OPTIMIZATION AND CHARACTERIZATION OF GLYCOLYSIS OF WASTE POLYETHYLENE TEREPHTHALATE (PET) WITH POLYETHYLENE GLYCOL (PEG)

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by

DINESH KUMAR A/L RAMAN

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for the degree of
Chemical Engineering

February 2013

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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Date   : 18 FEBRUARY 2013

STUDENT'S DECLARATION

I declare that this thesis entitled "optimization and characterization of glycolysis of waste Polyethylene Terephthalate (PET) with Polyethylene Glycol (PEG)" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature   :
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To my beloved family and friends

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

m   Meter

g   Gram

cm   Centimeter

mL   Milliliter

LIST OF ABBREVIATIONS

PET   Poly(ethylene) Terepthalate

EG   Ethylene Glycol

DEG   Diethylene Glycol

PEG   Polyethylene Glycol

PEO   Poly(ethylene oxide)

TEG   Triethylene Glycol

Gly   Glycerol

BHET   Bis(2-Hydroxyl eter) Terephthalate

DSC   Differential Scanning Calorimetry

TGA   Thermogravimetric Analysis

FTIR   Fourier Transform Infrared Spectroscopy

RSM   Response Surface Methodology

ANOVA   Analysis of Variance

LOF   Lack of fit

IUPAC   International Union of Pure and Applied Chemistry

OPTIMIZATION AND CHARACTERIZATION OF GLYCOLYSIS OF WASTE POLYETHYLENE TEREPHTHALATE (PET) WITH POLYETHYLENE GLYCOL (PEG)

ABSTRACT

Chemical recycling of poly (ethylene) terephthalate (PET) has been the subject of increased interest as a valuable feedstock for different chemical processes. In this research, the glycolysis of PET will be studied using excess Polyethylene Glycol (PEG) as depolymerization agent assisted by magnesium acetate as catalyst. The influence of several operating conditions covering temperature (165–215 ◦C), reaction time (0–4 h), and catalyst concentration and PEG to PET weight ratio was analyzed. The purified monomer was characterized by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Fourier Transform Infrared Spectroscopy (FTIR).Response surface methodology (RSM) software was used to predict the optimal condition of glycolysis process. The optimal condition of glycolysis time, temperature, amount of catalyst and amount of PEG were 205◦C, 2.49hr, 0.12g (2.4wt% of PET used) and 36.87g of PEG respectively. Where using this optimized condition the yield of the process can be reached up to 96.3%.

PENGOPTIMUMAN DAN PENCIRIAN PROSES "GLYCOLYSIS" (PENGITARAN SEMULA) "POLYETHYLENE TEREPHTHALATE (PET)" DENGAN POLIETILENA GLIKOL (PEG)

ABSTRAK

Mengitar semula bahan plastics (PET) telah menjadi subjek utama pada mas kini, dimana bahan yang dikitar semula boleh dijadikan sebagai bahan mentah berharga untuk pemprocessan yang berbeza. Dalam kajian ini, glikolisis PET akan dikaji menggunakan "Polyethylene Glycol" (PEG) sebagai ejen penyahpolimeran dibantu oleh "magnesium acetate" sebagai pemangkin. Pengaruh parameter yang meliputi suhu (165-215 ∘ C), masa reaksi (0-4 h), dan kepekatan pemangkin dan nisbah PEG yang digunakan telahpun telah dianalisis. Bahan glikolisis yang diperolehi telah dicirikan dengan mengunakan, "Differential Scanning Calorimetry" (DSC), "Thermogravimetric Analysis" (TGA), dan "Fourier Transform Infrared Spectroscopy" (FTIR). "Response Surface Methodology" (RSM) perisian telah digunakan untuk meramal keadaan optimum proses glikolisis. Dimana keadaan optimum glikolisis masa, suhu, jumlah pemangkin dan jumlah PEG adalah 205 ∘ C, 2.49hr, 0.12g (2.4wt% PET yang digunakan) dan 36.87g PEG masing-masing. Jika menggunakan keadaan ini hasil proses boleh mencecah sehingga kepada 96.3%.

CHAPTER 1

INTRODUCTION

1.1   BACKGROUND OF THE STUDY

Polyethylene terephthalate is a polyester material that is most often used to make fibers, containers for food and beverages, pharmaceuticals and make-up. Polyethylene terephthalate is often referred as PET or PETE and was previously called PETP or PET-P.

PET is a linear thermoplastic resin that is formed by the condensation of terephthalic acid and ethylene glycol. Because of its low cost (Thompson et al., 2009), excellent tensile strength, chemical resistance, clarity, processability, and reasonable thermal stability (Caldicott, 1999) the usage of PET is wide spread. The demand of PET is summarised in the Table 1.1 (Scheirs & Kaminsky, 2006). PET is suitable material for packaging of soft drinks, bakery products, frozen foods, cosmetics and household cleaner and many other products. Customers choose PET because it is inexpensive, resealable, shatter-resistant and recyclable (Carraher, 2000; ILSI Europe, 2000; Olabisi, 1997). Adding to that its excellent barrier characteristics to oxygen and carbon dioxide, it shows spurt growth in the soft drink industries.

Moreover PET's high toughness/weight property ratio make an added advantage over other other types of container materials (Welle, 2011).

The total global consumption has risen from 11.8 million metric tons in1997 (Paszun & Spychaj, 1997) to 23.6 million in 2005 (Pohler, 2005, as cited in Karayannidis& Achilias, 2007) and 54 million in 2010 (IHS, 2011). It is expected to grow by 4.5% per year from 2010 to 2015. In Europe and America, region the major cause of the demand and usage is the soft drink sector. While in Asia the usage is increased because of the fibre production. Recently the production trend of fibers has shifted from developed countries to developing countries (Pohler, 2005).

Table 1.1 The global demand and future prediction of PET by application. (Unit in thousand tons)

	1990	1995	2000	2005	2010
Fiber	8900	11700	18800	24200	33300
PET resin (for bottles)	1100	3100	7100	11900	18900
Film	1000	1100	1400	1400	1700
Others	700	800	1100	1900	2200
Total	11700	16700	28400	39400	56100

Since, the PET creates no harm to livings of earth and does not have adverse effect on the environment, large scale production cannot be avoided. But large scale of continual production implies dramatic effect in term of treatment of PET waste. With the increase in the amount of PET wastes, its disposal began to pose serious economical and environmental problems.

An important note that should be taken into account that out of 80 billion plastics bottles manufactured per year 85% is not recycled (The Container Recycling Institute). Most of the plastics bottles make their way to ocean or discarded in

landfill. And it is a important fact that the PET is completely non-biodegradable. In the year 2000, the global PET production capacity exceeded 33 million metric tons per year (Rieckmann, 2003). According to Greenpeace, 1.7 tons of CO_2 emissions are prevented for each ton of PET plastics recycled,

By considering, emerge societies awareness towards environmental safety issues, recycling becomes more preferable means of treatment of PET waste. Along with the added advantage in terms of energy conservation, recycling of PET is conducted in wide-scale (Nir et al., 1993).The recycling of PET does not only serve as a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical products and energy. It is estimated that every 1kg of production of PET requires 2kg of oil burning and raw material. Consequently burning of 1 kg oil for energy emits 3kg of carbon dioxide. Simply, per kg of plastic, about 6 kg carbon dioxide is created during production and incineration.

Present researches proven that, recently the PET bottles recycled at very low rate causing billion of bottles must be manufactured from fossil fuels itself to replace that were not recycled. Another problem rises here, where the trees are needed for making charcoal. So the production of new PET bottles without recycling will promotes carbon dioxide emission to the atmosphere (Paszun & Spychaj, 1997). Nevertheless, recycled products can results in 50-60% capital saving (Sinha et al., 2008).

Focussing on the recycling process, currently the PET is recycled by various techniques. Primary recycling also known as in-plant process, where uncontaminated PET scrap undergoes re-extrusion process. (Al-Salem, 2009; Al-Salem et al., 2009). Second is the Secondary recycling, where the Pet scraps undergo separation and processing into granules by mechanical means. One major disadvantage is that the processing involves extrusion by means of heat and heat, which will cause deterioration the properties each time it is recycled (Aguado & Serrano, 1999). Quaternary recycling is the thermal treatment of waste PET by incineration for the thermal recovery. The tertiary recycling involves chemical recycling where PET polymer breakdown into its respective monomer, oligomer and dimer. Chemical

processing method can be subdivided into hydrolysis, methanolysis, glycolysis and aminolysis (Carta et al., 2003)

Focussing on the chemical recycling, the major strategy is to increase the yield of the desired product at an optimized condition (reduced reaction time and temperature). Therefore the recovered product either can be integrated with production plant or can be used as parent material to synthesise other polymers with higher economical value such as unsaturated polyesters, polyurethane foams. This aids the reduction of sources used.
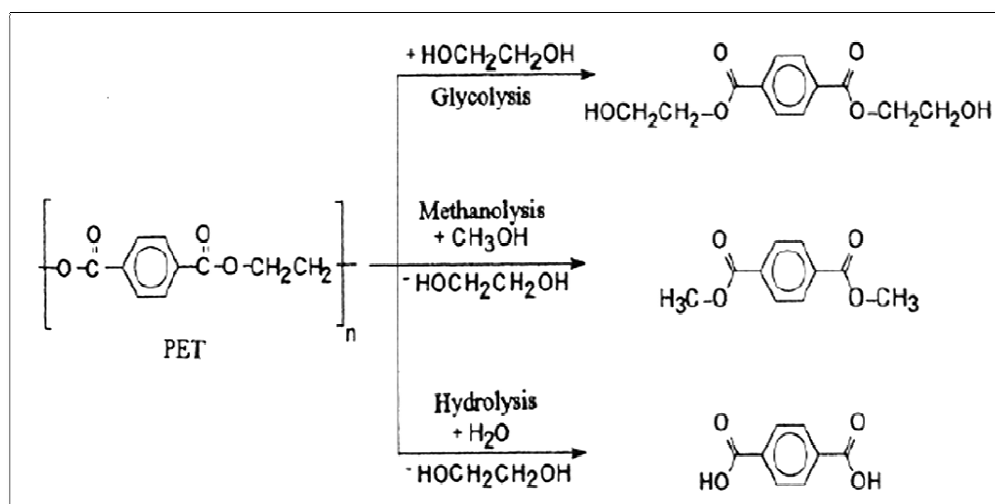
Figure 1.1 Chemical Recycling of PET

1.2 PROBLEM STATEMENT

PET plastic bottles are completely non-biodegradable. PET containers are not recycled and most of it makes their way into the ocean. Glycolysis has been identified as most profitable and less complex means of recycling of PET waste. A very limited work has been conducted on parameter-setting or optimization of the glycolysis process using Response Surface Methodology (RSM). A proper

understanding and development of mathematical model through RSM, may aid the glycolysis process become more profitable in term of economic value and environmental concern.

1.3   RESEARCH OBJECTIVE

The objectives in this present research are:

RO1. Identify the optimal process parameter for glycolysis of PET waste.

RO2. To characterize the end product of glycolysis process.

RO3. Investigate effect Polyethylene Glycol as depolymerising agent.

1.4   SCOPE OF RESEARCH

Survey shows very limited or almost no work on optimization of Glycolysis of PET waste using RSM. Adding to that almost all researches proposed the usage of Ethylene Glycol(EG), Diethylene Glycol(DEG) and mixture of DEG and EG as depolymerising agent and non of the research conducted detailed research on using Polyethylene Glycol (PEG) as depolymerising agent. Through this study, parameter-setting or optimization will be performed using Polyethylene Glycol (PEG) as depolymerising agent.In brief the scope of the study is stated as below;

1. Influence of reaction time on glycolysis yield.

2. Influence of reaction temperature on glycolysis yield.

3. Influence of catalyst concentration on glycolysis yield.

4. Influence of ratio of Polyethylene Glycol (PEG) to Poly (ethylene) Terephthalate (PET).

1.5   RATIONALE AND SIGNIFICANCE

This research is able to provide information about the possibility of PEG to be used in PET glycolysis process. Hence, by optimizing multiple responses/parameters that present the complexity of PET glycolysis can be resolved providing product with desirable quality and quantity. The novelty of the research is to change waste into wealth.

CHAPTER 2

LITERATURE REVIEW

2.1 POLYEHTYLENE TEREPHTHALATE

"Polyethylene terephthalate (PETE) is polymerized form of ethylene terephthalate ($C_{10}H_8O_4$) monomer units. PETE is a recyclable plastic with identification code "1". World-wide PETE-1 is used as a synthetic fiber, polyester, packaging materials, containers of soft drinks and etc". (Moinuddin Sarker et al., 2010).

"Capability for The world-wide use of PETE-1 has gradually increased and most of the waste PETE-1 is being dumped into the environment instead of recycling; this creates environmental problem" (Moinuddin Sarker et al., 2010). After the usage the PET plastics are being discarded in the landfill or make their way to oceans, hence causing various economical and environmental difficulties since it is known as non-biodegradable. Every day the plastics that have been left out in the landfill undergo photo- degradation and forming small solid particles. This might cause harmful health hazard if the food chain of entire surrounding habitant is affected by the solid complex (Moinuddin Sarker et al., 2010). Besides that another possible danger might be arise when these non-biodegradable substance undergo incineration (burning) causing release of harmful green house gases. When it comes

to recycling process, many researchers have been conducted and the thermal degradation with the aid of catalyst would be a better solution. (Moinuddin Sarker et al., 2010).

2.1.1 Properties and Synthesis of PET

Poly (ethylene) Terephthalate posses unique physical and chemical properties. It appears as amorphous glass-like material. Crystallinity and the rigidity of PET can be modified or enhanced by addictives or heat treatment of the molten polymer. The major added advantage of it properties is that, PET when heated above 72℃ PET in semi-crystalline state changes rubbery elastic form where it can be stretched or aligned into desired shape. Therefore, reforming followed by rapid quenching of reformed PET results in in extremely tough plastic (Sinha et al., 2008). Commercial PET melts between 255 and 265℃. Adding to that morphological and structural reorganization of PET leads to better crystal structures as the temperature increases (Awaja & Pavel, 2005).

Its monomer, BHET can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct (Fig 2.1). Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/ transesterification) with water as the byproduct (Fig 2.2).
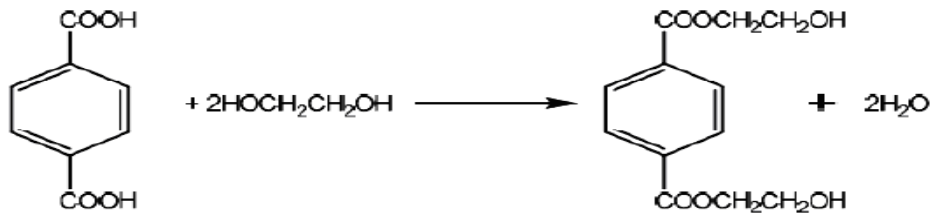
Figure 2.1 Chemical Reaction between ethylene glycol and terephthalic acid yields BHET.
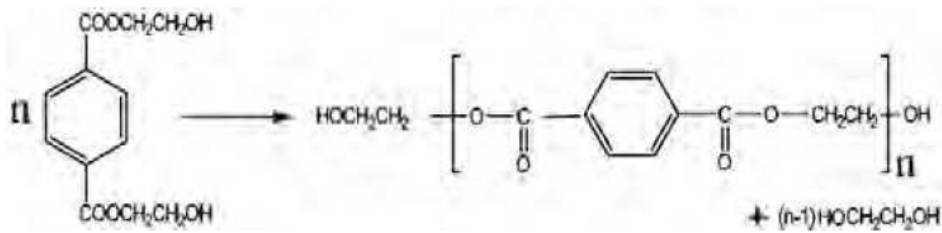
Figure 2.2 Polycondensation of BHET yields PET.

Table 1.2: Properties of PET

Physical Properties	ASTM Test Method	Units	PET
Density	D792	Lbs/ in.^{3}	0.0499
Water absorption ,24 hours	D570	%	0.10
MechanicalProperties			
Specific Gravity	D792	g/ cm.^{3}	1.38
Tensile Strength at break, 73° F	D638	psi	11,500
Tensile Modulus, 73°F	D638	psi	4×10^5
Elongation at break	D638	%	70
Coefficient of Friction @ 40psi, 50 fpm	-	Static/Dynamic	0.19/0.25
Thermal Properties			
Heat Deflection, 264 psi	D648	°F	175
Melting Point	---	°F	490
Coefficient of Linear Thermal Expansion	D696	in./in./-°F	3.9×10^{-5}

2.2 CHEMICAL RECYCLING OF PET

2.2.1 Hydrolysis

Karayannidis et al. (2006) discusses that hydrolysis is the one majorly used technique to recycle PET waste by the reaction between water in acid , alkaline or neutral medium to terephthalic acid (TPA). In common practice the TPA has been used to produce PET or can be converted into more valuable materials such as oxalic acid (Yoshioka et al., 2003). For acid catalysed hydrolysis process concentrated sulphuric acid have been practiced (Brown & O'Brien, 1976). While for the alkaline hydrolysis caustic soda is used (Alter, 1986). Meanwhile for the neutral hydrolysis water or steam is used (Campanelli et al., 1993). Nowadays hydrolysis means of recycling attracts a growing interest of PET production factories.
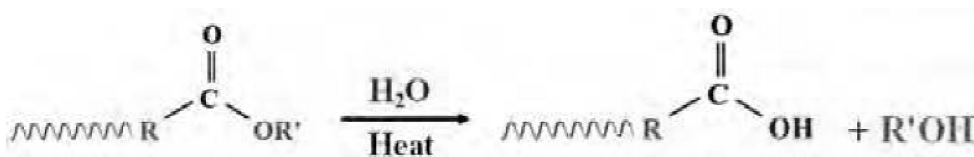
Figure 2.3 Hydrolysis Reaction

2.2.2 Methanolysis

Methanolysis is the degradation of PET to dimethyl terephthalate (DMT) and EG by methanol. Lotz et al. (1967) reported that PET was completely depolymerised using methanolysis into DMT and EG by the reaction of methanol and and molten PET at the temperature nearly 210°C. Finally the crude DMT is purified by vacuum distillation. Recent study on the methanolysis have proposed a new method of recycling by reacting PET waste with supercritical methanol above 300°C at 11 MPa for 30 min without a catalyst.

2.2.3 Glycolysis

Glycolysis is the depolymerisation reaction of PET into its respective its oligomers and monomers (bis(2-hydroxyethyl terephthalate)). The etherification reaction occurs where the ester linkage is replaced hydroxyl terminals (Shamsi R et al, 2009). Glycolysis is carried out using different glycols like; ethylene glycol, propylene glycol, 1, 4- butanediol and triethylene glycol, diethylene glycol (DEG), polyethylene glycol (PEG) dipropylene glycol (DPG), glycerol (Gly) and etc.
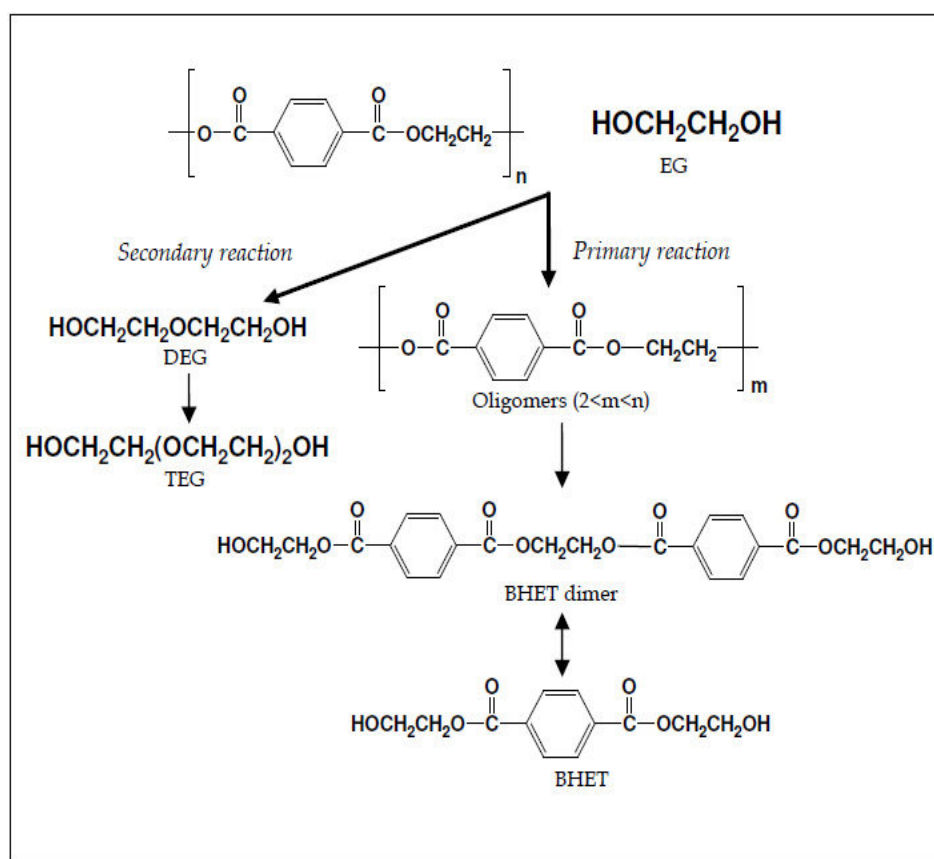
Figure 2.4 Reaction Scheme of Glycolysis using EG

2.2.4 Comparison between Methanolysis, Hydrolysis and Glycolysis

Focussing on hydrolysis, it is comparatively slower than the methanolysis and glycolysis. Among the three depolymerizing agents (i.e. water, methanol, ethylene glycol), water is the weakest nucleophile (Sinha et al, 2008). Addding to that hydrolysis process occur at elevated temperatures and pressure. On the other hand the recovery of monomer (TPA) which quite complex and indirectly affect the quality of end product.

While the major disadvantage of methanolysis is the cost of separation and refining process. Furthermore the water formed at the end causing poisonous effect on the catalyst meanwhile causing formation of various azeotropes (Patterson, 2007). Before glycolysis , methanolysis is major commercial mode of PET recycling but now the process not practiced in commercial because complexity in term of recovering DMT causing it to become obsolete (Paszun, 1997).

One major added advantage of glycolysis is that the monomer produced (BHET) can be mixed with fresh BHET, and the mixture can be used for the other (DMT-based or TPA-based) PET production lines. Glycolysis presents lower environmental impacts than hydrolysis of PET packaging waste (Calero et, al). Adding to that glycolysis is the least complex, and capital-intensive process. For that reason glycolysis attract researcher interest and more focus has been given out for the development of recycling of Pet through glycolysis. In recent year many researches has been publish using wide range of temperature and reaction time, and some researchers have devoted their time on the investigation and development of efficient glycolysis catalyst (Challa, 1960; As cited in Patterson, 2007).

2.3   CATALYZED GLYCOLYSIS

Recent studies reported that, glycolysis may conducted at relatively low reaction temperature , reaction time and either under pressure or at atmospheric pressure (Zahedi et al, 2009). The glycolysis process is very sluggish without catalyst. Therefore recent works more focussed on development of catalyst. Frequently is zinc acetate is reported to posses higher yield over the depolymerisation of PET. Other than that there are many other metal salts that have been investigated such as, cobalt acetate (Baliga et al., 1989), lead acetate (Chen.C.H, et al., 2001). Their works have proved that the order of activity of the catalysts increases from zinc to lead acetate. ($Zn+2 > Mn+2 > Co+2 > Pb+2$). Some metal chlorides such as zinc chloride, lithium chloride, magnesium chloride and ferric chloride also proved to catalyse the process (Troev. K et al, 2003).

In recent years researchers are more focussed on the development on milder catalyst which presents no harm to the environment. Lately in year 2009 an interesting study has been made on the catalytic effect of ionic liquids on trans-etherification of PET (Wang H. et al., 2009). The Figure below show the effect of catalysed and non-catalysed depolymerisation of PET with EG (Ethylene Glycol).
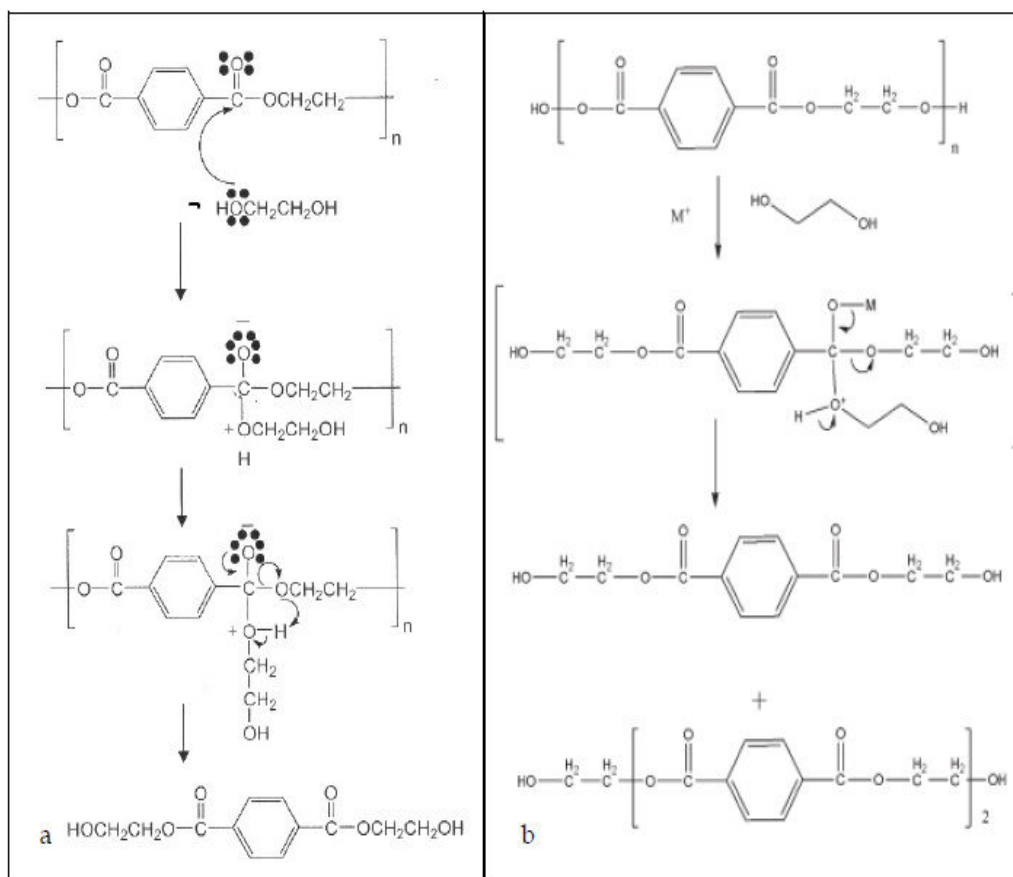
Figure 2.5 Catalyst effect on the depolymerization of PET

According to figure 2.5, a free electron pair on presence on polyether oxygen initiates the reaction by attacking the ester linkage of the PET. Thus forming bond between the hydroxyethyl group of polyether and carbonyl carbon of polyester, eventually breaks into short chains.

Meanwhile with metal based catalysts, the reaction is initiated by forming a complex with the carbonyl group of polyester. Thus, the polyether will be facilitated and bondage between carbonyl group of polyester and hydroxyl group of polyether. Relatively few works only have been made on the optimizing the   glycolysis process, which is depends upon parameters such as temperature, pressure, PET/ Depolymerization agent ratio and amount of catalyst. Majorly the all the focussed on

either the development of new catalyst or kinetic study of the glycolysis process (all of them with zinc acetate as catalyst). Considering the zinc acetate as catalyst, it has an adverse effect on the environment because of non-biodegradability of zinc cation. Presently there is research on optimization of glycolysis using magnesium acetate as catalyst.

2.4   OPTIMIZATION OF GLYCOLYSIS

Chen.C.H, et al. (2001) found out that the glycolysis process is depend upon the reaction parameter such as reaction time, temperature and catalyst concentration. The effect of these parameters can be sequenced in the following descending order: catalyst concentration>glycolysis temperature>glycolysis time.

2.4.1 Effect of reaction temperature

Optimization study conducted by Katoch.S et al. (2009) suggested that   the conversion increases with increasing temperature of the system while the reaction temperature is maintained. Then the trend reaches a maximum, the conversion percentage reaches a steady state. They suggest that at lower temperature (approximately below 140°C) the reaction seems to be very sluggish. This is due to the presents of thermodynamic equilibrium state between corresponding liquid states causing slow rate of release partially depolymerised PET from solid phase into liquid phase. When the temperature is raised   (approximately above than 180°C) causing acceleration of non-polymerized or partially polymerized polyester from solid phase to the liquid phase. (Katoch.S et al., 2012),

In one of their studies, Pardal and Tersac (2007) examined the influence of temperature, the presence of a catalyst and the morphology of the PET. The observation that reactivity is much greater at 220 ∘C suggests that the diffusion of diethylene glycol in the PET is favoured at this temperature, increasing the reaction rate as compared to reactions at lower temperatures. Wang H et al. (2009) states that the selectivity of glycolysis process towards BHET is very low at lower temperature. When reaction temperature increased from 170℃ to 180℃, the selectivity towards BHET increased drastically. Therefore, the researcher concludes that high temperature is beneficial in term of formation of BHET (Wang H. et al., 2009).

Therefore, the glycolysis temperature is a critical factor in the glycolysis of PET .Most of the research employed the glycolysis temperature from the range 165-200∘C.
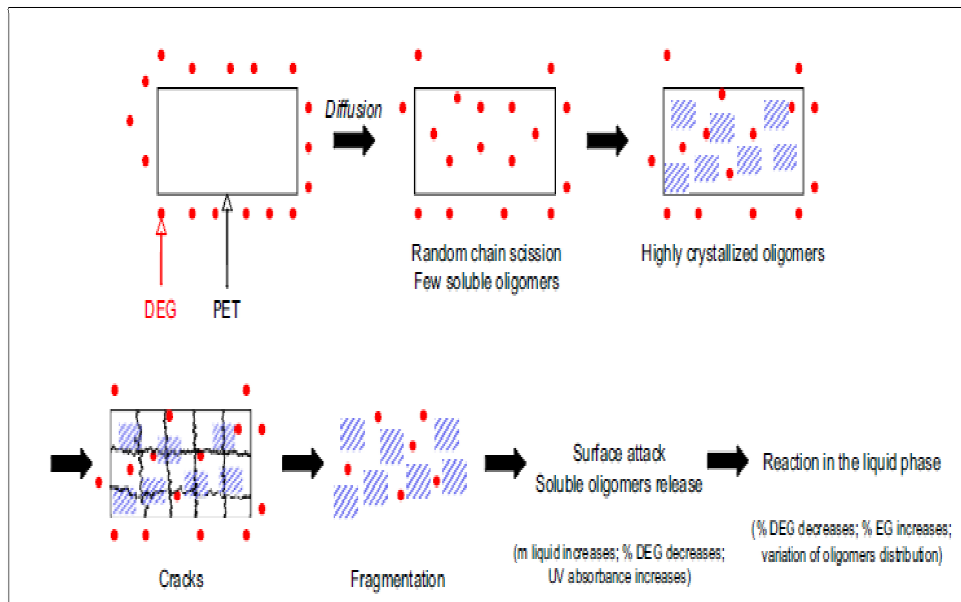
Figure 2.6 Schematic evolution of PET/DEG system during glycolysis

2.4.2 Effect of the reaction time

Recently Buasri , et al. (2011) presented a research on the characterization of PET co polyester. The influence of the variation of reaction time on percentage conversion of PET-PLA was clearly discussed. The study was carried out by maintaining the temperature at 180℃ and catalyst amount as 0.4% by weight of PET. Trend of the conversion of reaction observed to be proceeding in a higher rate, and pace is decreased when the reaction reached certain point. Therefore the yield observed after the optimum point become constant.

Meanwhile in the recent research on glycolysis of poly(ethylene terephthalate) catalyzed by ionic liquids states that the weight percentage of BHET (yield) initially increased and then decreased. From the study the researchers conclude that at first PET is depolymerised into oligomers and dimers which would increase the tendency for the formation of BHET then in the presence of excess depolymerising agent the reaction tend to shift to opposite direction where BHET is further depolymerised into dimer and oligomer (Wang H. et al., 2009).

2.4.3 Effect of amount of catalyst

As previously discussed catalyst has strong impact on the glycolysis process. The observation of Zhou et al states that the conversion of Pet and the selectivity towards BHET increase with increasing catalyst amount. Meanwhile increased addition of catalyst attributes to the repolymerization and BHET selectivity is decreased. Adding to that López-Fonseca et al., et al states that PET degradation into BHET was favoured with increasing temperature and catalyst concentration. But the effect of

temperature was strong compared to the catalyst amount. The result obtained showed that the yield of the process is increased to certain point when the catalyst amount is increased and only increase to a maximum limit when temperature of the system is increased (López-Fonseca et al., 2011)

2.4.4 Effect of PET/ Depolymerization agent Ratio

The effect of the PET/ Depolymerizing agent ratio cannot be neglected. At lower concentration of depolymerisation agent, the reaction becomes very sluggish. This is due to the surface reactivity, which is rate-determining process. Increasing the amount attributes to the acceleration of surface reactivity and formation of BHET the monomer. Meanwhile excess amount of the depolymerising agent aids the formation of BHET and minimize the formation of oligomers (Idris. S.E and Yassin K.E.,2012)

2.4.5 Effect of stirring rate

Studies proves that the conversion of PET glycolysis is considerably lower for the lower stirring speed, and increased significantly up to certain point when the stirring speed is increased. Further increase in stirring speed does not gives any noticeable effect on the conversion. (López-Fonseca et al., 2011)

2.4.6 Effect of PET scarp size

In some studies the effect of size of PET scrap also evaluated. As discussed before surface reactivity may be the rate determining step for the glycolysis process. The

particle size attributes to the lower conversion at a fixed time and temperature. Granulated PET scrapa promises high surface contact for the reaction therefore the conversion of PET increased. On the other hand it is proven that the effect of particle size towards PET degradation is comparatively stronger than the effect of stirring rate.

2.4.7 Optimization using RSM

In this advanced era, technologies have been developed drastically for the for the customer satisfaction. Due to customers demand and high expectation product/process design become extremely complicated. Therefore, manufacturing/processing industries prioritize optimizing multiple responses/parameters.

To resolve the problem design of experiments (DOE) is extensively adopted in industries for the optimal parameter setting which attributes to improved process conduction. Response Surface Methodology (RSM) is one of majorly used tools of DOE to obtain the optimal parameter settings. In RSM, analysis of variance (ANOVA) is used in indentifying significant factors. Based on experimental data, RSM can generate an equation representing the relationship between controlled and manipulated variable.

Recently RSM also been used for predicting the optimal condition glycolysis process of waste PET. At beginning of this year a journal article presented by Katoch.S et al. (2009) thoroughly discussed about the optimization of glycolysis time and temperature of PET scrap. Until now there is no research that discusses

about all the parameters (catalyst amount and depolymerising agent ratio) that can be considered in the glycolysis of PET.

2.5   CHARACTERIZATION OF GLYCOLYSIS PRODUCTS

2.5.1 Thermal Characterization

2.5.1.1 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is one of most widely used method of thermal analysis. Throughout thermal analysis thermodynamic data such as heat capacity, phase transition, enthalpy and kinetic data can be obtained. The added advantage of thermal analysis is the easy handling and the amount of sample would require is small. Meanwhile DSC is used to measure the energy would require to obtain a zero temperature difference between sample and a inert reference substance.

Meanwhile for the glycolysis process, DSC is widely used for the characterization of the polymeric materials. At first Wolf et al. (2003) Investigated and invented DSC based method to study the effect of catalyst activity towards depolymerisation reaction to produce BHET from PET. Then Johnson and Teeters further studied the DSC characterization technique to analyse the glycolysis process.

2.5.1.2 Thermo Gravimetric Analysis

Thermogravimetric analysis (TGA) also thermal analysis technique employed to characterize or analyse wide variety of polymeric materials. TGA analyses the rate mass change of the sample as a function of temperature or time. Commonly these

data would be useful in-term of analysing the thermal stability and compositional properties.

For the characterization of polymeric material of PET glycolysis Gamlen et al. (1999) have been expanded the research of Wolf et al. (2003) the precursor of PET thermal characteristic. With the development of DSC method together with TGA, the observation on the effectiveness of the catalyst towards depolymerisation follows the data of conventional method. However, the thermal analysis techniques are more convenient. Nowadays almost every research regarding characterization of degradation of PET involves DSC and TGA analysis.

2.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform infrared spectroscopy accounts for the frequencies of vibration between the bonds of atom. Each material has a unique arrangement and attachment of atoms, therefore a infrared spectrum of a compound cannot be matched with the other. Adding to that the size of the peaks accounts for the amount of material presents in the sample.

In recent study on the Fourier transform infrared spectrophotometer (FTIR) was used to identify the chemical bonds in the digested polyethylene terephthalate obtained from the glycolysis. The chemical bonds in the sample were identified at the peaks of the displayed infrared spectra for a specific transmittance and wave number (López-Fonseca et al., 2011).

2.6   DEPOLYMERIZING AGENT

Almost every work done on the depolymerization of PET is based on Ethylene glycol as the depolymerimization agent. Diethylene Glycol also been analyzed past decade. On the other hand , mixture of both EG and DEG also being studied (Viksne and Kalnins, 2002) nowdays. Adding to that, recently an optimization study conducted by Katoch.S et al. (2009) proved that propylene glycol also gives significant effect on the glycolysis of PET.

Focussing on Poly (ethylene glycol) (PEG), Garrci'a et al. (2007) stated that is a biodegradable biopolymer that possesses hydroxyl terminal groups. Adding to that the hydrophilic character of that terminal group it is very sensitive towards hydrolysis. Therefore PEG has the potential to be applied as the depolymerising agent for the glycolysis process. Recently Patel et al., investigated Glycolysis of PET waste was carried out using poly(ethylene glycol) (PEG) of various molecular weights (200, 400, 600). Followed by Ristić. I et al. (2007) have conducted research on the potential use of recycled poly ethylene terephthalate in polyurethane synthesis, using polyethylene Glycol as the depolymerization agent. Until now there is limited work have been done on the PEG as the depolymerization agent.

CHAPTER 3

RESEARCH METHODOLOGY

3.1   INTRODUCTION

In this chapter, the experimental materials and apparatuses, setup and procedures will be explained in details. The glycolysis of PET waste will be conducted at different reaction time (30-240 min), reaction temperature (175-215℃), amount of catalyst (0.01-0.15), and PEG to PET ratio (10:5,15:5,20:5,30:5). Then obtained PG (glycolysis product) will be subjected to thermal characterization (TGA and DSC) and FTIR. For the comparison purpose glycolysis process with DEG catalysed by zinc acetate will be compared.

3.1   RAW MATERIALS

3.2.1 Polyethylene Glycol (400)

Polyethylene glycol is a condensation polymers of ethylene oxide and water with the general formula H (OCH2CH2)nOH. Polyethylene glycols present in various molecular weights. PEG with a mean molecular weight up to 400 is non-volatile liquids at room temperature. While PEG 600 poses a lower melting range and appear

as pasty solution in ambient condition. The mean molecular weight above PEG 600 appears as solid or in the flakes form. PEG up to mean molecular weight of 600 is completely miscible in water. PEG – 400 is widely used in commercial industry because it's a thermally stable medium due to its higher molecular weight (higher specific heat). Therefore it is more preferred to hot bath applications. Since this glycolysis process is highly affected by temperature difference. Therefore PEG 400 is chosen as depolymerising agent.

Table 3. 1 Properties of Polyethylene Glycol (PEG- 400)

Characteristics	Test Method	Unit	PEG 400
Moles of Ethylene Oxide	-	-	8EO
Appearance	Visual	-	Colourless
Viscosity @ 40℃	ATM D-445	Cst	31-35
Hydroxyl Number	ASTM D-4252	Mg KOH/gr	340-415
pH	ASTM-1172		5-7
Molecular Weight	Calculated	Kg/Kmol	270-330
Water Content	Ballestra B-Z6	Wt%	0.5max

3.2.2 Magnesium Acetate

As discussed earlier in the survey, any metal acetate can aid the transesterification process.

Table 3. 2 Properties of Magnesium Acetate Tetra hydrate

Characteristics	Magenesium Acetate Tetrahydrate
Molecular Formula	C4H6O4Mg.4H2O
Molecular Weight	214.3982g
Appearance	White
Specific Gravity	1.454
Melting point	80 ℃
Solubility	120% in water.
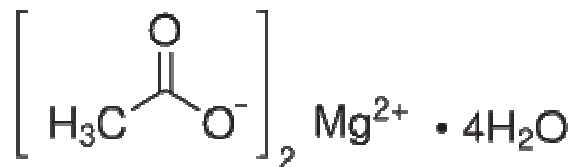
Figure 3.1: Molecular Structure of Magnesium Acetate Tetra hydrate

3.2.3 Raw Material Purchasing

Polyethylene Glycol (PEG-400), Magnesium acetate tetra hydrates $C_4H_{14}MgO_8$, Diethylene Glycol (DEG), Zinc acetate $C_4H_6ZnO_4$ was purchased in Sigma Aldrich Co.

3.3 EXPERIMENTAL

3.3.1 Preparation of PET scrap

Clear postconsumer bottles of PET wastes were collected .The collected samples were crushed into small pieces using waste plastic crusher. Then samples were conditioned with 1 wt % aqueous solution of sodium hydroxide for about 1hour.Conditioning with sodium hydroxide solution would remove any surface impurities presents along with the crushed scraps. After conditioning, the PET scraps washed thoroughly and dried in the oven at 80℃. PET scraps with particle size within 3 and 5 mm are separated then subjected to glycolysis process.

3.3.2 Glycolysis Process

This study will include two different glycols (PEG 400 and DEG) as depolymerising agent in the presence of magnesium acetate and zinc acetate respectively as a

transesterification catalyst. A 50 mL round-bottom three-necked flask equipped with a thermometer and a reflux condenser was initially loaded with 5.0 g of PET, 20.0 g of polyethylene glycol, and certain amount of magnesium acetate (0.05-0.15g). The reaction was carried out in atmospheric pressure condition and the reaction temperature was varied from 175-215℃. The reaction time (30-240min) for the glycolysis process also varied for the optimization process. The flask is placed in a heating mental and the temperature and time is set as per desired. The undepolymerized PET is separated quickly from the gycolysed product by means of mechanical separation to prevent the precipitation of product doring the cooling down process. Then excess cold distilled water is used to wash the undepolymerized PET and mixed with the product fraction. The washed undepolymerized Pet is then dried and weighed. The conversion of PET is defined by Eq. (1):

Conversion percentage of PET = $\frac{W_0 - W_1}{W_0} \times 100\%$ (Eq   3.1)

Where W_0 resembles the initial weight of Pet that charged into the flask. While W_1 represents the weight of undepolymerized PET (after dried and weighed).

The product that was mixed with cold water is then subjected to vigorous agitation where is tend to dissolve the remaining PEG, magnesium acetate, and the monomer. The mixture is then filtered, dried and and labelled as fraction B Meanwhile, the collected filtrate after the vigorous agitation followed by filtration was then concentrated to about 100ml by boiling it. The concentrated filtrate was stored in refrigerator at 4℃ for 24hours. Continual refrigeration will cause the the monomer to separate out (formation of white crystalline). The white crystalline is the

separated using vacuum filtration, dried and weighed. This fraction was labelled as fraction A.

The yield of monomer (Y) was defined as

$$Y\ (\%) = \frac{W_{monomer,t}/MW_{monomer}}{W_{PET,O}/MW_{PET}} \times 100\% \qquad \text{(Eq 3.2)}$$

Where $W_{PET,O}$ represents the initial weight of PET charged into the flask and $W_{monomer,t}$ represents weight of monomer at a specific reaction time. Meanwhile the $MW_{monomer}$ and MW_{PET} are the molecular weights of monomer (640 gmol−1) and the PET (192 gmol−1)per repeating unit.

3.3.3 Experimental Setup
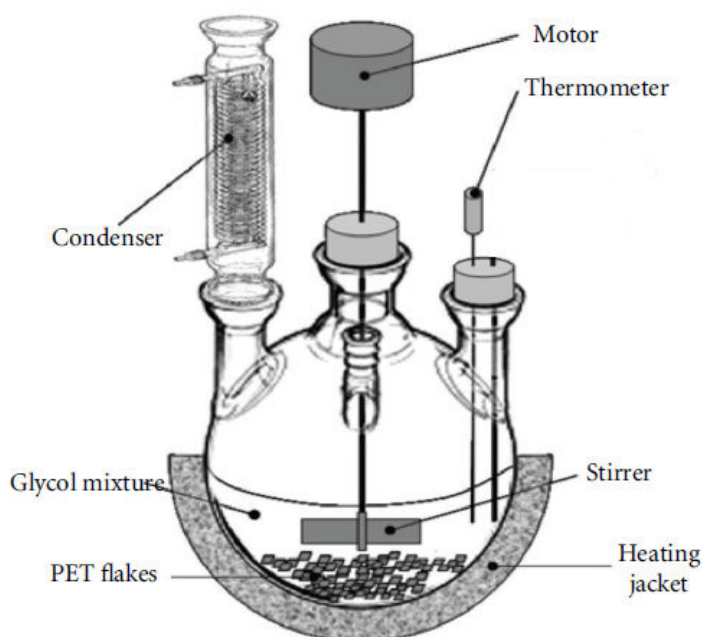
Figure 3.2 Three neck Glass Reactor for Glycolysis

3.4   ANALYSIS

The analysis was conducted on the product obtained for the characterization process. Three types of characterization techniques have been adapted. Which is Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA), and Fourier Transform Infrared Spectroscopy (FTIR)

3.4.1 Differential Scanning Calorimetry

DSC scans of the products were obtained using DSC-1000 by heating from room temperature to 200℃ at a rate of 10 ℃/min in an atmosphere of nitrogen.

3.4.2 Thermogravimetric analysis (TGA)

A thermogravimetric analyzer (TGA-500) was used to analyse the weight loss of the products in a nitrogen atmosphere during a temperature range from room temperature to 500℃ at a heating rate of 10 ℃/min.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis is conducted with Q1000 model with ATR attachment**.**

CHAPTER 4

RESULTS AND DISCUSSION

The effect of process conditions such as reaction temperature, reaction time, the molar ratio of PEG and amount of catalyst were investigated in this study. The collected data from the experimental procedure were optimizatized using RSM to have a proper visual upon the results obtained to gain a better understanding on the relationship between manipulated variables.

4.1   INFLUENCE OF REACTION TIME

The effects of glycolysis time on the conversion of PET and selectivity of monomer were presented in fig 4.1. When glycolysis time increase the conversion of PET increases and eventually reaches 100% when the reaction time almost 3hours. As described before conversion is the function of degree of degradation of PET. Meanwhile the selectivity of monomer reaches it maximum around one and hour of reaction time and decreases as the conversion increases. This is due presents of equilibrium between the dimer ,oligomer and the monomer .The depolymerisation reaction can be represented as

Fig 4.2 illustrates the effects of time on product distribution. It is very clear that, initially the presents of oligomer and dimer (fraction B) is higher compared to the monomer, indicating the initiation of PET depolymerisation and formation of oligomer and dimer. Correspondingly, at initial state the weight percentage of monomer (fraction A) is less and increasing rapidly after 30 minutes. After 2 hour there is minute decrease in the monomer weight percentage, causing the selectivity towards fraction A to be decreased. Meanwhile the weight percentage of dimer and oligomer decreases with increasing glycolysis time. As stated by Bartolome .L. et al. (2001) prolonging the reaction after the equilibrium tends to shift the reaction backward causing the formation of dimer.

In term of the yield of the process, the trend of fig 4.3 illustrates the amount of fraction A with time. After one hour of reaction time the yield is maintained at a specific value while the conversion is increased. Therefore it can be concluded that, initially PET was depolymerised into oligomer and dimer fractions and eventually to monomer in the presence of polyethylene glycol. With increasing reaction time more oligomers and dimmers are formed while the amount of monomer formed is constant.
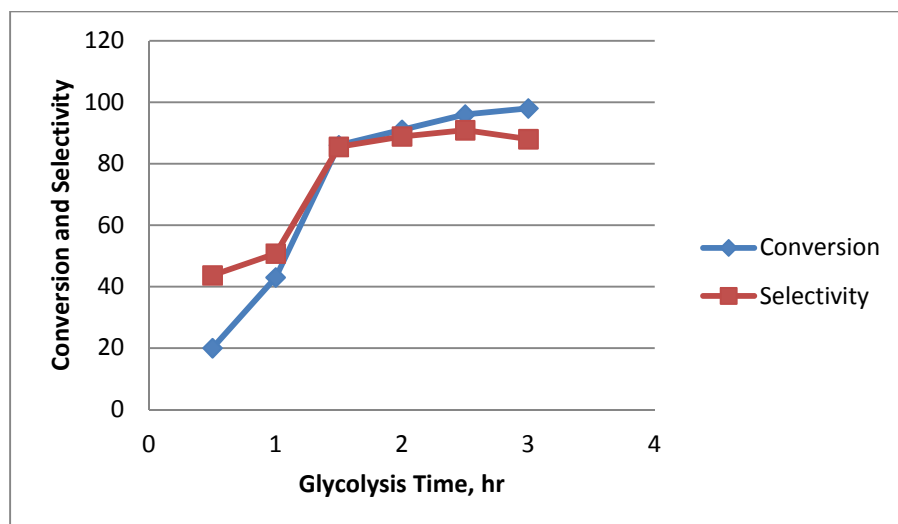
Figure 4.1 Effects of glycolysis time on the conversion of PET and selectivity of monomer (1atm, 185C, with 0.05 g of catalyst and 20g PEG)
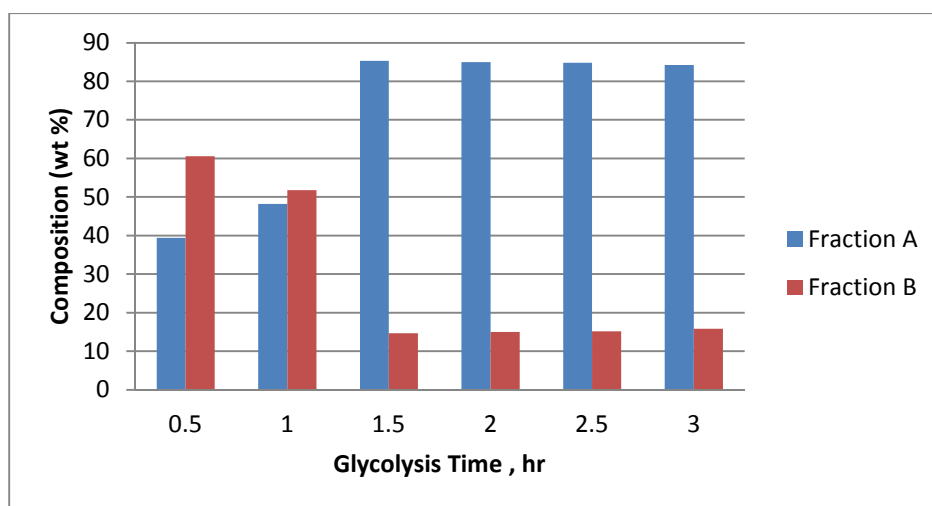
Figure 4.2 Effect of glycolysis time on distribution of the products (1atm, 185C, with 0.05 g of catalyst and 20g PEG)
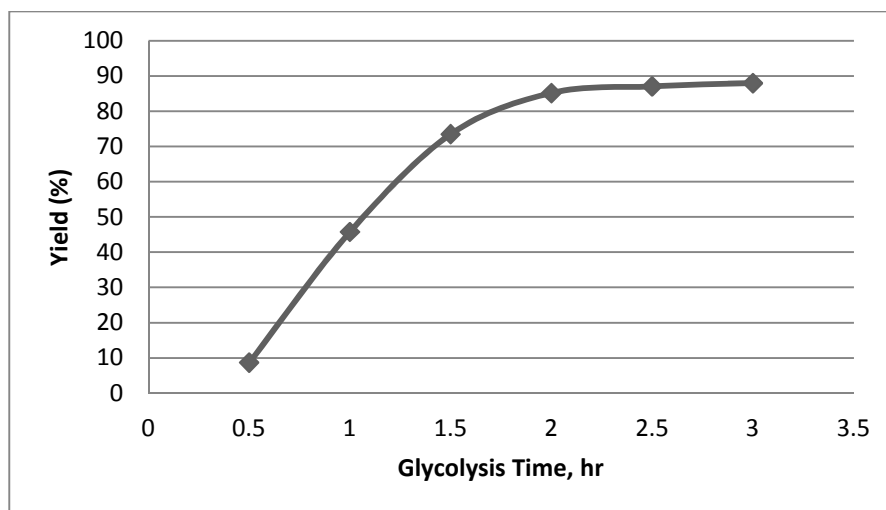
Figure 4.3 Effect of glycolysis time on yield of monomer (1atm, 185C, with 0.05 g of catalyst and 20g PEG)

4.2   INFLUENCE OF REACTION TEMPERATURE

The effects of glycolysis temperature on conversion of PET and selectivity of monomer were presented in fig 4.4. Meanwhile the fig4.5 shows the effect of reaction temperature on the distribution of products. It clearly show the conversion of PET increases as the when the reaction temperature is risen. Meanwhile the amount of monomer produced reaches to a steady state after 185°C. Thus, the selectivity of monomer is initially increased as the product is starting to form and eventually decrease as the conversion is increased at the same rate of product formation. The graph of product distribution over the temperature shows that the amount of oligomers and dimer (fraction B) to increase slightly while the weight percentage of monomer is decreased slightly. To further support this statement, the effect of temperature on the yield of monomer is plotted. Where the graph clearly shows that the amount/yield of monomer becomes constant after 185°C. Therefore it can be concluded that, initially PET was depolymerised into oligomer and dimer fractions and eventually to monomer in the presence of polyethylene glycol. With

increasing reaction temperature more oligomers and dimmers are formed while the amount of monomer formed is constant.
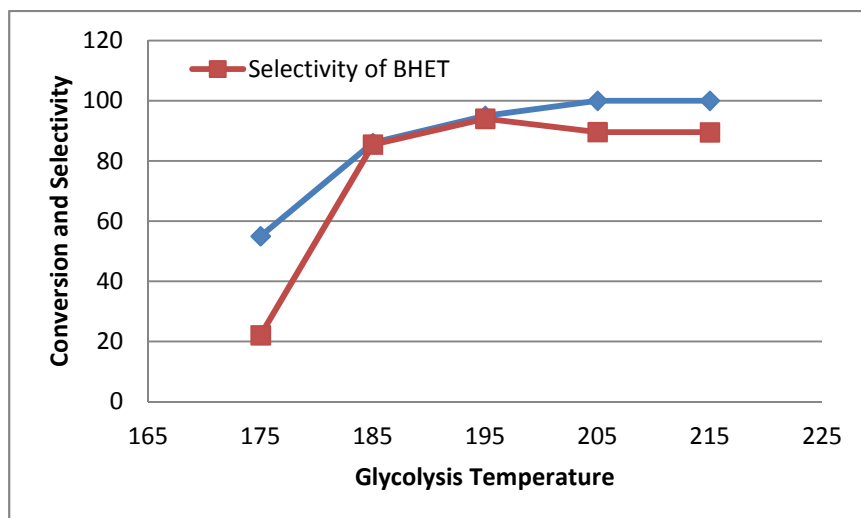
Figure 4.4 Effects of reaction temperature on the conversion of PET and selectivity of monomer (1 atm, 90min with 0.05g of catalyst and 20g PEG)
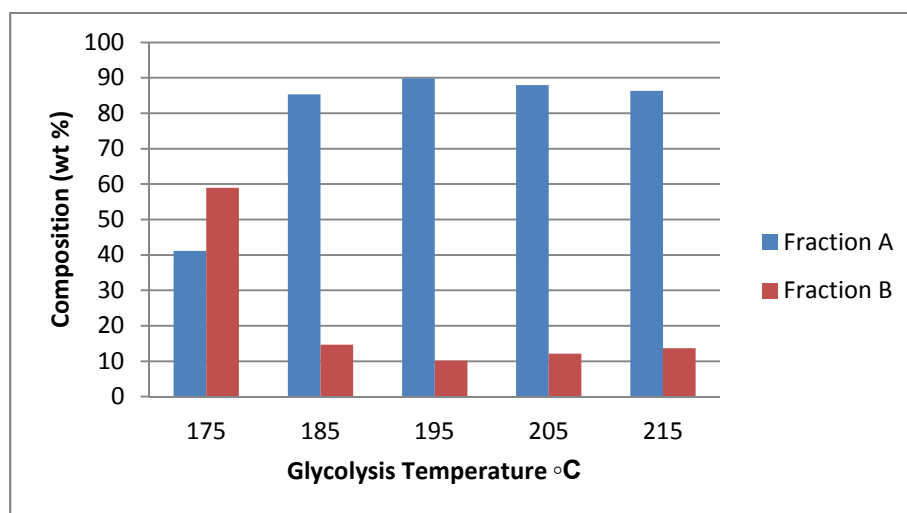
Figure 4.5 Effect of reaction temperature on distribution of the products (1 atm, 90min with 0.05g of catalyst and 20g PEG)
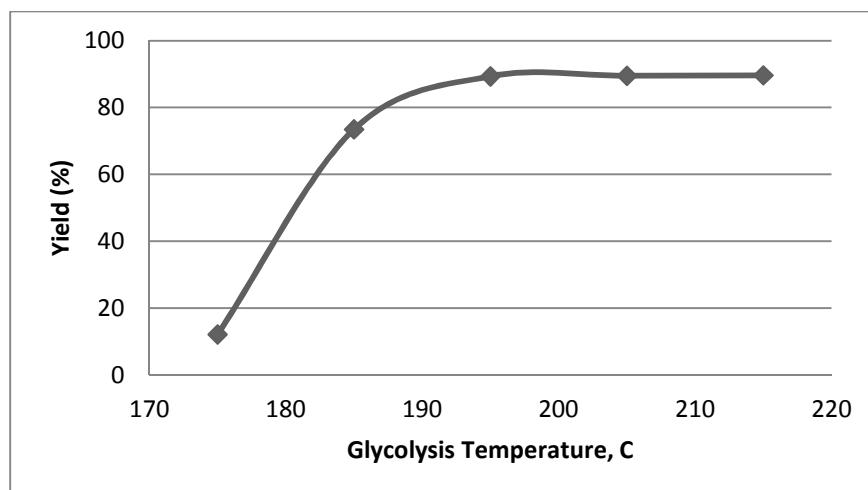
Figure 4.6 Effect of reaction temperature on yield of the process (1 atm, 90min with 0.05g of catalyst and 20g PEG)

4.3 INFLUENCE OF AMOUNT OF CATALYST

The fig 4.7 shows the effects of catalyst amount on the amount of monomer (fraction A). While fig 4.8 shows the effect of catalyst amount on the product distribution The experiment is conducted by maintaining the mass of PET used to be 5g and PEG used is 20g at 185°C for a reaction time of 90min. Initially the amount of catalyst used causes abrupt increase in the yield of the monomer, then the yield is increased gradually and reaches to a steady state as the amount of catalyst fed to reactor is increased. Focussing on the product distribution the amount of dimer and oligomer formed (fraction B) is decreased and reaches a steady state value. As described earlier in the survey that the metallic catalyst forms complex with the carbonyl group of ester (CO double bond present in PET), aiding the attack of PEG on PET to form monomer (refer section 2.3 and fig 2.5). As the amount of catalyst increased the saturation point between catalyst and PET is reached, where any excess of catalyst does affect the depolymerisation of PET to either dimer ,oligomer nor BHET. Therefore the amount of monomer, oligomer and dimer does not change.

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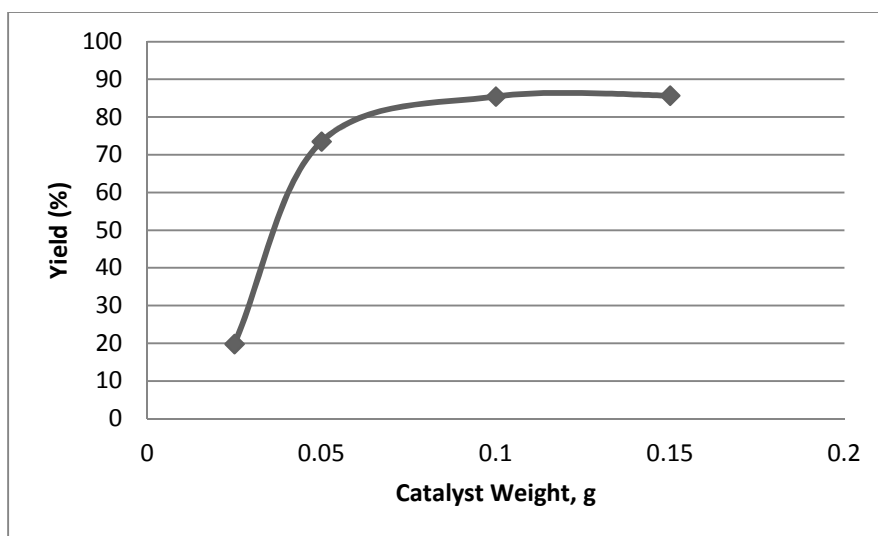
Figure 4.7 Effect of catalyst amount on yield of monomer (1 atm, 185C, 90min with 20g PEG)
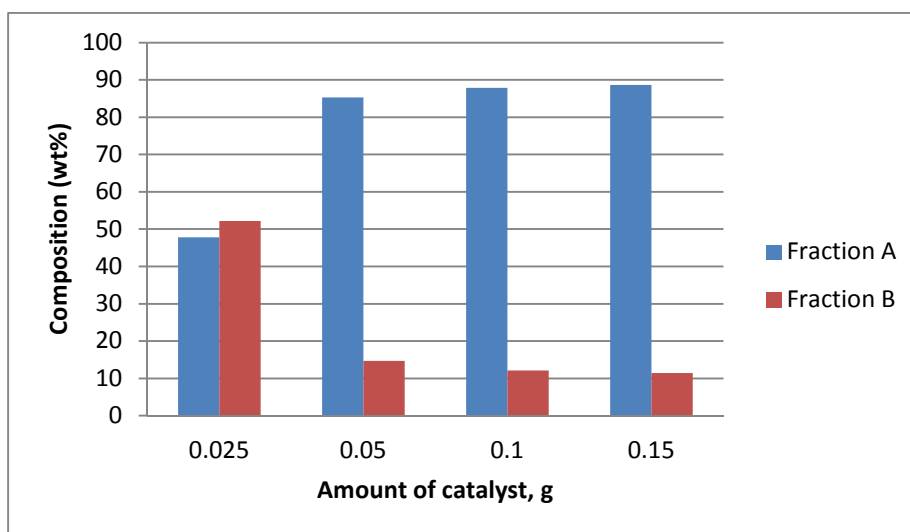
Figure4.8 Effect of catalyst amount on product distribution (1 atm, 185C, 90min with 20g PEG)

4.4 INFLUENCE OF AMOUNT OF PEG

The fig 4.8 shows the effect of PEG on the the yield of monomer. At initial stage the amount of PEG used for the glycolysis process increase the yield of monomer when the saturation limit is reached the quantity of PEG used does not affect the yield of the process.
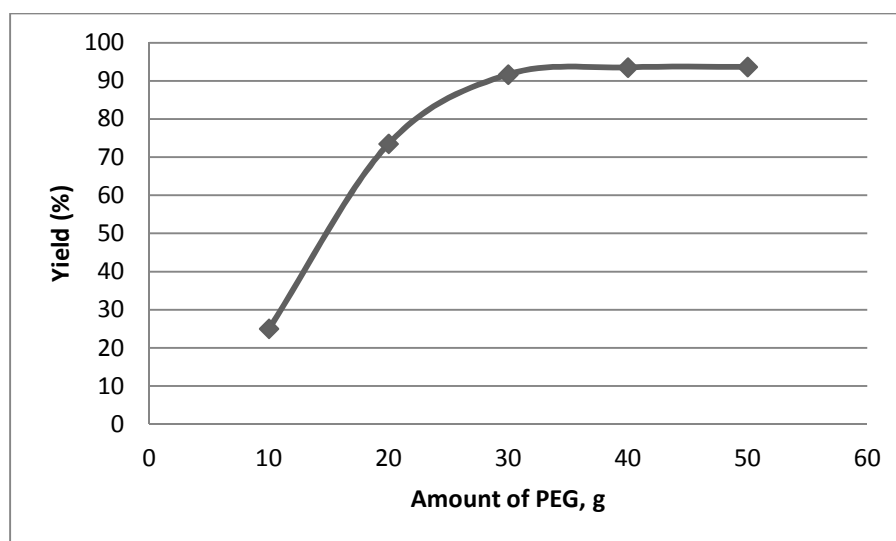
Figure 4.9 Effect of PEG amount on yield of monomer (1 atm, 185C, 90min with 0.05g of catalyst)

4.5 REACTION MECHANISM AND CHARACTERIZATION

4.5.1 Reaction Mechanism

The alcoholysis reaction can be denoted as

$$R1CO2R2 + R3OH \Leftrightarrow R1CO2R3 + R2OH \qquad \text{(Eq 4.1)}$$

Thus the polyether (glycol) can be used as agent of depolymerisation of polyesters such as PET. (Katoch.S. et al., 2012). In the presence of catalyst, the polyether (glygols) which consist of hydroxyl end group will attack the ester linkage in the

polymeric structure of PET (Meiyan et al., 1986). Thus, polyester (PET) chain will break and forming low molecular compounds.
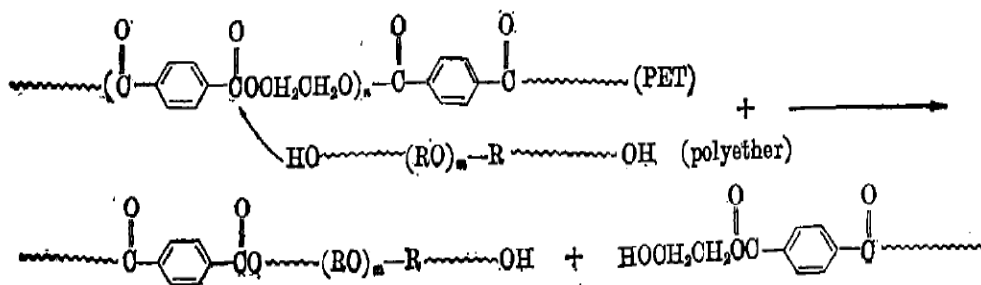
Figure 4.10 Mechanism of Alcoholysis (source: Meiyan et al., 1986)

4.5.2 Characterization
4.5.2.1 Differential Scanning Calorimetry (DSC)
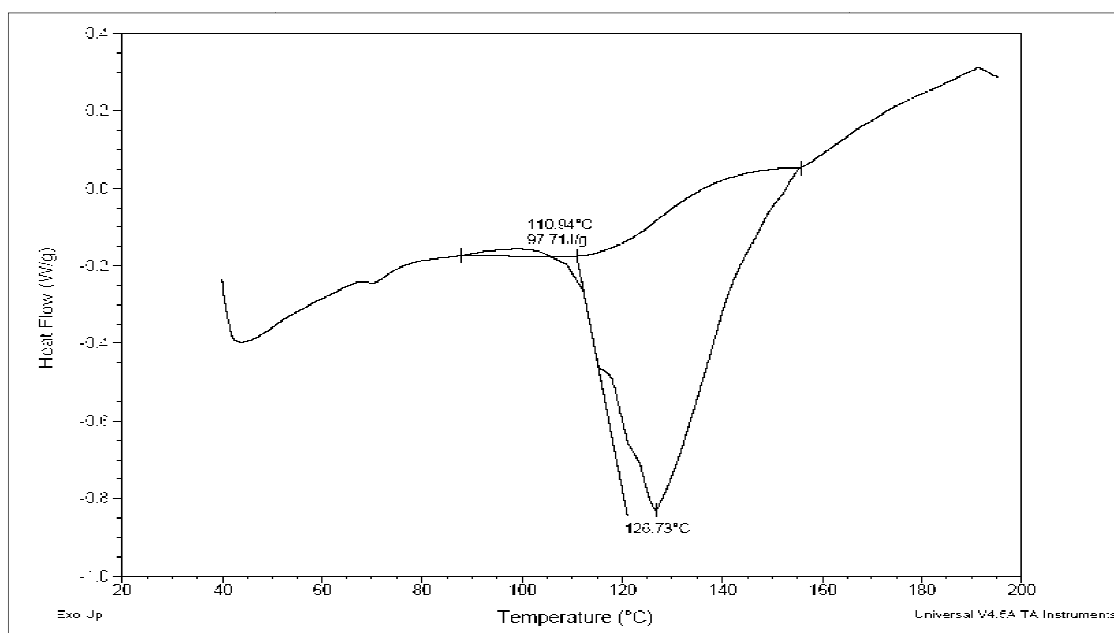
Figure 4.11 DSC thermograms (10°C per min ~ heating rate) of glycolysed product (monomer)

4.5.2.2 Thermogravimetric Analysis (TGA)

The thermal property of product of glycolysis is discussed in comparison with BHET (monomer of glycolysis process with ethylene glycol). The standard TGA for BHET is shown in the figure. The Figure 4.12 shows TGA curve for the glycolysed product (monomer) obtained. TGA curve for BHET composes of two decomposition region. Where the first decomposition region is around 190-220°C and the second decomposition region occurred at 380-400°C.

Meanwhile the TGA curve for the glycolysed product (monomer) poses a similar trend with the standard curve of BHET. The sample exhibits three decomposition region, first occurred around 80 to 120°C, the second region occurred around 190-240°C and completely decompose around 390-430°C. The first decomposition region occurred due of presents of water along with the sample. Improper drying after the filtration may cause the sample contains some portion of water. The first decomposition occurred at 190-220°C is due to thermal degradation of BHET. Comparing with the sample's TGA curve the second mass loss around 190-240°C is due to the presents of lower molecular weight component. Where BHET exhibit a rapid decomposition about 25% meanwhile the sample exhibit just 7-8% of mass loss. Indicating the presence of low molecular weighted component is less. The second mass loss occurred in BHET TGA, is about 55wt%. This is due to the formation of oligomers, dimer and PET results of thermal polymerization. Meanwhile the sample exhibit drastic mass loss about 80wt% at 390-430°C. Thus indicate the presence of component with higher molecular weight.
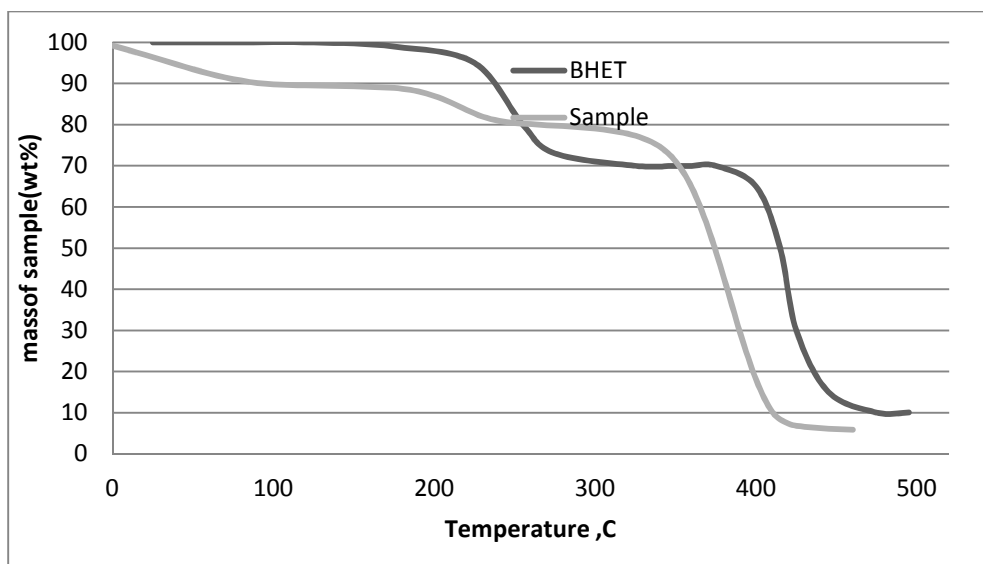
Figure 4.12 TGA curve of glycolysed sample (monomer) and standard BHET

4.5.2.3 Fourier Transform Infrared Spectroscopy

The Figure 4.13 illustrates the FTIR spectral analysis of of glycolysed product (monomer) and Figure 4.14 illustrates the spectrum of PET and PEG. The gycolysed product shows a band between 3000cm-1 to 3100cm-1 resembles stretching frequencies of hydroxyl groups. Referring to the PET spectrum the stretching of –OH (3000-3600cm-1) group is quite intense but in the glycolysed product spectrum is isn't,which proves the glycolysis have been occurred. Stretching frequencies for CH2 (-CH streching) groups may stand at 2850-3000 cm-1. The sharp bend around 1720 cm−1 stands carbonyl –C=O stretching results from the formation of ester linkage. Meanwhile PEG FTIR does not contain any spectra around 1700cm-1. The spectra tend to become sharper if number of ester linkage presents in the sample is higher. Frequency around frequencies 1100 cm-1 and 600-900 cm-1 stand for etheric linkage and for the aromatic ring, respectively due to ester. Overall it confirms that the glycolysis have occurred using PEG.

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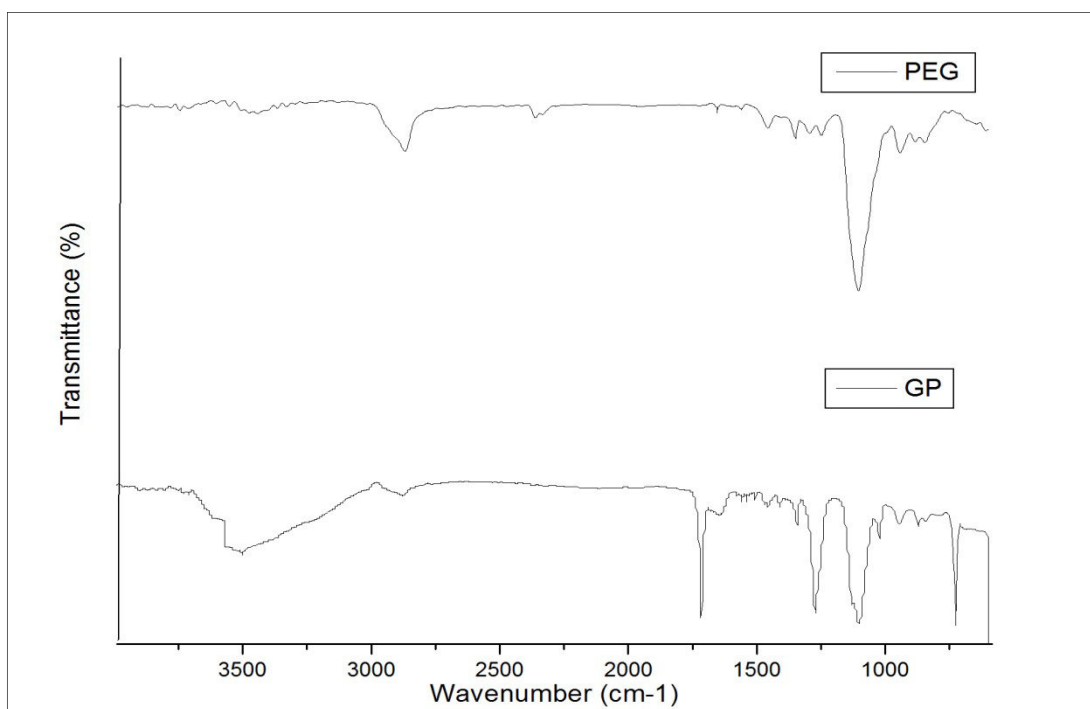
Figure 4.13 FTIR spectra of glycolysed product (monomer) and PEG
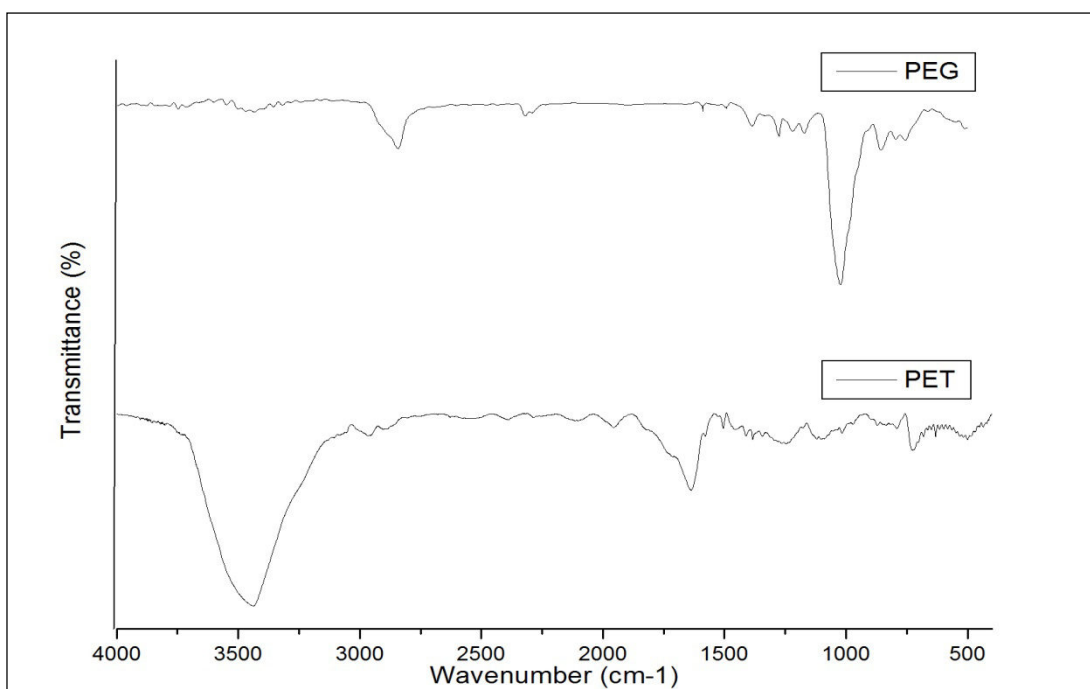
Figure 4.14 FTIR spectrums of PET and PEG

Table 4.1 Experimental values of responses and variables for glycolysis process.

No Run	Temperature, x_1 (°C)	Time, x_2 (hr)	Catalyst Weight, x_3 (g)	Amount of PEG, x_4 (g)	Yield , Y_1 (%)
1	185	2	0.15	30	93.05
2	195	2.5	0.1	40	96.14
3	195	2	0.05	20	80.55
4	205	2	0.15	30	94.55
5	195	2	0.1	30	94.14
6	195	2.5	0.1	20	93.61
7	195	2	0.1	30	94.2
8	185	2	0.1	20	86.64
9	195	2.5	0.15	30	95.6
10	205	2.5	0.1	30	95.41
11	195	1.5	0.05	30	81
12	195	1.5	0.1	20	91.29
13	205	2	0.1	20	92.64
14	185	1.5	0.1	30	91.59
15	195	2.5	0.05	30	83.32
16	205	2	0.05	30	82.35
17	185	2	0.05	30	80.85
18	195	1.5	0.15	30	93.2
19	185	2	0.1	40	93.77
20	195	2	0.15	20	92.75
21	205	1.5	0.1	30	93.09
22	195	2	0.15	40	95.28
23	195	2	0.05	40	83.08
24	195	1.5	0.1	40	93.82
25	185	2.5	0.1	30	93.91
26	205	2	0.1	40	95.07

4.6 DEVELOPMENT OF REGRESSION MODEL EQUATION

A polynomial regression equation was developed by using Three level factorial design to analyze the factor interactions by identifying the significant factors contributing to the regression model. The complete design matrix together with the response values obtained from the experimental works are given in Table 4.1. The yield of the glycolysis process was found to be 81 to 96.14%.

According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. For yield of the process, quadratic models was suggested by the software and selected due to higher order polynomial. The final empirical models in term of coded factor for the yield of the process (Y_1) are shown in Eq. 2:

$$Y_1 = 93.34 + 1.11x_1 + 1.17x_2 + 6.11x_3 + 1.64x_4 - 0.58x_1[2] + 0.56x_2[2] - 5.24x_3[2] - 0.36x_4[2] - 1.18\ x_1\ x_4 + 0.020x_2\ x_3 \qquad \text{(Eq 4.2)}$$

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient value. The R_2 value for the equation was 0.9851. This indicated that 98.51% of the total variation in the yield of the glycolysis process. The closer the R_2 value to unity, the better the model will give predicted values which are closer to the actual values for the response. The R_2 of 0.9851 for Eq. 2 was considered relatively high, indicating that there was good agreement between the experimental and the predicted yield of glycolysis process.

Table 4.2 Analysis of variance (ANOVA) for response surface quadratic model for yield of glycolysis process

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	712.022	14	50.85872	65.89067	< 0.0001	significant
X_1	14.74083	1	14.74083	19.09768	0.0006	
X_2	16.33333	1	16.33333	21.16086	0.0004	
X_3	447.4965	1	447.4965	579.7599	< 0.0001	
X_4	32.2752	1	32.2752	41.81455	< 0.0001	
X_1^2	2.162035	1	2.162035	2.801053	0.1164	
X_2^2	1.9992	1	1.9992	2.59009	0.1298	
X_3^2	178.4321	1	178.4321	231.17	< 0.0001	
X_4^2	0.851581	1	0.851581	1.103277	0.3113	
$X_1 X_2$	0	1	0	0	1.0000	
$X_1 X_3$	0	1	0	0	1.0000	
$X_1 X_4$	5.5225	1	5.5225	7.154746	0.0181	
$X_2 X_3$	0.0016	1	0.0016	0.002073	0.9643	
$X_2 X_4$	0	1	0	0	1.0000	
$X_3 X_4$	0	1	0	0	1.0000	
Residual	10.80611	14	0.771865			
Lack of Fit	8.086833	10	0.808683	1.189555	0.4700	not significant
Pure Error	2.71928	4	0.67982			

Table 4.3 Summary of results in analyzing lack of fit (LOF) foryiled of glycolysis process

Source	Sum of Squares	DF	Square	Value	Prob > F
Linear	203.7388648	14	14.55277606	21.40680777	0.0046
2FI	8.086833333	10	0.808683333	1.189555078	0.4700
Quadratic	1.628033333	2	0.814016667	1.197400292	0.3913
Pure Error	2.71928	4	0.67982		

4.7   STATISTICAL ANALYSIS

The result of the surface quadratic model in the form of analysis of variance (ANOVA) was given in Table 4.2 for the yield of glycolysis process. ANOVA is required to justify the significance and adequacy of the models. The mean squares

were obtained by dividing the sum of the squares of each of the variation sources, the model and the error variance, by the respective degrees of freedom. If the value of Prob $> F$ less than 0.05, the model term are considered as significant. For an example, in the Table 4.2 the model F-value is 50.8587 and Prob. < 0.0001 implied that this model was significant. In this case X_1, X_2, X_3, X_4, X_3^2, and X_1X_4 factors was significant model term X_1^2, X_2^2, X_4^2, X_1X_2 , X_1X_3 ,X_2X_3, X_2X_4, X_3X_4 whereas were insignificant to the response. From the statistical results obtained, it was shown that the above models were adequate to predict the yield of the process within the range of variables studied. Fig. 4.10 shows the predicted values versus the experimental values for yield of the glycolysis process. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the models developed were successful in capturing the correlation between operating parameter to the response.
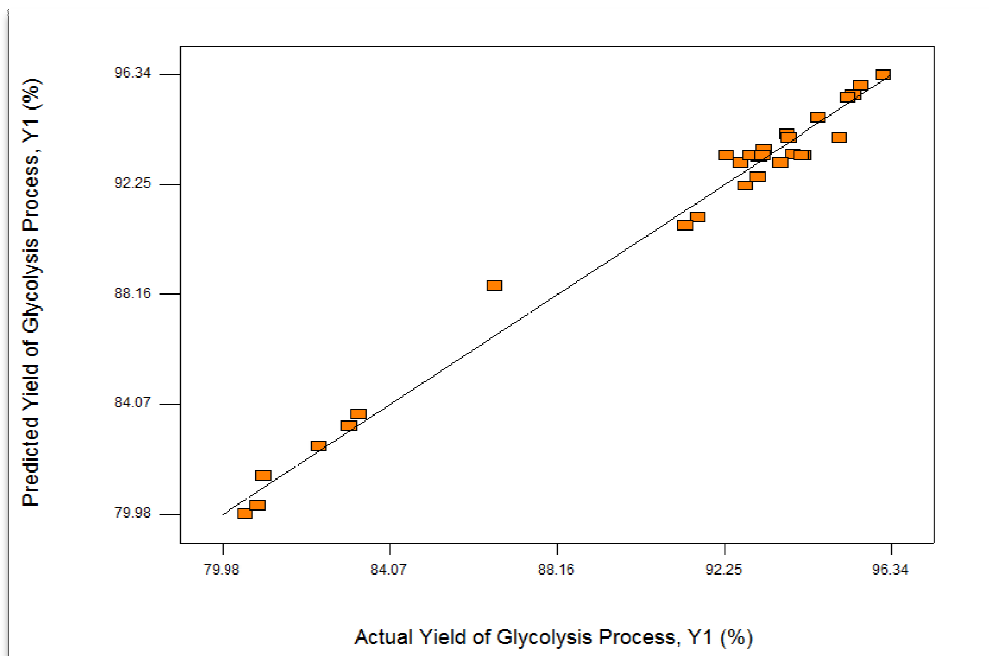
Figure 4.15 Linear Correlation Plot between Actual and Predicted Response

4.8   INFLUENCE OF PROCESS VARIABLES ON THE STIMULATED RESPONSE

The data tabulated in Table 4.2 shows that the catalyst plays an important role in term of the yield of the glycolysis process, where the F-value of that factor is 447.4965 the largest among the factors. But the effect of time is comparatively insignificant (14.74083). Meanwhile the F-value for the amount of PEG used and the temperature is 32.2752 and 16.33333 respectively. The results obtained compromises the investigation of Chen .C.H, et al, where they concluded that the effect of glycolysis process parameters can be sequenced into: catalyst concentration>glycolysis temperature>glycolysis time.

4.8.1 Comparison between influence of time and temperature

Referring to the figure 4.16 increasing the temperature (while maintain the time at 1.5hr) will increase the yield of the process up to 82.5%. At lower temperature (approximately below 180°C) the reaction seems to be very sluggish. This is due to the presents of thermodynamic equilibrium state between corresponding liquid states causing slow rate of release partially depolymerised PET from solid phase into liquid phase (Pardal and Tersac, 2007). Even though the reaction time is increased, the response towards the yield of the process is not satisfying. According to Katoch.S et al, when the temperature is raised (approximately above than 180°C) causing acceleration of non-polymerized or partially polymerized polyester from solid phase to the liquid phase. Meanwhile the temperature is maintained low (185℃) and the time of reaction is increased the yield obtained increased slowly up to 79.12%. The highest yield is obtained when the temperature is increased up to 205℃ and reaction is conducted for 2.5hr.
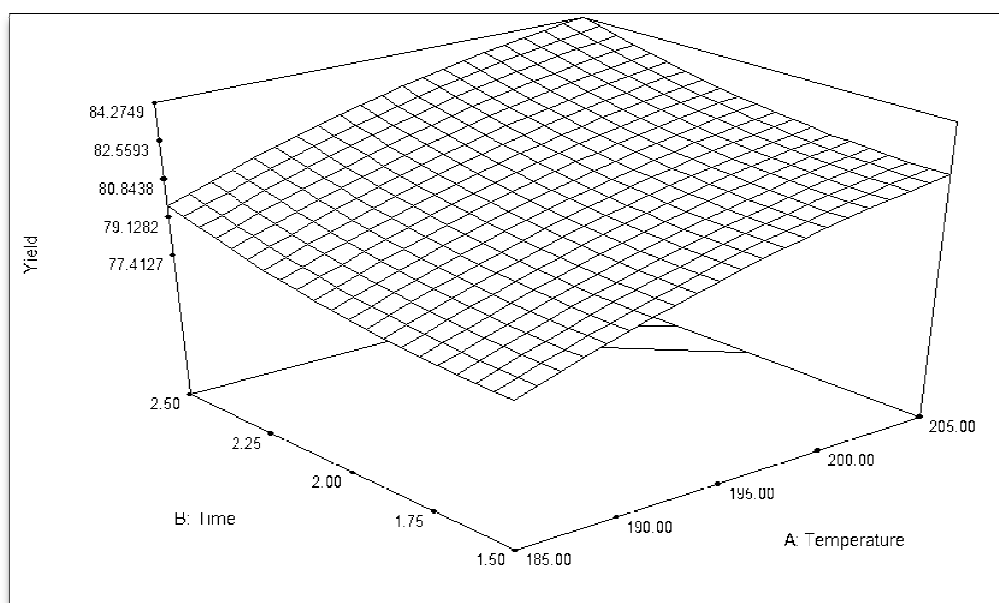
Figure 4.16 Surface Plot (3D) showing variation in response with glycolysis time and temperature (with 20g of PEG and 0.05g of catalyst)

4.8.2 Comparison between influence of catalyst amount and temperature

Referring to the figure 4.17 increasing the temperature (while maintaining the catalyst amount) will increase the yield of the process up to 80.94%. Meanwhile increasing the catalyst amount (while maintaining temperature) will cause abrupt increase the yield to a steady state. Further increase in the catalyst amount does not influence the response. As described earlier in the survey that the metallic catalyst forms complex with the carbonyl group of ester (CO double bond present in PET), aiding the attack of PEG on PET to form monomer (refer section 2.3 and fig 2.5). As the amount of catalyst increased the saturation point between catalyst and PET is reached, where any excess of catalyst does affect the depolymerisation of PET. One should notice that even though the effect of temperature is less than catalyst amount, but the response does not show any saturation point between the process parameter.

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Further increase in temperature may lead to higher yield towards the process. According to Wang H. et al. high temperature is beneficial in term of formation of monomer. The highest yield is obtained when the temperature is increased up to 205℃ and catalyst amount of 0.10 (2wt %)
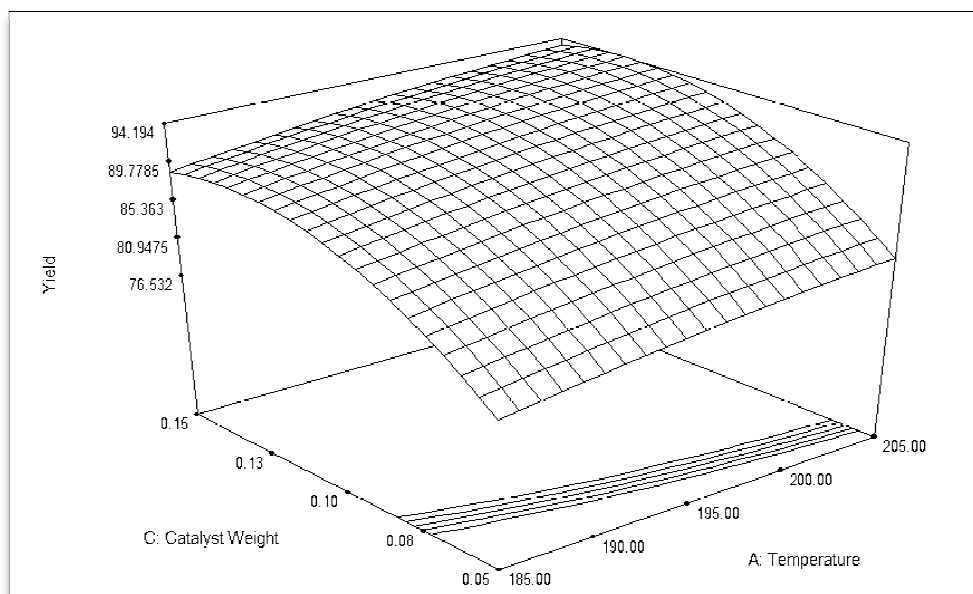
Figure 4.17 Surface Plot (3D) showing variation in response with catalyst amount and glycolysis temperature (with 20g of PEG and 1.5hr of reaction time)

4.8.3 Comparison between influence of PEG amount and the temperature

Referring to the figure 4.18 increasing the temperature (while maintaining the PEG amount) will increase the yield of the process up to 80.48%. Meanwhile increasing the PEG amount (while maintaining temperature) will cause abrupt increase the yield to a steady state.

The equation below shows the mechanism suggested by Chen et al.(1991). Where the depolymerisation reaction can be divided into two steps

PET+EG →BHET + oligomers   (Eq 4.3)

BHET ↔ oligomers + EG   (Eq 4.4)

This mechanism was well explained by Carta et al (2003). Where they stated that, the glycolysed product consists of PET, dimer, trimer/oligomers. Eq 3 is extremely fast, and it is reversible reaction. In the excess usage of EG (glycol), the amount of oligomer and dimer formed is insignificant because the depolymerisation reaction occur quickly and randomly. In lower EG/PET amount of oligomer formed is higher. (Carta et.al., 2003). They have concluded that EG/PET can be used to regulate the degree of polymerization. The investigation by both party suggest that amount of depolymerisation agent have strong influence on the yield of desired product (monomer). Adding to that higher temperature the synergetic effect of both amount of PEG and glycolysis temperature can increase the yield up to 83.5% with 0.05g of catalyst 1.5hr of reaction time.
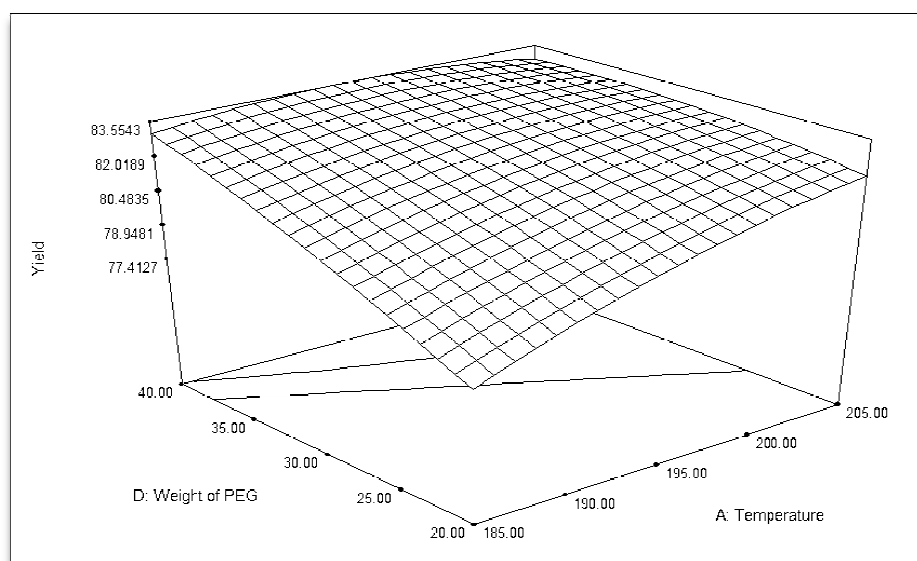
Figure 4.18 Surface Plot (3D) showing variation in response with PEG amount and glycolysis temperature (with 0.05g of catalyst and 1.5hr of reaction time)

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4.8.4 Comparison between influence of catalyst amount and time of reaction

Referring to the figure 4.19 increasing the catalyst amount (while maintaining the reaction time at 1.5 hr) will increase the yield of the process up to a steady state (88.12%). As discussed earlier the metallic catalyst forms complex with the carbonyl group of ester (CO double bond present in PET), aiding the attack of PEG on PET to form monomer. As the amount of catalyst increased the saturation point between catalyst and PET is reached, where any excess of catalyst does affect the depolymerisation of PET. Meanwhile increasing catalyst amount accelerates (to a certain extent) glycolysis process and shorten the equilibrium time (X. Zhou et al., 2012) Thus the reaction time does not influence the response, since the catalyst amount determines the equilibrium time /point. But the synergized effect of catalyst amount and reaction time can promise the yield up to 91.98% at 185℃ and 20 g of PEG
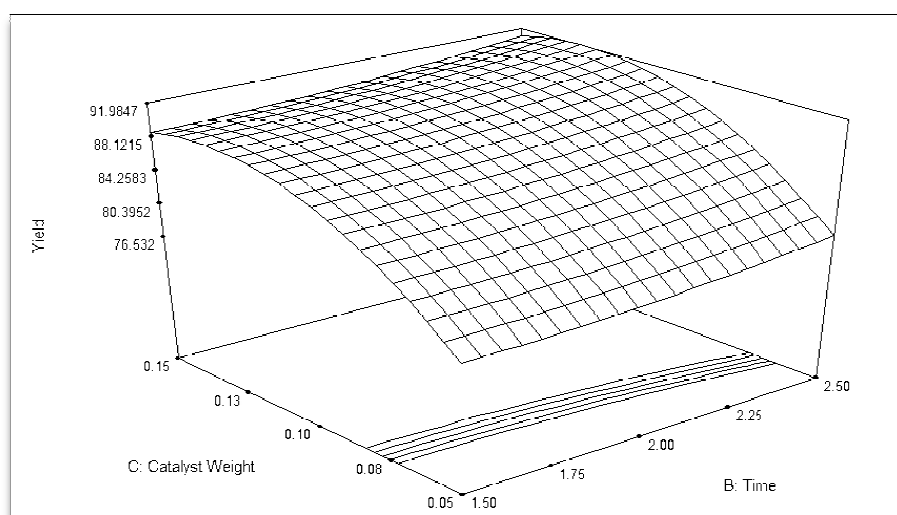
Figure 4.19 Surface Plot (3D) showing variation in response with catalyst amount and glycolysis time (with 0.05g of catalyst and 185℃ of reaction time)

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4.8.5 Comparison between influence of amount of PEG and time of reaction

Referring to the figure 4.20 increasing the amount of PEG (while maintaining the reaction time at 1.5 hr) will increase the yield of the process up to 83.36%. For the longer reaction time (2.5hr) the yield can be increased just up to 85.34%. Increasing reaction time does not give significant effect on the glycolysis process. As explained earlier, the formation of monomer and oligomer (Eq 4.3, refer to section 4.8.3) is extremely fast, and the excess of PEG used will suppress the degradation of monomer formed into glycols and oligomers. Therefore the effect of time is considerably small compared to influence of amount of PEG.
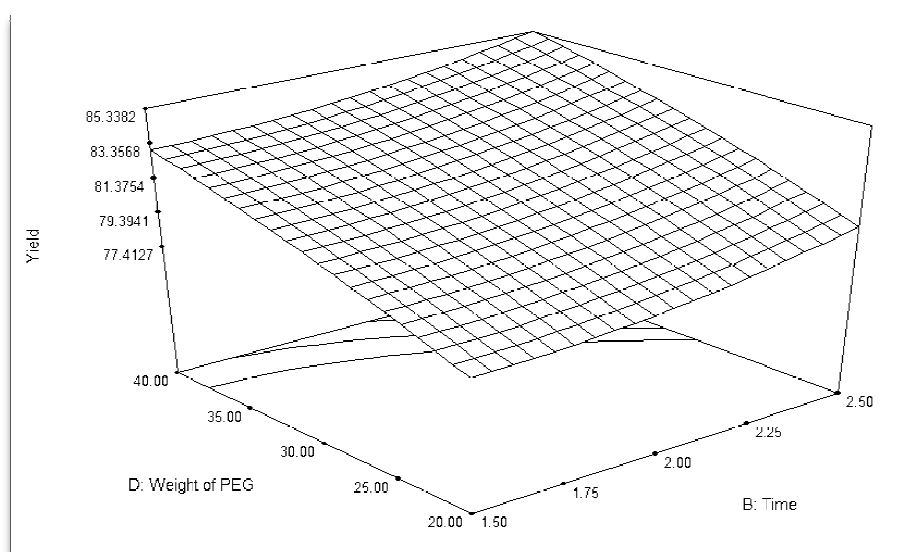
Figure 4.20 Surface Plot (3D) showing variation in response with PEG amount and glycolysis time (with 0.05g of catalyst and 185℃ of reaction temperature)

4.8.6 Comparison between influence of amount of PEG and amount of catalyst

Referring to surface plot, both parameter have significant effect towards the response. Where increasing PEG amount results in increase of yield from 76.5 to 81.2%, meanwhile the amount of catalyst is maintained at 0.05g. Furthermore increasing amount of catalyst cause the yield to be increased and attain steady state. One should notice that, at steady state (catalyst amount >0.1g) further increase in the PEG ratio or amount cause the yield to be increased up to 95.2% and attain a steady state. It's clearly illustrates that the presence of saturation between the PEG and catalyst. Thus increasing amount of PEG in the presence of higher catalyst will increase the yield of glycolysis process. As explained earlier this statement identical to investigation of X.Zhou et al. (2012) about the influence of catalyst.
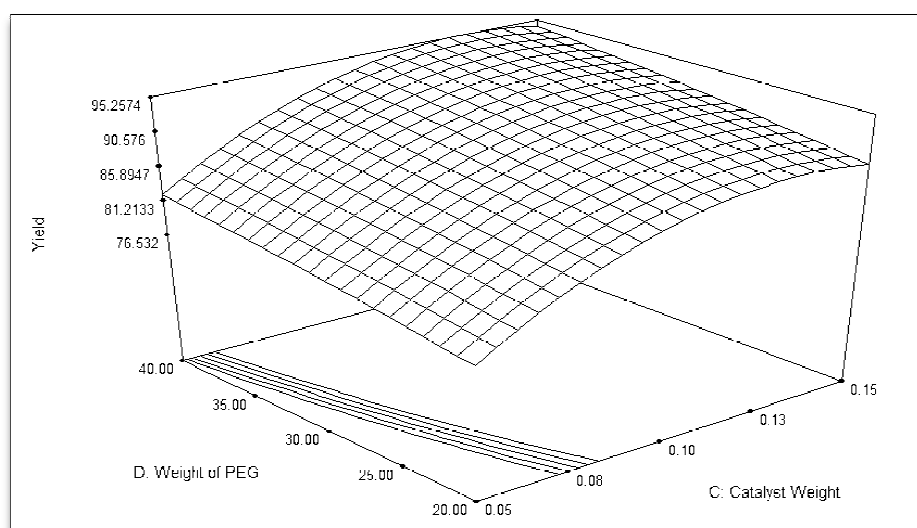
Figure 4.21 Surface Plot (3D) showing variation in response with PEG amount and glycolysis time (with 0.05g of catalyst and 185℃ of reaction time)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1   CONCLUSION

The presented work includes Polyethylene Glycol is used to study the influence of process parameter towards the glycolysis process due to limited work done on the PEG as deploymerizing agent of PET. In particular, experimental work includes preparation of PET scrap including collecting and treating and glycolysis of treated PET. Then the glycolysed product is separated using cold distilled water by means of vacuum distillation.

Obtained product is then subjected to thermal and FTIR characterization. FTIR shows an intense dropping around 1700-1750cm-1 resembling the stretching of carbonyl group. Which confirm the formation of glycolysed product. From Thermogravimetric Analysis carried out the sample shows approximately 80% of mass loss around 390-430℃ which resembles the sample contain compound with long chain. The weight loss around 190-240℃ is just 7-8wt%. To support the characterization DSC analysis also has been conducted. It clearly shows the sample

has higher melting point compared to standard BHET melting point, confirms formation of compound with higher molecular chain.

For the optimization process the Research Surface Methodology is used visualize the results obtained upon the combined effect of process condition. To gain a better understanding on the relationship between manipulated variables. The optimal condition of glycolysis time, temperature, amount of catalyst and amount of PEG were 205∘C, 2.49hr, 0.12g (2.4wt% of PET used) and 36.87g of PEG respectively. Where using this optimized condition the yield of the process can be reached up to 96.3%. The stimulated values were in good agreement with experimental value, revealing the constructed/stimulated model is completely reliable.

5.2   RECOMMENDATION

It is strongly recommended for future work that the study should be done in wide scope on certain experimental parameter such as type of catalyst. The catalyst used in this research is a conventional catalyst, where separation and refining process is quite complex. Since glycolysis of PEG with PET is an intermediate reaction to produce various types of polyurethanes and block copolymers, optimizing it with various kind of catalyst would be economically beneficial. Furthermore developing an eco-friendly catalyst towards glycolysis process, would be the real motive of recycling process which is to provide a unpolluted environment, major concern in this eco-friendly era.

Rather than developing and optimizing an eco-friendly catalyst, the method research itself can be improved to get the accurate results. It is suggested the experiment can be conducted using pilot plant where the small experimental setup does not resembles the commercially available plants and optimization with obtained results would deviate from the actual.

Furthermore, in term of characterization, hydroxyl and acid value can be adopted. Hydroxyl value denotes the hydroxyl terminal presents in the oligomers while acid value denotes for the carbonyl terminated oligomers. Thus, the degree of depolymerization can be determined.

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APPENDIX A1

EXPERIMENTAL RESULTS

Run	Temp, degree C	Time, hr	Mass of A ,g	Mass of B ,g	Conversion (%)	Weight of catalyst, g	Fraction of PEG used to PET	Yield (%)
1	215	1 ½	3.91	0.48	100	0.050	20/5	89.66
2	205	1 ½	3.90	0.47	100	0.050	20/5	89.50
3	195	1 ½	3.89	0.44	95	0.050	20/5	89.35
4	185	3	3.83	0.72	98	0.050	20/5	87.97
5	185	2 ½	3.80	0.68	96	0.050	20/5	87.05
6	185	2	3.52	0.62	91	0.050	20/5	85.15
7	185	1 ½	3.20	0.55	86	0.050	20/5	73.50
8	185	1	0.95	1.02	43	0.050	20/5	45.78
9	185	½	0.39	0.60	20	0.050	20/5	8.72
10	185	1 ½	3.72	0.51	95	0.100	20/5	85.44
11	185	1 ½	3.73	0.48	100	0.150	20/5	85.70
12	185	1 ½	3.28	0.76	100	0.200	20/5	75.20
13	185	1 ½	0.87	0.95	48	0.025	20/5	19.82
14	185	1 ½	1.09	0.06	54	0.050	10/5	25.03
15	185	1 ½	3.99	1.20	97	0.050	30/5	91.64
16	185	1 ½	4.07	0.21	100	0.050	40/5	93.50
17	185	1 ½	4.08	0.25	100	0.050	50/5	93.66
18	175	1 ½	0.53	0.76	55%	0.050	20/5	12.17
19	185	2	4.05	0.09	100	0.150	30/5	93.05
20	195	2 ½	4.18	-	100	0.100	40/5	96.14
21	195	2	3.50	0.08	90	0.050	20/5	80.55
22	205	2	4.12	-	100	0.150	30/5	94.55
23	195	2	4.09	-	100	0.050	20/5	94.14
24	195	2 ½	3.77	0.09	95	0.100	20/5	86.64
25	185	2	4.16	-	100	0.150	30/5	95.6
26	205	2 ½	4.15	-	100	0.100	30/5	95.41
27	195	1 ½	3.52	0.13	91	0.050	30/5	81.00
28	195	1 ½	3.97	0.08	100	0.100	20/5	91.29
29	205	2	4.03	0.05	100	0.100	20/5	92.64
30	185	1 ½	3.99	0.06	100	0.100	30/5	91.59
31	195	2 ½	3.63	0.21	93	0.050	30/5	83.32
32	205	2	3.59	0.13	93	0.100	30/5	82.35
33	185	2	3.52	0.15	90	0.050	30/5	80.85
34	195	1 ½	4.06	0.05	100	0.150	30/5	93.2
35	205	1 ½	4.05	0.07	100	0.100	30/5	93.09
36	195	2	4.14	-	100	0.150	40/5	95.28
37	195	2	3.62	0.12	92	0.050	40/5	83.08
38	195	1 ½	4.08	0.08	100	0.100	40/5	93.82
39	185	2 ½	4.09	0.07	100	0.100	30/5	93.91
40	205	2	4.14	-	100	0.100	40/5	95.07

APPENDIX A2

WEGHT DISTRIBUTION

Composition A $_{T=185C}$ = $\frac{3.20}{3.20+0.55}$

=85.3wt%

Composition B $_{T=185C}$ = $\frac{0.55}{3.20+0.55}$

=14.7wt%

Table A2.1:Distribution of the products vs reaction temperature (1atm, 1.5hr, with 0.05 g of catalyst and 20g PEG)

Run	Temperature	Mass of A	Mass of B	Composition A (wt%)	Composition B (wt%)
1	175	0.53	0.76	41.1	58.9
2	185	3.20	0.55	85.3	14.7
3	195	3.89	0.44	89.8	10.2
4	205	3.90	0.47	91.7	8.3
5	215	3.91	0.48	93.3	6.7

Table A2-2: Distribution of the products versus reaction time (1atm, 185°C, with 0.05 g of catalyst and 20g PEG)

Run	Time	Mass of A	Mass of B	Composition A (wt%)	Composition B (wt%)
1	½	0.39	0.60	39.4	60.6
2	1	0.95	1.02	48.2	51.8
3	1 ½	3.20	0.55	85.3	14.7
4	2	3.52	0.62	85.8	14.2
5	2 ½	3.80	0.68	86.3	13.7
6	3	3.83	0.72	87.0	13.0

Table A2-3: Distribution of the products versus catalyst amount (1atm, 1.5hr, 185C with 20g PEG)

Run	Catalyst amount	Mass of A	Mass of B	Composition A (wt%)	Composition B (wt%)
1	0.025	0.87	0.95	47.8	52.2
2	0.05	3.20	0.55	85.3	14.7
3	0.1	3.72	0.51	87.9	12.1
4	0.15	3.73	0.48	88.6	11.4

APPENDIX B1

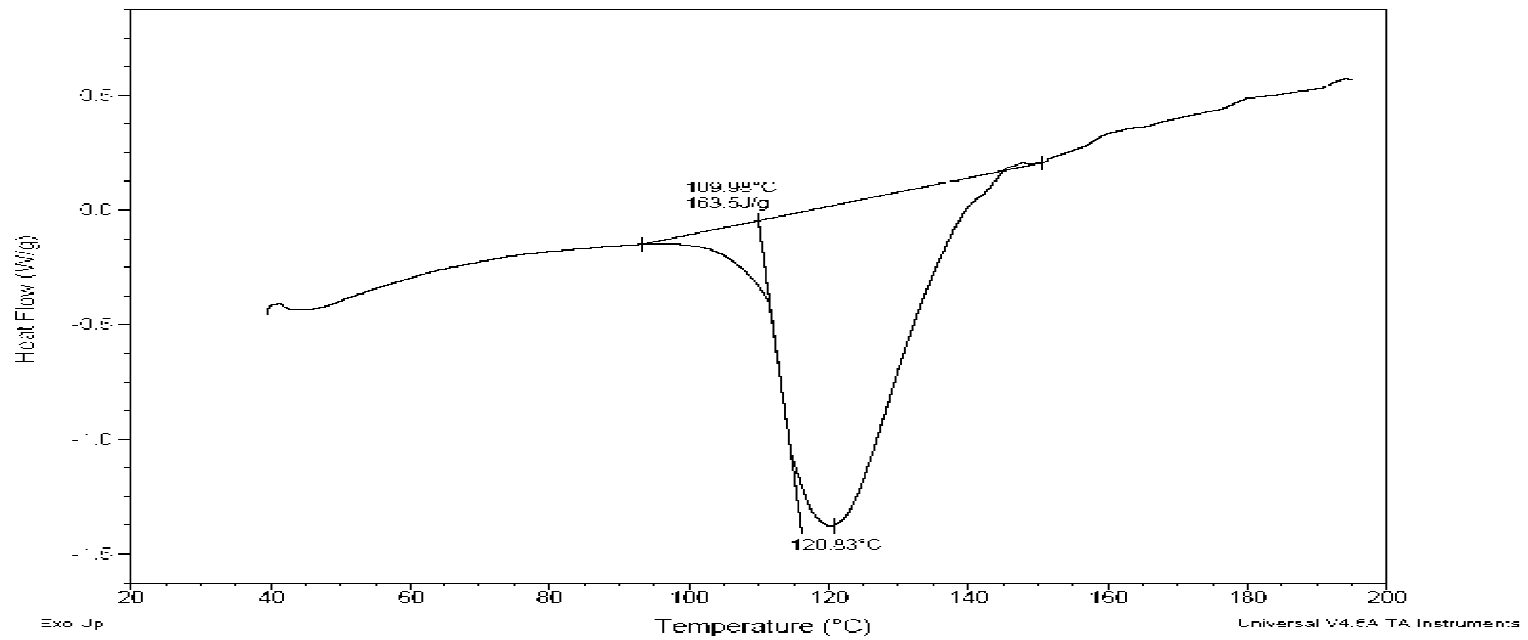# ANALYSIS RESULTS: DSC THERMOGRAMS

Sample: PEG/PET(1)
Size: 3.2000 mg
Method: Ramp

DSC

File: C:...\dinesh kumar\PEGPET_1.001
Operator: fiza
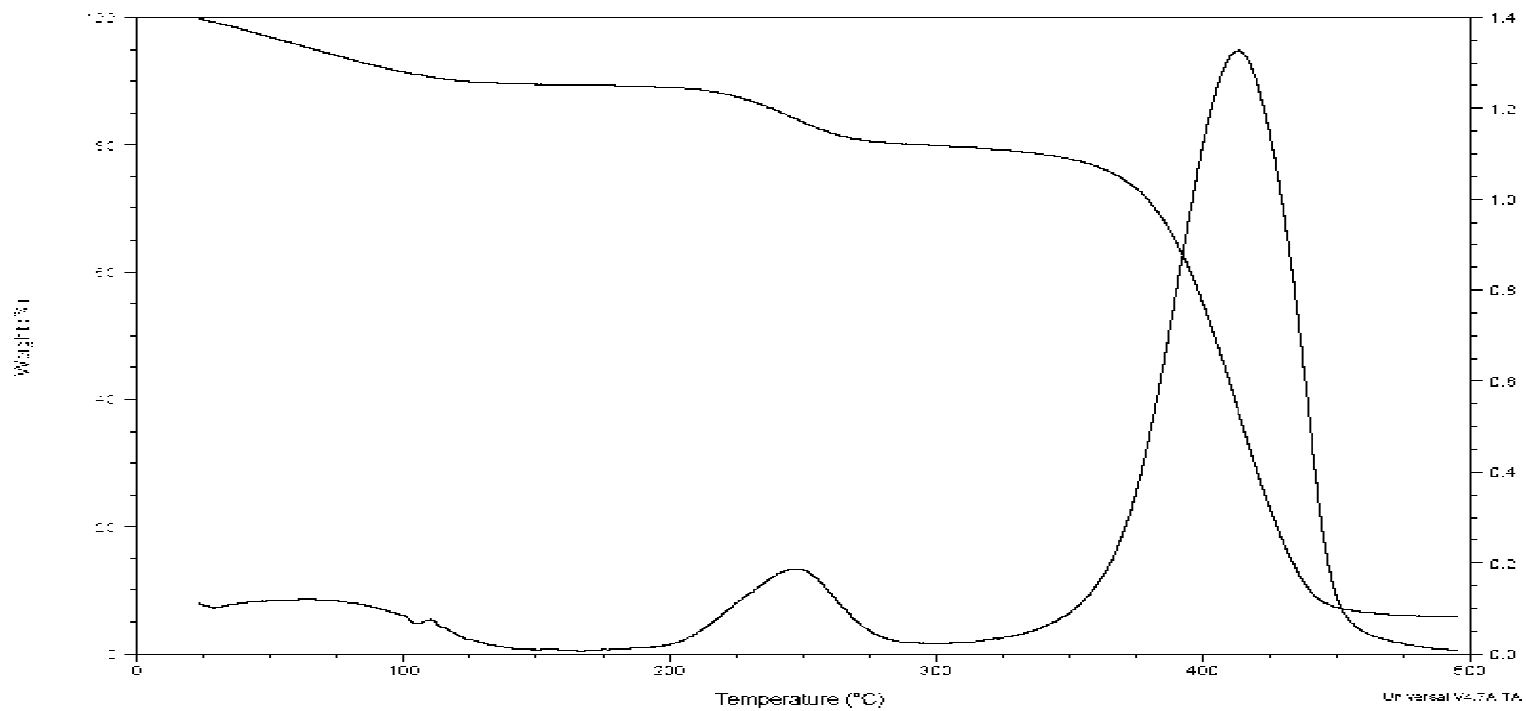Run Date: 07-Dec-2012 09:28
Instrument: DSC Q1000 V9.9 Build 303

109.98°C
163.5J/g

120.93°C

Exo Up

Temperature (°C)

Heat Flow (W/g)

Universal V4.5A TA Instruments

APPENDIX B2

ANALYSIS RESULTS: TGA

APPENDIX B3

ANALYSIS RESULTS: FTIR
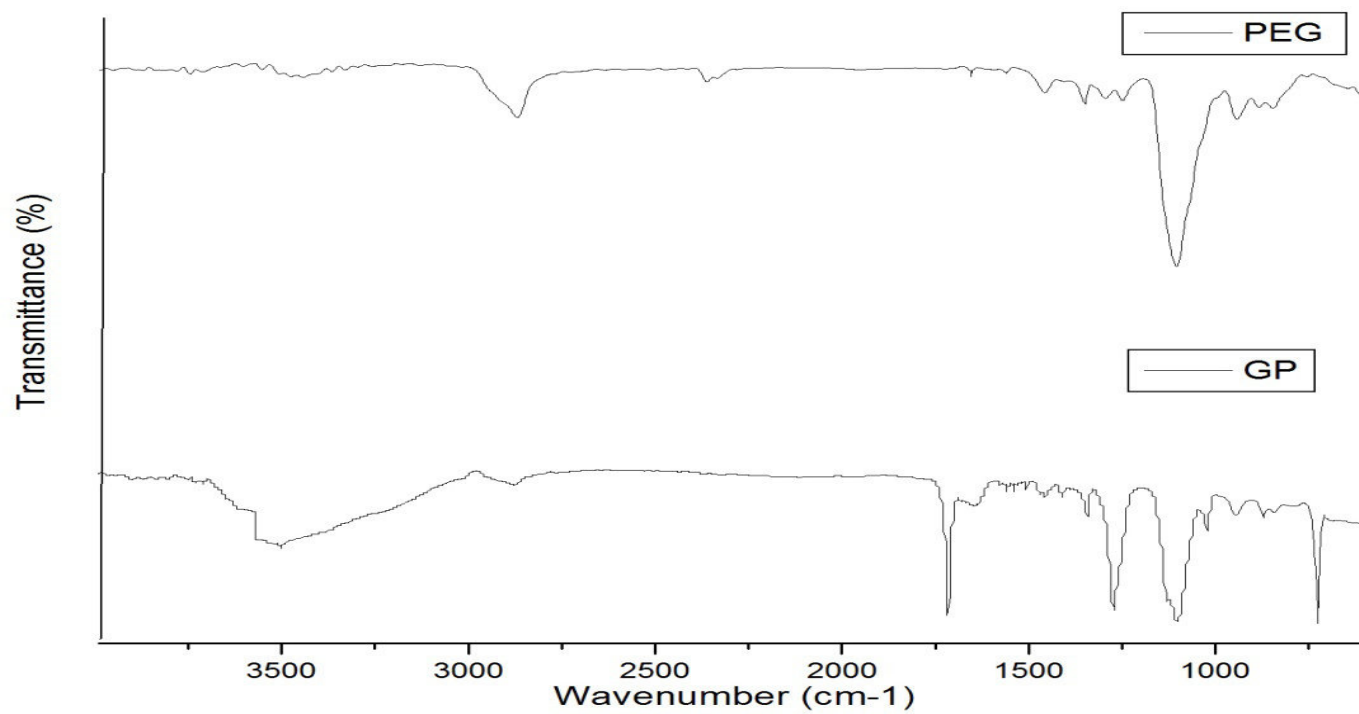
APPENDIX C1

RSM: LAYOUT DESIGN

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A:Temperature deg C	B:Time hr	C:Catalyst Weight g	D:Weight of PEG	Yield
19	1	185	2	0.15	30	93.05
24	2	195	2.5	0.1	40	96.14
5	3	195	2	0.05	20	80.55
20	4	205	2	0.15	30	94.55
26	5	195	2	0.1	30	94.14
22	6	195	2.5	0.1	20	93.61
28	7	195	2	0.1	30	93.18
25	8	195	2	0.1	30	94.2
9	9	185	2	0.1	20	86.64
16	10	195	2.5	0.15	30	95.6
4	11	205	2.5	0.1	30	95.41
13	12	195	1.5	0.05	30	81
21	13	195	1.5	0.1	20	91.29
29	14	195	2	0.1	30	92.29
10	15	205	2	0.1	20	92.64
1	16	185	1.5	0.1	30	91.59
14	17	195	2.5	0.05	30	83.32
18	18	205	2	0.05	30	82.35
17	19	185	2	0.05	30	80.85
15	20	195	1.5	0.15	30	93.2
11	21	185	2	0.1	40	93.77
6	22	195	2	0.15	20	92.75
2	23	205	1.5	0.1	30	93.09
27	24	195	2	0.1	30	92.88
8	25	195	2	0.15	40	95.28
7	26	195	2	0.05	40	83.08
23	27	195	1.5	0.1	40	93.82
3	28	185	2.5	0.1	30	93.91
12	29	205	2	0.1	40	95.07

APPENDIX C2

RSM: FIT SUMMARY

Response: Yield

Table C2-1: Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Mean	240194.502	1	240194.502		
Linear	510.8459	4	127.711475	14.4591138	< 0.0001
2FI	5.5241	6	0.92068333	0.08026954	0.9975
Quadratic	195.652031	4	48.9130079	63.3698805	< 0.0001
Cubic	6.4588	8	0.80735	1.11427441	0.4605
Residual	4.34731333	6	0.72455222		
Total	240917.33	29	8307.49415		

I+"Sequential Model Sum of Squares"0+: Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Table C2-2: Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Linear	209.262965	20	10.4631482	15.3910568	0.0084
2FI	203.738865	14	14.5527761	21.4068078	0.0046
Quadratic	8.08683333	10	0.80868333	1.18955508	0.4700
Cubic	1.62803333	2	0.81401667	1.19740029	0.3913
Pure Error	2.71928	4	0.67982		

I+"Lack of Fit Tests"0+: Want the selected model to have insignificant lack-of-fit.

Table C2-2: Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS
Linear	2.97196796	0.70673217	0.65785419	0.56086143	317.421715
2FI	3.38672363	0.71437451	0.55569368	0.14461239	618.298239
Quadratic	0.87855861	0.98505023	0.97010046	0.92968033	50.829035
Cubic	0.85120633	0.99398569	0.97193321	0.66978918	238.685675

I+"Model Summary Statistics"0+: Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".