FINAL REPORT
FUNDAMENTAL RESEARCH GRANT SCHEME (FRGS)
Laporan Akhir Skim Geran Penyelidikan Fundamental (FRGS)
Pindaan 1/2015

KEMENTERIAN PENDIDIKAN MALAYSIA

A | **RESEARCH TITLE: KINETIC MODELLING OF THE SYNTHESIS OF SORBITOL-BRANCHED POLYESTER FOR THE PRODUCTION OF BIO-BASED POLYURETHANE**

PHASE & YEAR: 01/2014

START DATE: 01 JULY 2014
END DATE: 30 JUN 2016
EXTENSION PERIOD (DATE): RMC LEVEL: 31 DEC 2016
KPM LEVEL:

PROJECT LEADER:
I/C / PASSPORT NUMBER: 770810-14-5422

PROJECT MEMBERS:
(including GRA)
1. Cheng Chin Kui
2. Chua@Yeo Gek Kee
3. Hayder A. Abdul Bari
4. Mohd Sabri Bin Mahmud
5. Muhammad Ridzuan Kamaruzaman

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE			
Project progress according to milestones achieved up to this period	0 - 50%	51 - 75%	76 - 100%
Percentage (please state #%)			100

RESEARCH OUTPUT		
Number of articles/ manuscripts/ books *(Please attach the First Page of Publication)*	Indexed Journal	*Non-Indexed Journal*
	2 (As Attachment 1 and Attachment 2)	-
Conference Proceeding *(Please attach the First Page of Publication)*	International	*National*
	-	-
Intellectual Property *(Please specify)*	-	

HUMAN CAPITAL DEVELOPMENT					
Human Capital	**Number**				**Others** (please specify)
	On-going		**Graduated**		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
No. PHD STUDENT	1				
Student Fullname: IC / Passport No: Student ID:	Muhammad Ridzuan Kamaruzaman 880219065035 PKC16021				
No. MASTER STUDENT					
Student Fullname: IC / Passport No: Student ID:					
No. UNDERGRADUATE STUDENT	1		2		
Student Fullname: IC / Passport No: Student ID:	Nurwadiah Bt. Azizan KE13011		Elaine Pui Chiew Ling KA12107 Jasmin A/P Tramarajh KA12006		
Total					

EXPENDITURE *(Perbelanjaan) as Borang K1(RMC)*

C   **Budget Approved** *(Peruntukan diluluskan)* : **RM 120,000.00**
     Amount Spent *(Jumlah Perbelanjaan)* : **RM 112,966.58**

     Balance *(Baki)* : **RM 7033.42**
     Percentage of Amount Spent :   94.14 %
     (Peratusan Belanja)

ADDITIONAL RESEARCH ACTIVITIES THAT CONTRIBUTE TOWARDS DEVELOPING SOFT AND HARD SKILLS
(Aktiviti Penyelidikan Sampingan yang menyumbang kepada pembangunan kemahiran insaniah)

D

International

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	-	-

National

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	Creation, Innovation, Technology & Research Exposition (CITREX-2015), 9-10 March 2015	UMP

E | **PROBLEMS / CONSTRAINTS IF ANY** *(Masalah/ Kekangan sekiranya ada)*

-

F | **RECOMMENDATION (***Cadangan Penambahbaikan***)**

-

G | **RESEARCH ABSTRACT – Not More Than 200 Words** (*Abstrak Penyelidikan – Tidak Melebihi 200 patah perkataan*)

A bio-based polyester polyol was synthesised through the esterification of azelaic acid and sorbitol catalysed by tin (II) oxide. The chemical equilibrium, reaction kinetics and parametric studies were carried out. Different reaction parameters were studied in order to determine the best reaction conditions. The best operating condition with reaction temperature of 433K, sorbitol to azelaic acid molar ratio of 4:1 and catalyst loading of 2wt%, yielded a conversion of 72%. The formation of sorbitol based branched polyester with its backbone incorporated with sorbitan and isosorbide was affirmed. The mathematical form of Eley Rideal (ER) model gave good agreement with the experimental data. The activation energy was found to be 47.62 kJ/mol.

Date :
Tarikh

Project Leader's Signature:
Tandatangan Ketua Projek

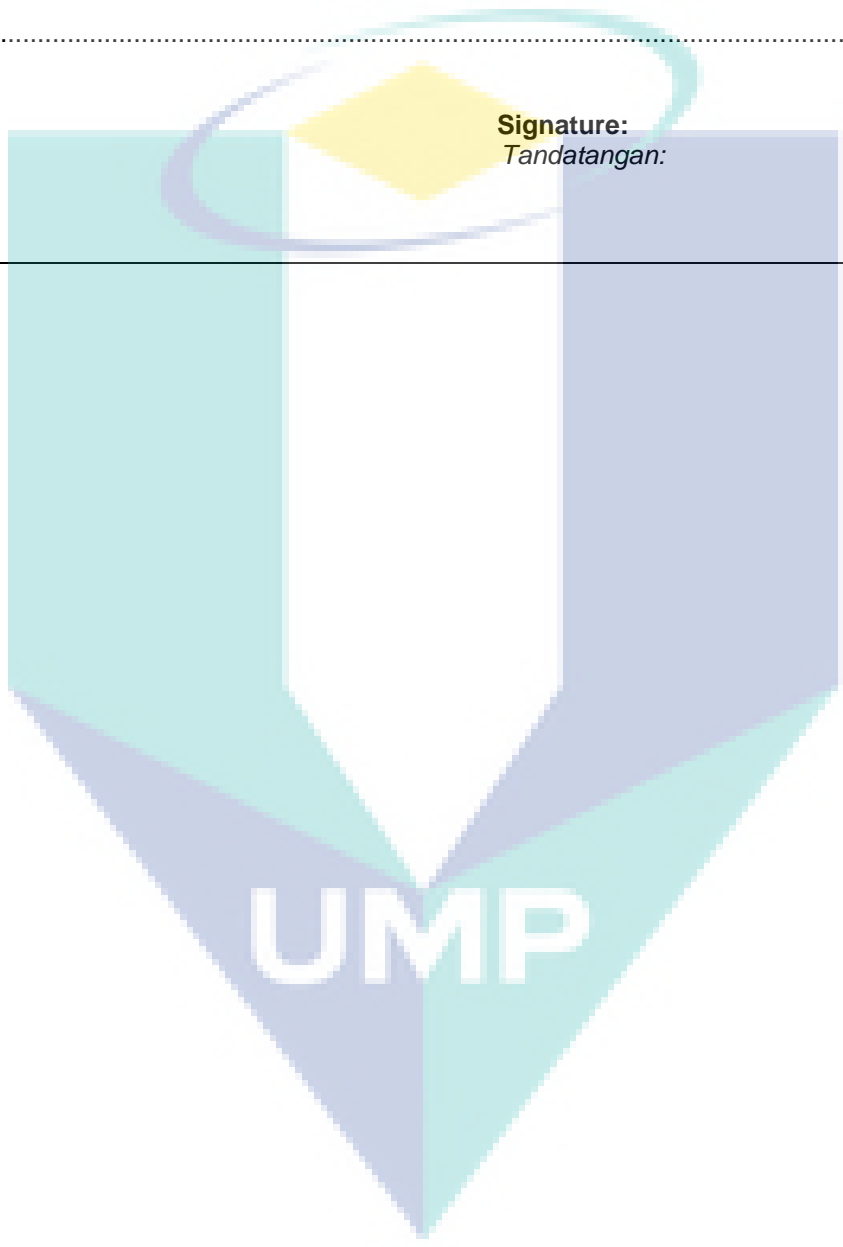| H	**COMMENTS, IF ANY/ ENDORSEMENT BY RESEARCH MANAGEMENT CENTER (RMC)** *(Komen, sekiranya ada/ Pengesahan oleh Pusat Pengurusan Penyelidikan)*
	.... **Name:** **Signature:** *Nama:* *Tandatangan:* **Date:** *Tarikh:*

SENARAI DAFTAR HARTA MODAL DI BAWAH DANA PENYELIDIKAN FUNDAMENTAL KEMENTERIAN PENDIDIKAN TINGGI (FRGS)

BIL	IPT	JENIS GERAN (FRGS/ERGS/LRGS/PRGS/NRGS/RAGS/RACE/TRGS)	FASA (CONTOH 2/2014)	TAJUK PROJEK PENYELIDIKAN	NAMA KETUA	NAMA ASET	BILANGAN UNIT	NO SIRI PENDAFTARAN	TARIKH PEROLEHAN	HARGA PEROLEHAN ASAL (RM)
1	UMP	FRGS	1/2014	Kinetic Modelling of the Synthesis of Sorbitol-Branched Polyester for the Production of Bio-based Polyurethane	Chin Sim Yee	Thermal oil pump	1	FTA1000-PB104(R)-1602-0001-00004		2200
2	UMP	FRGS	1/2014	Kinetic Modelling of the Synthesis of Sorbitol-Branched Polyester for the Production of Bio-based Polyurethane	Chin Sim Yee	Peristaltic pump for transfering raw material	1	FTA1000-PB104(R)-1602-0001-00001		400
3	UMP	FRGS	1/2014	Kinetic Modelling of the Synthesis of Sorbitol-Branched Polyester for the Production of Bio-based Polyurethane	Chin Sim Yee	Peristaltic pump for transfering raw material	1	FTA1000-PB104(R)-1602-0001-00002		400
4	UMP	FRGS	1/2014	Kinetic Modelling of the Synthesis of Sorbitol-Branched Polyester for the Production of Bio-based Polyurethane	Chin Sim Yee	Furnace	1	FTA1000-PB104(R)-1602-0001-00007		900
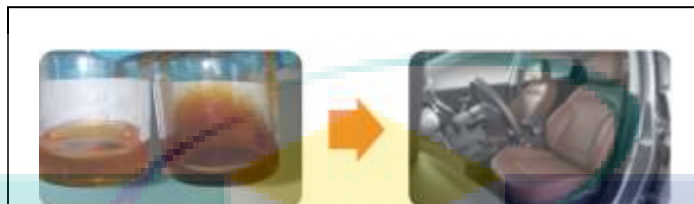
KINETIC MODELLING OF THE SYNTHESIS OF SORBITOL-BRANCHED POLYESTER FOR THE PRODUCTION OF BIO-BASED POLYURETHANE

Project leader: Chin Sim Yee
Co-researchers: Cheng Chin Kui, Chua@Yeo Gek Kee, Hayder A. Abdul Bari, Mohd Sabri Bin Mahmud
UMP/ Faculty of Chemical and Natural Resources Engineering
chin@ump.edu.my
Technology and Engineering: Energy and Green Technology

ABSTRACT

A bio-based polyester polyol was synthesised through the esterification of azelaic acid and sorbitol catalysed by tin (II) oxide. The chemical equilibrium, reaction kinetics and parametric studies were carried out. Different reaction parameters were studied in order to determine the best reaction conditions. The best operating condition with reaction temperature of 433K, sorbitol to azelaic acid molar ratio of 4:1 and catalyst loading of 2wt%, yielded a conversion of 72%. The formation of sorbitol based branched polyester with its backbone incorporated with sorbitan and isosorbide was affirmed. The mathematical form of Eley Rideal (ER) model gave good agreement with the experimental data. The activation energy was found to be 47.62 kJ/mol.

1 INTRODUCTION

Polyurethanes (PUs) are one of the most versatile groups of polymers suitable for the application in the area of foams, elastomers, thermoplastics, adhesives, coatings, sealants and fibers. Conventionally, PUs is produced by reacting petro-based polyester polyol with diisocyanate. Uncertainty in terms of price and availability of petroleum, in addition to global political and institutional tendencies toward the principles of sustainable development, has prompted the continuing effort to identify bio-based PUs. Sorbitol-based polyester is one of the potential polyester polyol for the production of biobased PUs possessing comparable properties with the petro-based PUs. Sorbitol based polyesters can be produced by direct, acid or base-

catalysed or acid-catalysed esterification reaction of sorbitol with fatty acids at elevated temperature. It can also be produced through the basic catalysed transesterification of sorbitol with triglycerides or fatty acid methyl esters. In recent years, most of the researches for the synthesis of sorbitol based polyester were carried out using the route of acid catalysed esterification since the base catalysed reaction attributes to the unwanted highly coloured products. Moreover, the anhydrization degree of sorbitol increases in the presence of an acid catalyst, and therefore producing the mixtures with a high proportion of esters of sorbides. The isosorbide ester produced possesses rigid molecular structure which improving the mechanical properties of the PUs [1]. Giacometti et al. [2] prepared the surfactant through the esterification of sorbitol with lauric acid using p-toluene sulfonic acid as a catalyst. Enzyme such as lipase has also been employed as a catalyst in the esterification of sorbitol anhydrides (sorbitol and isosorbide) with oleic acid and decanoic acid [3-4]. The sorbitol based polyesters were also prepared through the process with and without the pre-process of sorbitol dehydration prior to esterification reaction. A better conversion was reported for the esterification of lauric acid with the pre-dehydrated sorbitol. A kinetic model of reversible second order reaction was proposed for the esterification of lauric acid with the sorbitol anhydrides produced through the pre-dehydration sorbitol. To the best of our knowledge, very limited information about the heterogeneously catalyzed esterification of sorbitol with di-carboxylic acid can be found in the open literature. In the present study, parametric and kinetic studies of the esterification of sorbitol with azelaic acid were carried out. Azelaic acid is industrially used in the manufacturing of pharmaceutical products, plasticizers,

2   RESEARCH METHODOLOGY

2.1 Materials
Azelaic acid (90%), potassium hydroxide (KOH) pellets and potassium hydrogen phthalate (KHP) were purchased from Merck. Sorbitol solution (70%) and ethanol (99.7%) were obtained from R&M Chemicals. Tin (II) oxide (99%) was supplied by Alfa-Chemistry. All chemicals were used without further purifications.

2.2 Methods
2.2.1 Experimental procedure for the esterification reaction study
The esterification reaction of sorbitol and azelaic acid catalysed by tin (II) oxide was carried out in a three neck flask equipped with condenser, temperature controller and temperature probe. The sorbitol and azelaic acid were charged into two distinct flasks for heating to desired temperature. Subsequently, the sorbitol and azelaic acid were mixed and the catalyst was introduced. The samples were withdrawn every 30 minutes for the first hour and every 1 hour for the subsequent 6 hours. The important reaction parameters were varied during the reaction study. These parameters included molar ratio of sorbitol to azelaic acid ($M_{SL:AA}$) of 1:1 to 6:1, reaction temperature of 403 to 433K and catalyst loading of 1 to 8wt%.

The procedure for the equilibrium study was identical to esterification reaction study at different temperatures but the reaction time was prolonged until the conversion achieved equilibrium. The sample after 6 hours was taken in every two hours. The reaction was in equilibrium when the acid value was constant.

2.2.2 Analysis
The acid value (AV) of the sample was determined by titration using KOH with phenolphthalein as indicator. The KOH solution was standardised using KHP. AV was calculated using Eq. 1.
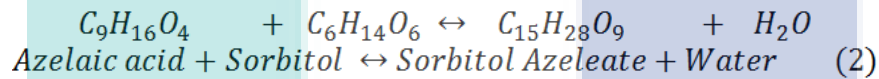
$$AV = \frac{A \times N \times 56.1}{W} \qquad (1)$$

Where A is amount of 0.1M of KOH consumed for sample in ml, N is KOH concentration in mol/L and W is sample weight in g.

The gas chromatography (GC) analysis was limited to certain component in the reaction mixture attributing to the commercially unavailability of the GC standard. The reaction products (sorbitan and isosorbide) were determined by GC-FID using CP-TAP CB column with 25m in length, 0.10 μm of film thickness, and 0.25m of inner diameter. The oven temperature was ramped from 423K to 493K with the rate of 278K/min. The split ratio was 20:1. The injector and detector temperature was set at 523K and 653K respectively.

2.2.3 Kinetic study
The esterification reaction of sorbitol and azelaic acid is shown in Eq 2.

$$C_9H_{16}O_4 \quad + \quad C_6H_{14}O_6 \leftrightarrow \quad C_{15}H_{28}O_9 \quad + \quad H_2O$$
$$Azelaic\ acid + Sorbitol \leftrightarrow Sorbitol\ Azeleate + Water \qquad (2)$$

The reaction rate was determined by the differentiating the azelaic acid concentration-time profile. The non-linear regression program (Polymath Profession 6.0) was used to find the best fitted rate law models. The reaction mechanism was elucidated using different types of kinetic models (Pseudohomogeneous (PH) model, Eley Rideal (ER) model and Langmuir Hinshelwood Hougen Watson (LHHW) model) as shown in Eq. 3, 4 and 5 respectively.

$$r_A = k_f(C_{AA}C_{SL} - \frac{C_{SA}C_W}{K_{eq}}) \qquad (3)$$

$$r_A = \frac{k_f(C_{AA}C_{SL} - \frac{C_{SA}C_W}{K_{eq}})}{1 + K_{AA}C_{AA} + K_WC_W} \qquad (4)$$

$$r_A = \frac{k_f(C_{AA}C_{SL} - \frac{C_{SA}C_W}{K_{eq}})}{(1 + K_{AA}C_{AA} + K_{SL}C_{SL} + K_{SA}C_{SA} + K_WC_W)^2} \qquad (5)$$

Where k_f is the forward rate constant, K_{eq} is the equilibrium constant, C is the concentration, K_i is the adsorption constant for species i, the subscript of AA, SL, SA and W are azelaic acid, sorbitol, sorbitol azeleate and water respectively.

The kinetic parameters of the models were estimated at various temperature using non-linear regression techniques based on Lavernberg Marquardt algorithm in the non-linear regression program. The model was evaluated based on squared of the calculated and experimental rate of reaction ($min\ \varphi$) and mean relative error percentage between calculated and experimental mole fraction (MRE) as shown in Eq. 6 and 7 respectively.

$$\min \varphi = \sum_{all\ data\ samples}(r_{calc} - r_{exp})^2 \qquad (6)$$

$$MRE = \frac{\sum_{all\ data\ samples}\frac{|x_{exp}-x_{calc}|}{x_{exp}}}{n_{sample}} \times 100 \qquad (7)$$

The activation energy (Ea) and pre-exponential (A) factor was obtained from Arrhenius equation as shown in Eq. 8.

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (8)$$

The Gibbs free energy, enthalpy (ΔH) and entropy (ΔS) were determined using Eq. 9-11.

$$\Delta G° = -RT\ln K_{eq} \quad (9)$$
$$\Delta G° = \Delta H - T\Delta S° \quad (10)$$
$$\ln K_{eq} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (11)$$

The standard deviation as shown in Eq. (12) can be used as a measure of the quality of fit.

$$\sigma(K) = \sqrt{\sum_{i=1}^{N} \frac{\left(K_i^{exptl} - K_i^{calc}\right)^2}{n-m}} \quad (12)$$

Where n is the number of experimental points and m is the number adjusted parameters.

3   LITERATURE REVIEW

3.1 Overview
Esterification is a well-studied reaction that is of both scientific and industrial importance. This reaction produces esters that can be used to produce wide range of products especially in polyester for polyurethane productions. Conventional production of polyesters is via esterification of acids and petrol-based polyols. However, petrochemical feedstocks that are used to produce petro-based polyols are decreasing in the face of growing demand from developing countries; hence a sudden spike in energy price. In lieu of this, bio-based polyol from renewable sources is worth exploring as a reactant for polyester synthesis. In this section, previous studies related to the polyol polyester synthesis process, catalysts for the esterification process and catalyst preparation techniques for the selected catalyst are presented.

3.2 Polyols and Polyesters
Polyols are polyhydroxyl compounds (with molecular weight between 200 and 12000 and OH functionality of two or more) that are derived conventionally from two classes of products: polyethers and polyesters. However, they can also be derived from acrylic [21]. Polyols can exist as either solid or liquid, but they are commonly found as liquid at room temperature.

Polyesters are among the most important categories of polymers in use today. Simplistically, polyesters are synthesized by the polyesterification of a glycol with a dicarboxylic acid. The dimer acid based polymers are reported to be useful in both rigid and flexible foam formulations. They are commonly used in surface coating applications, they are also useful in a whole lot of other applications, for instance hot melts adhesives, lubricants and films applications. The major applications for the dimer acid based polyester films so far is in food packaging materials and shrink labels [21]. For polyurethane flexible foams where acid value must be low, an excess of diol has to be used in order to ensure minimum carboxylic terminations in the polyester.

Polyesterification is highly influenced by the presence of water which is in equilibrium with the reactants and the polymer. The removal of water in the later part of the reaction process is vital for the development of the required molecular weight (MW). During polyesterification, resins normally lose between 5 and 12% of initial weight as condensate, depending on the final MW [22].

The presence of water can cause some degree of degradation in polyesters (by the cleavage of ester bonds) due to the equilibrium of the esterification reaction. However, aromatic polyesters possesses strong hydrophobic properties which can repel water from the proximity of the ester bonds. Hence, only aliphatic polyesters will degrade over observable time scale. Therefore, this is the one of the many reasons why aliphatic polyesters are considered as one of the most used biodegradable polymers in use today [23].

3.3 Polyester Polyol Synthesis Process

The easiest way to synthesize a polyester is to heat a hydroxycarboxylic acid, or a mixture of a glycol with a dicarboxylic acid, to a temperatures between 150 ºC and 250ºC, where both polyester and water are produced through the polyesterification reaction. The esterification reaction is the elementary step in polyesterification. It is an equilibrium process and hence the efficiency of continuous elimination of water from the reaction system is highly important to the development and increase in molecular weight of the polyester. Depending on the desired degree of polymerisation different measures have to be taken. When the desired degree of polymerization is in the range 5-20 (common for polymeric plasticisers or for polyurethane precursors), the flow of a dry inert gas such as nitrogen can be applied to remove the water from the reactor. However, to obtain higher degrees of polymerization, or in cases that the removal of water is more difficult for some reason, the reaction can be carried out with a small amount of a boiling inert organic solvent (e.g. DMF (dimethylformamide) , DMA (N,N-dimethylacetamide) , xylene and DMSO. Combinations of solvents may also be employed.) with azeotropic entrainment of the produced water. To obtain high conversion of polymerization, similar numbers of reactive groups should be present at all stages of the reaction. In the reaction between dicarboxylic acids and glycols the latter are often relatively volatile and some quantity may be lost by distillation of the glycol that can be carried in the gaseous stream out of the reactor [24].

Transesterification reaction also takes place during the process, and this contributes to the high molecular weight distribution in the final polyester polyol. In the case of the formation of polyester when the reaction consists of two or more glycols, they will be added to the polymer chain in a statistical distribution. Nonetheless, careful monitoring of the ratio of ingredients should be done to ensure that the final product contains a suitable hydroxyl and not acidic end groups [23].

In order to have terminal hydroxyl groups, an excess of glycol is should be used. The reaction can take place in an uncatalysed reaction condition (self-catalyzed by the acidic carboxyl groups), however, the best performances (low reaction time, low final acidity) are obtained in the presence of specific catalysts [25].

Stirred batch process is commonly used to synthesize polyester polyols. The raw materials are heated up in an inert atmosphere. Reaction temperature range is of 150-220ºC. Temperature is vital in the production of these polyester polyols. Reaction happens faster at high temperatures that makes the process shorter, apart from leading to higher MW in the products. In the case of low temperatures 120-140ºC, the reaction is very slow (changing the acid number is negligible) [26].

3.4 Reactants for the Bio-Based Polyester Polyol Synthesis

3.4.1 Diols and Polyols
The bio-based polyol used for the production of polyol polyesters includes glycerol, sorbitol, xylitol, maltitol and mannitol. Among the bio-based polyols, esterification of glycerol is the most commonly studied due to its abundance attributed to the biodiesel production. Glycerol esterification with diacid such as azelaic acid, glutaric acid and succinic acid to synthesize hyperbranched polyester has been studied in [27] to produce unique properties of polymer as compared to linear polymer such as the unique three-dimensional architecture. According to [28], esterification of sorbitol with sebacic acid can produce poly(sorbitol sebacate) that has high biodegradability due to the formation of hydrolyzable esters in polycondensation polymerizations. Therefore, it is worthy to investigate the potential of using sorbitol to produce biodegradable polyester which can subsequently be used to produce environmental friendly biodegradable polyurethane.
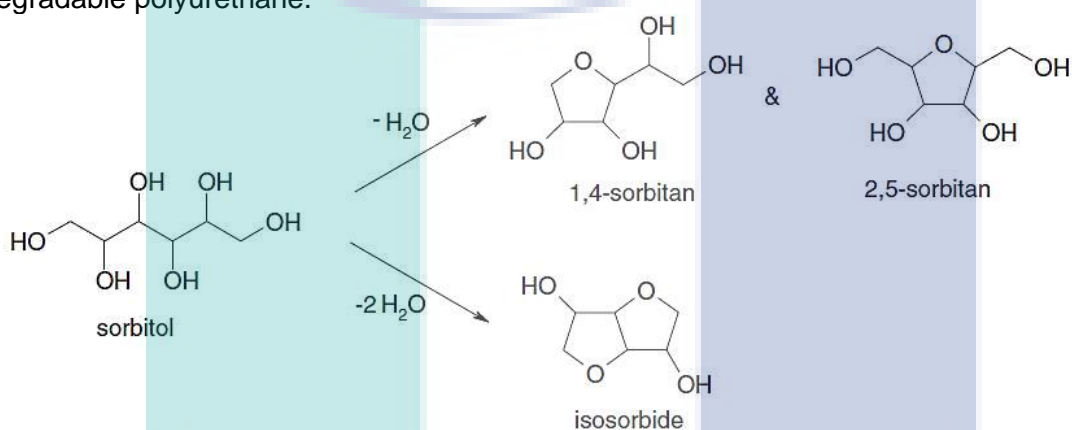
Figure 3-1: Anhydrization of sorbitol

Sorbitol is a molecule (a hexitol) that contains six hydroxyl groups which can be esterified with carboxylic acids. It is derived from glucose is thus a functional monomer based on natural resources. However, as shown in Figure 3-1, this molecule dehydrates partially or in other words undergoes anhydrization by forming internal ethers at moderate temperature, subsequently forming the main products the hexitans (mainly 1,4-sorbitan and minor amounts of 2,5-sorbitan), which contain four hydroxyl groups, and hexides (isosorbide), which contain two hydroxyl groups [1]. The isosorbide (diol) is thermally stable, of low cost and available in large quantities and may prove a valuable monomeric reagent for the synthesis of green polymers such as polyesters and polyurethane [29]. Sadler et al. [30] has esterified isosorbide with ethylene glycol to synthesize bio-based unsaturated polyester that can be used as thermosetting resins. High glass transition as well as improved mechanical properties of the polymer produced are observed due to rigid structure and chirality of the isosorbide [30].

3.4.2 Diacids/ Dicarboxylic Acids
Dicarboxylic acids are organic compounds that contain two functional groups of COOH. General formula for aliphatic dicarboxylic acids is HOOC-(CH2) n-COOH. Dicarboxylic acids and monocarboxylic acids have similar properties and chemical. However, second ionization of the carboxyl group in dicarboxylic acids is much more difficult than the ionization of the first carboxyl group. This is due to the reason that more energy is required to separate a positive hydrogen

ion from the anion than in the neutral molecule. For short-chain dicarboxylic acids, fatty acids can include those that are of major importance in the general metabolism and until n = 3 cannot be treated as lipids since their water solubility is very good. The simplest of these is oxalic acid, whose IUPAC name is ethanedioic acid (n = 0), n=1 is malonic acid (acid propanedioic), succinic (butanedioic acid) contains the n=2, pentanedioic acid also now as glutaric (n=3) acids. Dicarboxylic fatty acids have "n" value from 4 to 21. Adipic acid, with n=4 (hexanedioic acid) is a product of oxidative rancidity (lipid peroxidation). Dicarboxylic acids are also commonly used in surface preparation of organic acids for pharmaceutical and food industries. Furthermore, they are useful materials for the preparation of aromatic polyamides, adhesives, lubricants [25].

Aliphatic fatty acid dicarboxylic acids that are commonly used in the synthesis of polyesters are glutaric acid (n=3), adipic acid (n=4), azelaic acid (n=7), sebacic acid (n=8) as shown in Table . Although azelaic acid has been used in the study of hyperbranched polyester through the esterification with glycerol, the use of azelaic acid in esterification with sorbitol is still nonexistence. Azelaic acid belongs to a family of a naturally occurring saturated dicarboxylic fatty acid [5]. It can be derived from oleic acid by using ozonolysis method [31], or through new environmentally friendly oxidative scission of oleic acid [32]. Azelaic acid is industrially used as component in a series of applications such as biodegradable polyesters, polyamides, pharmaceuticals, plasticizers, lubricants, or hydraulic fluids. It has excellent solubility in organic solvents and water compared to other even chain dicarboxylic acids, which is advantageous in formulation of high solids or solvent free systems. The polyester made from azelaic acid has high-dimensional stability [6]. Hence, the use of azelaic acid in sorbitol esterification to produce polyester polyol is worth exploring.

Table 1: Aliphatic dicarboxylic acids used for polyester polyol synthesis

Dicarboxylic acid	Formula	MW	Acid number, mgKOH/g
Adipic acid	HOOC(CH2)4COOH	146.14	767.78
Glutaric acid	HOOC(CH2)3COOH	132.12	849.2
Succinic acid	HOOC(CH2)2COOH	118.09	950.1
Sebacic acid	HOOC(CH2)8COOH	202.0	555.4
Azelaic acid	HOOC(CH2)7COOH	186.0	603.2

3.5 Heterogeneous Catalysts Used In Esterification
The common types of catalyst used in esterification process are acidic homogeneous and heterogeneous catalyst. Acidic catalysts are more suitable in the esterification whereas basic catalysts are more suitable for transesterification process. Basic catalysts such as alkaline hydroxides and alkaline metal oxides are not favourable in the synthesis of fatty acid esters due to the high sensitivity of the catalysts to water and free fatty acids and formation of soap [1].

Sorbitol based esters can be produced by direct [33], base- [34] or acid-catalyzed [2] reaction of sorbitol with fatty acids at elevated temperature, or by transesterification of sorbitol with triglycerides or fatty acid methyl esters catalysed by basic compounds. The use of a nitrogen atmosphere or vacuum is required to remove the water and avoid excessive oxidation of the reagents. Table 2 shows the effect of using acidic, basic, the combination of acidic and basic catalysts, as well as the condition where no catalyst is used, in the esterification reaction between sorbitol and fatty acids. The anhydrization degree of sorbitol increases in the presence of an acid, and therefore acid catalysts tend to produce mixtures with a high proportion of esters of sorbides, while alkaline catalysts lead mainly to esters of sorbitans. A disadvantage of the

base-catalyzed direct reaction is that the product is usually highly colored [1]. Therefore, treatment with a bleaching agent such as hydrogen peroxide and adsorbents is required to obtain acceptable color values. Two-step processes have been established where the acid-catalyzed anhydrization of sorbitol takes place before the esterification or transesterification reaction [34]. It has also been reported that lower color values are obtained when reducing acids, like phosphorous and hypophosphorous acids, are used as catalysts [34-35), or by addition of reducing agents like sodium borohydride [34].To produce esters of sorbitans and sorbides of approximate equal amounts, the use of catalyst should be excluded [33]. Seeing that esterification of sorbitol with diacid will produce several products due to sorbitol anhydrization, superacidic catalyst can be used to reduce the production of by-products by increasing the dehydration or anhydrization of sorbitol to the maximum extent to encourage the production of the diol, isosorbide and hence selectively producing more isosorbide ester. The isosorbide produced possesses rigid molecular structure which will improve the mechanical properties of the polymer produced through the esterification of isosorbide with fatty acid.

Regardless of whether an acid or a base catalyst is used, homogeneous catalysts present certain inherent disadvantages. The replacement of homogeneous catalysts with heterogeneous solid catalysts is on the increase [36].

Transesterification occurs as the esterification reactions proceeds to produce polyester polyol. Thus, it would be an advantage to use catalyst that could catalyse both reactions. Amphoteric catalyst possesses both acidic and basic properties, which can cater to both esterification and transesterification. However, acidity of amphoteric catalyst is lower than acidic acid, this would lead to incomplete anhydrization of sorbitol. Both sorbitan and isosorbide would be present, causing the formation of polyester containing both sorbitan and isosorbide. In addition, unanhydrized sorbitol itself would also involve in the polyester formation. A complex sorbitol based hyperbranched polyester would be synthesized, due to sorbitol and sorbitan incorporated into the backbone of the polyester. Branched polyester polyol contributes to flexible polyurethane properties such as low temperature flexibility, high tensile strength, high tear strength, high elongation, abrasion resistance, solvent resistance and the like, to ensure that the products made therefrom can withstand the environments in which they are used [37]. Study of amphoteric catalyst tin (II) oxide in esterification between sorbitol and azelaic is non-existent, thus it is worth exploring.

Table 1: Catalysts for the sorbitol ester synthesis

Fatty acid	Fatty acid/ sorbitol ratio	Catalyst	Reaction temperature (ºC)	Fatty acid conversion	Ester composition	Reference
Coconut oil fatty acids	1	-	235	~100	70% sorbitan monoester	[33]
Coconut oil fatty acids	1	H_3PO_4 (pH=2.0)	225	~100	Mostly sorbide monoester	[33]
Oleic acid	1	KOH	200-220		Mostly sorbitan diester	[34]
Oleic acid	1.45	H_3PO_4+ NaOH	245	~100	Mostly sorbitan diester	[35]
Lauric acid	6	Sulfonic acid functionaliz-ed MCM-41	110	33	95% isosorbide diester	[38]
Lauric acid	1	p-toluenesulfo-nic acid	160		Isorbide monolaurate, sorbitan monolaurate	[2]

4 FINDINGS

4.1 Effect of Important Operating Parameters

4.1.1 Effect of Temperature

The effect of temperature was investigated by carrying out the esterification reaction in the temperature range between 403 to 433K, $M_{SL:AA}$ of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm. The conversion of azelaic acid increased with temperature as depicted by the conversion-time profile in Figure 1. It can be observed from Figure 2 that the initial reaction rate increased more than 35% with the increment of 10°C in the reaction temperature. The temperature rise causes more frequent collision of the reactant which resulting more successful collision to break the bonds to form the sorbitol azeleate [9]. The reaction temperature of 433K was used for the subsequent studies.

Figure 1: Azelaic acid conversion-time profile for the reaction at various reaction temperature with $M_{SL:AA}$ of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm.

Figure 2: Effect of reaction temperature on initial rate of reaction.

4.1.2 Effect of Molar ratio
The effect of molar ratio was studied to determine the best molar ratio for the esterification of sorbitol with azelaic acid with other parameters remained constant. The usage of excess alcohol

can shift the reaction equilibrium towards ester formation and shorten the time required to achieve equilibrium. The determination of best molar ratio is to prevent the increasing cost in recovery process when too much alcohol is used [10-12]. Figures 3 and 4 show that the conversion and initial reaction rate were increased with the increase of $M_{SL:AA}$ from 1:1 to 4:1. The similar finding was found by Gulati et al. [20] in their studies on the esterification of sorbitol with stearic acid. Further increasing the molar ratio, the negative effect towards the conversion because the excess sorbitol has blocked the active sites on the catalyst surface and subsequently prevent it from nucleophilic attack [13]. Despite the identical conversion at 6th hour, the $M_{SL:AA}$ of 4:1 was chosen and used for subsequent studies due to its superior initial rate of reaction.
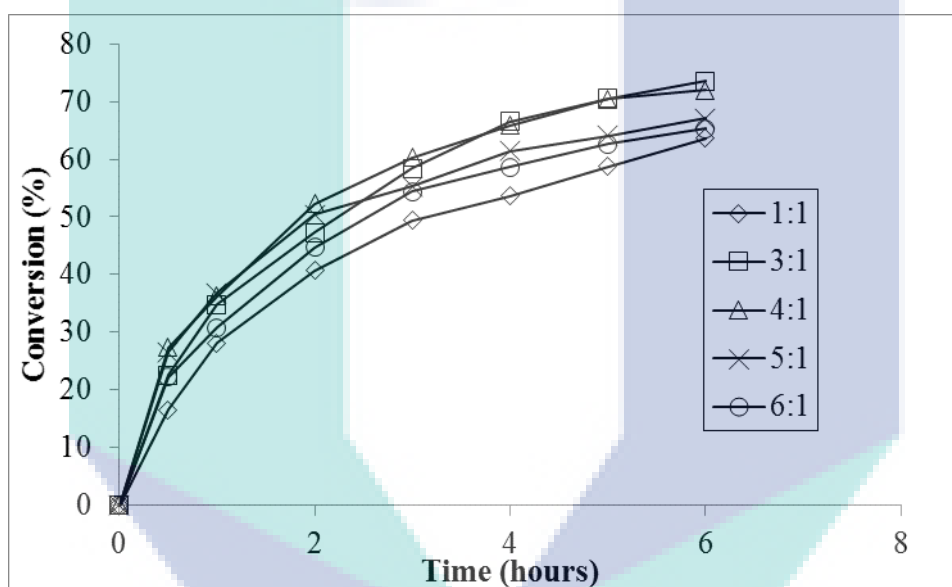
Figure 3: Azelaic acid conversion-time profile for the reaction at different $M_{SL:AA}$ with stirring rate of 600rpm, reaction temperature of 433K and catalyst loading of 4wt%.
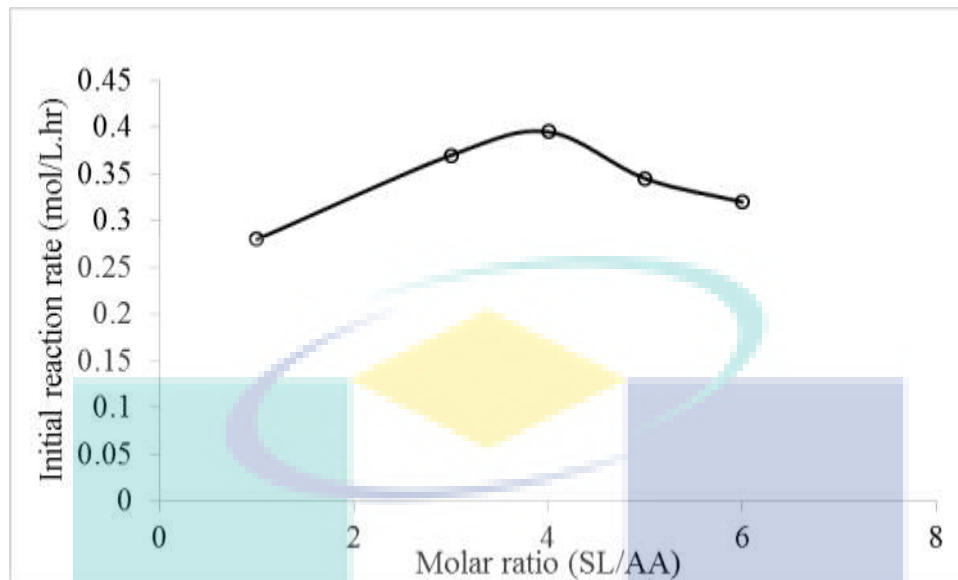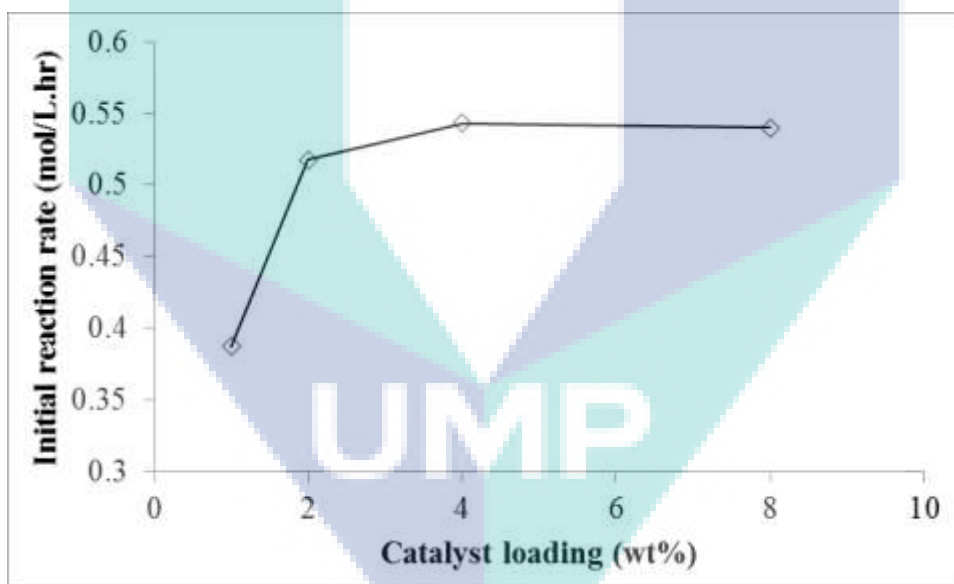
Figure 4: Initial reaction rate for the reaction at different $M_{SL:AA}$ at stirring rate of 600rpm with reaction temperature of 433K and catalyst loading of 4wt%.

4.1.3 Effect of Catalyst Loading

The catalyst loading was varied from 1wt% to 8wt% to study its effect towards esterification reaction. The other parameters were kept constant. Figure 5 shows that the increase of catalyst loading has led to a rise in conversion because of the increase of catalyst sites that promoting reaction [14-16]. No significant change in conversion was observed when the catalyst loading was changed from 4wt% to 8wt%. The initial reaction rate for the reaction with the catalyst loadings of 4 wt% and 8 wt% were identical as shown in Figure 6. This occurrence was ascribed to the sufficient active sites provided by the 4 wt% of catalyst in the reaction mixture. The catalyst loading of 4wt% was the best condition since it provided sufficient active site to accommodate the reaction of the reactants molecules [17,18].
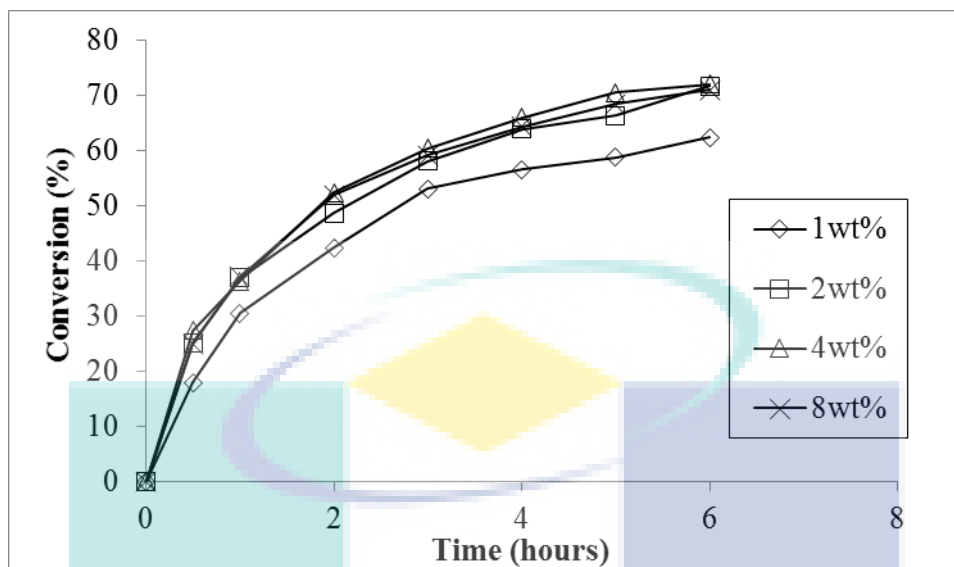
Figure 5: Azelaic acid conversion-time profile for the reaction at different catalyst loading of tin (II) oxide with stirring rate of 600rpm, reaction temperature of 433K and $M_{SL:AA}$ of 4:1.

Figure 6: Initial reaction rate for the reaction at different catalyst loading with stirring rate of 600rpm, reaction temperature of 433K and $M_{SL:AA}$ of 4:1.

4.2 Equilibrium Study

The esterification process is limited by equilibrium conversion. The equilibrium constant, K_{eq} was calculated experimentally according the Eq. 13.

$$K_{eq} = \frac{C_{SA}C_W}{C_{AA}C_{SL}} \quad (13)$$

Figure 7 shows the concentration profile for the equilibrium study carried out at the reaction temperature of 403, 413, 423 and 433K, molar ratio ($M_{SL:AA}$) of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm as shown in Figure 7. The equilibrium conversion, X_e and the corresponding K_{eq} are shown in Table 3. The K_{eq} and X_e increase with implying the esterification of sorbitol with azelaic acid catalysed by tin (II) oxide was endothermic. The current findings are in agreement with studied of Giacometti et al. [2] on the esterification of sorbitol with lauric acid catalysed by p-toluenesulfonic acid.
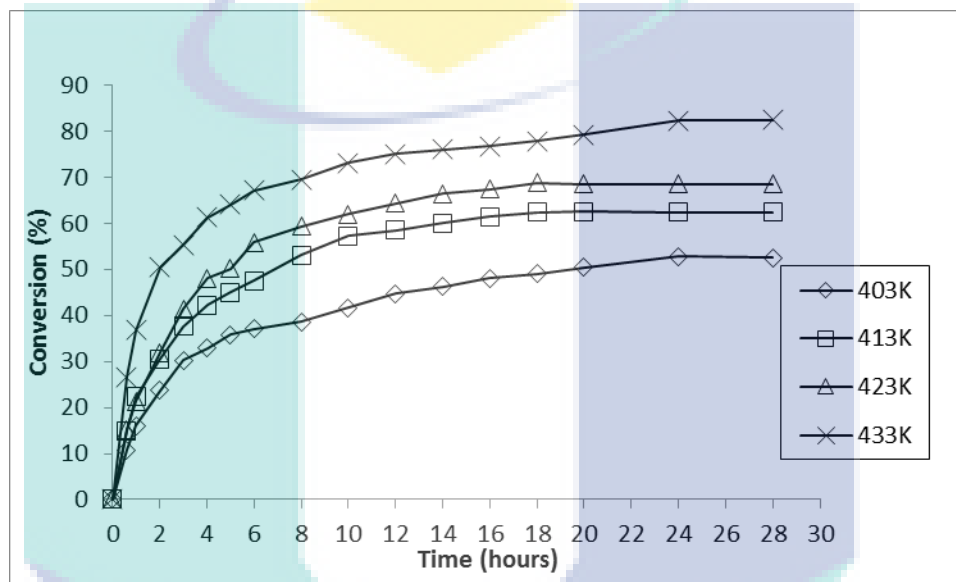
Figure 7: Azelaic acid conversion-time profile for equilibrium study at different reaction temperature with $M_{SL:AA}$ of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm

Table 3: Equilibrium constant and equilibrium conversion at different temperature

Temperature (K)	K_{eq}	X_e (%)
403	52.4804	0.1295
413	62.4519	0.2374
423	68.5449	0.3462
433	82.4012	0.9239

Based on the Van't Hoff plot in Figure 10, the ΔH was 90706 J/mol while ΔS was 208 J/mol.K. Gibbs free energy (ΔG) was 840 J/mol at 433K. The positive value of ΔS reflects that the amount of disorder or randomness in the system is increased as a consequence of the reaction.
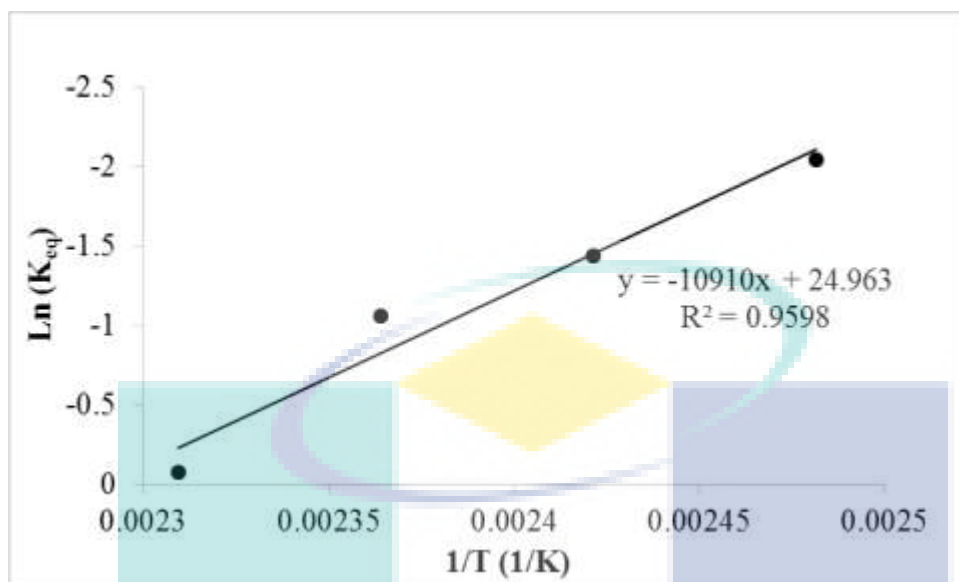
Figure 10: Van't Hoff plot for the synthesis of sorbitol azeleate at different reaction temperature

4.3 Kinetic Modelling

Table 4 shows the kinetic parameter for each kinetic model. The fitting of kinetic data to ER and LHHW models has shown the coefficient of determination, R^2 of closest to one and lowest values of min φ and MRE. ER model was preferred due to its simple mathematical form the superior adsorption equilibrium constant of water indicated that water was more prone to adsorption on the catalyst surface than the azelaic acid attributing to the higher polarity of the water. It showed the inhibiting effect of water to esterification reaction [20-23].

Table 4: Kinetic parameters of the models to fit experimental data

Model	Temp. (K)	k_f (mol/L.hr)	$\sigma(k_f)$ (mol/L.hr)	MRE (%)	Min φ	K_W (L/mol)	K_{AA} (L/mol)	K_{SL} (L/mol)	K_{SA} (L/mol)	R^2
PH	403	0.024	0.003	8.13						0.90
	413	0.035	0.002	5.78	0.010					0.98
	423	0.044	0.003	4.66						0.98
	433	0.065	0.008	9.17						0.92
ER	403	0.250	0.028	7.47						0.93
	413	0.374	0.024	5.20	0.009	16.020	10.618			0.98
	423	0.467	0.027	4.03						0.98
	433	0.695	0.091	8.26						0.92
LHHW	403	0.527	0.059	7.43						0.93
	413	0.787	0.052	5.18	0.009	2.913	1.485	0.560	0.397	0.98
	423	0.982	0.056	3.99						0.98
	433	1.463	0.192	8.15						0.92

Figure 8: Arrhenius plot for the synthesis of sorbitol azeleate at different reaction temperature

The activation energy was determined using Arrhenius plot as given in Figure 8 and the corresponding Arrhenius equation is shown in Eq. 14. The activation energy for the present study (47.62 kJ/mol) was lower than the activation energy (50.8 kJ/mol) of the polyesterification of sorbitol with lauric acid catalysed by p-TSA in the study of Giacometti et al. [2]. This reveals that the sorbitol azeleate is easier to be formed in the esterification of sorbitol with azelaic acid catalysed by tin (II) oxide.

Figure 9: Parity plot of Eley Rideal model of ±10% error.

The parity plot in Figure 9 shows that the errors between experimental data and predicted results were within ±10%, signifying that the esterification of sorbitol and azelaic acid catalysed by tin (II) oxide occurred based on the ER mechanism. The azelaic acid first adsorbed onto the active sites in tin (II) oxide before reacting with

sorbitol in the bulk fluid. The adsorbed azelaic acid accepted a protons from tin (II) oxide. Sorbitol molecule attacked the protonated carbonyl group to give a tetrahedral intermediate and water. A proton was lost at one oxygen atom and it was gained by another oxygen atom to form another intermediate which further loses a molecule of water that gives a protonated ester. A proton was transferred to a water molecule to give the sorbitol azeleate ester.

$$k \left(\frac{mol}{L}.hr\right) = 376247\ exp\frac{-47618.44}{RT} \tag{14}$$

5   CONCLUSION

The kinetic behaviour of the esterification of azelaic acid and sorbitol catalysed by tin (II) oxide has been studied. The best operating conditions were 433K, MAA:S of 4:1 and 2wt% of catalyst loading. The kinetic data were correlated with different models and ER model was the best model to describe the esterification reaction. It indicated that the reaction was controlled by the surface reaction. The activation energy was found to be 47.62 kJ/mol.

ACHIEVEMENT

i)   Name of articles/ manuscripts/ books published

Kamaruzaman, M.R, Chin, S. Y. and Pui, E. C. L. (2017). Synthesis of Bio-based Polyester Polyol for Polyurethane Production: Esterification of Sorbitol with Azelaic Acid Catalysed by Tin (II) Oxide- A Kinetic Modelling Study. Chinese Journal of Chemical Engineering. Under Review. (As Attachment 1)

Kamaruzaman, M.R, Hong, C. S., Chua@Yeo G. K. and Chin S. Y. (2017). The separation and characterisation of azaleic acid, sorbitol and its anhydrides using gas and liquid chromatographic techniques. *Journal of Chromatography A. Under Preparation Process.* (As Attachment 2)

ii)   Human Capital Development

No. of PhD students	1
PhD Student's Details	
Name	Muhammad Ridzuan Kamaruzaman
Student No.	PKC16021
Status	On-going
No. of undergraduate students	3
Name	Elaine Pui Chiew Ling
Student No.	KA12107
Status	Graduated
Name	Jasmin A/P Tramarajh
Student No.	KA12006
Status	Graduated
Name	Nurwadiah Bt. Azizan
Student No.	KE13011
Status	On-going

iii)   Awards/ Others
Gold Medal. Bio-based Polyester Production through the Esterification of Sorbitol and Azelaic Acid over Tin(II) Oxide Catalyst. Creation, Innovation, Technology & Research Exposition (CITREX-2015), UMP

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Manuscript Details

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Abstract

A sustainable and renewable bio-based polyester polyol for the polyurethane production was synthesised through the esterification of azelaic acid and sorbitol catalysed by tin (II) oxide. The chemical equilibrium, reaction kinetics and parametric studies were carried out. Different reaction parameters such as temperature (403K to 433K), molar ratio of sorbitol to azelaic acid (1:1 to 6:1) and catalyst loading (1wt% to 8wt%) were studied in order to determine the best reaction conditions. The polyester polyol synthesised was tested for its fatty acid content through titration. The best operating condition found was at reaction temperature 433K, sorbitol to azelaic acid molar ratio of 4:1 and 2wt% of catalyst loading, yielding 72% of conversion. The presence of sorbitan and isosorbide have been affirmed by the analysis through gas chromatography with flame injection detector, indirectly proving the formation of sorbitol based branched polyester with its backbone incorporated with sorbitan and isosorbide. The simple mathematical form of Eley Rideal (ER) model gives good agreement with the experimental data. The activation energy was found to be 47.62 KJ/mol.

Keywords	kinetic modelling; esterification; azelaic acid; sorbitol; polyurethane
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Order of Authors	Muhammad ridzuan kamaruzaman, chin sim yee, pui Elaine Chiew Ling
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PM Dr. Chin Sim Yee

University Malaysia Pahang,

Lebuhraya Tun Razak,

26300 Kuantan Pahang, Malaysia

chin@ump.edu.my

Prof. Dr. Weiyang FEI

Editor-in-Chief

Chinese Journal of Chemical Engineering

Dear Prof Dr Weiyang FEI,

I am pleased to submit an original research article entitled "Synthesis of Bio-based Polyester Polyol for Polyurethane Production: Esterification of Sorbitol with Azelaic Acid Catalysed by Tin (II) Oxide- A Kinetic Modelling Study" by M.R. Kamaruzaman, Chin Sim Yee and Elaine Pui Chiew Ling for consideration for publication in the *Chinese Journal of Chemical Engineering*.

The novelty of this paper is new kinetic knowledge on esterification of azelaic acid with sorbitol which a new potential of bio-based polyester for production of polyurethane. There is no open literature on esterifation of this reaction based on our knowledge.

We believe that this manuscript is appropriate for publication in your prestige journal because of its potential of new process and new catalytic reaction. This manuscript has not been published and is not under consideration for publication elsewhere. We have no conflicts of interest to disclose.

Thank you for your consideration.

Sincerely,

Chin Sim Yee, PhD

Associate Professor,

Faculty of Chemical and Natural Resources Engineering,

University Malaysia Pahang.

Synthesis of Bio-based Polyester Polyol for Polyurethane Production: Esterification of Sorbitol with Azelaic Acid Catalysed by Tin (II) Oxide- A Kinetic Modelling Study

M.R. Kamaruzaman, *S.Y. Chin, Elaine Pui Chiew Ling

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, LebuhrayaTunRazak, 26300 Kuantan, Pahang, Malaysia.

duanz88@yahoo.com.my, chin@ump.edu.my

Abstract

A sustainable and renewable bio-based polyester polyol for the polyurethane production was synthesised through the esterification of azelaic acid and sorbitol catalysed by tin (II) oxide. The chemical equilibrium, reaction kinetics and parametric studies were carried out. Different reaction parameters such as temperature (403K to 433K), molar ratio of sorbitol to azelaic acid (1:1 to 6:1) and catalyst loading (1wt% to 8wt%) were studied in order to determine the best reaction conditions. The polyester polyol synthesised was tested for its fatty acid content through titration. The best operating condition found was at reaction temperature 433K, sorbitol to azelaic acid molar ratio of 4:1 and 2wt% of catalyst loading, yielding 72% of conversion. The presence of sorbitan and isosorbide have been affirmed by the analysis through gas chromatography with flame injection detector, indirectly proving the formation of sorbitol based branched polyester with its backbone incorporated with sorbitan and isosorbide. The simple mathematical form of Eley Rideal (ER) model gives good agreement with the experimental data. The activation energy was found to be 47.62 KJ/mol.

Keywords

Kinetic modelling, esterification, azelaic acid, sorbitol, polyurethane

1.0 Introduction

Polyurethanes (PUs) are one of the most versatile groups of polymers suitable for the application in the area of foams, elastomers, thermoplastics, adhesives, coatings, sealants and fibers. Conventionally, PUs is produced by reacting petro-based polyester polyol with diisocyanate. Uncertainty in terms of price and availability of petroleum, in addition to global political and institutional tendencies toward the principles of sustainable development, has prompted the continuing effort to identify bio-based PUs.

Sorbitol-based polyester is one of the potential polyester polyol for the production of bio-based PUs possessing comparable properties with the petro-based PUs. Sorbitol based polyesters can be produced by direct, acid or base-catalysed or acid-catalysed esterification reaction of sorbitol with fatty acids at elevated temperature. It can also be produced through the basic catalysed transesterification of sorbitol with triglycerides or fatty acid methyl esters. In recent years, most of the researches for the synthesis of sorbitol based polyester were carried out using the route of acid catalysed esterification since the base catalysed reaction attributes to the unwanted highly coloured products. Moreover, the anhydrization degree of sorbitol increases in the presence of an acid catalyst, and therefore producing the mixtures with a high proportion of esters of sorbides. The isosorbide ester produced possesses rigid molecular structure which improving the mechanical properties of the PUs [1]. Giacometti *et al*. [2] prepared the surfactant through the esterification of sorbitol with lauric acid using *p*-toluene sulfonic acid as a catalyst. Enzyme such as lipase has also been employed as a catalyst in the esterification of sorbitol anhydrides (sorbitol and isosorbide) with oleic acid and decanoic acid [3,4]. The sorbitol based polyesters were also prepared through the process with and without the pre-process of sorbitol dehydration prior to esterification reaction. A better conversion was reported for the esterification of lauric acid with the pre-dehydrated sorbitol. A kinetic model of reversible second order reaction was proposed for the esterification of lauric acid with the sorbitol anhydrides produced through the pre-dehydration sorbitol.

To the best of our knowledge, very limited information about the heterogeneously catalysed esterification of sorbitol with di-carboxylic acid can be found in the open literature. In the present study, parametric and kinetic studies of the esterification of sorbitol with azelaic acid were carried out. Azelaic acid is industrially used in the manufacturing of pharmaceutical products, plasticizers,

lubricants and hydraulic fluids. It belongs to a family of a naturally occurring saturated dicarboxylic fatty acid. It is a superior raw material in the formulation of high solids or solvent free systems ascribing to its excellent solubility in organic solvents and water [5]. The polyesters made from azelaic acid was reported to have high-dimensional stability [6]. In the present study, the polyesterification of azelaic acid with sorbitol is to produce bio based polyester as the potential source for PUs production.

2.0 Materials and Methods

2.1 Materials

Azelaic acid (90%), potassium hydroxide (KOH) pellets and potassium hydrogen phthalate (KHP) were purchased from Merck. Sorbitol solution (70%) and ethanol (99.7%) were obtained from R&M Chemicals. Tin (II) oxide (99%) was supplied by Alfa-Chemistry. All chemicals were used without further purifications.

2.2 Methods

2.2.1 Experimental procedure for the esterification reaction study

The esterification reaction of sorbitol and azelaic acid catalysed by tin (II) oxide was carried out in a three neck flask equipped with condenser, temperature controller and temperature probe. The sorbitol and azelaic acid were charged into two distinct flasks for heating to desired temperature. Subsequently, the sorbitol and azelaic acid were mixed and the catalyst was introduced. The samples were withdrawn every 30 minutes for the first hour and every 1 hour for the subsequent 6 hours. The important reaction parameters were varied during the reaction study. These parameters included molar ratio of sorbitol to azelaic acid ($M_{SL:AA}$) of 1:1 to 6:1, reaction temperature of 403 to 433K and catalyst loading of 1 to 8wt%.

The procedure for the equilibrium study was identical to esterification reaction study at different temperatures but the reaction time was prolonged until the conversion achieved equilibrium. The sample after 6 hours was taken in every two hours. The reaction was in equilibrium when the acid value was constant.

2.2.2 Analysis

The acid value (AV) of the sample was determined by titration using KOH with phenolphthalein as indicator. The KOH solution was standardised using KHP. AV was calculated using Eq. 1.
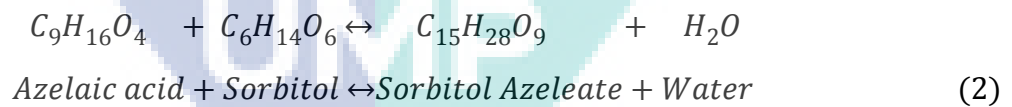
$$AV = (A \times N \times 56.1)/W \tag{1}$$

where A is amount of 0.1M of KOH consumed for sample in ml, N is KOH concentration in mol/L and W is sample weight in g.

The gas chromatography (GC) analysis was limited to certain component in the reaction mixture attributing to the commercially unavailability of the GC standard. The reaction products (sorbitan and isosorbide) were determined by GC-FID using CP-TAP CB column with 25m in length, 0.10 µm of film thickness, and 0.25m of inner diameter. The oven temperature was ramped from 423K to 493K with the rate of 278K/min. The split ratio was 20:1. The injector and detector temperature was set at 523K and 653K respectively.

2.2.3 Kinetic Study

The esterification reaction of sorbitol and azelaic acid is shown in Eq 2.

$$C_9H_{16}O_4 + C_6H_{14}O_6 \leftrightarrow C_{15}H_{28}O_9 + H_2O$$
$$Azelaic\ acid + Sorbitol \leftrightarrow Sorbitol\ Azeleate + Water \tag{2}$$

The reaction rate was determined by the differentiating the azelaic acid concentration-time profile. The non-linear regression program (Polymath Profession 6.0) was used to find the best fitted rate law models. The reaction mechanism was elucidated using different types of kinetic models (Pseudohomogeneous (PH) model, Eley Rideal (ER) model and Langmuir Hinshelwood Hougen Watson (LHHW) model) as shown in Eq. 3, 4 and 5 respectively.

$$r_A = k_f(C_{AA}C_{SL} - C_{SA}C_W/K_{eq}) \tag{3}$$

$$r_A = k_f(C_{AA}C_{SL} - C_{SA}C_W/K_{eq})/(1 + K_{AA}C_{AA} + K_W C_W) \tag{4}$$

$$r_A = k_f(C_{AA}C_{SL} - C_{SA}C_W/K_{eq})/(1 + K_{AA}C_{AA} + K_{SL}C_{SL} + K_{SA}C_{SA} + K_W C_W)^2 \tag{5}$$

where k_f is the forward rate constant, K_{eq} is the equilibrium constant, C is the concentration, K_i is the adsorption constant for species i, the subscript of *AA, SL, SA* and *W* are azelaic acid, sorbitol, sorbitol azeleate and water respectively.

The kinetic parameters of the models were estimated at various temperature using non-linear regression techniques based on Lavernberg Marquardt algorithm in the non-linear regression program. The model was evaluated based on squared of the calculated and experimental rate of reaction (*min φ*) and mean relative error percentage between calculated and experimental mole fraction (*MRE*) as shown in Eq. 6 and 7 respectively.

$$\min \varphi = \sum_{all\ data\ samples} (r_{calc} - r_{exp})^2 \tag{6}$$

$$MRE = \frac{\displaystyle\sum_{all\ data\ samples} \frac{|x_{exp} - x_{calc}|}{x_{exp}}}{n_{sample}} \times 100 \tag{7}$$

The activation energy (*Ea*) and pre-exponential (*A*) factor was obtained from Arrhenius equation as shown in Eq. 8.

$$\ln k = -E_a/RT + \ln A \tag{8}$$

The Gibbs free energy, enthalpy (ΔH) and entropy (ΔS) were determined using Eq. 9-11

$$\Delta G^\circ = -RT \ln K_{eq} \tag{9}$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \tag{10}$$

$$\ln K_{eq} = -\Delta H^\circ/RT + \Delta S^\circ/R \tag{11}$$

The standard deviation as shown in Eq. (12) can be used as a measure of the quality of fit.

$$\sigma(K) = \sqrt{\sum_{i=1}^{N} \frac{\left(K_i^{exptl} - K_i^{calc}\right)^2}{n - m}} \tag{12}$$

Where n is the number of experimental points and m is the number adjusted parameters.

3.0 Results and Discussion

3.1 Effect of important operating parameters

3.1.1 Effect of temperature

The effect of temperature was investigated by carrying out the esterification reaction in the temperature range between 403 to 433K, $M_{SL:AA}$ of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm. The conversion of azelaic acid increased with temperature as depicted by the conversion-time profile in Figure 1. It can be observed from Figure 2 that the initial reaction rate increased more than 35% with the increment of 10°C in the reaction temperature. The temperature rise causes more frequent collision of the reactant which resulting more successful collision to break the bonds to form the sorbitol azeleate [7]. The reaction temperature of 433K was used for the subsequent studies.
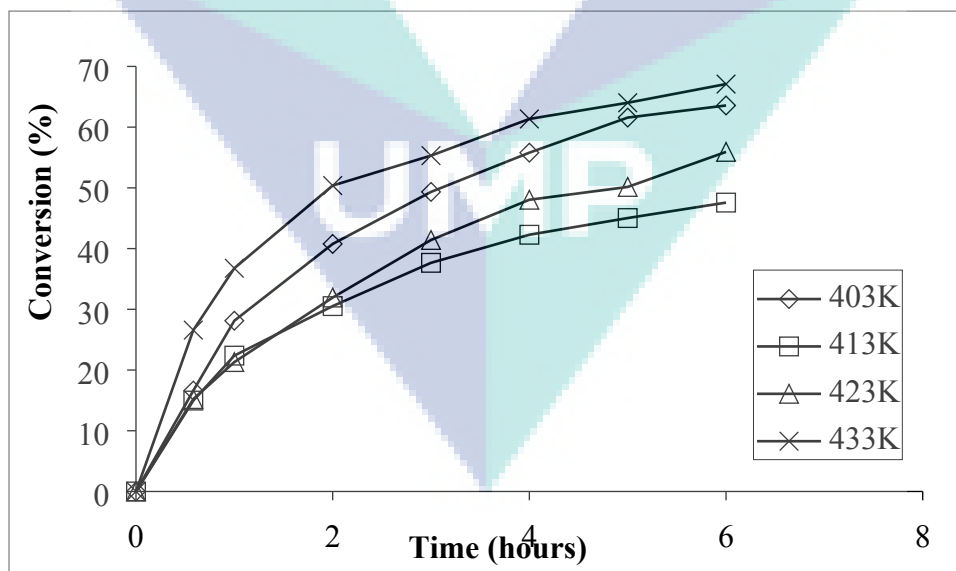
Figure 1: Azelaic acid conversion-time profile for the reaction at various reaction temperature with $M_{SL:AA}$ of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm.
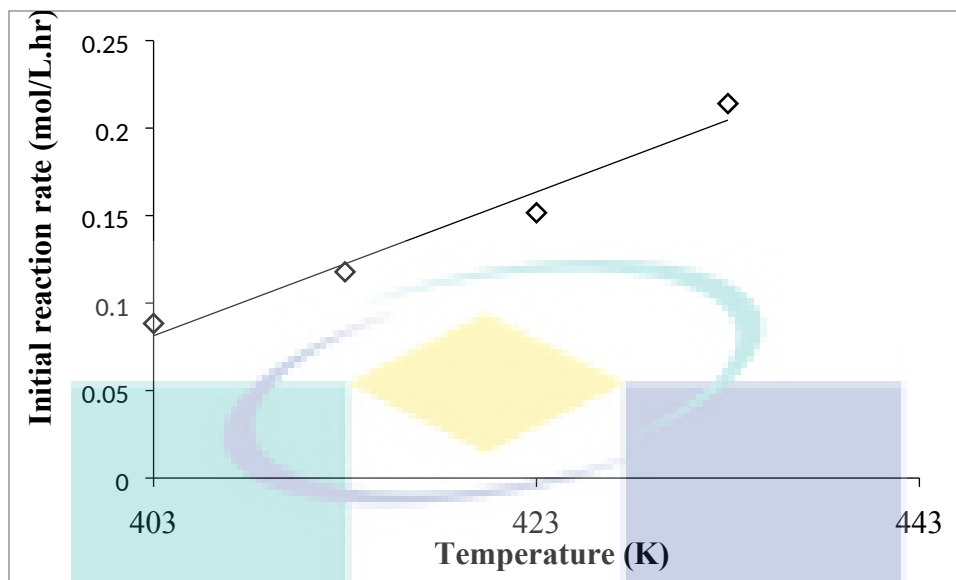
Figure 2: Effect of reaction temperature on initial rate of reaction

3.1.2 Effect of Molar ratio

The effect of molar ratio was studied to determine the best molar ratio for the esterification of sorbitol with azelaic acid with other parameters remained constant. The usage of excess alcohol can shift the reaction equilibrium towards ester formation and shorten the time required to achieve equilibrium. The determination of best molar ratio is to prevent the increasing cost in recovery process when too much alcohol is used [8-10]. Figures 3 and 4 show that the conversion and initial reaction rate were increased with the increase of $M_{SL:AA}$ from 1:1 to 4:1. The similar finding was found by Gulati *et al.* [11] in their studies on the esterification of sorbitol with stearic acid. Further increasing the molar ratio, the negative effect towards the conversion because the excess sorbitol has blocked the active sites on the catalyst surface and subsequently prevent it from nucleophilic attack [12] Despite the identical conversion at 6th hour, the $M_{SL:AA}$ of 4:1 was chosen and used for subsequent studies due to its superior initial rate of reaction.
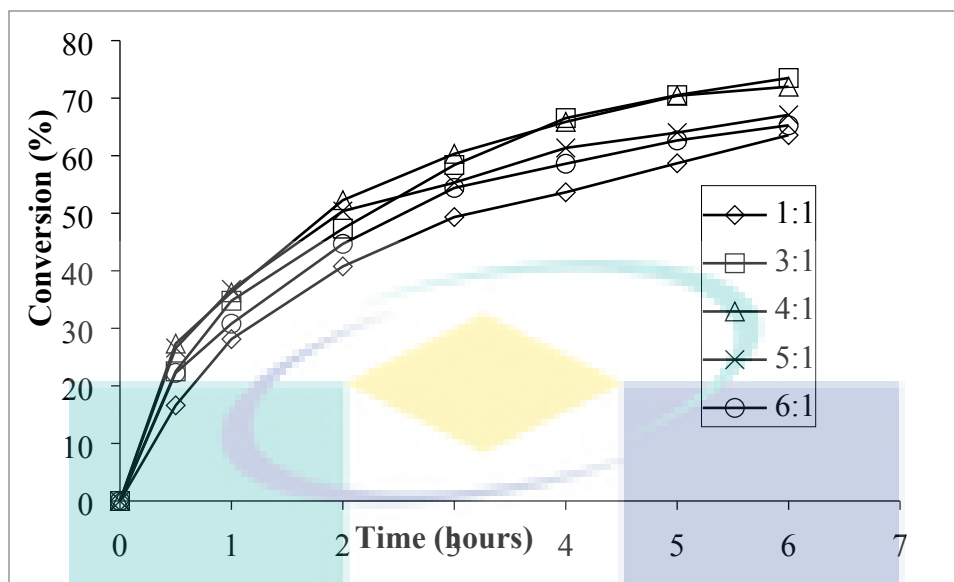
Figure 3: Azelaic acid conversion-time profile for the reaction at different $M_{SL:AA}$ with stirring rate of 600rpm, reaction temperature of 433K and catalyst loading of 4wt%
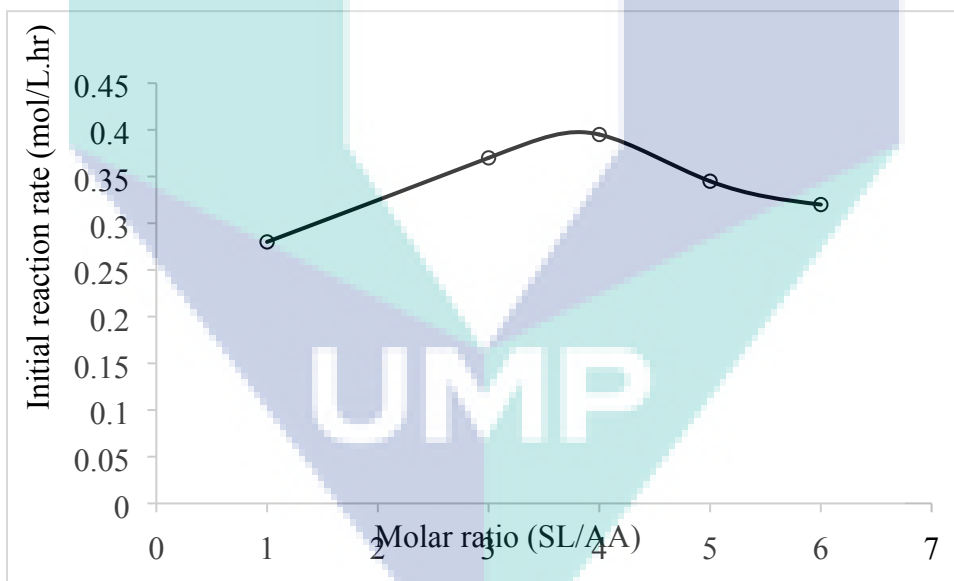

Figure 4: Initial reaction rate for the reaction at different $M_{SL:AA}$ at stirring rate of 600rpm with reaction temperature of 433K and catalyst loading of 4wt%

3.1.3 Effect of Catalyst Loading

The catalyst loading was varied from 1wt% to 8wt% to study its effect towards esterification reaction. The other parameters were kept constant. Figure 5 shows that the increase of catalyst loading has led to a rise in conversion because of the increase of catalyst sites that promoting reaction [13-15]. No significant change in conversion was observed when the catalyst loading was changed from 4wt% to 8wt%. The initial reaction rate for the reaction with the catalyst loadings of 4 wt% and 8 wt% were identical as shown in Figure 6. This occurrence was ascribed to the sufficient active sites provided by the 4 wt% of catalyst in the reaction mixture. The catalyst loading of 4wt% was the best condition since it provided sufficient active site to accommodate the reaction of the reactants molecules [16, 17].
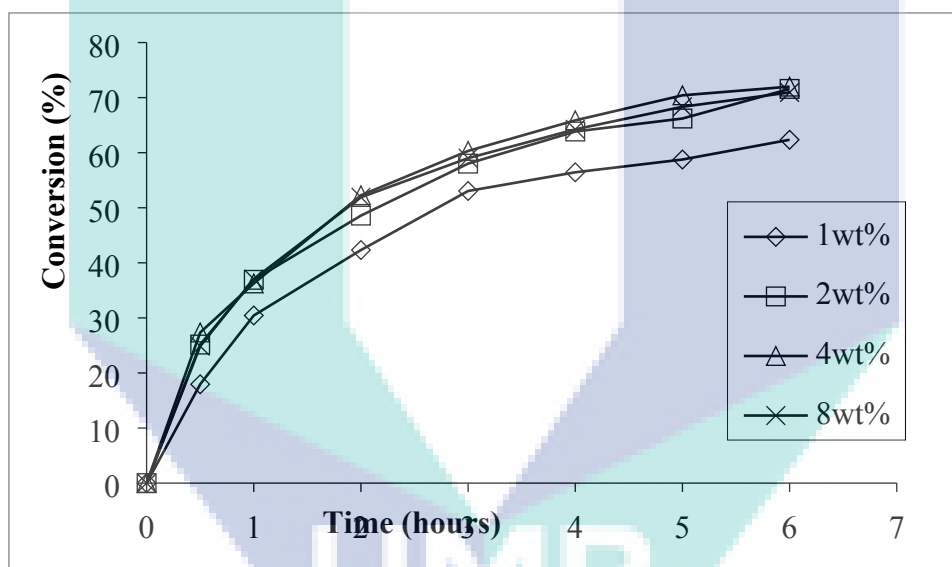
Figure 5: Azelaic acid conversion-time profile for the reaction at different catalyst loading of tin (II) oxide with stirring rate of 600rpm, reaction temperature of 433K and $M_{SL:AA}$ of 4:1
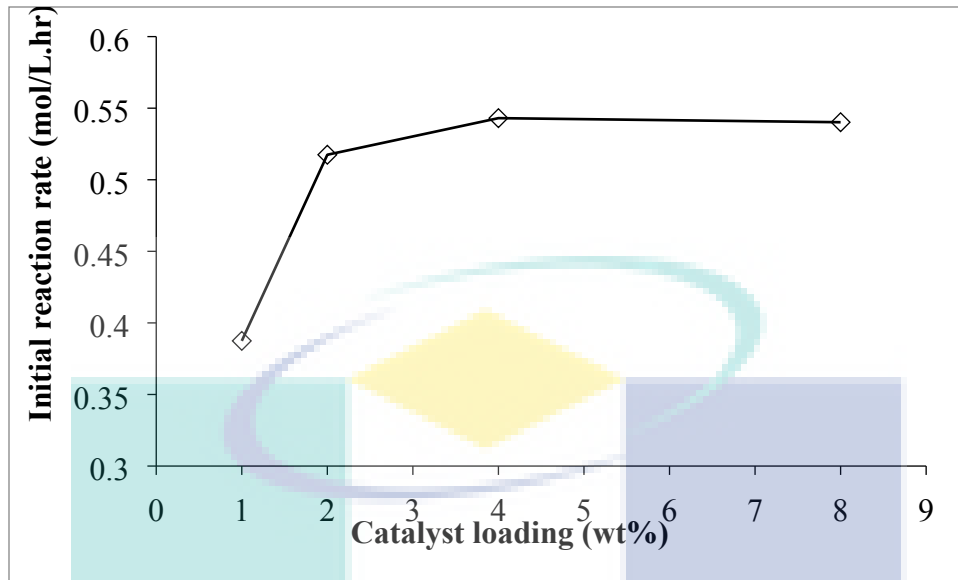
Figure 6: Initial reaction rate for the reaction at different catalyst loading with stirring rate of 600rpm, reaction temperature of 433K and $M_{SL:AA}$ of 4:1

3.4 Equilibrium Study

The esterification process is limited by equilibrium conversion. The equilibrium constant, K_{eq} was calculated experimentally according the Eq. 13.

$$K_{eq} = (C_{SA}C_W)/(C_{AA}C_{SL}) \tag{13}$$

Figure 7 shows the concentration profile for the equilibrium study carried out at the reaction temperature of 403, 413, 423 and 433K, molar ratio ($M_{SL:AA}$) of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm as shown in Figure 7. The equilibrium conversion, X_e and the corresponding K_{eq} are shown in Table 1. The K_{eq} and X_e increase with implying the esterification of sorbitol with azelaic acid catalysed by tin (II) oxide was endothermic. The current findings are in agreement with studied of Giacometti et al. [2] on the esterification of sorbitol with lauric acid catalysed by p-toluenesulfonic acid.
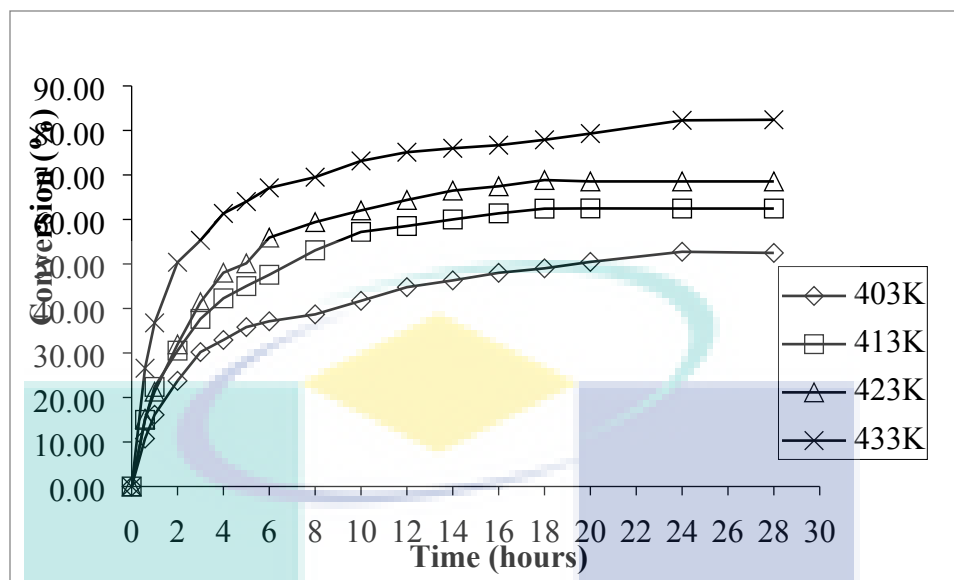
Figure 7: Azelaic acid conversion-time profile for equilibrium study at different reaction temperature with $M_{SL:AA}$ of 5:1, catalyst loading of 4 wt% and stirring rate of 600rpm

Table 1: Equilibrium constant and equilibrium conversion at different temperature

Temperature (K)	K_{eq}	X_e (%)
403	52.4804	0.1295
413	62.4519	0.2374
423	68.5449	0.3462
433	82.4012	0.9239

Based on the Van't Hoff plot in Figure 10, the ΔH was 90706 J/mol while ΔS was 208 J/mol.K. Gibbs free energy (ΔG) was 840 J/mol at 433K. The positive value of ΔS reflects that the amount of disorder or randomness in the system is increased as a consequence of the reaction.
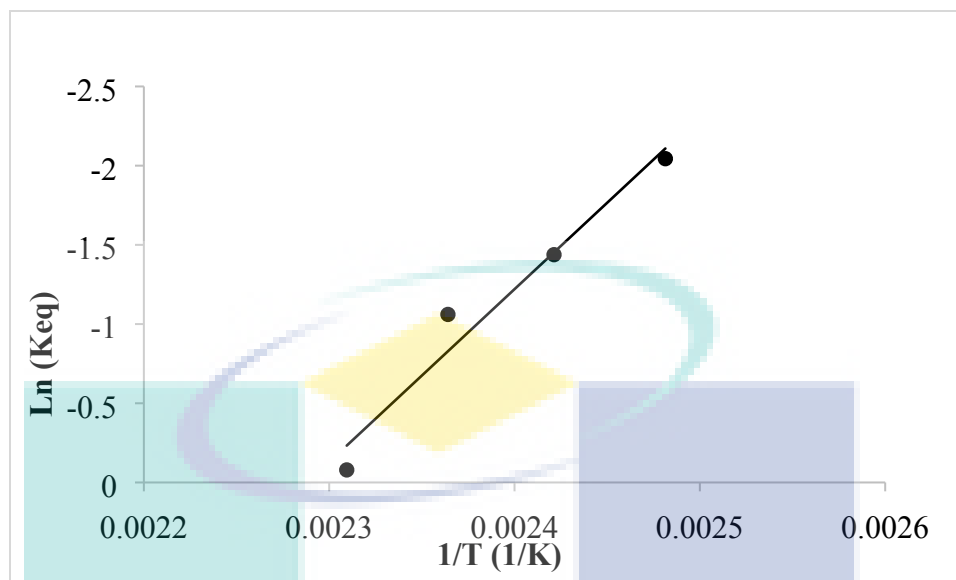
Figure 10: Van't Hoff plot for the synthesis of sorbitol azeleate at different reaction temperature

3.5 Kinetic Modelling

Table 2 shows the kinetic parameter for each kinetic model. The fitting of kinetic data to ER and LHHW models has shown the coefficient of determination, R^2 of closest to one and lowest values of *min φ* and *MRE*. ER model was preferred due to its simple mathematical form the superior adsorption equilibrium constant of water indicated that water was more prone to adsorption on the catalyst surface than the azelaic acid attributing to the higher polarity of the water. It showed the inhibiting effect of water to esterification reaction [18-20].

Table 2: Kinetic parameters of the models to fit experimental data

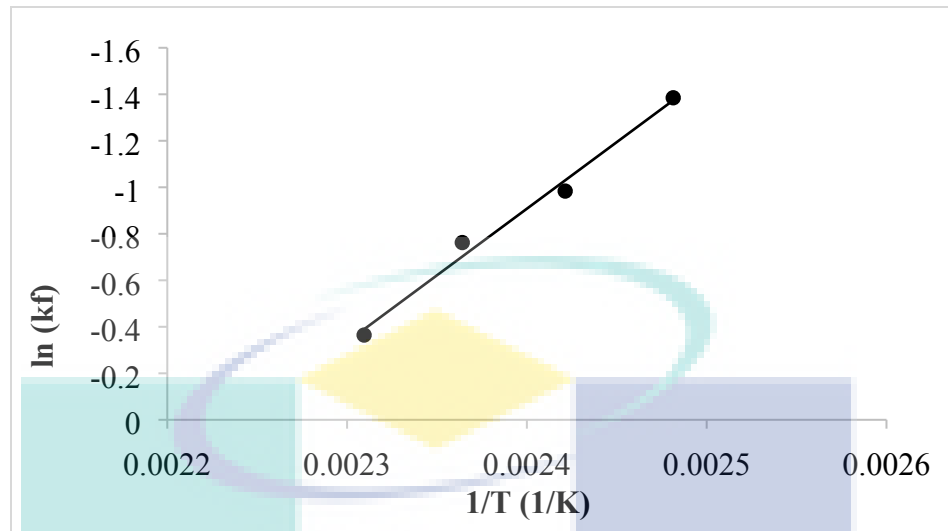| Model	Temp. (K)	k_f (mol/L.hr)	$\sigma(k_f)$ (mol/L.hr)	MRE (%)	Min φ	K_W (L/mol)	K_{AA} (L/mol)	K_{SL} (L/mol)	K_{SA} (L/mol)	R^2
PH	403	0.024	0.003	8.13	0.010					0.90
	413	0.035	0.002	5.78						0.98
	423	0.044	0.003	4.66						0.98
	433	0.065	0.008	9.17						0.92
ER	403	0.250	0.028	7.47	0.009	16.020	10.618			0.93
	413	0.374	0.024	5.20						0.98
	423	0.467	0.027	4.03						0.98
	433	0.695	0.091	8.26						0.92
LHHW	403	0.527	0.059	7.43	0.009	2.913	1.485	0.560	0.397	0.93
	413	0.787	0.052	5.18						0.98
	423	0.982	0.056	3.99						0.98
	433	1.463	0.192	8.15						0.92

Figure 8: Arrhenius plot for the synthesis of sorbitol azeleate at different reaction temperature

The activation energy was determined using Arrhenius plot as given in Figure 8 and the corresponding Arrhenius equation is shown in Eq. 14. The activation energy for the present study (47.62 kJ/mol) was lower than the activation energy (50.8 kJ/mol) of the polyesterification of sorbitol with lauric acid catalysed by *p*-TSA in the study of Giacometti *et al*. [2] This reveals that the sorbitol azeleate is easier to be formed in the esterification of sorbitol with azelaic acid catalysed by tin (II) oxide.

Figure 9: Parity plot of Eley Rideal model of ±10% error.

The parity plot in Figure 9 shows that the errors between experimental data and predicted results were within ±10%, signifying that the esterification of sorbitol and azelaic acid catalysed by tin (II) oxide occurred based on the ER mechanism. The azelaic acid first adsorbed onto the active sites in tin (II) oxide before reacting with sorbitol in the bulk fluid. The adsorbed azelaic acid accepted a protons from tin (II) oxide. Sorbitol molecule attacked the protonated carbonyl group to give a tetrahedral intermediate and water. A proton was lost at one oxygen atom and it was gained by another oxygen atom to form another intermediate which further loses a molecule of water that gives a protonated ester. A proton was transferred to a water molecule to give the sorbitol azeleate ester.

$$k \ (mol/L.hr) = 376247 \exp \left(-47618.44/RT \right) \qquad (14)$$

4.0 Conclusion

The kinetic behaviour of the esterification of azelaic acid and sorbitol catalysed by tin (II) oxide has been studied. The best operating conditions were 433K, $M_{AA:S}$ of 4:1 and 2wt% of catalyst loading. The kinetic data were correlated with different models and ER model was the best model to describe the esterification reaction. It indicated that the reaction was controlled by the surface reaction. The activation energy was found to be 47.62 kJ/mol.
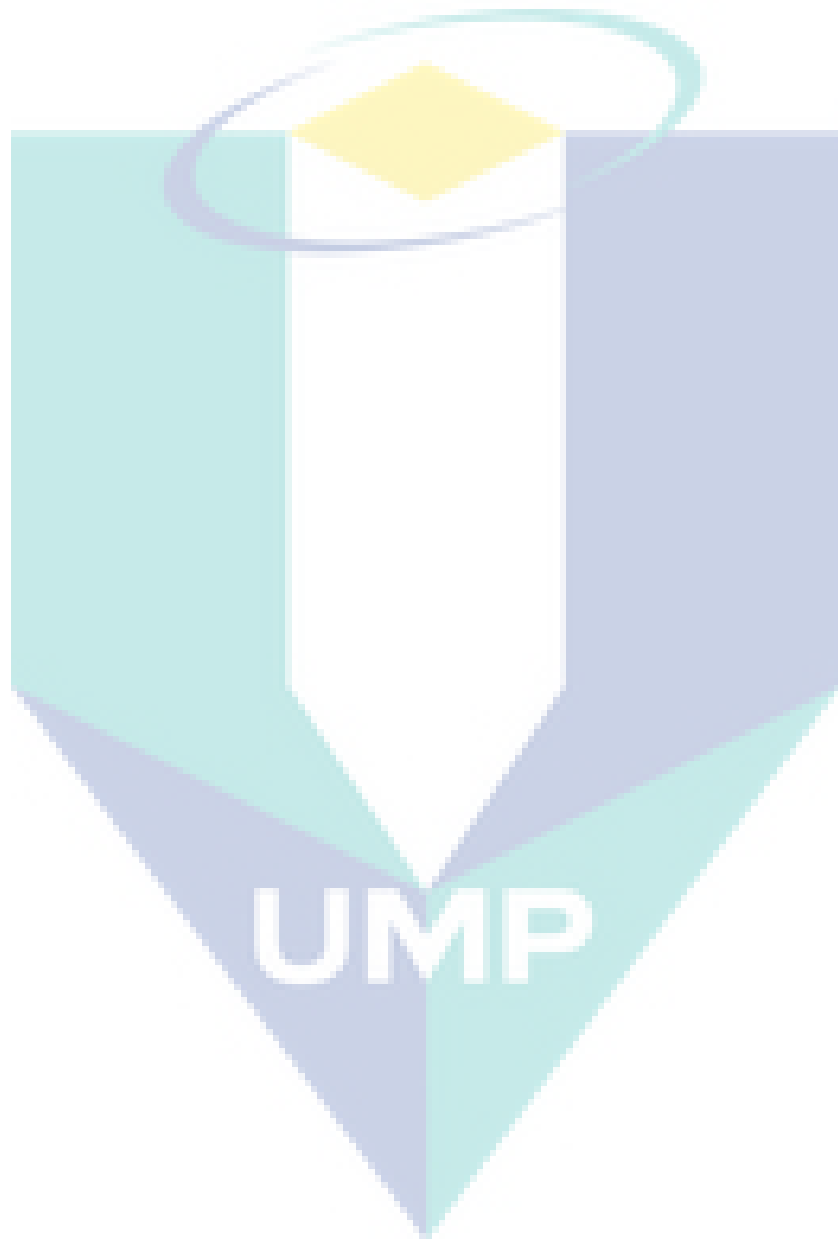
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Q., 2015, **29**, 549-557.

Highlights

- One pot esterification of sorbitol and azelaic acid catalysed by tin (II) oxide.

- Production of sorbitol branched polyol ester from esterification

- The reaction mechanism follows Eley Rideal model.
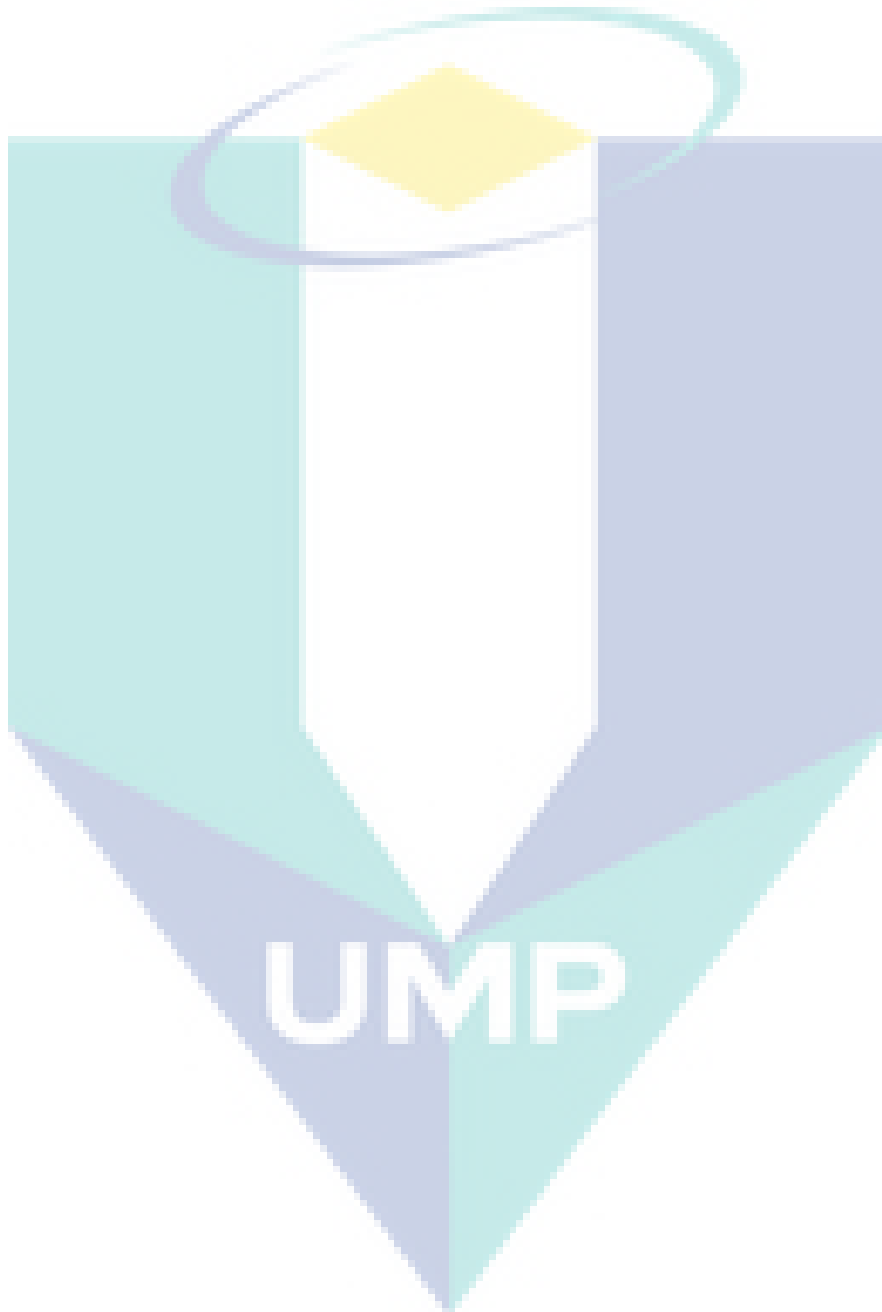
The separation and characterisation of azaleic acid, sorbitol and its anhydrides using gas and liquid chromatographic techniques

1.0 Introduction

The demand of polyurethanes (PU) produced from dwindling fossil resources is increasing in recent years especially in automotive sectors, constructions and furniture industries which estimated 33.1 billion pounds by 2020 (Fang et al., 2013; Gustini et al., 2015). The conventional PU is produced by reacting oligomeric polyol and diisocyanate which come from petroleum. The growing interest in usage of renewable resources because of reduction of the environmental impact, decrease in the dependence on petroleum, reduction of the carbon footprint and improvement of the Life Cycle Analysis in agreement with sustainable development (Orgiles-Calpena et al., 2016).

Previous study has used natural oil which show the potential of bio-based polyester polyol derived from palm oil (Badri et al., 2001; Ng et al., 2017), jatropha oil (Hazmi et al., 2013), castor oil (Gao et al., 2012; Luong et al., 2016; Moghadam et al., 2016) soybean oil (Sun et al., 2012) and rapeseed oil (Zieleniewska et al., 2015) for polyurethane production. Meanwhile, to produce PU with special properties such as such as elasticity, flexibility, hydrophobicity, hydrolytic stability, and lower glass transition temperature, the used of dicarboxylic acid as raw material is encouraged (Hill et al., 2000). The polycondensation reaction to produce polyester polyol needs dicarboxylic acid and diol. The sorbitol (diol) that abundance and renewable reacted with dicarboxylic acid will gives the comparable properties with petro-based polyol (Alvarez et al., 2005). The reaction between sorbitol and azelaic acid (dicarboxylic acid) have potential to produce good bio-based polyester polyol which has not reported elsewhere.

The quality of these bio-based polyester polyol is determined by the distribution of polyester polyol of sorbitol and its derivatives. Usually, the sugar is analysed using by HPLC but the demand for simultaneous analysis of acid and sugar is contemporaneous. The quantification method using GC has several advantages which using single procedure, using one apparatus, one detector and one column which saving time, cost, and work by using single elution procedure of high selectivity. Although the analyte needs derivatisation, this method is high desirable compared to HPLC which need more than one column, more than one eluent system, more than one detector and more than one apparatus to achieve same results (Perl, 1999).

The previous study by Giacometti et al. (1996) has confirmed that the polyester polyol can be monitor by GC. Further studied by Humprey (2007), which quantify the sorbitol polyester

polyol using GC for which showed promising results. Unfortunately, the quantification for the azelaic acid, sorbitol ester and its derivatives are not available in literature. The standard for this polycondensation reaction are also not available. So, present studies will determined the reactants and dehydrated sorbitol (sorbitan and iso-sorbide) which can give information about the ester conversion which lead to the quality of the polyester polyol that can compare with the existing petro-based polyester polyol.

2.0 Methodology

2.1 Materials

Azelaic acid (90%), sorbitol (97%), dianhydro-D-glucitol (98%), 1,4 anhydro-D-sorbitol (97%), pyridine (99.5%), acetic anhydride (98.5%), dimethylformamide (99.5%), hexamethyldisilazane (98%) and trimethylchlorosilane were used without further purifications.

2.2 Dilution

A known amount of sample was dissolved in dimethylformamide. The dissolved sample will filtered through membrane filter before injecting to GC-FID.

2.3 Sample derivatisation

Acetylation

2 grams of sample was dissolved in 5ml of pyridine and mixed with acetic anhydride. The mixture was reflux for 1hour. The mixture is filtered before injected to GC-FID.

Silylation

50mg of samples was dissolved in 1ml of dimethylformamide (DMF). 0.3ml of the dissolved samples was mixed with 0.1ml of Tri-sil reagent which prepared by mixing hexamethyldisilazane, trimethylchlorosilane and pyridine with ratio of 2:1:9. The mixture was shake and stand for 15 minutes. The mixtures was filtered before injected to GC-FID.

Silylation II

50 to 100mg of samples was dissolved in 3ml of pyridine in stopped vials. The 0.4 ml of hexamethyldisilazane was added. Then 0.3 ml of trimethylchlorosilane was added slowly to the mixture and shake vigorously for 30 seconds. The mixture was stand for 5 minutes. The supernatant was filtered and injected to GC-FID.

2.3 GC Analysis

The samples that has been derivatisation were analysed using GC-FID using CP-TAP CB column with 25m in length, 0.10 μm of film thickness and 0.25 μm of inner diameter. The oven temperature of 150°C to 250°C with ramping 8°C/min. The column flow rate was set for 1ml/min. the split ratio of 10:1. The injector and detector temperature are set at 250°C and 380°C respectively.

3.0 Results and discussion

The findings of analysis methods using GC-FID for esterification of azelaic acid with sorbitol is important to determine the percent of azelaic, sorbitol, dianhydro-D-glucitol (iso-sorbide) and 1,4 anhydro-D-sorbitol (sorbitan). Thus, can quantifying the conversion of each ester which led to the quality of the polyester that has been produced.

3.1 Dilution

The solute needs to prepare before injecting to GC and simple dilution is used to see whether the column can separate the solute. Figure 1 shows the solutes can be separated as each solute has different retention time. The chromatogram shows the fronting peaks of each materials which indicates the amount of solute in (or on the stationary phase is comparatively large (large injection or low volatile solute). The amount of solute is reduced but the peaks pattern is same shown in figure 1 which indicates the fronting peaks is due to low volatility of the solute. This type of peaks has difficult to measure, the retention time also increases with larger samples and the small size of solute may eliminate the peak which show the precision or reliability is poor (Cazes 2005).

The low volatile of solute (AA, SL and SB) condensed and acts like stationary phase. In this localized section, the apparent stationary phase volume (Vs) is higher than the apparent mobile phase volume (Vm). Solute molecules in the mobile phase are now affected differently depending their position in that solute band. Those at the front are retained in normal fashion and exhibit 'normal' solute retention factor (k), as the carrier sweeps them forward over virgin stationary phase where the column phase ratio has not been affected. Solute molecules in the mobile phase that not advancing front of the band continue to chromatograph in 'localized' region where the 'apparent phase ratio a progressively increasing concentration of the less retained molecules, gradually tapering into a higher concentration of more retained molecules, followed by an abrupt return to baseline as the last of the latter elute from the column. (Jennings et al., 1997).

This involatile materials should be avoided because will cause column degradation due to residue build up or attack of stationary phase over a period of time (Poole, 2012).
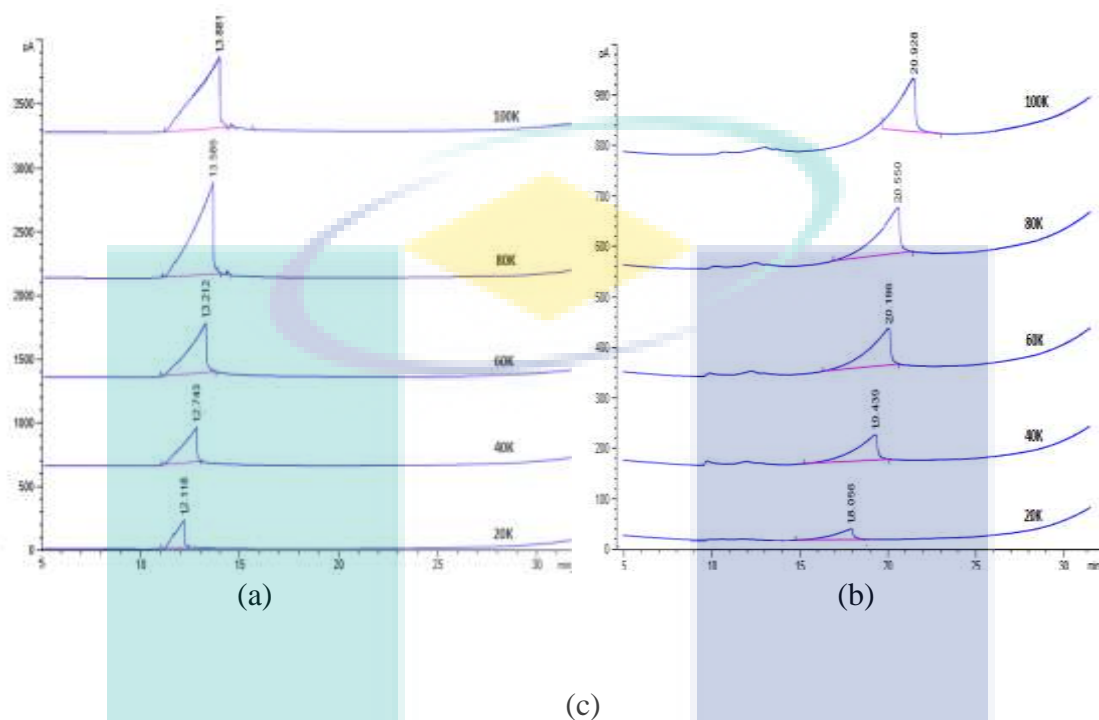

(a)   (b)

(c)

Figure 1: Chromatogram peaks for dilution of, a) azelaic acid; b) sorbitol; and c) isosorbide.

The polar nature, low stability and low volatility of solutes required derivatisation prior to their analysis to increase the volatility. The acetylation by acetic anhydride is common and simple.

3.2 Acetylation

There are several studies on derivatisation of sorbitol using acetylation (Humprey, 2007 & Li et al., 2013) but not for AA. This acetylation is substitution the hydrogen with acyl group (Ruiz-Matute et al., 2010) as shown in Eq 1.

$$ROH + Ac\text{-}X \rightarrow R\text{-}O\text{-}Ac + HX \qquad (1)$$

The acetylated sorbitol and sorbitan can be separated with the different retention time shown in Figure 2. The chromatogram shows slightly fronting peaks which better than sample preparation by dilution with DMF. Usually the fronting happened when column is overload which can reduced by reducing the sample amount by dilution or increase the split ratio and/or increasing thickness of the stationary phase, internal diameter of the column or the column temperature (Engewald and Dettmer-Wilder, 2014; Gad, 200) but the chromatogram for acetylate azelaic acid shows no peaks. The acetylated sorbitol also crystalise over a period of

time which can cause the concentration of solute is differ from the actual. The crystallite solute also may stuck in the injector needle.
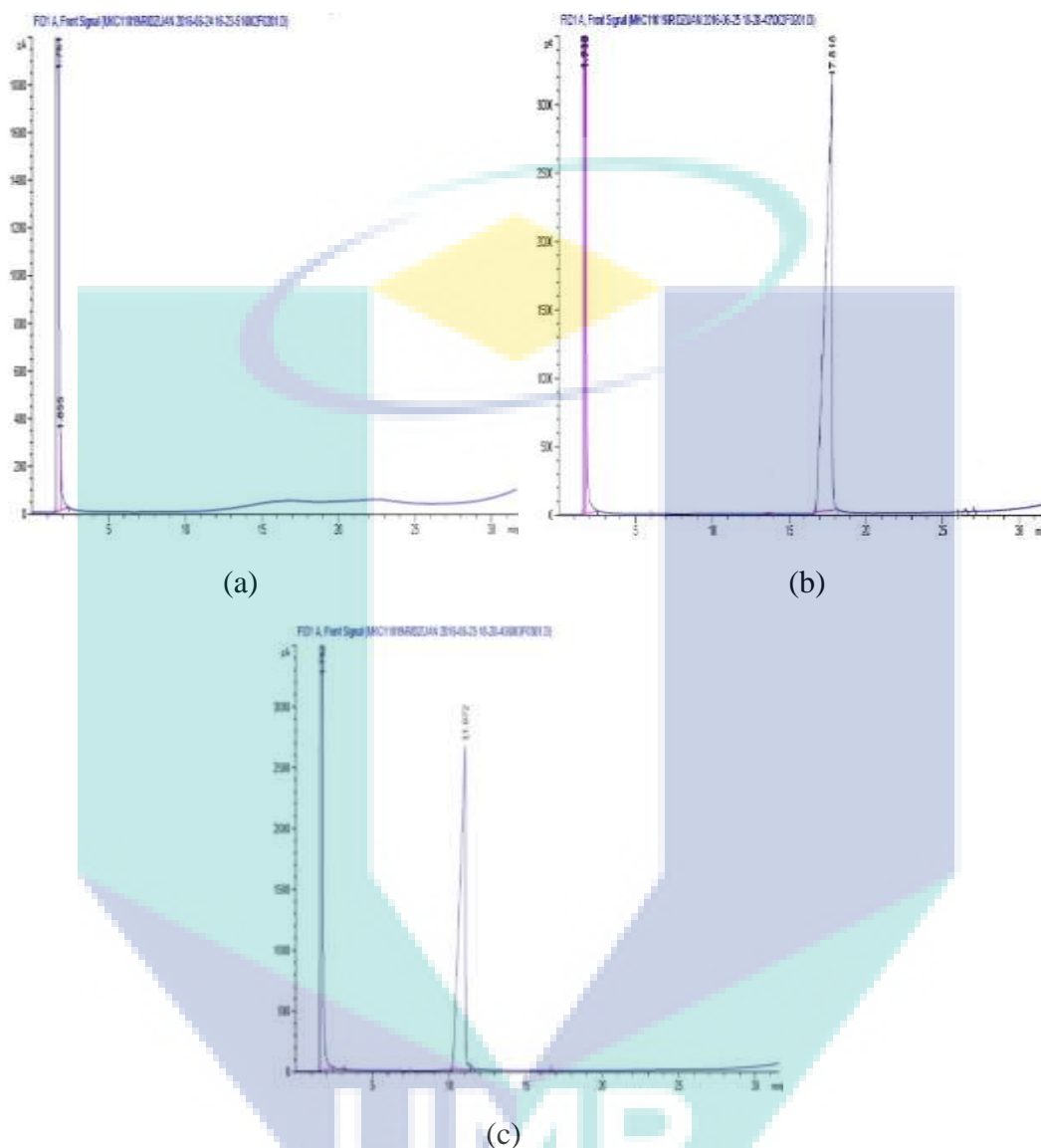

(a)

(b)

(c)

Figure 2: Chromatogram peaks for acetylation of, a) azelaic acid; b) sorbitol; and c) isosorbide.

3.3 Silylation

The reaction for silylation is simple and quantitative without any undesirable side-reactions (Giacometti et al., 1995). The mechanism involved the replacement of the active hydrogen with trimethylsilyl group (Ruiz-Matute et al 2010; Orata) as shown in Eq 2.

$$R\text{-}OH + (CH3)3Si\text{-}X \rightarrow R\text{-}O\text{-}Si(CH3)3 + HX \qquad (2)$$
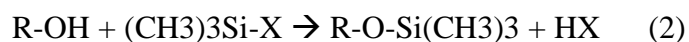
The previous silylation method by Giacometti et al. (1995) can be separate the solute using the CP-TAP column but with fronting peaks as shown in figure 3. The method seems promising with shorter time required for reaction and much simples. The previous method by Robert (1965) is introduced because more simple and several modification has been made. A good chromatograph is produced with symmetric peaks for silylated azelaic acid and isosorbide shown in figure 4.
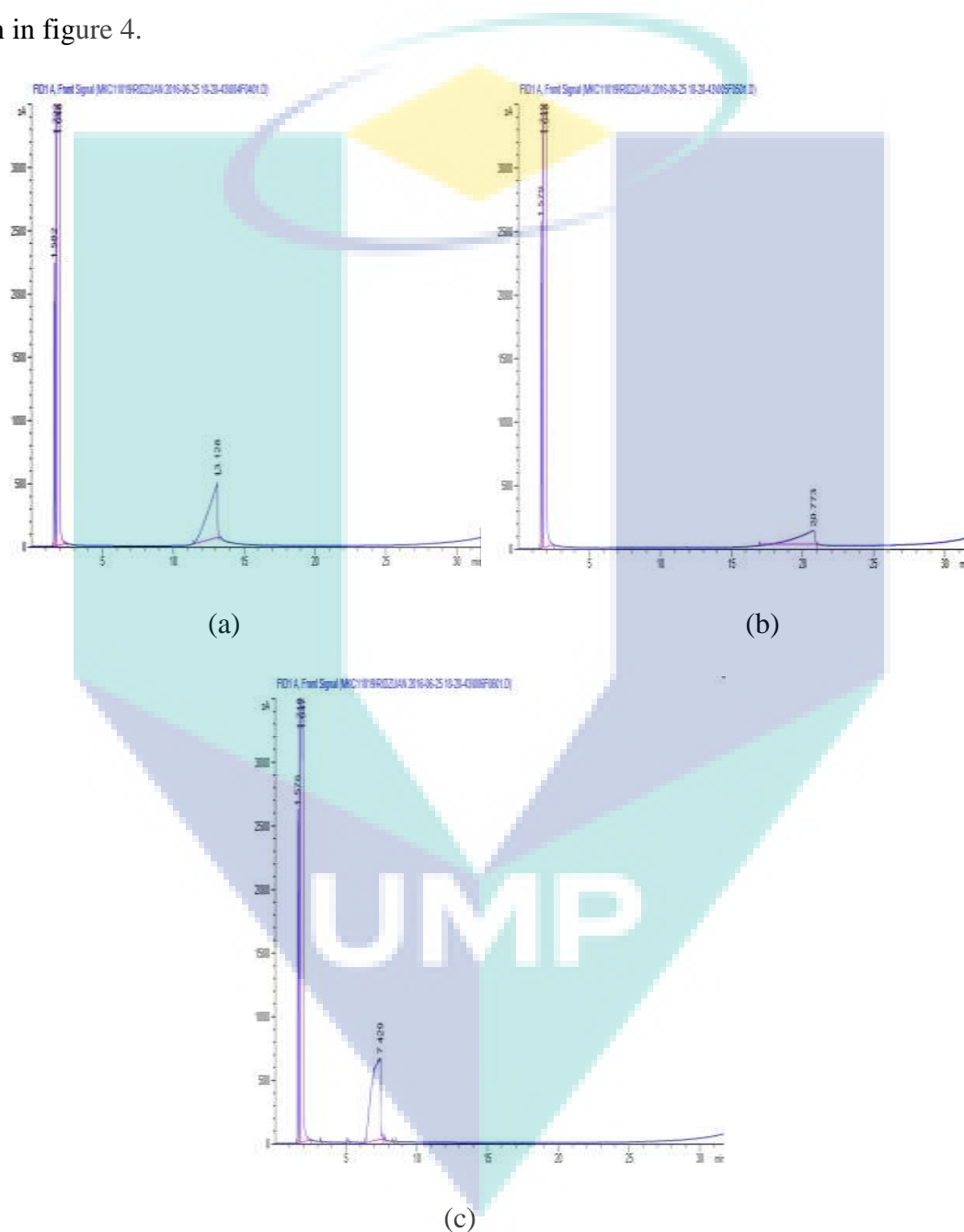
(a)

(b)

(c)

Figure 3: Chromatogram peaks for silylation of, a) azelaic acid; b) sorbitol; and c) isosorbide.
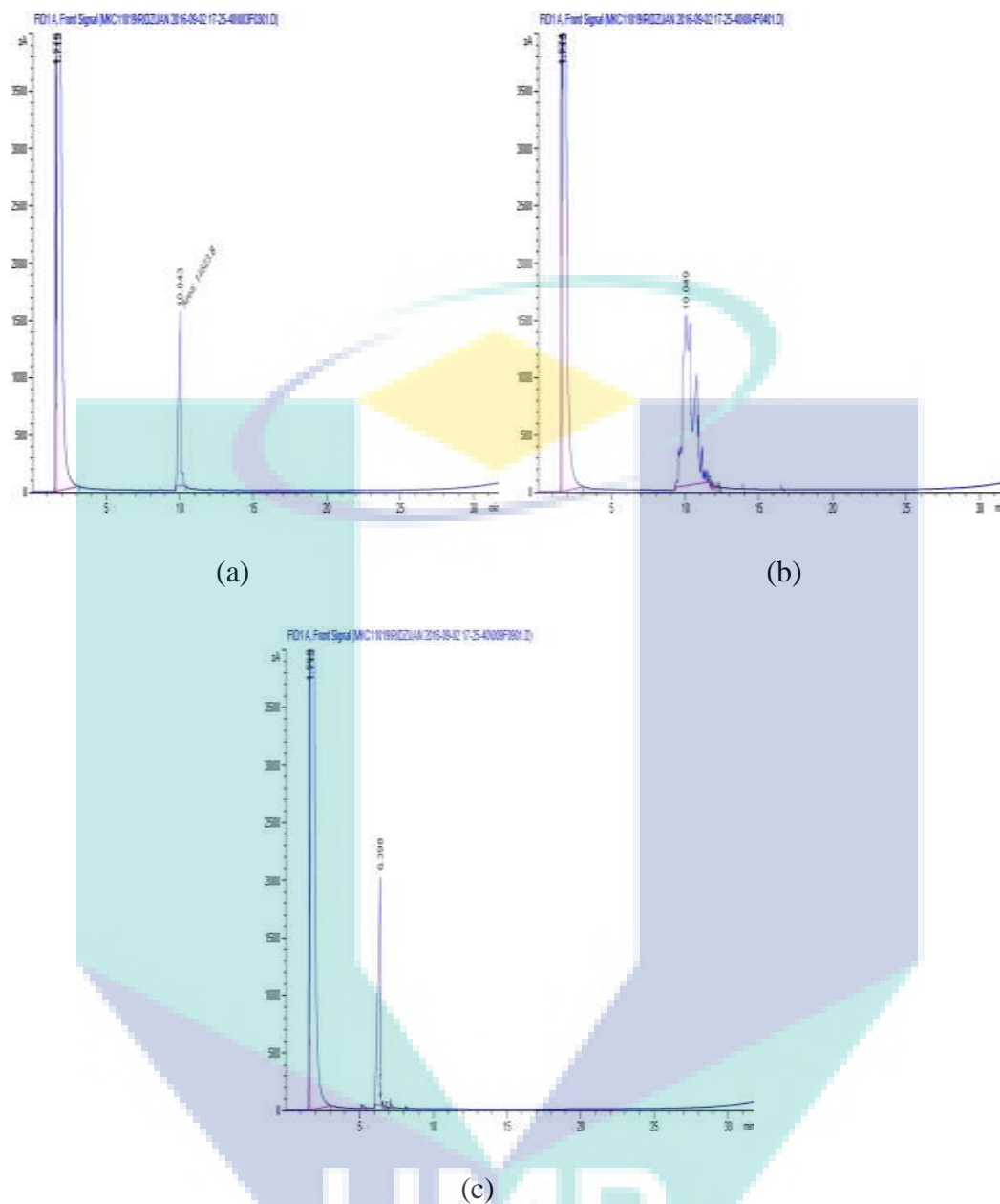
(a)

(b)

(c)

Figure 4: Chromatogram peaks for silylation II of, a) azelaic acid; b) sorbitol; and c) isosorbide.

The silylated sorbitol shows 'christmas tree effects' in figure 4(b). These happened when high programming rates necessitate powerful heating of the column. The very hot air produced at heating filaments of ovens may no longer mixed well enough with the cooler air in the oven. As a consequences, the column hit alternately by cooler then hot air. The fluctuating temperature in column leads to expansion/contraction of the carrier gas and rapid changes in retentive power, causing jumping chromatography of the solutes and distorted (Grob., 2008). The GC conditions is changed to make sure the heating condition in oven is steady by holding the initial temperature for 7 minutes. The column flow rate is reduced to

0.2ml/min to make sure the acetylate azelaic acid and sorbitol is well separated since the retention time are closed in figure 4. The chromatogram for conditioning shown in figure 5. The sorbitan is tested using the previous method and the chromatogram is shown in figure 5(d).
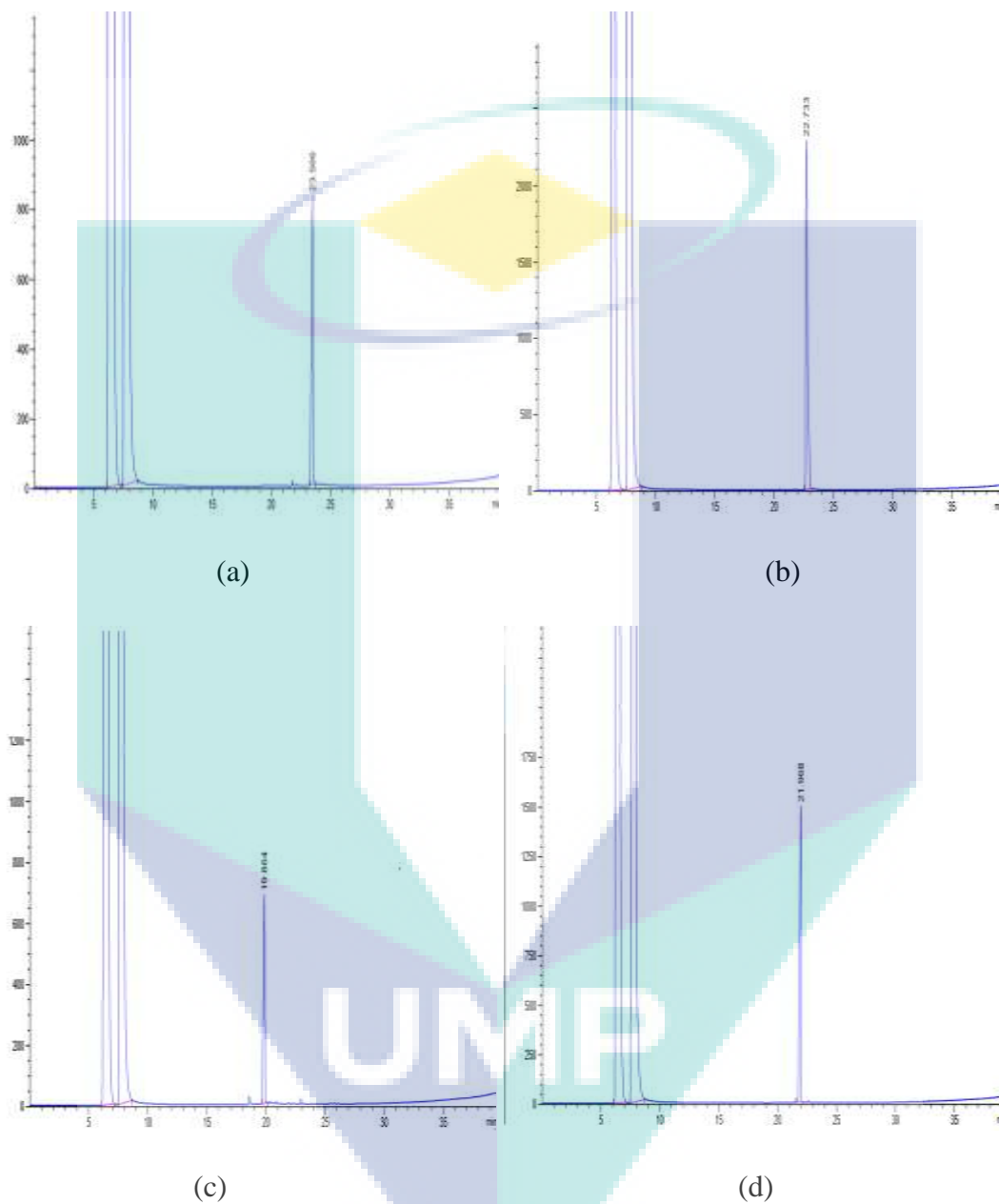

(a)

(b)

(c)

(d)

Figure 5: Chromatogram peaks of, a) azelaic acid; b) sorbitol; and c) isosorbide; d) sorbitan.

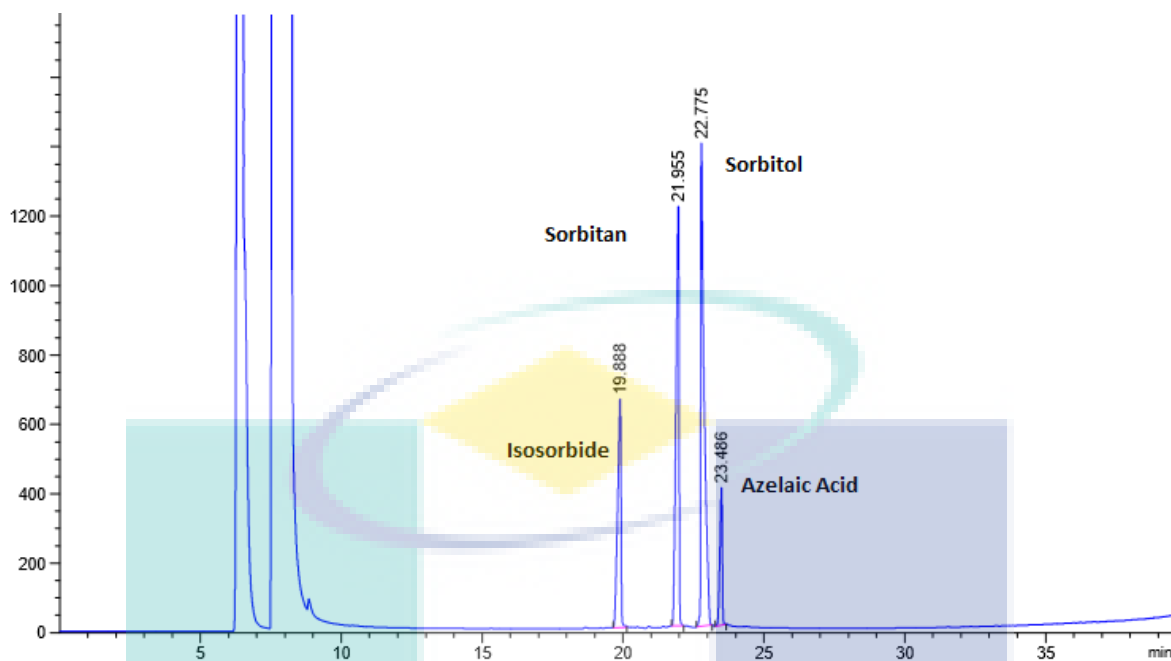The figure 6 shows the good and well separated solute using single analysis by GC-FID.

Figure 6: Chromatogram peaks for derivatisation using modified silylation.

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