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

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“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	: ....

**Potong yang tidak berkenaan*

NOVEMBER 2006

DECLARATION

"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	: RIDUAN ABD. GHANI
Date	: 20 November 2006

DEDICATION

To my beloved father, mother,

brothers and sisters……

ACKNOWLEDGEMENTS

Bismillahirrahmanirrahim

First of all praise and gratitude to Allah S.W.T for giving me strength went through many difficulties and successful finished my project industrial. After all the hardwork and difficulty, I personally would like to acknowledge the many wonderful people that have guided me and support me in completing this thesis.

In preparing this thesis, I was in contact with many people, academicians and practitioners. They have contributed toward my understanding and thoughts during this project development. In particular, I wish to express my sincere appreciation to my thesis supervisor, Mr. Mohd Sabri bin Mahmud for his encouragement, guidance, critics and advise. Without their continued support and interest, this thesis would not be a success.

I am also indeed gratitude to all personnel in the Faculty of Chemical Engineering & Natural Resources (FKKSA) for their support and motivation in completing my undergraduate project.

My fellow friends especially Sharulnizam Jamen, Shahbudin Sobki and Jedidiah Johnny should also be recognized for their support. Their view and tips are indeed 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-tetradodecanoate (PETD) was used as an essential varnish additive in magnetic wire production, It recently been conducted in many foreign countries, but in Malaysia it's still not yet localized by any local company. The objective of this research is to study effects of temperature in catalytic PETD reactor. Method was applied by using reactive distillation as the main unit operation involving the mixture of lauric acid and pentaerythritol substrates occurred at the range 180°C to 230°C. The product from the experiment is analyzed with Gas Chromatography (GC). The result from analysis shows that the optimum temperature is at 200°C. From observation, 200°C is an optimum temperature, where it is suitable to obtain maximum reaction and higher production of PETD. From GC analysis also shows that high production of PETD when catalyst was used if compare to experiment without catalyst. Outcome from this research can be considered as pioneer process in localizing the technology, scale up and commercialization of PETD production especially in Malaysia.

ABSTRAK

Pentaerythritol Tetradodecanoate (PETD) adalah ester baru yang digunakan dalam pembuatan wayar magnetic. Di negara-negara luar, penghasilan PETD telah dijalankan namun di Malaysia, teknologi penghasilan PETD masih belum diterokai oleh mana-mana syarikat di Malaysia. Objektif kajian ini adalah untuk mengkaji kesan suhu terhadap penghasilan PETD dengan penggunaan mangkin. Eksperimen dijalankan menggunakan penyulingan reaktif sebagai unit operasi melibatkan campuran asid laurik dan pentaerythritol dengan enam suhu yang berbeza dari 180°C hingga 230°C. Hasil produk dari eksperimen ini kemudiannya dianalisis dengan menggunakan Kromatografi gas. Keputusan analisis menunjukkan suhu optimum adalah 200°C. Daripada pemerhatian yang dilakukan, suhu 200°C adalah suhu yang sesuai untuk mendapatkan kadar penghasilan PETD yang tingggi. Selain itu dengan penggunaan pemangkin ia juga dapat menambahkan kadar penghasilan PETD Hasil dari kajian ini boleh dianggap sebagai langkah awal dalam mengkomersialkan penghasilan PETD ini.

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PETD	= Pentaerythritol Tetradodecanoate
RD	= Reactive Distillation
GC	= Gas Chromatography
w/w %	= weight per weight percent

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Ester is essentially applied in a variety of areas such as solvents, plasticizers, pharmaceuticals and intermediates. Pentaerythritol-Tetradodecanoate (PETD) also known as Pentaerythritol-Tetralaurate is one of the ester was used as varnish additive in the magnetic wire coating [4]. PETD is produced from esterification process by using the mixture pentaerythritol and lauric acid as reactant.

Esterification is the general name for a chemical reaction in which two chemicals (typically an alcohol and an acid) form an ester as the reaction product. Different approaches have obviously been employed to prepare esters. Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an acid catalyst. The equilibrium can be driven to completion by using an excess of either the alcohol or the carboxylic acid, or by removing the water as it forms.

A common method of operating equilibrium-limited reactions is to use one excessive reactant in order to increase the conversion of the limiting reactant. In reactive distillation, the continual separation of products from reactants forces the reaction to surpass the equilibrium conditions.[1] Reactive distillation is a process where separation of the components of a reaction system is accompanied by a chemical reaction in a column. The combination of a reversible reaction and distillation is a widely used technique to increase the conversion of the reactants to levels above equilibrium conversion. The reactive distillation is becoming more and more popular in chemical industries.

Catalysts provide an alternative pathway of lower activation energy, for a reaction to proceed whilst remaining chemically unchanged them. A catalyst is a substance that accelerates the rate (speed) of a chemical reaction. Chemical catalysts participate in reactions but are neither chemical reactants nor chemical products.

1.2 PROBLEM STATEMENT

Malaysia is gearing towards achieving industrialized and developed nation. PETD has been used as a varnish additive in production of magnetic wire for a few years ago. The product of PETD as a varnish additive is recently produced and supplied directly from Japan by KANEKA. The esterification of PETD has been produced in many foreign countries, but the process technology is still not yet localized by local company to support manufacturing needs especially in reducing the product price. Local companies has still not known the technology to produce the fine chemical at an optimum output in terms of purity, production rate, energy consumption and process minimization.

This study is considering the production of PETD using esterification. Esterification is a reversible reaction, so the suitable instrument was reactive distillation because the application of Le Chateliers' principle. In reactive distillation, the reaction occurs and at the same time separates the product. Meanwhile, temperature is affected in the term of reaction in reactive distillation.

From the problem arise; it is essential to study in the process of PETD production. The hypothesis of the study is the temperature of reaction and the production of PETD is increased proportionally until the optimum temperature that occurs at 200 °C.

1.3 OBJECTIVE

The aim of this study is to study the effect of temperature on the performance of catalytic reaction in PETD production.

1.4 SCOPE RESEARCH

To achieve the objective of this research, there are three scopes that have been identified:

a) This study was on the effects of difference temperature to the reaction. Six sample were tested at temperature was range between 180^{o}C to 230^{o}C. at 1 atm, 16 hours and same rig. The range is used because in the past literature review, the optimize temperature is 190^{o}C. From experiment, the conversion in PETD production is the main idea to make a conclusion by observing the relation of temperature and PETD production.

b) Identify the temperature for optimum reaction. The optimum is the point which the amount of PETD is the most favorable. The optimum temperature is decided when the sample is analyze. The sample is analyzed with Gas Chromatography (GC). The optimum temperature is the temperature that enhanced the conversion to its maximum. The analysis of the sample can give the idea to predict the outcome of result.

c) Next scope is effect of catalyst in PETD reaction. Homogeneous catalyst is use in the experiment. The effect of catalyst is compared with the control test to see the difference. Catalysts reduce the activation of the energy and accelerate speed of reaction. So, the time of production is reduced to minimum as possible.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Magnet wire is an insulated electrical conductor, usually copper or aluminum that when wound into a coil and energized creates a useful electrical field. Electricity is essentially useless without magnet wire. 90% of all electrical energy requires modification through the use of magnet to be of use. It plays an important role in the machine function. Enameled wires are used to make electrical coils for the conversion (interchange between electrical & magnetic energy) of electrical energy to electromagnetic energy and this is why enameled wire is also called magnet wire.

At the moment Kaneka Chemical has patent the PETD as one of its product. The product of PETD as a varnish additive is recently produced and supplied directly from Japan.

2.2 Pentaerythritol Tetradodecanoate

PETD is an ester that was produced by esterification reaction in many foreign countries; the production of PETD used pentaerythritol and lauric acid as the raw material. It involves the mixture of lauric acid and pentaerythritol substrates occurred at the range 180^{o}C to 230^{o}C.

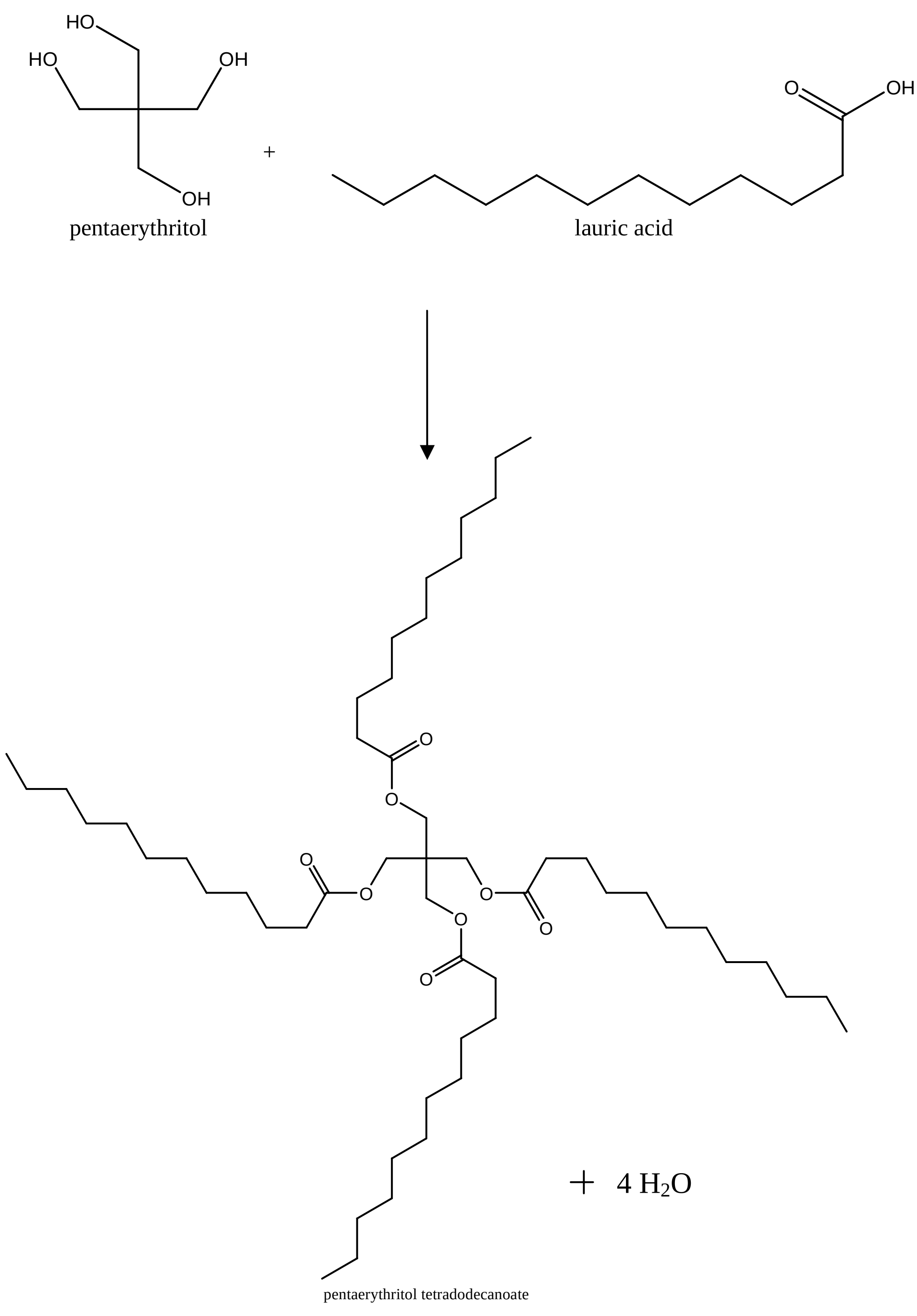


Figure 2.1: The general reaction of PETD with Pentaerythritol and Lauric acid as raw material.

2.3 Esterification

Esterification is the general name for a chemical reaction in which two chemicals (typically an alcohol and an acid) form an ester as the reaction product. These are commonly used as fragrance or flavour agents.

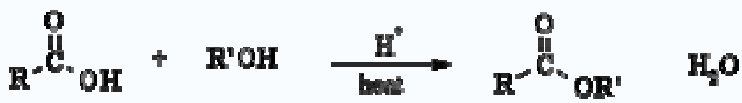
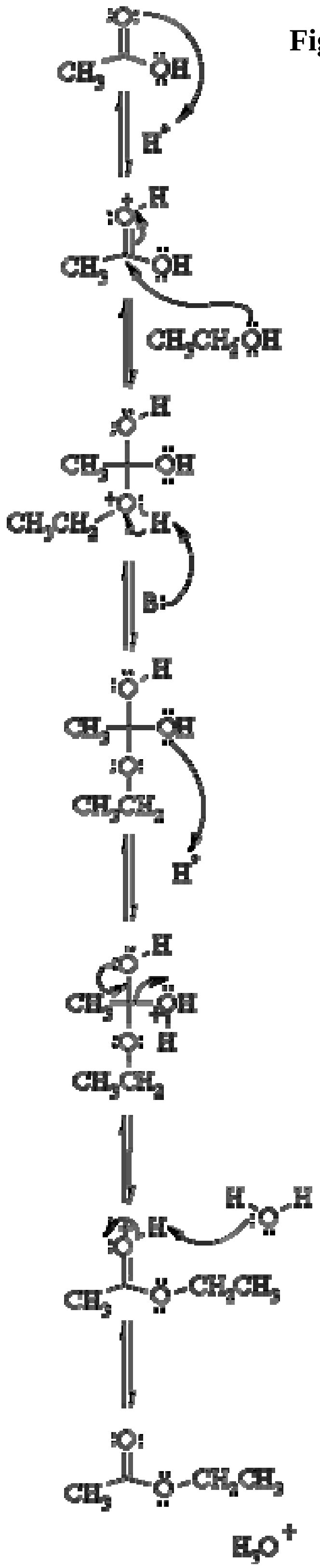


Figure 2.2: General equations of esterification

2.3.1 Acid-Catalyzed Esterifications

Acid-catalyst esterifications are called Fischer esterifications. They proceed very slowly in the absence of strong acids, but they reach equilibrium within a matter of a few hours when an acid and an alcohol are refluxed with a small amount of concentrated sulfuric acid or hydrogen chloride. Since the equilibrium controls the amount of the ester formed, the use of an excess of either the carboxylic acid or the alcohol increases the yield based on the limiting reagent. Just which components we choose to use in excess will depend on its availability and cost. The yield of an esterification reaction can also be increased by removing water from the reaction mixture as it is formed.

Figure 2.3: Reaction type: Nucleophilic Acyl Substitution



Step 1:
An acid/base reaction. Protonation of the carbonyl makes it more electrophilic.

Step 2:
The alcohol O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3:
An acid/base reaction deprotonate the alcoholic oxygen.

Step 4:
An acid/base reaction. Need to make an -OH leave, it doesn't matter which one, so convert it into a good leaving group by protonation.

Step 5:
Use the electrons of adjacent oxygen to help "push out" the leaving group, a neutral water molecule.

Step 6:
An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the ester product.

2.4 Catalyst

Estimates are that 60% of all commercially produced chemical products involve catalysts at some stage in the process of their manufacture. [3] A **catalyst** is a substance that accelerates the rate (speed) of a chemical reaction. Chemical catalysts participate in reactions but are neither chemical reactants nor chemical products. More generally, one may sometimes call anything which accelerates a reaction without itself being consumed or transformed a catalyst.

Catalysts provide an alternative pathway of lower activation energy, for a reaction to proceed whilst remaining chemically unchanged them. This can be observed on a Boltzmann distribution and energy profile diagram. This means that catalysts reduce the amount of energy needed to start a chemical reaction. Molecules that would not have had the energy to react or that have such low energies that they probably would have taken a long time to react are able to react in the presence of a catalyst. Thus, more molecules that need to gain less energy to react will go through the chemical reaction.

Catalysts cannot make energetically unfavorable reactions possible; they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are equally affected.

A catalyst is not destroyed or changed during a reaction, so it can be used again. This is the ideal situation. In reality, catalyst will also involve in reaction and hard to be recovered. The catalyst will disturb the reaction by form the complex medium. The traditional homogenous catalysed reactions are less favoured owing to the attendant problems of separation and reuse. [5] There for many other catalysts that used for esterifications such as acidic ion exchange resin.

Catalysts can be either heterogeneous or homogeneous. Heterogeneous catalysts are present in different phases from the reactants (e.g. a solid catalyst in a liquid reaction mixture), whereas homogeneous catalysts are in the same phase (e.g. a dissolved catalyst in a liquid reaction mixture). A simple model for heterogeneous catalysis involves the catalyst providing a surface on which the reactants (or substrates) temporarily become adsorbed. Bonds in the substrate become weakened sufficiently for new bonds to be created. The bonds between the products and the catalyst are weaker, so the products are released. Homogeneous catalysts generally react with one or more reactants to form a chemical intermediate that subsequently reacts to form the final reaction product, in the process regenerating the catalyst. This experiment use homogeneous type of catalyst.

In research of esterifcation of Acetic Acid with Ethanol Catalysed by an Acidic Ion-Exchange Resin by S Ismail Kirbaslar, Z. Baris Baykal and Umur Dramur [1], they observed that percentage of equilibrium between acetic acid and ethanol is increasing due to increasing the amount catalyst. The graph below shown increasing of percentage of equilibrium by temperature profiles.

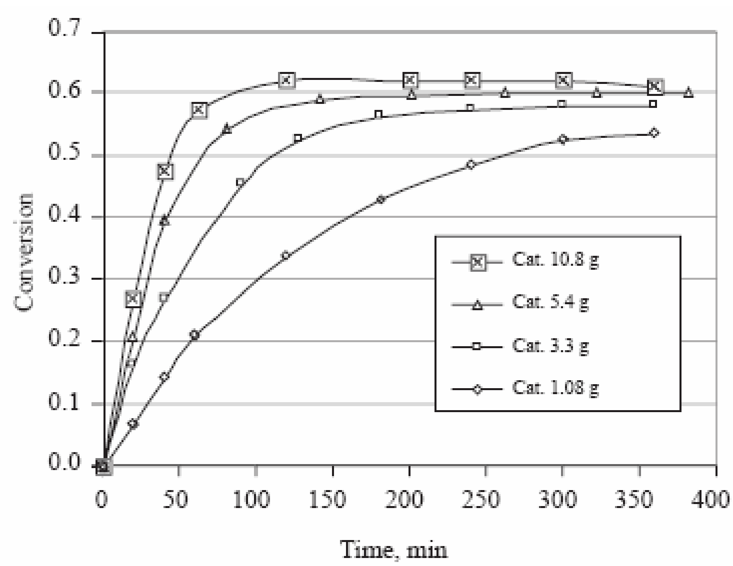


Figure 2.4: Effect of changing catalyst concentrations on the conversion of example (molar ratio of acetic acid and ethanol (M= 1/1) and temperature 353 K)

2.5 Reactive Distillation

Reactive distillation comprises the processes of catalytic reaction and multistage distillation carried out simultaneously in a single vessel.[9] A reactive distillation column replaces the reactor and a series of distillation columns, thereby reducing the number of process vessels and materials transfer and control equipment required.

Benefits of reactive distillation include:

- Increased speed and improved efficiency
- Lower costs – reduced equipment use, energy use and handling
- Less waste and fewer byproducts
- Improved product quality – chemicals are exposed to heat only once, reducing opportunity for degradation

Reactive distillation is a complex technology that is not right for every project. Generally, normal operating conditions for distillation and reaction, such as temperature and pressure conditions, should overlap, and other specific requirements must be met.

Reactive distillation can be used with a wide variety of chemistries, including the following:

- Acetylation
- Aldol condensation
- Alkylation
- Amination
- Dehydration
- Esterification
- Etherification
- Hydrolysis
- Isomerization
- Oligomerization
- Transesterification

2.5.1 Concept of Reactive Distillation

Reactive distillation is used with reversible, liquid phase reactions. Suppose a reversible reaction had the following chemical equation:

$$A + B \rightleftharpoons C + D$$

For many reversible reactions the equilibrium point lies far to the left and little product is formed:

$$A + B \rightleftharpoons C + D$$

However, if one or more of the products are removed more of the product will be formed because of Le Chatlier's Principle:

$$A + B \rightleftharpoons C + D$$

Removing one or more of the products is one of the principles behind reactive distillation. The reaction mixture is heated and the product(s) are boiled off. However, caution must be taken that the reactants won't boil off before the products.

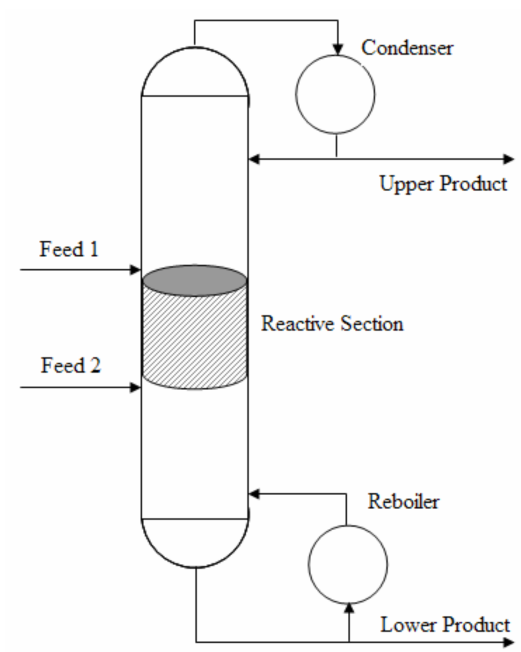


Figure 2.5: Typical Reactive Distillation Column

2.6 Le Chatelier's Principle

In chemistry, Le Chatelier's principle can be used to predict the effect of a change in conditions on a chemical equilibrium.

Chemical equilibrium is the state in which a chemical reaction proceeds at the same rate as its reverse reaction; the rates of the forward and reverse reactions are equal, and the concentration of the reactants and products stop having net change. When this condition is met, there is no change in the proportion; i.e., concentrations of the various compounds involved, and it appears that the reaction ceases to progress. However the forward and the reverse reactions continue to occur at the same rates. This process is known as dynamic equilibrium [2].

A statement of Le Chatelier's Principle

- If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

Le Chatelier's Principle can be summarized, if a chemical system at equilibrium experiences a change in concentration, temperature or total pressure the equilibrium will shift in order to minimize that change.

2.7.1 Using Le Chatelier's Principle with a change of concentration

Suppose you have an equilibrium established between four substances A, B, C and D.

$$A + 2B \rightleftharpoons C + D$$