KINETIC STUDY OF
CATALYTIC GLYCOLYSIS OF PET WASTES
WITH ZINC ACETATE

CHAN WEI TATT

UNIVERSITI MALAYSIA PAHANG

KINETIC STUDY OF
CATALYTIC GLYCOLYSIS OF PET WASTES
WITH ZINC ACETATE

CHAN WEI TATT

A thesis submitted in fulfillment of the requirements
for the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang

February 2013

TABLE OF CONTENTS

KINETIC STUDY OF CATALYTIC GLYCOLYSIS OF PET WASTES WITH ZINC ACETATE

ABSTRACT

Poly(ethylene terephthalate) (PET) was depolymerized by di-ethylene glycol (DEG) in the presence of zinc acetate. Qualitative analysis showed that the main product from glycolysis was bis(hydroxylethyl) terephthalate. Fourier Transform infra-red (FTIR) was used for characterization of product while thermo-gravimetry analysis (TGA) and differential scanning calorimetry (DSC) were used for thermal analysis. The respond surface methodology (RSM) was used to predict the optimum conditions of reaction which includes time, temperature, amount of catalyst and amount of DEG. Besides that, the analysis of variance (ANOVA) was employed to evaluate the validity of the developed model. The maximum conversion obtained from RSM was 99.79%, The optimum temperature, time, amount of catalyst and amount of DEG were 183.37 ℃, 0.82 hour, 0.09 g and 10.33 g respectively. Lastly, a simple theoretical power-law model was developed to predict the time evolution of conversion. This kinetic model was found to be consistent with the experimental data. From the study, activation energy and enthalpy of reaction of 38.24 kJ/mol and 14.87kJ/mol were obtained, respectively.

KAJIAN KINETIC TERHADAP PEMANGKINAN GLIKOLISIS BAHAN BUANGAN PET DENGAN ASETAT ZINC

ABSTRAK

PET diuraikan dengan menggunakan di-ethylene glycol (DEG) dengan kehadiran zinc acetate sebagai pemangkin. Produk yang dihasilkan daripada glikolisis adalah BHET telah dipastikan melalui analisis kualitatif. FTIR telah digunakan untuk pencirian manakala TGA dan DSC telah digunakakn untuk melaksanakan analisis haba. Sementara itu, RSM telah digunakan untuk mendapatkan keadaan optima untuk tindak balas glikolisis seperti masa, suhu, jumlah pemangkin dan juga jumlah DEG. Selain itu, ANOVA telah digunakan untuk mengesahkan model yang dicadangkan oleh RSM. Pada keadaan optima, penukaran setinggi 99.79% telah direkodkan. Keaddan optima untuk tindak balas glikolisis adalah pada 183.37^{o}C, 0.82 jam, 0.09g zinc asetat dan 10.33g DEG. Daripada pengajian tersebut, tenaga pengaktifan dan entalpi tindak balas yang ditentukan adalah 38.24 kJ/mold dan 14.87 kJ/mol masing-masing.

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
BHET	-	bis(2-hydroxyethylene) terephthalate
CV	-	Coefficient of variance
DEG	-	Di-ethylene Glycol
DMT	-	Dimethyl terephthalate
DSC	-	Differential Scanning Calorimetry
EG	-	Ethylene glycol
FTIR	-	Fourier Transform Infra-Red
n. d.	-	no date
PE	-	Polyester
PEG	-	Polyethylene glycol
PET	-	Polyethylene terephthalate
PP	-	Polypropyl
R^2	-	Correlation coefficient value
R^2_{adj}	-	Adjusted correlation coefficient value
RSM	-	Response Surface Methodology
TGA	-	Thermo-Gravimetry Analaysis
TPA	-	Terephthalic acid
UF	-	Urea formaldehyde
UV	-	Ultraviolet

LIST OF SYMBOLS

%	-	percent
atm	-	atmosphere
C	-	concentration
cm	-	centimetre
g	-	gram
h	-	hour
Hg	-	mercury
K	-	Kelvin
kg	-	Kilogram
kJ	-	kilojoule
L	-	litre
m	-	meter
mL	-	mililitre
mm	-	milimeter
^{o}C	-	degree celcius
t	-	time

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of research

The usage of industrial synthesized polymer are widely discovered in many consumer end products, especially the polyethylene terephthalate (PET), being one of the most popular in the polyester families. According to a reported technical paper, PET consumption was approximately 15.3 million tons in 2009 (GBI, 2010). As the population increases from year to year, the usage of PET may be doubled, and most likely will be tripled in the future. PET is characterized by its high strength, low density, low gas permeability and good aesthetic appearance (Liu, Wang, and Pan, 2011). The products of PET cover a wide range of application, which includes plastic drinking bottles, plastic bags, food containers, and even toys for kids. Indeed, the invention and commercial application of PET has brought a lot of benefits and conveniences to mankind in the aspect of improvement on the standard of life; however, the excess usage of PET has also caused a lot of serious environmental issues. These environmental issues can be reviewed from various aspects, such as recycling, landfill disposal, incineration as well as marine pollution. Out of the issues arisen, the disposal of PET products can be considered as a very critical issue and needed to be solved as soon as possible. PET can be classified into two categories, namely biodegradable and non-biodegradable PET. Due to the economical factor, majority of the PET produced are non-biodegradable, as they are much cheaper in the production cost. Actually, the biodegradable PET has been existed for a long time, but the high expense has never made it become a commercial option (Chong and Kim, 2007). When the amount of produced PET increases from years to years and yet no better alternatives to deal with the environmental issues arisen, it will eventually lead to serious environmental problems. For an example, the villagers in the rural areas disposed the PET products such as bottles and plastic bags by open burning, which is a very unwise decision and action since the toxic fumes are released to the air and it will harm both the environment and mankind significantly.

The productions of PET are most probably encouraged by the economic factor, which is a critical and vital aspect to be considered in any production processes. The low manufacturing and processing costs of PET is definitely an important factor behind the progressive development of PET usages. When the amount of PET increases, the problems of PET wastes disposal are created. Among all the alternatives available, recycling is the most well-known, commercial and common solution. Since most of the PET products are non-biodegradable, it is always a wise decision to recycle or reuse the PET products (waste to wealth). More and more researches are currently directed towards the recycling of PET waste, and they are mainly encouraged and motivated by both the environmental and economic reasons. The recycling of plastic became popular in the era of 1990s. Two classes of plastics are thermosetting and thermoplastics. For thermoplastics, they were melted and remoulded to form new products; for thermosetting plastics, they were normally ground up and used as filler.

In this research, the collected PET waste will be recycled using glycolysis process, in which the di-ethylene glycol (DEG) is used as the main glycol chemical and zinc acetate is used as trans-esterification agent (catalyst).

1.2 Problem statement

The varieties of PET products seem to be an endless list as they can be found commonly all around the world. Most of the manufacturers will choose to produce non-biodegradable PET rather than those with biodegradable one since the cost of production between these two PETs is considerably huge in their difference. As the production of PET products give a profitable return to the country, however, when the amount of PETs produced are growing more rapidly than the amount of PETs disposed or recycled, it started to create environmental problems.

Malaysia is one of the countries that facing this problem. A clear indication can be observed that the PET products such as plastic bottles and containers occupy the majority quantities of the trash collected. There are many alternatives available nowadays to deal with the PET waste, utilizes them by turning them from waste to wealth being the wisest choice. However, before they can be integrated into particular product, it is necessary to go through the characterization process so that their chemical and physical properties can be determined. It helps the experts to decide whether they can be integrated into which products by looking at the characterization results.

1.3 Research objectives

Based on the problem statement that had been identified, the following objectives are proposed:

i. To carry out the glycolysis process using the DEG as glycol and zinc acetate as trans-esterification agent.
ii. To investigate the impacts of reaction parameters on the glycolysis process of PET.
iii. To carry out the optimization of parameters for the glycolysis process.
iv. To perform the kinetics study of glycolysis process.

1.4 Research scopes

By identifying the scopes of the study, it provides a guideline in conducting the experiment. The study concentrates on the scopes as listed as below in order to achieve the objectives stated above.

i. The glycolysis process will be conducted using di-ethylene glycol (DEG), and zinc acetate as trans-esterification agent (catalyst).

ii. Fourier Transform Infrared Spectrometry (FTIR), Thermogravimetry analysis (TGA) and Differential Scanning Calorimetry (DSC) will be used for characterization of glycolyzed PET.

iii. The Response Surface Methodology (RSM) will be used to perform the optimization for glycolysis reaction.

iv. The kinetic study of glycolysis was developed using a simple theoretical power-law model.

1.5 Expected outcomes

By doing this research, the following expected outcomes are formulated:

i. It is expected that the glycolysis of PET wastes can be carried out successfully.
ii. It is expected that the characterization of PET waste can be done so that it can provide useful information about the glycolysis process.
iii. It is expected that the optimization of reaction variables can be performed so that optimum glycolysis reaction can be achieved.
iv. It is expected the kinetics study can be developed to provide insight into the glycolysis reaction.

1.6 Significance of research

This research is able to provide information about the changes to PET waste in glycolysis process. The qualitative and quantitative analysis of the chemical process will also provide useful information about the PET waste and optimum temperature and time can be obtained. The optimization carried out will help researchers to perform the same experiment more effectively. Furthermore, the kinetics study is able to provide useful information that will help people to understand more about the glycolysis reaction.

1.7 Summary of chapter

Overall, this chapter gives explanation and elaboration about the research that is going to be conducted. In early stage, there are some descriptions on the background of the problem that exists currently. This includes the environmental issues brought upon the vast usage of PET products. After all the problems had been clarified, the next step is to set the expected outcomes to achieve the objectives within the scopes of research. Finally in this chapter is the significance of the research, which provides explanation on the importance of conducting this research to provide useful information about the glycolysis process.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Literature review is a preliminary study for related topics before developing a research, in this case. It is one of the important techniques used in gathering data and information, as well as facts in a research development. Literature review can be done through researching and study of previous and similar researches. Study on the previous researches will help to generate solutions for improving or create new innovative ideas in the functions of the research, and hence new implementation can be done for the benefits of mankind.

2.2 Polyethylene Terephthalate (PET)

Polyethylene Terephthalate (PET) is one of the members from the polyester family, which is also an industrially important thermoplastic resin. PET is mainly formed from terephthalic acid (HOOC-C_6H_4-COOH) and ethylene glycol (HO-C_2H_4-OH), in which both were the derivatives of oil feed stocks. The formation of PET can be illustrated by the figure shown below. The average molecular weight for commercial PET (bottle grade) is 192 g mol^{-1} (Lόpez-Fonseca et *al*, 2011).

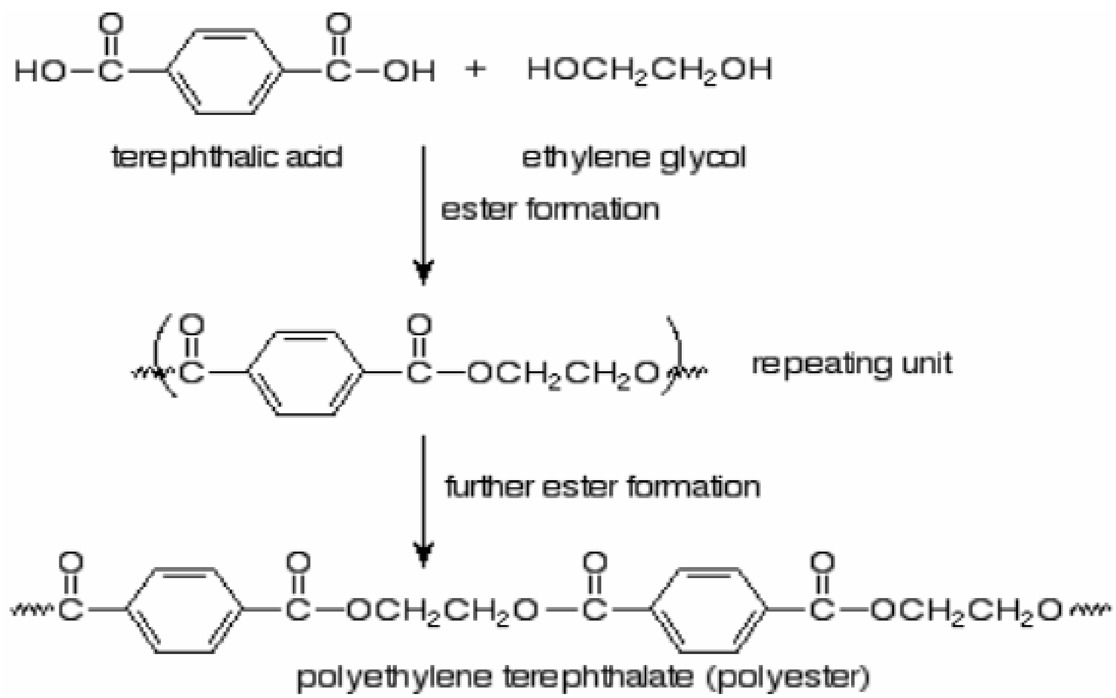

Figure 2.1 Formation of commercial PET
(Source: Vedula, 2005)

PET is a semi-crystalline polymer composed of both crystalline and amorphous regions, as well as a versatile engineering plastics material with excellent thermal and chemical resistance and mechanical performance (Vedula, 2005). Due to its properties of chemically flexible nature which can be modified and applied commercially, the PETs have been studied extensively since a long time ago. It has a high melting point of 250^{o}C and glass transition temperature of 80^{o}C, PETs can still retain its excellent mechanical properties up to 175 - 180^{o}C. Because PET exists as a semi crystallizer, its crystallinity varies from amorphous to fairly high crystalline degree. It can be highly transparent and colourless, but thicker samples are usually opaque and off-white. Overalls, PET is a hard, stiff, strong, dimensionally stable material that absorb very little amount of water. Furthermore, it has good barrier properties and has good chemical resistance except to alkalis, which it can be recycled chemically using alkaline hydrolysis process (Vedula, 2005).

The application of PET can be found almost everywhere. Its product varies from the manufacture of video and audio tapes, X-ray films, high strength fibres, food packaging, especially of soft-drink bottles (Joshi, 2011; Kao, Cheng, and Wan, 1996). Typical applications of PET include in the automotive, electrical, and packaging fields. For the automotive field, PET is applied in the production of sunroof rails and wiper blade supports. For the electrical field, PET is produced as computer fans, fuse holder and insulated housings. On the other hands, PET is used a soft drink container and packaged food containers. Generally, the usage of PET almost can be seen everywhere surrounding the mankind.