EFFECTS OF TEMPERATURE IN REACTIVE DISTILLATION OF VAPOR
FROM NON-CATALYTIC PENTAERYTHRITOL TETRADODECANOATE
(PETD) REACTOR

SHAHRULNIZAM JAMEN

A report submitted in partial fulfillment of the requirements for the award of the
Degree of Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resource Engineering
University College of Engineering and Technology Malaysia
“Saya/Kami* akui bahawa saya/kami* telah membaca karya ini dan pada pandangan saya/kami* karya ini adalah memadai dari segi skop dan kualiti untuk tujuan Penganugerahan Ijazah Sarjana Muda Kejuruteraan Kimia.”

Tandatangan : ...........................................................
Nama Penyelia : Mr Mohd Sabri Mahmud
Tarikh : ...............................................................
“I declare that this thesis is the result of my own research except as cited references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any degree”

Signature : ............................
Name of Candidate : SHAHRULNIZAM JAMEN
Date : 20 November 2006
DEDICATION

Special dedication to my beloved father, mother, brothers and sister......
ACKNOWLEDGEMENTS

Bismillahirrahmanirrahim

In preparing this thesis, I was in contact with many people, researchers, academicians and practitioners. They have contributed towards my understanding and thoughts during this research. First of all praise and gratitude to Allah S.W.T for giving me strength went through many difficulties to successfully finishing my project industrial. Next, I wish to express my sincere appreciation to my supervisor, Mr. Mohd Sabri Bin Mahamud for his valuable encouragement, guidance, and critics. Without his continued support and interest, this project would not be a success.

I am also indeed indebted to all the lecturers and teaching engineering especially Mr. Mohd Hasbi bin Abdul Rahim in FKKSA for his support during project development

My fellow friend especially Riduan Abd Ghani, Shahbudin Sobki, Jedidiah Johny and other should also be recognized for their support. Their view and tips are indeed very useful. I am also grateful to my family member for their continuous support from starting of this project until the end of it.
ABSTRACT

Pentaerythritol Tetradecanoate (PETD) is a new ester which used as varnish addictive in magnetic wire production. In many foreign countries, production of PETD has been conducted but in Malaysia, the technology of PETD production still not localized by any Malaysia company. The objective of this research is to study effects of temperature in non-catalytic PETD reactor. Method for experiment of this research is using reactive distillation as unit operation and six different temperatures from 180°C to 230°C will be manipulated. The products from the experiment has been analysed using Gas Chromatography (GC). Results show that at 200°C is an optimum temperature for non-catalyst PETD production. It may observe that at 200°C is the maximum temperature for this production of PETD. So, for best temperature for producing PETD using reactive distillation is at 200°C because at this temperature, there are maximum reaction and higher conversion for PETD. Outcome from this research can be considered as pioneer process in localizing the technology, scale up and commercialization of PETD production.
ABSTRAK

TABLE OF CONTENT

CHAPTER   TITLE                PAGE

DECLARATION             ii
DEDICATION             iii
ACKNOWLEDGEMENT            iv
ABSTRACT                  v
ABSTRAK                  vi
TABLE OF CONTENTS           vii
LIST OF TABLE              x
LIST OF FIGURES              xi
NOMENCLATURE               xii
LIST OF APPENDICES           xiii

1  INTRODUCTION

1.0 Introduction                1
1.1 Problem Statement         2
1.2 Objective                3
1.3 Scope Research            3

2  LITERATURE REVIEW

2.0 Introduction               5
2.1 Phase Rule                8
2.2 Distillation Principles  9
## METHODOLOGY

### 3.0 Introduction

### 3.1 Experiment

- 3.1.1 Chemical
- 3.1.2 Apparatus
- 3.1.3 Lab Methodology

### 3.2 Analysis

- 3.2.1 Gas Chromatography
- 3.2.2 Preparation of Calibration Standard
- 3.2.3 Preparation of Analysis Sample
- 3.2.4 Gas Chromatography Method

## RESULT AND DISCUSSION

### 4.0 Result

### 4.1 Standard Calibration of Dodecanoic Acid

### 4.2 Chromatogram Result

### 4.3 PETD Analysis on Dodecanoic Acid Calibration Curve

### 4.4 Error and Prevention Step
5 CONCLUSION

5.0 Conclusion 32
5.1 Recommendation 33

REFERENCES 34

APPENDICES A-N 37
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>Chemical properties</td>
<td>20</td>
</tr>
<tr>
<td>3.1</td>
<td>Concentration weight per weight %</td>
<td>22</td>
</tr>
<tr>
<td>3.2</td>
<td>Gas Chromatography Method</td>
<td>23</td>
</tr>
<tr>
<td>4.0</td>
<td>Percentage of dodecanoic acid in every sample</td>
<td>29</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.0</td>
<td>Reactive Distillation</td>
<td>06</td>
</tr>
<tr>
<td>2.1</td>
<td>Boiling-Point Diagram</td>
<td>09</td>
</tr>
<tr>
<td>2.2</td>
<td>Uniform vapor-liquid equilibrium</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Non-ideal systems</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Maximum boiling point and minimum boiling point</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>Heterogeneous azeotropic</td>
<td>13</td>
</tr>
<tr>
<td>2.6</td>
<td>Effect of temperatures on mole fraction of n-Hexyl</td>
<td>16</td>
</tr>
<tr>
<td>2.7</td>
<td>Effect of reaction temperature on the synthesis of oleyl oleate</td>
<td>17</td>
</tr>
<tr>
<td>2.8</td>
<td>Equilibrium conversion by temperature profiles</td>
<td>18</td>
</tr>
<tr>
<td>3.0</td>
<td>Block Diagram Flow</td>
<td>19</td>
</tr>
<tr>
<td>3.1</td>
<td>Apparatus Setting</td>
<td>21</td>
</tr>
<tr>
<td>4.1</td>
<td>Standard Calibration Curve</td>
<td>25</td>
</tr>
<tr>
<td>4.2</td>
<td>Sample 180°C</td>
<td>26</td>
</tr>
<tr>
<td>4.3</td>
<td>Sample 190°C</td>
<td>26</td>
</tr>
<tr>
<td>4.4</td>
<td>Sample 200°C</td>
<td>27</td>
</tr>
<tr>
<td>4.5</td>
<td>Sample 210°C</td>
<td>27</td>
</tr>
<tr>
<td>4.6</td>
<td>Sample 220°C</td>
<td>28</td>
</tr>
<tr>
<td>4.7</td>
<td>Sample 220°C</td>
<td>28</td>
</tr>
<tr>
<td>4.8</td>
<td>Temperature profile versus percentage of dodecanoic acid in sample of product</td>
<td>29</td>
</tr>
</tbody>
</table>
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETD</td>
<td>Pentaerythritol Tetradodecanoate</td>
</tr>
<tr>
<td>RD</td>
<td>Reactive Distillation</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Standard Calibration Chromatogram</td>
<td>37</td>
</tr>
<tr>
<td>B</td>
<td>Standard Calibration Curve</td>
<td>38</td>
</tr>
<tr>
<td>C</td>
<td>GC Chromatogram - 180°C</td>
<td>39</td>
</tr>
<tr>
<td>D</td>
<td>GC Chromatogram Curve - 180°C</td>
<td>40</td>
</tr>
<tr>
<td>E</td>
<td>GC Chromatogram - 190°C</td>
<td>41</td>
</tr>
<tr>
<td>F</td>
<td>GC Chromatogram Curve - 190°C</td>
<td>42</td>
</tr>
<tr>
<td>G</td>
<td>GC Chromatogram - 200°C</td>
<td>43</td>
</tr>
<tr>
<td>H</td>
<td>GC Chromatogram Curve - 200°C</td>
<td>44</td>
</tr>
<tr>
<td>I</td>
<td>GC Chromatogram - 210°C</td>
<td>45</td>
</tr>
<tr>
<td>J</td>
<td>GC Chromatogram Curve - 210°C</td>
<td>46</td>
</tr>
<tr>
<td>K</td>
<td>GC Chromatogram - 220°C</td>
<td>47</td>
</tr>
</tbody>
</table>
L    GC Chromatogram Curve - 220°C  48

M    GC Chromatogram - 230°C       49

N    GC Chromatogram Curve - 230°C 50
CHAPTER 1

INTRODUCTION

1.0 Introduction

In magnetic wire production such as Kaneka chemical, pentaerythritol tetradodecanoate (PETD) has been used as an essential addictive vanish. In foreign country, like Japan, the esterification of PETD has been produced but in Malaysia the process technology is still not yet localized by any Malaysian company to support the country’s manufacturing needs especially in reducing the product price, at the moment. Dodecanoic acid and Pentaerythritol are used as the raw material to produce this varnish additive using esterification process.

Esterification is a general name for a chemical reaction which an ester is the reaction product. Carboxylic acid reacts with alcohols to form esters through a condensation reaction

\[
\text{Alcohol} + \text{Carboxylic Acid} \rightleftharpoons \text{Ester} + \text{Water}
\]  

Esterification is a reversible reaction which the products can react to produce the original reactants. In a closed system where none of the reactants or products can escape, reversible reactions reach equilibrium. At equilibrium, the reactions are still happening but at the same rate, so the concentrations of reactants and products do not change. Esterification of PETD in this research will carried out in reactive distillation.

In the chemical process industries, chemical reaction and the purification of the desired products by distillation are usually carried out sequentially. In many
cases, the performed of this classis chemical process structure can be significantly improved by integration of reaction and distillation in a single process unit. This concept is called reactive distillation. Sundamacher [1] give an overview on advantages of this integration are chemical equilibrium limitation can be overcome, higher selectivity can be achieved, the heat of reaction can be used in situ for distillation, auxiliary solvents can be avoid, and azeotropic or closely boiling points mixtures can more easily separated than in common distillation. Beside that this reactive also increased process efficiently and reduction of investment and operational costs are direct result of this approach. Some of these advantages were realized by using reaction to improve separation and others are realized by using separation to improve reaction [1]

Due to the interaction of reaction and distillation in one single unit, the steady state and dynamic operational of reactive distillation can be very complex. Therefore, suitable process control strategies have to be developed and applied, ensuring optimal and safe operation.

In this research, focus was mainly to the effects of temperature in esterification of PETD depending on conversion rate of products. From the research done by Salina, Mahiran, Abu Bakar, Arbakariya, Basyaruddin, Raja Noor Zaliha (2005), in esterification process, effects of temperature can be apportioned to its effect on substrate solubility as well as its direct influences on the reaction.

1.1 Problem Statement

Pentaerythritol tetradodecanoate (PETD) is a new ester, which is produced from reaction between pentaerythritol (alcohol) and dodecanoic acid (carboxylic acid). Pentaerythritol tetradodecanoate has been used as an essential varnish additive in magnetic wire production. In many foreign countries, the esterification of pentaerythritol tetradodecanoate has been conducted but in our country, the technology process for this esterification still not yet localized by any Malaysia company.
Therefore, the products of pentaerythritol tetradecanoate as additives vanish were supply from Japan for Malaysia’s company especially which involved in magnetic wire production such as Kaneka Chemical. That will make the price of pentaerythritol tetradecanoate products is high. As alternative for reducing the product of pentaerythritol tetradecanoate price in market, new research for develop technology process of esterification of pentaerythritol tetradecanoate at optimum output must carry out to support our country’s manufacturing needs.

In this research for esterification of pentaerythritol tetradecanoate using reactive distillation unit, the temperature will be manipulated to find higher conversion rates for pentaerythritol tetradecanoate product. The effect of the temperature to the production of pentaerythritol tetradecanoate will be studied further. According to la Chatelier principle if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change. So, by increasing temperatures at pressure 1 atm and 24 hours of reaction times between temperatures range 180°C to 230°C, the conversion rates of pentaerythritol tetradecanoate products will increase too. The optimum temperature state from previous work was 190°C by using catalyst. In this research by non-catalytic reaction, the optimum temperature assumes to be at 200°C.

1.2 Objective

To study the effects of temperature in Pentaerythritol Tetradecanoate reactor

1.3 Scope Research

Scope of this research is to find which temperatures that given higher conversion rates of pentaerythritol tetradecanoate production. So, temperatures is a
manipulate variable between 180°C to 230°C. Six experiments will be run to studies which temperatures given higher conversion rates;

1) 1<sup>st</sup> run at 180°C
2) 2<sup>nd</sup> run at 190°C
3) 3<sup>rd</sup> run at 200°C
4) 4<sup>th</sup> run at 210°C
5) 5<sup>th</sup> run at 220°C
6) 6<sup>th</sup> run at 230°C

The constants factors in this experiment are pressure, times of reaction and set up of apparatus. All experiments will be run at 1 atm, 600 rpm, 24 hours and same set up of apparatus. Apparatus that used in this experiment are;

1) Reaction Flask 500 ml
2) Fractionating Columns Vigreux 20cm
3) Motor Stirrer
4) Condenser 20cm
5) Distillation Chemistry Kit
6) Digital Thermometer
7) Beaker 500 ml
8) Heating Mantle 2L

The products from experiment will analysis by gas chromatography (GC) for testing the purity of product from experiment where gas chromatography is a one of the most useful instrument tools for separating and analyzing organic compounds that can be vaporized without decomposition.
CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

In the chemical process industries, chemical reaction and purification of the desired products by distillation are usually carried out sequentially. In many cases, the performances of this classic chemical process structure can be significantly improved by integration of reaction and distillation in a single multifunctional process unit. This integration concept is called ‘reactive distillation’ [1].

Chemical reaction is a process involving one, two or more substances called reactant to become product by chemical change. It can be character by a chemical change and yield in one or more product(s) which are different from reactant, while distillation is a process for separating the various component of a liquid solution which depend upon the distribution of these components between vapor phase and liquid phase [2]. This process is based on the fact that the vapor of a boiling mixture will be richer in the components that have lower boiling points. Therefore when this vapor is cooled and condensed, the condensate will contain more volatile components and at the same time, the original mixture will contain more of the less volatile material [5].

As advantages of this integration, chemical equilibrium limitations can be overcome, higher selectivity can be achieved, the heat of reaction can be used in situ for distillation, auxiliary solvents can be avoided, and azeotropic or closely boiling mixtures can be more easily separated than in non-reactive distillation. Increased process efficiency and reduction of investment and operational costs are results of
In standard reactive distillation, reactant A and B enters the column in Fig 2.0. If the reactant is liquid, it flows down to sieve tray or stage. Vapor enters the tray and bubbles through the liquid on this tray as entering liquid flow flows across. Reactant A and B will react in reaction section. The vapor and liquid leaving the tray are essentially in equilibrium. The vapor continues up to the next tray or stage, where it is again contacted with a downflowing liquid. In this case the concentration of the more volatile component (the lower-boiling component A) is being increased in the vapor from each stage going upward and decreased in the liquid from each stage going downward the final vapor product coming overhead is condensed in a condenser and portion of the liquid product (distilled) is removed, which contains a high concentration of A. The remaining liquid from condenser is returned (reflux) as a liquid to the top tray. The liquid leaving the bottom tray enters the reboiler, where it this approach. Some of these advantages are realized by using improve separation; others are realized by using separation to improve reaction [1].
is partially vaporized and the remaining liquid which is lean in A or rich in B, is withdrawn as liquid product.

Reactive Distillation is used with reversible reaction which reversible reactions are reactions in which the products can react to produce the original reactants. In a closed system where none of the reactants or products can escape, reversible reactions reach equilibrium. At equilibrium, the reactions are still happening but at the same rate, so the concentration of reactants and products do not change.

If the forward reaction is exothermic and the temperature is increased, the yield of products is decreased. Exothermic means to release energy in the form of heat. It refers to a transformation in which a system gives heat to the surroundings: $Q < 0$. When the transformation occurs at constant pressure: $\Delta H < 0$; and constant volume: $\Delta U < 0$. If the system undergoes a transformation which is both exothermic and adiabatic, its temperature increases [3].

If the forward reaction is endothermic and the temperature is increased, the yield of products is increased. Endothermic means to absorb energy in the form of heat. It refers to a transformation in which a system receives heat from the surroundings: $Q > 0$. When the transformation occurs at constant pressure: $\Delta H > 0$; and constant volume: $\Delta U > 0$. If the surroundings do not supply heat, an endothermic transformation leads to a drop in the temperature of the system [3].

Chemical reaction for reactive distillation:

$$A + B \rightleftharpoons C + D$$  \hspace{1cm} (2.1)

For many reversible reactions the equilibrium point lies far to the left and little product is formed. However, if one or more of the products are removed more of the product will be formed because of Le Chatelier's Principle:

$$A + B \rightleftharpoons C + D$$  \hspace{1cm} (2.2)
Le Chatelier's principle states that when a system in chemical equilibrium is disturbed by a change of temperature, pressure, or a concentration, the system shifts in equilibrium composition in a way that tends to counteract this change of variable. There are three ways that can affect the outcome of the equilibrium, changing concentrations by adding or removing products or reactants to the reaction vessel, changing partial pressure of gaseous reactants and products, and changing the temperature [4].

2.1 Phase rule

Many chemical process materials and biological substances occur as mixtures of different component in gas, liquid, or solid phase. In order to separate or remove one or more of the component from its original mixture, it must be contacted with another. In order to predict the concentration of a solute of two phases in equilibrium, experimental equilibrium data must be available. If two phases are not at equilibrium, the rate of mass transfer is proportional to the driving force, which departure from equilibrium [12]. In all cases involving equilibria, two phases are involved such as gas-liquid or liquid-liquid. The important variables affecting the equilibrium of a solute are temperature, pressure and concentration [12].

The equilibrium between two phases in a given situation is restricted by the phase rule. Phase rule describes the possible number of degrees of freedom in a (closed) system at equilibrium, in terms of the number of separate phases and the number of chemical constituents in the system. It was deduced from thermodynamic principles by J. W. Gibbs in the 1870s.

\[ F = C - P + 2 \]  

(2.4)

Where F is the number of independent intensive variables that need to be specified in value to fully determine the state of the system or degrees of freedom. Typical such variables might be temperature, pressure, or concentration [13].
P is a number of phases at equilibrium. Phase is a component part of the system that is immiscible with the other parts. While C the number of total component in the two phases when no chemical reactions are occurring.

### 2.2 Distillation Principle

Separation of components from a liquid mixture via reactive distillation depends on the differences in boiling points of the individual components. Also, depending on the concentrations of the components present, the liquid mixture will have different boiling point characteristics. Therefore, distillation processes depends on the vapor pressure characteristics of liquid mixtures [11].

The boiling point diagram shows how the equilibrium compositions of the components in a liquid mixture vary with temperature at a fixed pressure. Consider an example of a liquid mixture containing two components (A and B) - a binary mixture. This has the following boiling point diagram [11].

![Boiling-Point Diagram](image)

**Figure 2.1: Boiling-Point Diagram [11].**

The boiling point of A is that at which the mole fraction of A is 1. The boiling point of B is that at which the mole fraction of A is 0. In this example, A is the more volatile component and therefore has a lower boiling point than B. The upper curve in the diagram is called the dew-point curve while the lower one is called the bubble-