyst was about 91% after 24 hours of reaction at 120^{o}C. The selectivity of monoacetin, diacetin and triacetin in glycerol conversion was 38%, 28% and 24% respectively. However, the selectivity and the conversion of glycerol acetylation are still affected by the time, temperature and the molar ratio of glycerol to acetic acid (Khayoon and Hameed, 2011)

The use of sulfated zirconia catalysts showed acetylation yields up to 63% and 91% of glycerol conversion after 24 h of reaction. This catalyst also shows the selectivity result of 38% for mono-acetin, 28% for di-acetin and 34% for tri-acetin with the optimized conditions at 120 ^{o} C and 3 hours of reaction time.

CHAPTER 3

METHODOLOGY

3.1 Overview of Experiment

In this study, the main purpose was to investigate the optimal conditions which could result in highest yield of Triacetin for acetylation with catalyst which where sulphuric acid (H_2SO_4) act as a homogenous catalyst. The parameters involved for preliminary study reaction temperature (90 and 120 ^oC), reaction time (30 – 60 minutes), glycerol to acetic acid ratio (1:3, 1:6 and 1:9), and glycerol to sulphuric acid ratio (1:0.00, 1:0,02 and 1:0.04). Full factorial design was used to study the effects of those parameters.

3.2 Material and Chemicals

The material used in this research is glycerol which is a colourless liquid. While the chemicals used throughout the whole research are listed in Table 3.1.

Table 3.1: List of Chemicals Used in Research Experiment

Chemicals	Supplier	Purpose
Glycerol	R & M Chemical, Malaysia	Solvent in Acetylation
Acetic acid	R & M Chemical, Malaysia	Solvent in acetylation
Sulphuric acid	QReC, Malaysia	Catalyst for acetylation
Ethanol	Chem Sol, Malaysia	Internal standard for GC

3.3 Equipment

The equipment used throughout this research studies are listed as in Table 3.2. Besides, the supplier of the equipment is provided as well.

Table 3.2: List of equipment used in this research study

Equipment	Brand
Gas Chromatography	Perkin Elmer, USA
Gas Chromatography-Mass Spectrometry	Shimadzu, Japan
Heating Mantle	Favorit, Malaysia
Hot Plate	Favorit, Malaysia
Rotary Evaporator	Buchi, Switzerland
Reflux Condensation Reactor	Favorit, Malaysia
Fourier Transform Infrared Spectroscopy	Perkin Elmer, USA

3.4 Reactant and Catalyst Preparation

All the chemicals were obtained commercially and used without any further purification. 98% of Acetic acid was obtained from R & M Chemical, Malaysia, 93% of glycerol was obtained from R & M Chemical, Malaysia and 98.9% of sulfuric acid was obtained from QReC, Malaysia. 99.9% of GC grade ethanol used for Gas chromatography (GC) test was made from Chem Sol, Malaysia.

3.5 Acetylation

Synthesis of triacetin in the presence and absence of catalyst was carried out in a stirred reactor at atmospheric pressure and 290 rpm of stirring speed, temperatures of 90 to 120 ^{o}C. Synthesis of triacetin has been carried out previously by using different types of catalyst which including the heterogeneous catalyst and homogenous catalyst. In this research, the catalyst used is homogeneous catalyst sulfuric acid. It was revealed that this catalyst has functionalized as the best homogeneous catalyst among several types of catalyst used.

The reaction carries out in three-neck flask equipment with heating mantle, stirrer and thermometer as shown in Figure 3.1. The reactants glycerol and acetic acid were mixed directly into the three neck flask along with the sulfuric acid catalyst. The reaction carries out at a mixing time from 30 minutes to 60 minute. The mixing was continuously stirred during the reaction using a magnetic stirrer. Next, the products which contain sulfuric acid catalyst were neutralized by adding same ratio of sodium hydroxide in container. After neutralized, the contaminated catalyst was removed by using the recirculating water respirator equipment as shown in Figure 3.2. Lastly, the product containing mono-acetin, di-acetin, tri-acetin, glycerol and unreacted acetic acid were poured into a rotatory evaporator to remove the solvent from the product as shown in Figure 3.3.

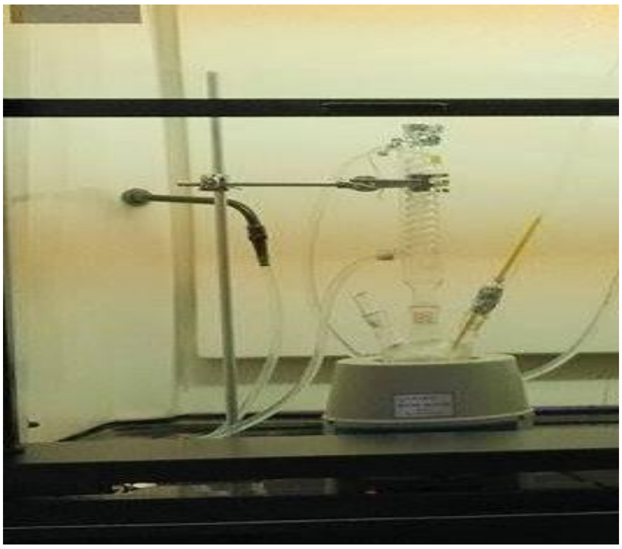


Figure 3.1: Reflux Condensation Set Up

Figure 3.2: Recirculating Water Respirator

Figure 3.3: Rotatory Evaporator

3.6 Design of Experiment (DOE)

Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was employed to utilize Response Surface Methodology (RSM) for acetylation of glycerol. This design method allowed analysis of statistical data and optimization of desired response to be determined. There are three major steps involved in this experimental design, including statistical design experiments, validation of a mathematical model with response prediction and optimization of response. Central composite design (CCD) was selected as the experimental design to study the effect of operating parameters (independent variables) on the acetylation of glycerol with acetic acid into triacetin (response). The optimum operating parameters for acetylation were determined in order to maximize the triacetin yield. The independent variables studied in this experimental design were reaction time, reaction temperature, molar ratio of glycerol to acetic acid and molar ratio of glycerol to sulphuric acid catalyst.

Table 3.3 lists the range and levels of the four independent variables studied.

Table 3.3: Range and levels of independent variables

Code	Variable	Units	Low	High
A	Reaction Temperature	^{o}C	90	120
B	Molar Ratio of Glycerol to Acetic Acid	mol/mol	0.00	0.04
C	Reaction Time	minutes	30	60
D	Molar Ratio of Glycerol to Sulphuric Acid	mol/mol	3	9

Therefore, 29 runs of experiment were conducted where the first 24 runs were organized in a factorial design and additional 5 runs were carried out at the center points to estimate the overall curvature effect. Statistical analysis and regression analysis of the experimental data of the experimental data were conducted by using Design Expert software. The response (Y) or yield of triacetin obtained in each acetylation process was utilized to develop a mathematical model that correlates the conversion of glycerol with acetic acid into triacetin (response) as a function of the independent variables.

Successively, correlation coefficient (R-Square) was employed to evaluate the quality of the proposed model whereas the statistical significance of the model and the ‘Lack of Fit’ test of the model were evaluated using analysis of variance (ANOVA). In addition, interactions between independent variables were studied in two-dimensional and three-dimensional plots and the region of optimum conditions was evaluated.

Furthermore, numerical feature of Design Expert software was practiced in optimization study to identify the optimum operating parameters which lead to optimum yield of triacetin. The independent parameters were set within the range of low (-1) and high (+1) while the yield was set to maximum value. As a result, several solutions were generated and solution with the best desirability based on optimum yield was identified as the optimum parameters.

3.7 Product Analysis

The properties of the triacetin obtained from the glycerol acetylation went through several analytical tests which include Fourier transform infrared spectroscopy (FTIR) and Gas chromatography (GC) in order to identify the yield, components and impurity.

3.7.1 Triacetin Yield

Gas Chromatography (GC) equipped with flame ionization detector with model PerkinElmer Clarus 500 was used to determine Triacetin in the sample collected. The principle of GC is to study the different in retention time of vaporized component in sample though a capillary column. BPX5 capillary column used have 0.25 μm of film thickness, 0.25mm of internal diameter and 30 m length. Samples were prepared by mixing 500 μL of product with 20 μL of the ethanol (GC grade) as internal standard. About 0.5 μL of the sample was then injected into the column. Table 3.4 shows the summary of GC specification.

Table 3.4 Gas Chromatography Specification

Specification	(GC)
Analytical Column	BPX5 capillary column
Carrier Gas	Helium gas (38.3 mL/min)
Initial Temperature	60 ^{o}C (2 min)
Initial Ramp	10 ^{o}C/min to 260 ^{o}C
Final Ramp	30 ^{o}C/min to 300 ^{o}C
FIP	350^{o}C
Injection temperature	250^{o}C with split ratio 20

The area under the peak is proportional to the amount of triacetin present in the sample. Concentration of triacetin presented in the sample was determined through the area under peak obtained by referring the calibration curve prepared based on interval standard. Triacetin yield was calculated and the sample calculation was inserted in Appendix C.

3.7.2 Preparation of Diluted Triacetin Sample

Firstly, internal standard, GC ethanol was prepared. Samples were mixed 500 µL of product with 20 µl of ethanol as internal standard. Hence, the dilution factor of the sample was 20. About 1.5 µl of diluted sample was injected into the column of gas chromatography and the peak areas of each individual component and internal standard (IS) were recorded as $\text{Area}_{\text{sample}}$ and Area_{IS} respectively.

3.7.3 Determination of Yield of Triacetin

According to modified EN 14103 standard, the content of every individual component of sample could be obtained by using the following Equation 3.1:

$$C_i = \frac{A_i}{\sum A - A_{IS}} X\ 100\% \tag{3.1}$$

where

C_i = content of different component in the sample in %

A_i = component peak area

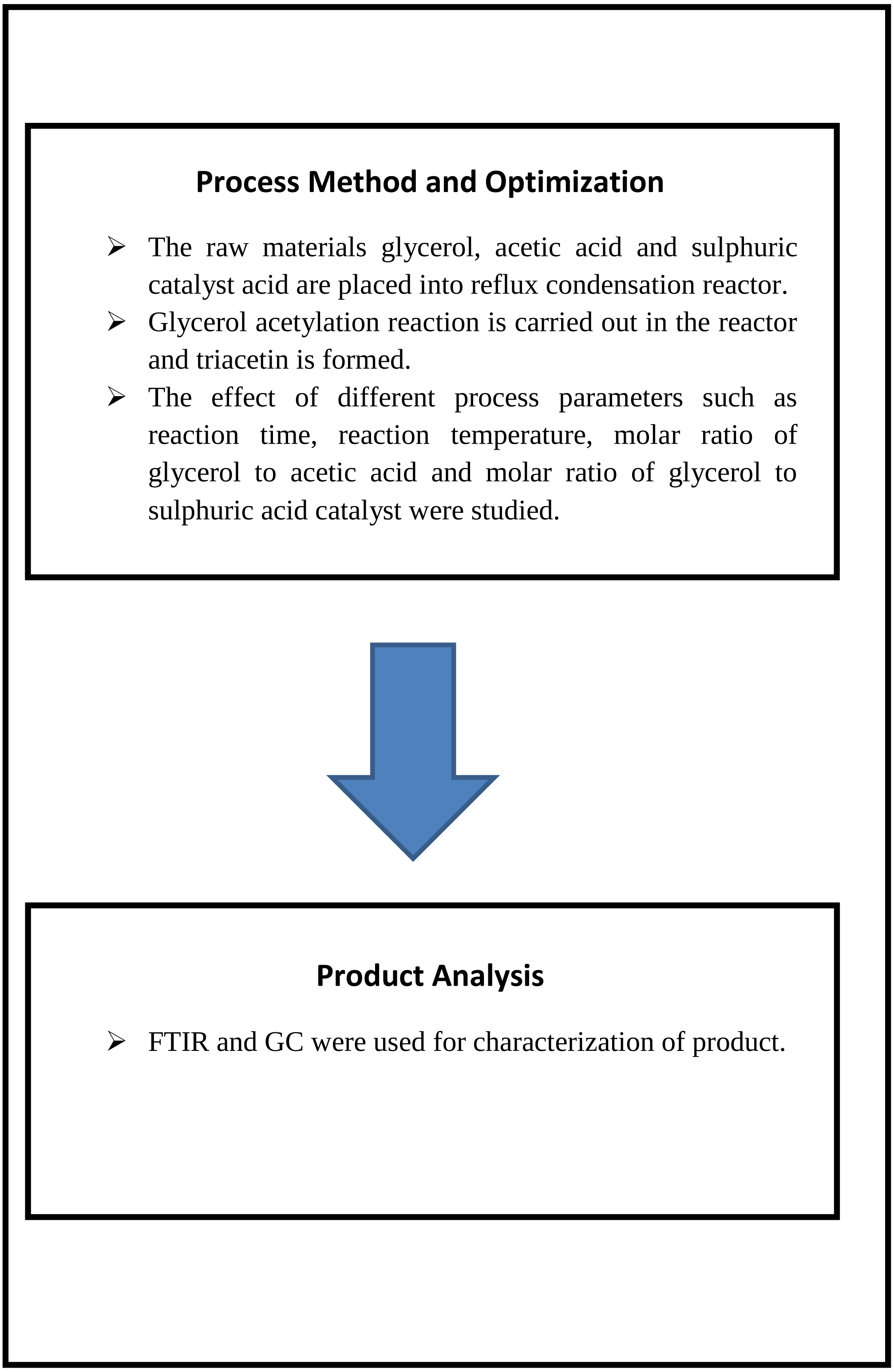
$\sum_A$ = total peak area

3.7.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was employed in this studies to determine the functional group of each component obtained in the triacetin. The analysis is carried out by using Perkin Elmer FTIR.

3.8 Research Flow Diagram

Figure 3.4 shows the flow diagram of the research experiments. This optimization of glycerol acetylation which involved four parameters and were carried out by utilizing Response Surface Methodology (RSM) to obtain their respective optimum conditions



Process Method and Optimization

- The raw materials glycerol, acetic acid and sulphuric catalyst acid are placed into reflux condensation reactor.
- Glycerol acetylation reaction is carried out in the reactor and triacetin is formed.
- The effect of different process parameters such as reaction time, reaction temperature, molar ratio of glycerol to acetic acid and molar ratio of glycerol to sulphuric acid catalyst were studied.

Product Analysis

- FTIR and GC were used for characterization of product.

Figure 3.4: Research Flow Diagram of this Study

CHAPTER 4

RESULT AND DISCUSSION

In this section, there were major parts which were preliminary study and optimisation study. In preliminary study, triacetin yield for prepared by those parameters would be studied. After decided the parameters, optimisation study would proceeded with. Thus, an optimum condition to produce triacetin yield could be determined.

4.1 Preliminary Study

Preliminary study investigated the relation between reaction time, reaction temperature, catalyst quantity and also glycerol to acetic ratio on the triacetin yield. Besides, preliminary study helped to define the feasible range for each process parameters before the optimisation. In preliminary study, the feasible range of reaction time, reaction temperature, catalyst ratio and glycerol to acetic acid ratio were defined. Thus the feasible range for those parameters will be used during the optimisation experiments.

During the preliminary study, 29 experiments runs were designed using Design Expert software. The reaction performance was defined based on biodiesel yield. Sample calculation for the biodiesel yield was shown in Appendix C.

Table 4.1: Experimental Condition and Triacetin Yield

Run	Reaction Temperature (^{o}C)	Glycerol To Sulphuric Acid Ratio	Reaction Time (minute)	Glycerol To Acetic Acid Ratio	Triacetin Yield (%)
1	105.00	1:0.02	45.00	1:6	25.50
2	105.00	1:0.02	45.00	1:6	28.80
3	105.00	1:0.02	60.00	1:3	29.76
4	105.00	1:0.04	45.00	1:9	26.71
5	105.00	1:0.02	45.00	1:6	25.26
6	90.00	1:0.02	45.00	1:3	18.65
7	105.00	1:0.02	45.00	1:6	26.78
8	120.00	1:0.02	60.00	1:6	31.12
9	90.00	1:0.02	30.00	1:6	17.58
10	105.00	1:0.00	60.00	1:6	6.56
11	105.00	1:0.02	60.00	1:9	31.89
12	120.00	1:0.04	45.00	1:6	21.98
13	105.00	1:0.02	30.00	1:9	18.45
14	120.00	1:0.02	30.00	1:6	30.53
15	105.00	1:0.02	45.00	1:6	25.55
16	120.00	1:0.00	45.00	1:6	5.67
17	105.00	1:0.00	45.00	1:3	4.45
18	120.00	1:0.02	45.00	1:3	21.45
19	105.00	1:0.00	30.00	1:6	4.65
20	105.00	1:0.02	30.00	1:3	15.76
21	105.00	1:0.04	45.00	1:3	30.76
22	90.00	1:0.02	45.00	1:9	19.47
23	105.00	1:0.04	60.00	1:6	31.34
24	105.00	1:0.04	30.00	1:6	21.76
25	90.00	1:0.00	45.00	1:6	2.34
26	120.00	1:0.02	45.00	1:9	32.5
27	105.00	1:0.00	45.00	1:9	5.76
28	90.00	1:0.04	45.00	1:6	23.45
29	90.00	1:0.02	60.00	1:6	25.30

4.2 Glycerol Acetylation Reaction

4.2.1 Screening Study via Statistical Analysis by using Design of Experiment (DOE)

The feasible range for each parameter (catalyst ratio, glycerol to acetic acid ratio, reaction temperature, and reaction time) was determined again using statistical analysis.

Table 4.1 displays the complete experimental design matrix and the corresponding yield of triacetin. As shown in the table, the yield ranged 2.34% to 31.89%. A reaction time of 60 minutes, molar ratio of glycerol to methanol of 1:9, molar ratio of glycerol to sulphuric acid catalyst of 1: 0.02 and reaction temperature of 105 ^{o}C gave the highest yield whereas a reaction time of 45 minutes, molar ratio of glycerol to methanol of 1:6, molar ratio of glycerol to sulphuric acid catalyst of 1:0.00 and a reaction temperature of 90 ^{o}C gave the lowest.

4.2.2 Statistical Analysis

Statistical analysis was done to determine how the variables affect the response. Table 4.2 shows the result of the sequential model sum of square analysis. As shown in the table, a quadratic model was suggested as the most appropriate approach to optimize the acetylation reaction with the ‘Prob > F’ value being 0.0001.

Table 4.2: Result of Sequential Model Sum of Square

Source	**Sum of Square**	**DF**	**Mean Square**	**F Value**	**p-valvue Prob > F**	
Mean	12818.00	1	12818.00			
Linear	1646.27	4	411.57	10.90	<0.0001	
2FI	66.36	6	11.06	0.24	0.9585	
Quadratic	665.03	4	166.26	12.34	0.0001	Suggested

Cubic	131.62	8	16.45	2.30	0.1625	Aliased
Residual	42.84	6	7.12			
Total	15370.13	29	530.00			

Data for ANOVA was summarized in Table 4.3. Prob > F less than 0.05 indicated the model terms are significant. In this case A, B, C, and B^2 were significant model terms. Thus, the triacein yield heavily dependents on the factors of reaction temperature, catalyst amount, and reaction time. Furthermore, the F-value of 13.63 indicates that the model is significant and is reliable in predicting the triacetin yield. For the model, the "Prob > F" value is only < 0.0001 which means that there is less than 0.0001% chance that a F-value this large could occur due to noise factor, further proving the reliability of the model. Besides, the F-value of lack of fit is only 7.59, this indicating that is insignificant. The "prob > F" value of 0.0328 proves that there is only 3.28% chance that " Lack of Fit" F-value this small could occur due to noise factor.

Table 4.3: Analysis of Variance (ANOVA) of the Variable

Source	**Sum of Square**	**DF**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	2377.66	14	169.83	13.63	< 0.0001	significant
A	110.78	1	110.78	8.89	0.0099	
B	1333.10	1	1333.10	106.97	< 0.0001	
C	185.97	1	185.97	14.92	0.0017	
D	16.43	1	16.43	1.32	0.2702	
A^2	22.02	1	22.02	1.77	0.2050	
B^2	639.58	1	639.58	51.32	< 0.0001	
C^2	0.000627	1	0.000627	0.00005033	0.9944	
D^2	8.69	1	8.69	0.70	0.4178	
AB	5.76	1	5.76	0.46	0.5077	
AC	12.71	1	12.71	1.02	0.3297	
AD	26.16	1	26.16	2.10	0.1694	
BC	14.71	1	14.7	1.18	0.2957	
BD	6.94	1	6.94	0.56	0.4678	

CD	0.078	1	0.078	0.00629	0.9379	
Residual	174.47	14	12.46			
Lack of fit	165.73	10	16.57	7.59	0.0328	significant
Pure Error	8.73	4	2.18			
Cor Total	2552.13	28				

Data for ANOVA Study for R-Square Value was summarized in Table 4.4**.**

Table 4.4 ANOVA Study for R-Square Value

R-Squared	0.9316
Adj R-Squared	0.8633
Pred R-Squared	0.6206
Adeq Precision	13.000

The R-Square value shown in Table 4.4 for the empirical model was 0.9316, which implies that 93.16% of the variation in the result was attributed by the independent variable studies. This indicated that the empirical model developed well fitted the experimental data. The “Pred R-Squared” of 0.6206 is in reasonable agreement with the “Adj R-Squared” of 0.8633.

As the R-Square value is relatively near to one, a good agreement between predicted and actual yield was achieved in this regression model. Figure 4.1 shows a graph of predicted yield against actual yield using the model development in order to show the correlation between these two parameters.

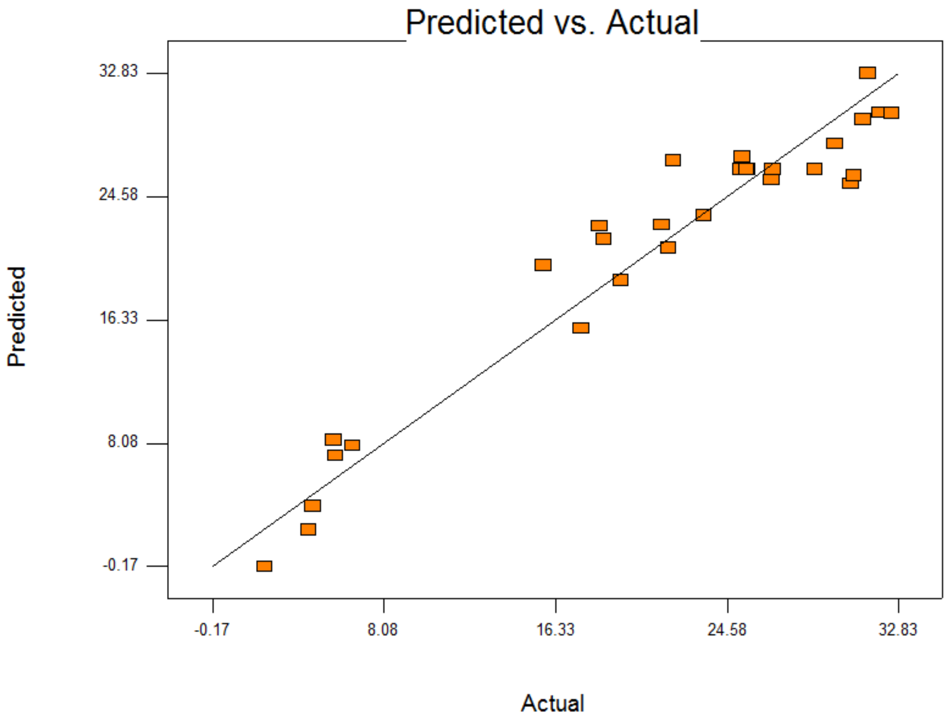


Figure 4.1: Predicted Yields against Experimental Yields for Acetylation Reaction

The final equation in term of coded factors after eliminating parts of the insignificant terms is outlined in Equation 4.1

$$\begin{aligned}\mathrm{TRIACETIN} = {} & 26.38 + (3.04 * \mathrm{A}) + (10.54 * \mathrm{B}) + (3.94 * \mathrm{C}) + (1.17 * \mathrm{D}) \\ & - (1.84 * \mathrm{A}^2) - (9.93 * \mathrm{B}^2\ ) - (0.009833 * \mathrm{C}^2) - (1.16\mathrm{D}^2) \\ & - (1.20 * \mathrm{A} * \mathrm{B}) - (1.78 * \mathrm{A} * \mathrm{B}) + (2.56 * \mathrm{A} * \mathrm{D}) + (1.92 * \mathrm{B} * \mathrm{C}) \\ & - (1.32 * \mathrm{B} * \mathrm{D}) - (0.14 * \mathrm{C} * \mathrm{D})\end{aligned} \tag{4.1}$$

Where:

A = Reaction temperature
B = Mole ratio of glycerol to sulphuric acid catalyst
C = Reaction time
D = Mole ratio of glycerol to acetic acid

From the Equation 4.1, terms with a positive sign indicates synergistic effects whereas terms with negative sign indicates antagonistic effect. According to Equation 4.1, parameter B which contains highest value of coefficient from 4 parameters plays an important role in reaction producing triacetin. The Final equation in terms of actual factors is outlined in Equation 4.2

Tricetin = -136.11838 + (2.02599 * reaction temperature) + (2120.57027 * mole ratio of catalyst) + (0.97559 * reaction time) – (3.40899 * mole ratio of glycerol to acetic acid) – (0.00818815 * reaction temperature^2) – (31296.24295 * mole ratio of catalyst^2) – (0.000004.3703 * reaction time^2) – (0.12859 * mole ratio of glycerol to acetic acid^2) – (4.4912 * reaction temperature * mole ratio of catalyst) – (0.0079222 * reaction temperature * reaction time) + (0.056833 * temperature * mole ratio of glycerol to acetic acid) + (7.17661 * mole ratio of catalyst * reaction time) - (24.65497 * mole ratio of catalyst * mole ratio of glycerol to acetic acid) - (0.000311111 * reaction time * mole ratio of glycerol to acetic acid)

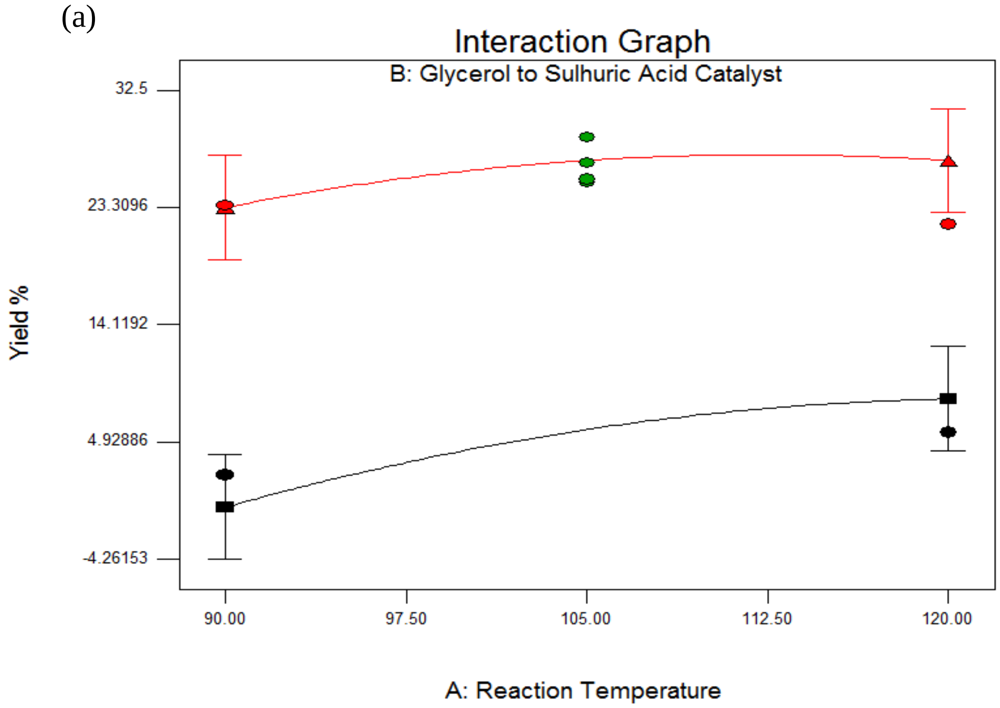
(4.2)

4.2.3 Variables Interaction

Variable interactions are important throughout the study to determine the optimum condition required to achieve desired result. Therefore, interactions of variable are studied.

Figure 4.2 shows the interaction between reaction temperature (A) and mole ratio of glycerol to sulphuric acid catalyst (B) on the yield of triacetin produced. Figure 4.2 (a) describes the plot in two-dimension and Figure 4.2 (b) in three-dimension. From the Figures 4.2 (a) and (b), when no catalyst was used in the reaction, the yield was its lowest. Furthermore, at lower reaction temperature, the yield seems to be at its lowest too. When the temperature increased from 90 ^{o}C to 120 ^{o}C, with an increment in the catalyst from a mole ratio of glycerol to sulphuric acid 1:0.02 mol/mol to 1:0.04 mol/mol, an increasing trend in yield is observed. The elevated temperatures enhanced the formation of higher glycerol acetates due to the protonation of the remaining hydroxyl groups of glycerol molecule by steric factors and/or interaction with the active sites on the catalyst surface (Khayoon and Hameed, 2011). The rate of formation of acylium ions on the catalyst surface represents the fastest and determining step during the acetylation reaction (Lilja et al., 2005). However, a decreasing trend in yield was observed when passing a temperature of 112.5 ^{o}C with a catalyst percent of 1:0.04. A desired yield is obtained when the temperature reaches its optimum value together with an optimum catalyst amount. Beyond 112.5 ^{o}C, the activity decreases in the reaction due to the certain chemical changes taking place between the catalysts in high temperature. An observation was made during this research. Addition of too much catalyst at a high temperature entirely changes the final product colour. Hence, the optimum temperature and catalyst amount are 105^{o}C with 1:0.02 mol/mol ratios.

(a)



(b)

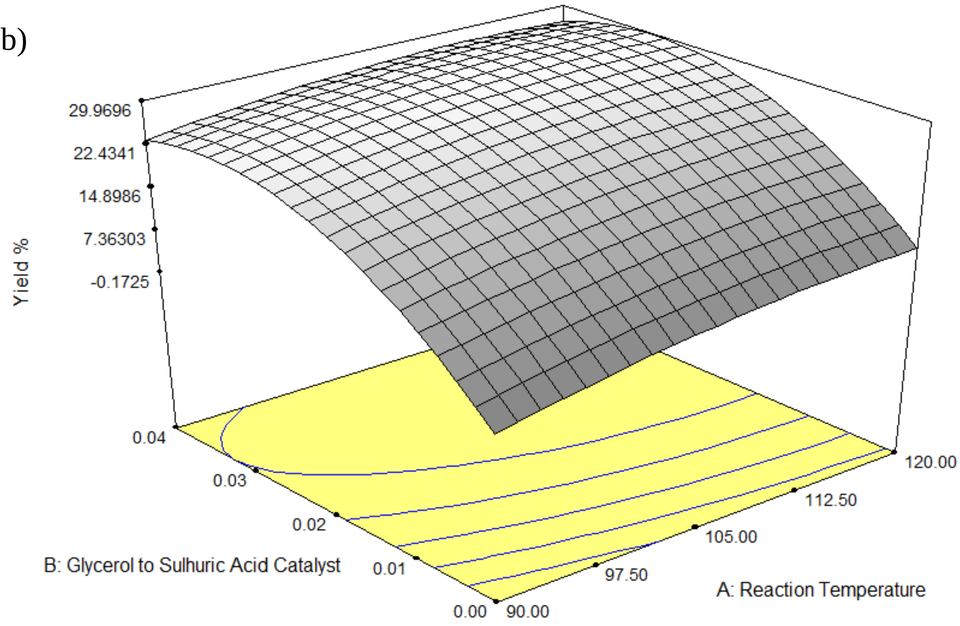
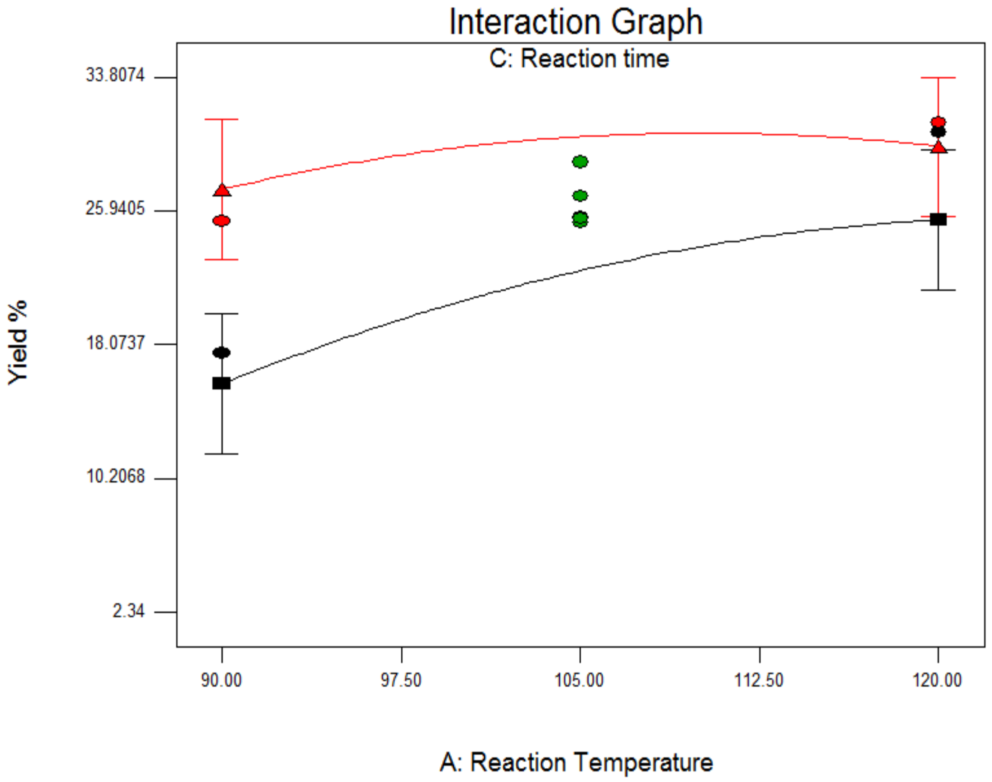


Figure 4.2: Effect of Reaction Temperature (A) and Glycerol to Sulphuric Acid Catalyst Mole Ratio (B) on the Triacetin Content in (a) Two-Dimension and (b) Three-Dimension Interaction Plots for Acetylation Reaction.

Figure 4.3 (a) and (b) illustrate the effect of reaction temperature (A) and reaction time (C) on the yield triacetin. Melero et al. (2007) have acclaimed that reaction temperature and molar ratio of glycerol with acetic acid are the most influential parameters on the esterification of glycerol, as evidence by multivariate analysis. Theoretically, a long reaction time and a higher reaction temperature produce a higher yield of the triacetin. Thus from Figures 4.3 (a) and (b), it is observed that the influence of reaction time in acetylation at 90 ^{o}C is more prominent compare to the reaction conducted at 120 ^{o}C. This shows that at a lower reaction temperature, longer reaction time is needed to enhance of yield of triacetin. Hence, at lower temperature, a longer time is needed to eliminate the yield of triacetin. Observation from Figures 4.3 (a) and (b), reviews after 118 ^{o}C, yield starts to deteriorate. This is because when the temperature exceeding 118 ^{o}C, the acetic acid tends to evaporate at a higher rate, disturbing the reaction hence resulting in a lower yield of triacetin. Therefore in this study, the optimum time for the reaction to take place is 60 minutes at 105 ^{o}C.

(a)



(b)

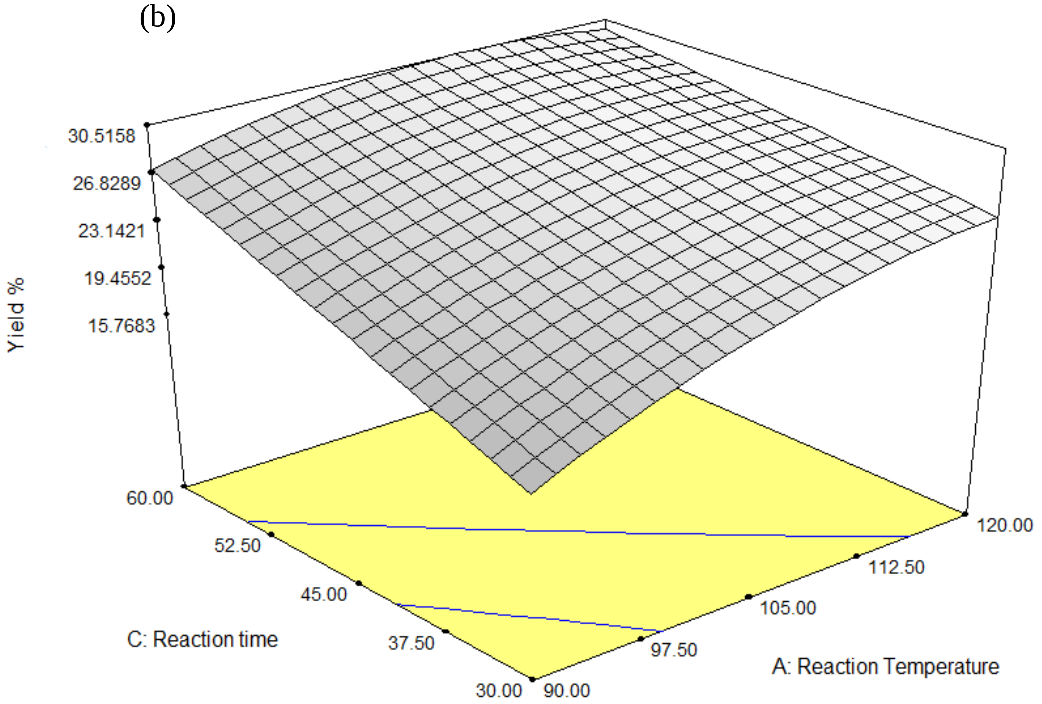
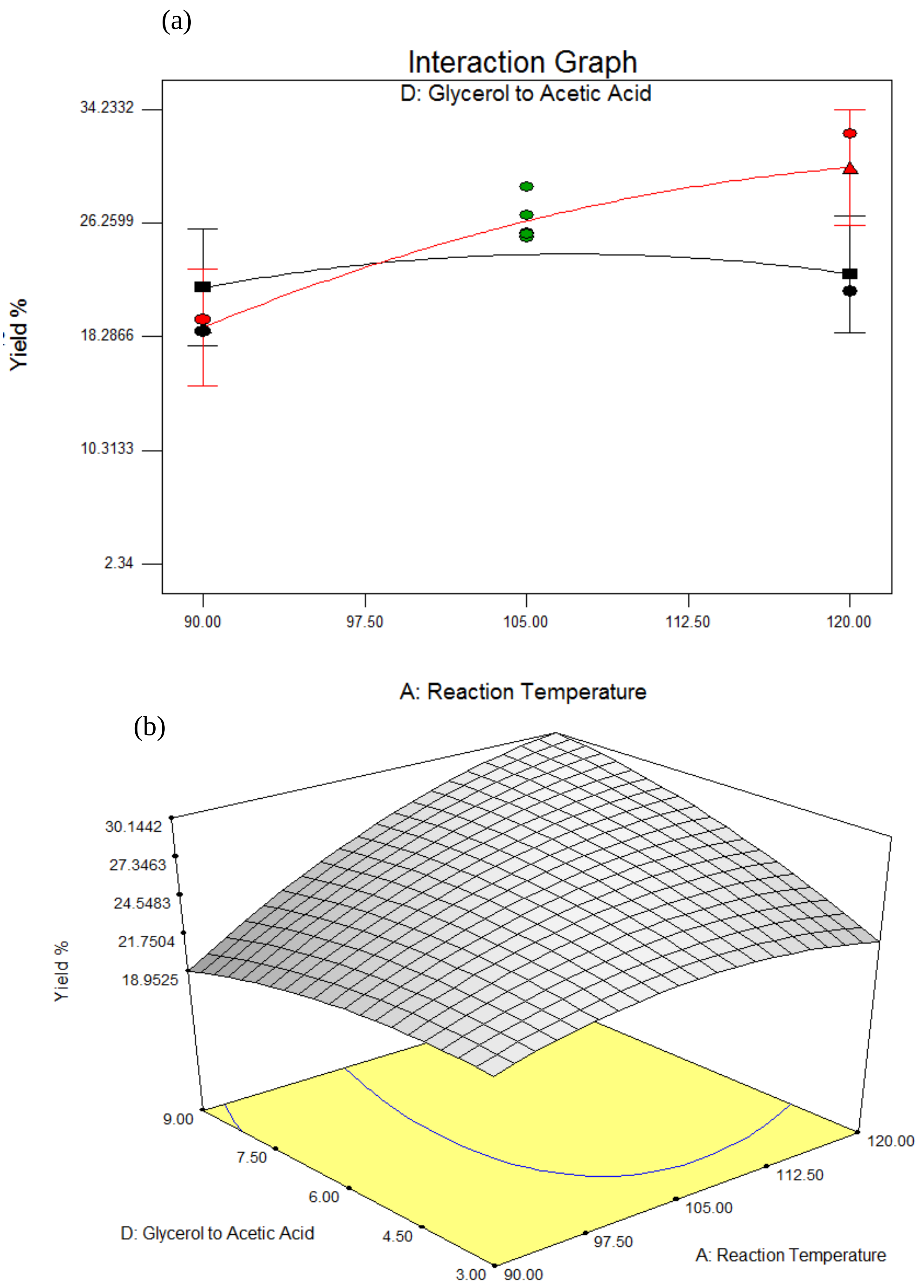


Figure 4.3: Effect of Reaction Temperature (A) and Reaction Time (C) on the Triacetin Content in (a) Two-Dimension and (b) Three-Dimension Interaction Plots for Acetylation Reaction.

Figure 4.4 shows the interaction between reaction temperature (A) and mole ratio of glycerol to acetic acid (D) on the yield of triacetin produced. Figure 4.4 (a) describes the plot in two-dimension and Figure 4.4 (b) in three-dimension. At higher molar ratio of glycerol to acetic acid (1:9 mol/mol), the increment of temperature from 90 ^{o}C to 120 ^{o}C encourages increase in triacetin yield. An excess of carboxylic acid utilized in acetylation reactions might shorten the time required to reach reaction equilibrium (Pagliaro et al., 2007) and provide more acetylating agent which undertakes the formation of tricetin through further acetylation reactions. These data correlates with those already reported (Balaraju et al., 2010; Ferreira et al., 2009). In contrast, at lower molar ratio a similar trend is observed, yield increases until the temperature of 105 ^{o}C and start decreasing at a higher temperature. This phenomena can be explained further because at a higher molar ratio and temperature, there is an excess of solvent thus evaporation of solvent doesn’t disturb the reaction whereas for a smaller molar ratio, when the solvent evaporates there is no excess to run the remaining reaction. Therefore in this study, the optimum temperature for the reaction to take place is 60 minutes with molar ratio of glycerol to acetic acid of 1:9.

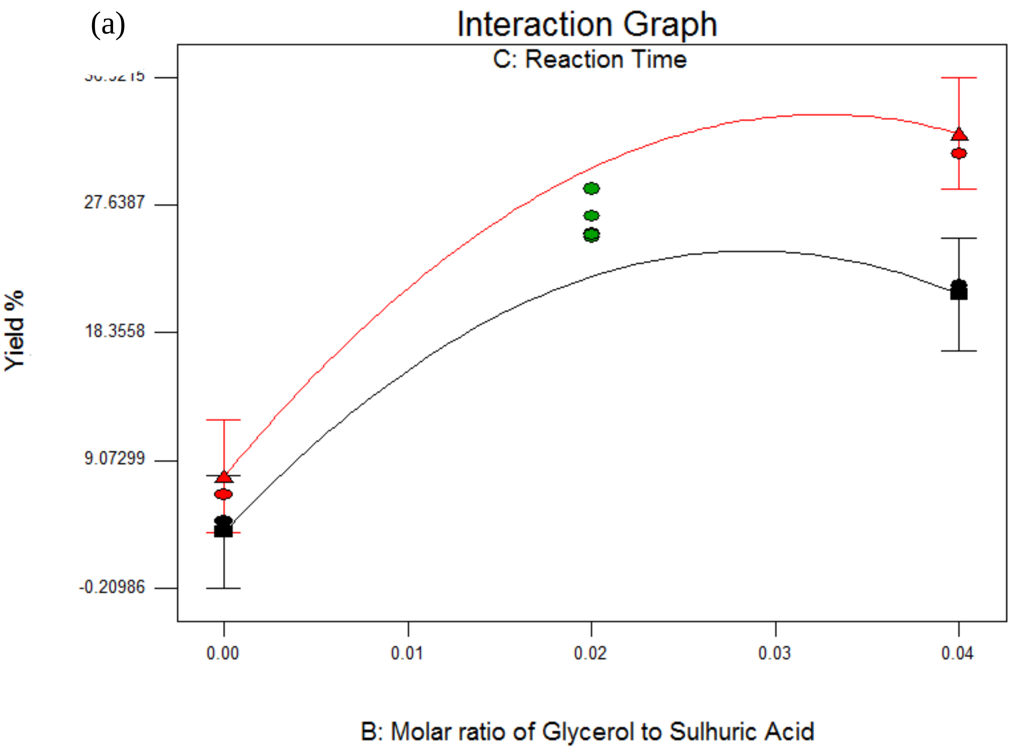


(a)

(b)

Figure 4.4: Effect of Reaction Temperature (A) and Molar Ratio of Glycerol to Acetic acid (D) on the Triacetin Content in (a) Two-Dimension and (b) Three-Dimension Interaction Plots for Acetylation Reaction.

Figure 4.5 (a) and (b) display the interaction between molar ratio of glycerol to sulphuric acid catalyst (B) and reaction time (C) on the yield of triacetin production in both two-dimensional and three-dimensional respectively. These figures revealed the effect of different amount of catalyst and reaction time on triacetin yield obtained. It is observed from the figures that increasing the molar ratio of catalyst not only increase the final triacetin content, but also increased the rate of reaction. From the figures (a) and (b), the triacetin yield increases as catalyst load and reaction time increases. The highest Triacetin yield of 31.89% was obtained in 60 minutes reaction time at a molar ratio catalyst of 1:0.02. It was explained by Liu et al., 2014 that the amount of catalyst represents the total number of acid sites or active sites available for reaction and the total surface area of the catalyst. But at the molar ratio of 1:0.04, the yield of triacetin started to decrease with the increment of time. This could be explained as increased in catalyst load, the acidity of the reaction also increased. Thus the adsorption of the product molecules by excessive of catalyst load could cause higher mass transfer resistance (Liu et al., 2014). However, in Figure 4.5 (a) and (b), the highest amount of triacetin yield was obtained at 60 minutes reaction times, and for longer reaction time, the triacetin yield started to decrease after 60 minutes. Longer reaction time will cause the active sites of the catalyst to be blocked by the product (Patel, Brahmkhatri and Singh, 2013). Thus, the optimum catalyst weight is molar ratio of 1:0.02 with a reaction time of 60 minutes.



(b)

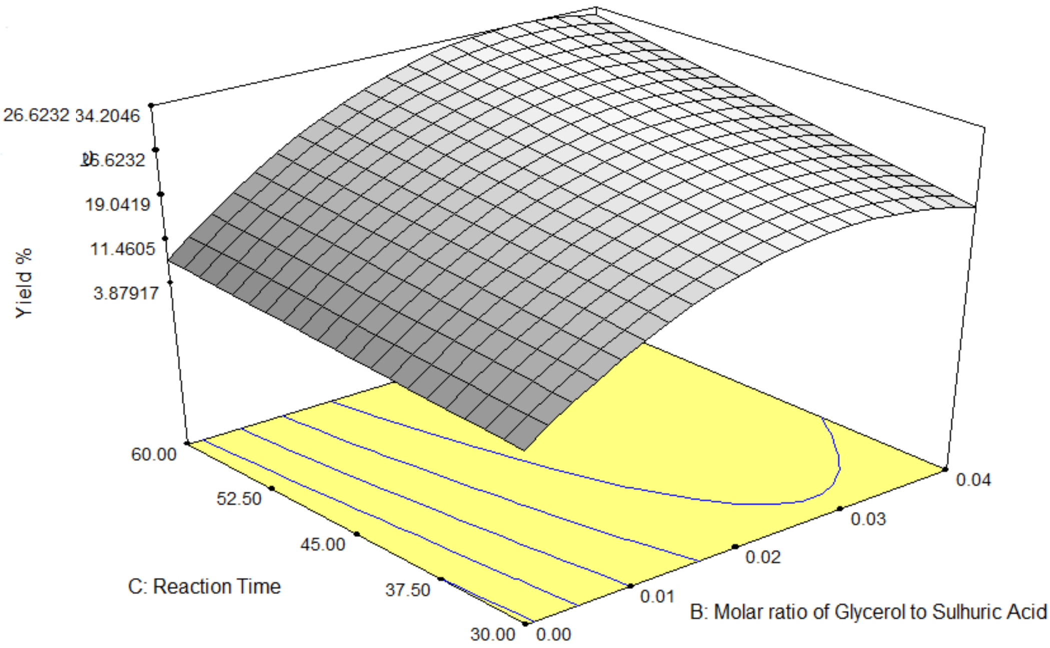


Figure 4.5: Effect of Molar Ratio of Glycerol to Sulphuric Acid Catalyst (B) and Reaction Time (C) on the Triacetin Content in (a) Two-Dimension and (b) Three-Dimension Interaction Plots for Acetylation Reaction.

Figure 4.6 (a) and (b) display the interaction between molar ratio of glycerol to acetic acid (D) and reaction time (C) on the yield of triacetin production in both two-dimensional and three-dimensional respectively. From the figures, it is observed the triacetin yield increased with the increase of molar ratio of glycerol to acetic acid and the reaction time. From Figure 4.6 (b), it shows that the interaction effect between reaction temperature (C) and molar ratio of glycerol to acetic acid (D) is insignificant. The effect of reaction time in the production of triacetin is more prominent at molar ratio of 1:9 mol/mol compared to at molar ratio at 1:3 mol/mol. This shows that at higher molar ratio with a longer reaction time induces high rate of reaction and subsequently increases the yield of triacetin content. However, the yield was still increasing when it approached 60 minutes of reaction time for both molar ratio of 1:3 mol/mol and 1:9 mol/mol. This implies that although a higher yield percent can be achieved by increasing the molar ratio of glycerol to acetic acid, a long reaction time is required. Thus, the optimum mole ratio of glycerol to acetic acid is 1:9 mol/mol with a reaction time of 60 minutes.

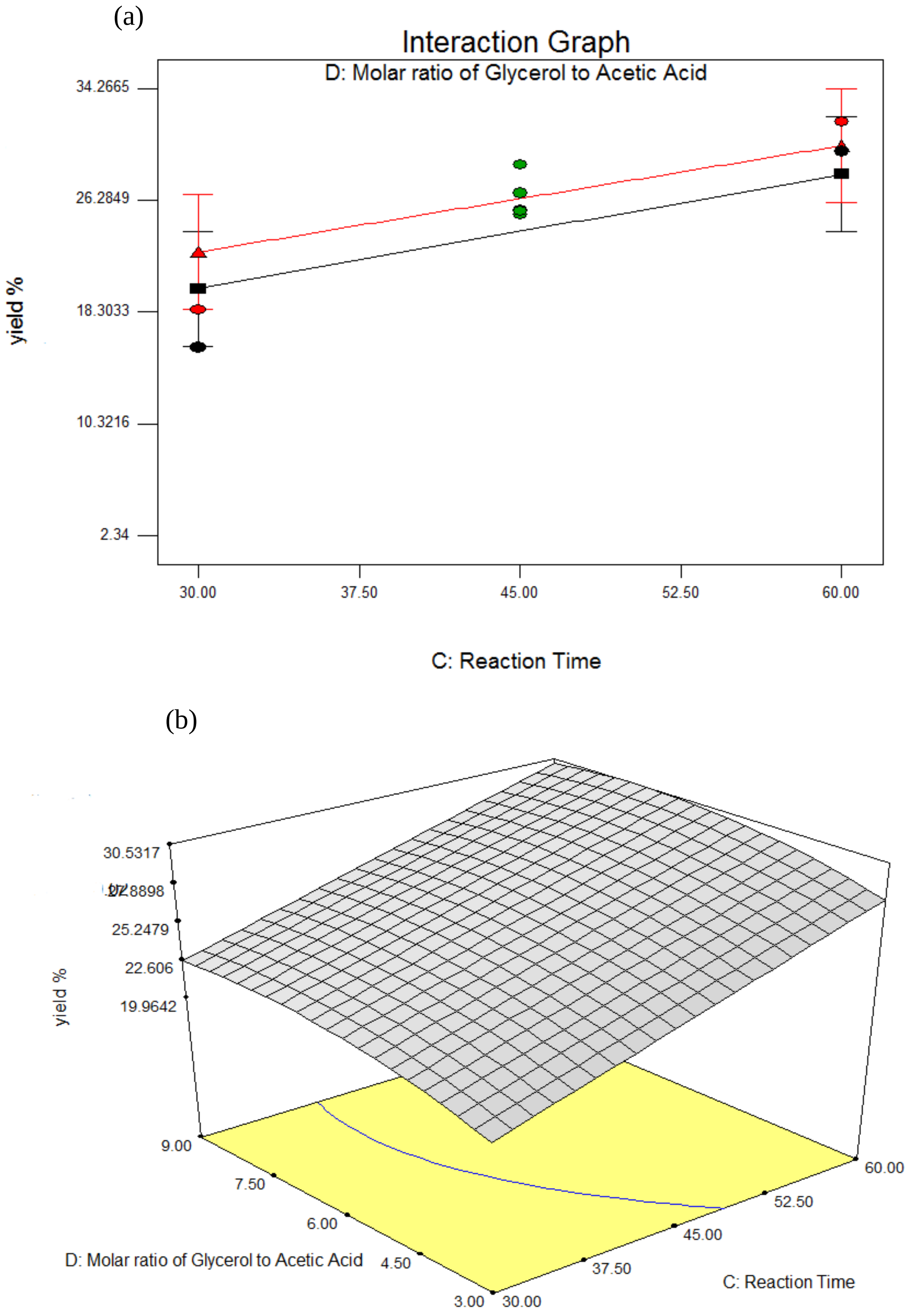
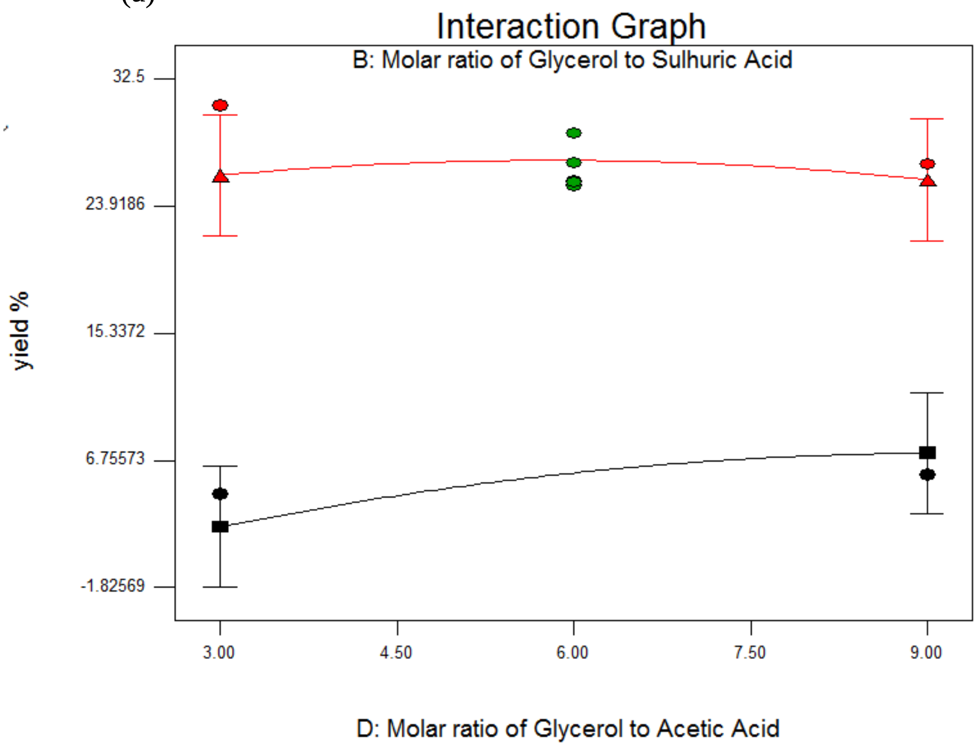


Figure 4.6: Effect of Molar Ratio of Glycerol to Acetic Acid (D) and Reaction Time (C) on the Triacetin Content in (a) Two-Dimension and (b) Three-Dimension Interaction Plots for Acetylation Reaction

Figure 4.7 (a) and (b) display the interaction between molar ratio of glycerol to sulphuric acid catalyst (B) and molar ratio of glycerol to acetic acid (D) on the yield of triacetin production in both two-dimensional and three-dimensional respectively. From Figure 4.7 (a), the molar ratio of glycerol to acetic acid 1:9 mol/mol has a higher yield compare to molar ratio of 1:3 mol/mol. This shows the molar ratio of glycerol to acetic acid affect the yield of triacetin is more than the molar ratio of catalyst used. Besides, there is no increment in rate of reaction and the yield when the molar ratio of catalyst is 1: 0.04 mol/mol with the increasing of molar ratio of glycerol to acetic acid. There will be unused active site when there is huge amount of active site with the limited amount of reactant. Therefore, further increment amount of catalyst will not affect the rate of reaction and the yield of the product and molar ratio of catalyst with 1:0.04 mol/mol is said to be overloaded. Both the plot did not intercept each other, indicating there was minimal interaction between the variables B and D. Thus, the optimum molar ratio of catalyst is 1:0.02 mol/mol with a molar ratio of glycerol to acetic acid of 1:9 mol/mol.

(a)



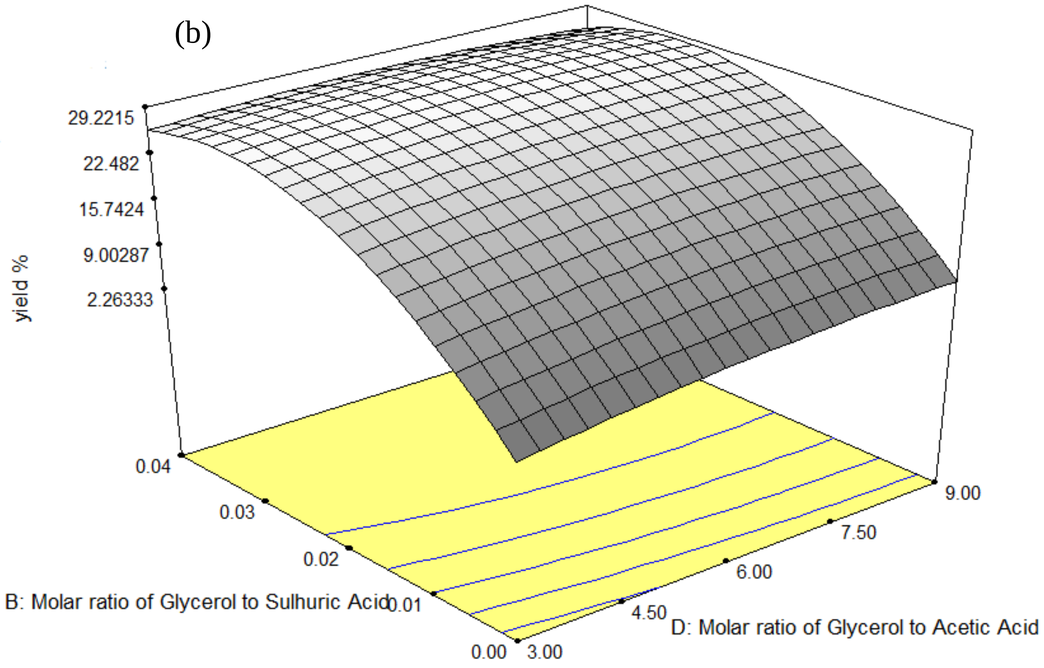


Figure 4.7: Effect of Molar Ratio of Glycerol to Acetic Acid (D) and Molar Ratio of Glycerol to Sulphuric Acid (B) on the Triacetin Content in (a) Two-Dimension and (b) Three-Dimension Interaction Plots for Acetylation Reaction

4.2.4 Optimization Study

From the Design Expert software, the combination of optimum conditions had been determined. The optimum conditions are listed in the Table 4.5.

Table 4.5 Summary of Optimum Conditions for Glycerol Acetylation and Predicted Yield

Condition	Value
Reaction Temperature (A), (^{o}C)	105
Glycerol to Sulphuric Ratio (B), mol/mol	1:0.02
Reaction Time (C), minute	60
Glycerol to Acetic Acid Ratio (D), mol/mol	1:9
Predicted Yield	29.378

Table 4.6 shows the comparison between the predicted and experimental yield of triacetin. Addition independent run was conducted to validate the proposed conditions. Actual experiment based on the optimum conditions produced 31.89 of triacetin with percent error of 8.55%. This small percent error proves that the actual values and predicted values are in strong agreement with each other. Thus, the regression model was successfully proven to be reliable in predicting the yield of triacetin content for the given conditions studied.

Table 4.6: Comparison between Predicted and Experimental Triacetin Content of Acetylation Reaction

Run	Predicted Triacetin Content (%)	Experimental Triacetin Content (%)	Error (%)
1	29.378	31.89	8.55%

4.3 Product Analysis

4.3.1 Fourier Transform Infrared Spectroscopy Analysis

Fourier transform infrared spectroscopy (FTIR) is used to identify the component and impurities in the triacetin obtained from the glycerol acetylation. As shown in Figure 4.8, several peaks can be obtained and each peak represents different functional group of different compounds

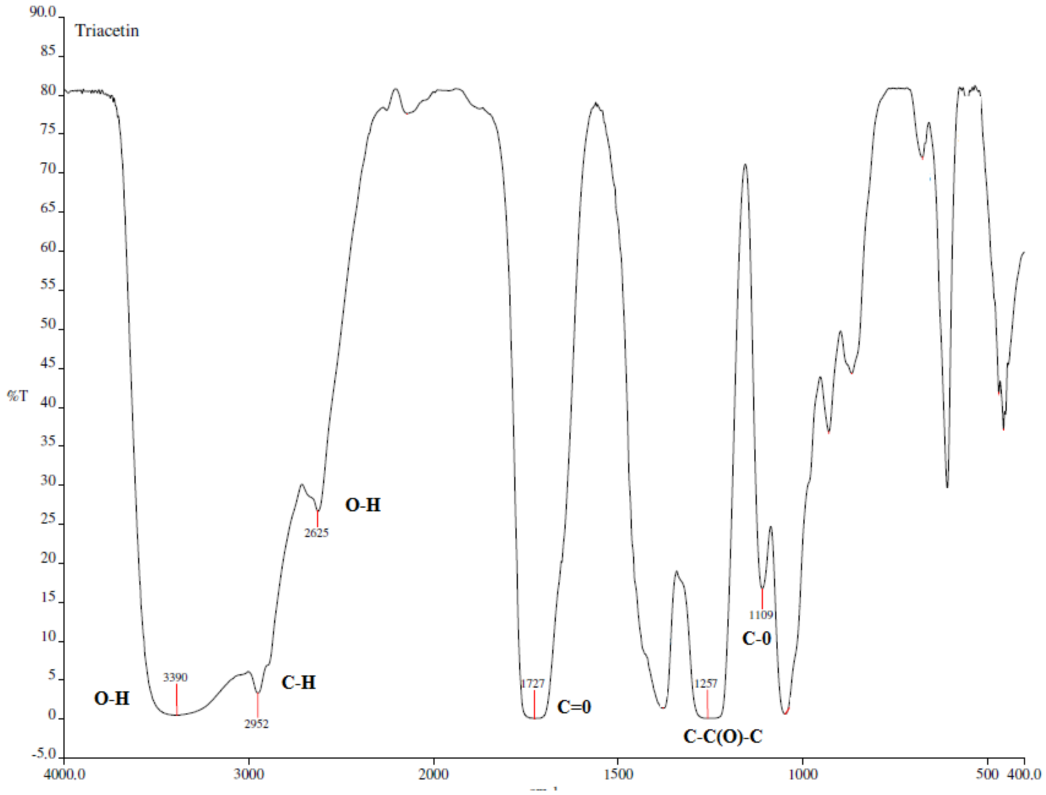


Figure 4.8: FTIR Analysis of Triacetin

The peak at 3390 cm^{-1} represents the functional group of O-H stretch of alcohol, this indicating there was unreacted ethanol in the product. Besides, the peak at 1625 cm^{-1} indicates O-H stretch of carboxylic acid, indicating the unreacted acetic acid in the product. The peak at 2952 represents a C-H stretch in an alkane hydrocarbon. On the other hand, the peak at 1727 cm^{-1} represents a C=O stretch represents the ester molecules. Lastly, the peak at 1257 cm^{-1} indicates a C-C(O)-C stretch of ester of acetates group, further proving the presence of the triacetin in the product.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The batch reaction of glycerol acetylation was conducted using the reflux condensation machine. The glycerol acetylation was optimized using different parameters. The parameter used to optimize the reaction were reaction temperature, reaction time, molar ratio of glycerol to acetic acid and molar ratio of glycerol to sulphuric acid catalyst. The highest yield of triacetin obtained in this research was 31.89% with the condition of 1:0.02 molar ratio of glycerol to sulphuric acid, 1: 9 molar ratio of glycerol to acetic acid, 60 minutes of reaction time and $105^{o}C$ of reaction temperature. The Fourier Transform Infrared Spectroscopy Analysis reviews that the present of triacetin is seen through the ester of acetates group stretch at 1257 cm^{-1} peak. Finally through the GC and FITR test conducted, it was proven that the experiment is a success.

5.2 Recommendation

The experiment was conducted in batch mode by using reflux condensation machine, although it is a convenient method to produce triacetin but the amount of triacetin production is limited due to the size of the machine. Therefore, increasing the size of the machine will take more advantages for the production of triacetin. Besides, batch reaction which may different from the condition in mass production, there for continuous reaction is recommended for further study.

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APPENDICES

APPENDIX A: Gantt Chart

Gantt Chart for First Long Trimester

Details/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Project Proposal/Selection	🟩	🟩	🟩											
Preliminary Research Work		🟩	🟩											
Project Work				🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Progress Report Submission												🟩		
Oral Presentation													🟩	🟩

Gantt Chart for Second Long Trimester

Details/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Project Work (continue)	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩		
Progress Report Submission								🟩						
Final Report Submission												🟩		
Oral Presentation													🟩	🟩
Hard bound submission														🟩

APPENDIX B: Triacein GC Analysis

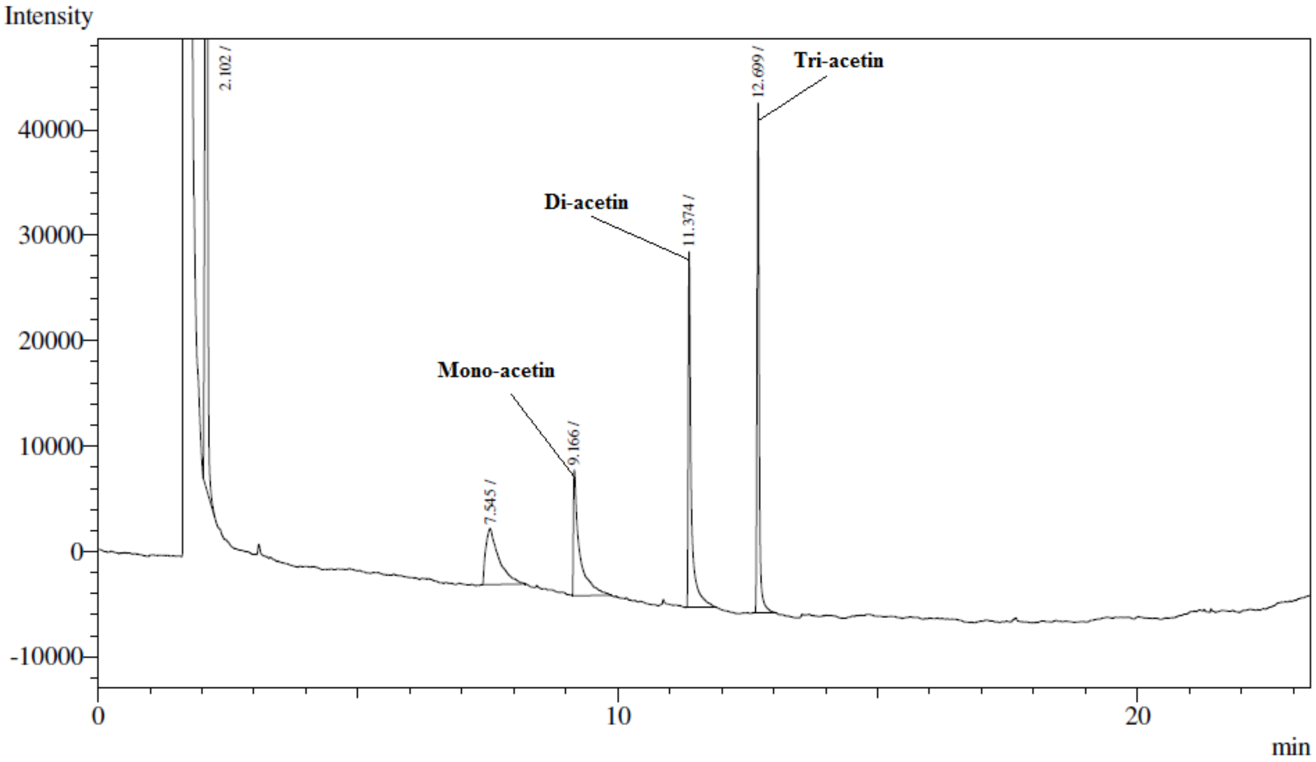

Figure B.1: Chromatograph Analysis of Mono-, di- and Tri-acetin

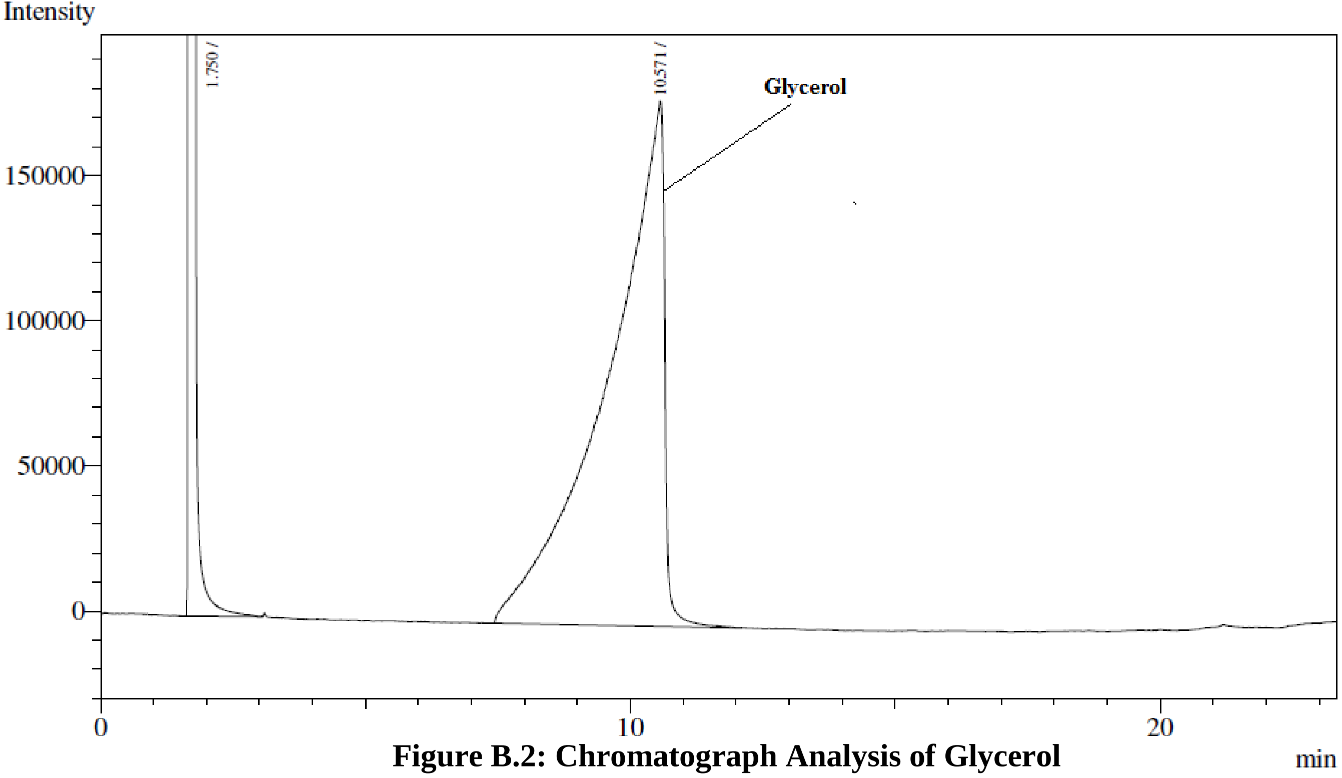

Figure B.2: Chromatograph Analysis of Glycerol

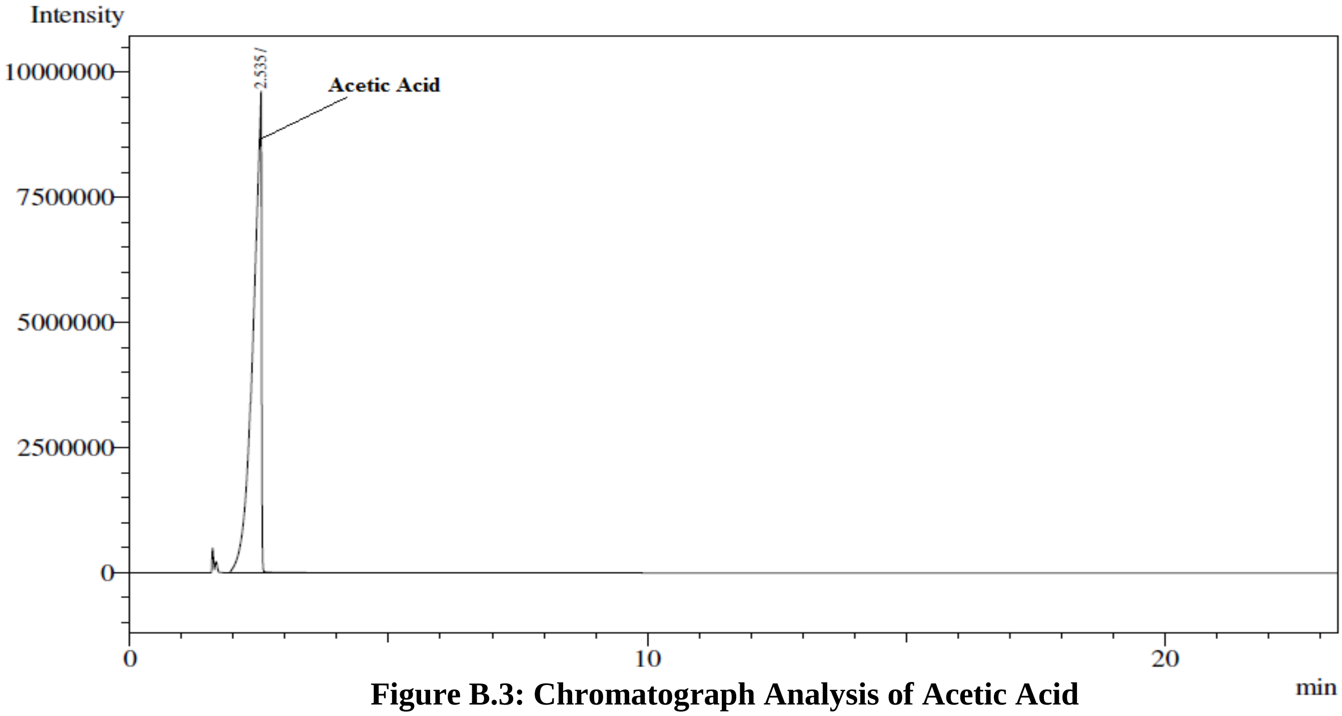

Figure B.3: Chromatograph Analysis of Acetic Acid

APPENDIX C: Sample Calculation

Based on Figure B, the area and retention time of Triacetin obtained for set number 11 in Table 4.2 was summarized in Table C.1. It is given that,

Total peak area = 803007

Table C.1: Retention Time and Area of Traicetin obtained in Figure B

Component	Retention Time (min)	Area	Content, C_i (%)
Triacetin	12.699	146414	31.89

According to modified EN 14103 standards, the content of each individual component of samples were calculated by using Equation 3.2.

$$C_i = \frac{A_i}{\sum A - A_{IS}} \times 100\%$$

<u>For example:</u>

Content of triacetin, C $= \frac{A_i}{\sum A - A_{IS}} \times 100\%$

$$= \frac{146414}{803307-344185} \text{ x } 100\%$$

= 31.89%