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Bio-based sorbitol azelaic acid ester synthesis through germanium (IV) oxide catalysed esterification

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Abstract. Conventionally, polyurethane (PU) is derived from the non-renewable petroleum feedstocks, polyol polyester and di-isocyanate. Bio-based polyol polyester is an alternate to reduce the environmental impacts of the petroleum-based polyol polyester. Bio-based reactants, sorbitol (SL) and azelaic (AA) acid were used in the esterification to produce sorbitol azelaic acid ester (SAAE) using germanium (IV) oxide (GeO_2) as a catalyst. The experimental studies set at various operating conditions were conducted to determine the best operating condition that gave product with highest AA conversion and acceptable colour. The best operating condition was achieved at a temperature of 200°C, SL/AA reactant ratio of 4:1 and catalyst loading of 0.5 wt%, with the corresponding AA conversion of 90.10%. The kinetic data was well fitted to the Langmuir Hinshelwood Hougen Watson (LHHW) model with the corresponding activation energy of 11.55 kJ/mol.

1. Introduction

Natural leathers, commonly obtained from animals, are popular because of its beautiful appearance, soft and porous structure. In recent years, a substitution of the natural leather with the synthetic leather was advocated due to the restricted source and expensive price of natural leather in addition to the awareness in protecting animal. Synthetic leather could be a nonwoven support material coated with polyurethanes (PU) [1].

PU is commonly used in the production of coating, elastomers, solid articles, films and foams. A robust development in key end-user industries such as construction, automotive, furniture and electronics has resulted remarkable growth in the demand of PU [2]. PU is required to exhibit properties such as low temperature flexibility, high tensile strength, tear strength, elongation, abrasion resistance and solvent resistance to fulfil the conditions of various applications [3].

Conventionally, PU is obtained by reacting polyol polyester with di-isocyanate in which both are derived from petroleum resources [4-5]. In addition to the expected depletion of natural petroleum resource and instability in the price of crude oil, the concern on environmental pollution due to the disposal of this non-biodegradable petroleum-derived PU has driven the researches to substitute petroleum-derived raw materials with the degradable raw materials such as bio-based polyol polyester [6].

Biodegradable polyol polyester can be synthesized by heating bio-based polyol with dicarboxylic acid derived from plant at a very high temperature in consideration of the melting temperature of both reactants. Esterification reactions are commonly carried out using homogeneous catalysts. Examples of homogenous catalysts used in esterification of polyol with fatty acid are p-toluene sulfonic acid, sulphuric acid and phosphoric acid. The homogeneous catalysts have caused higher capital and operating costs due to its corrosiveness and necessity to be separated from the product for reuse purposes. Comparing to the homogeneous catalyst, heterogeneous catalysts have many significant advantages such as different phase from the product, less corrosive and less toxic, leading to the reduced production cost and environmental problem [7].

In previous studies, heterogeneous catalysts zeolite and cation exchange resins were employed in the esterification of oleic acid with glycerol and trimethylolpropane respectively. The use of these catalysts restricted the reaction temperature below 190 °C due to its thermal stability [8-9]. The resultant oleic acid conversion was low (approximately 80%) and hence producing a product with high acid value [9]. Other researcher used germanium (IV) oxide as catalyst to produced polyester from natural polyol and sebacic acid at 160°C. It has promising results which produced high clarity and high molecular weight of polyester [10]. In view of this, a catalyst with higher thermal stability should be adopted to enable the esterification of fatty acid with polyol at higher reaction temperature. The polyol polyester with low acid value (≧25 mg KOH/g to ≦400 mg KOH/g) can then be produced to meet the specification of the raw material required for production of PU. Previously, the kinetic of sorbitol esterification with lauric, azelaic and linoleic acid catalysed by p-toluenesulfonic acid, tin (II) oxide and lipase, respectively had been fitted successfully with several model to elucidate the reaction mechanism. The models including Pseudohomogeneous model, Eley-Rideal model and Langmuir Hinshelwood Hougen Watson model [11-13].

In the present study, germanium (IV) oxide, a heterogeneous catalyst with high thermal stability, was used to catalyse the synthesis bio-based polyol polyester through the esterification of sorbitol (SL) with azelaic acid (AA). The objective of this research is to determine the reaction operating condition that yields the product with best quality and the kinetic values. The important operating parameters such as reaction temperature, SL/AA molar ratio and catalyst loading were investigated.

2. Materials and methods

2.1. Chemicals

Azelaic acid (98%) and sorbitol (97%) were used as the reactants while germanium (IV) oxide (99.99%, Alfa Aesar) was used as the catalyst for the esterification reaction. The acid value titration analysis adopted potassium hydroxide (85%) dissolved in distilled water as the titrant and phenolphthalein dissolved in ethanol (99.5%) as the titration indicator. Potassium hydrogen phthalate (99.5%) was used to standardize the self-prepared potassium hydroxide solution. All the chemicals were purchased from Sigma Aldrich except germanium (IV) oxide and phenolphthalein that were supplied by Alfa Aesar and R&M Chemicals, respectively.

2.2 Experimental procedure for esterification reaction study

The esterification of sorbitol (SL) and azelaic acid (AA) in batch-mode was conducted in a 500 mL three-necked round bottom flask. The reactor was fitted with reflux condenser to condense the vapour released during the reaction by using cooling water. The temperature probe was used to detect the reaction temperature while the temperature controller was used to control the reaction temperature. Rotamantle was used to supply heat to the reaction and magnetic stirrer was used as the source of stirring. Figure 1 shows the experimental setup for the esterification reaction study.

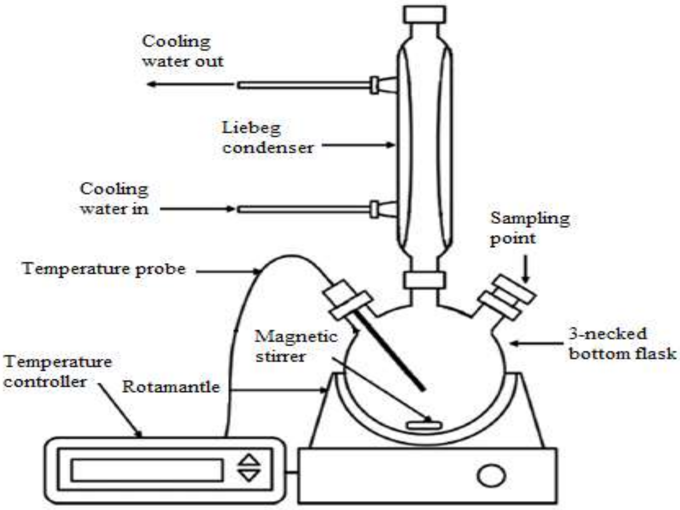


Figure 1. The experimental setup of esterification reaction study.

The esterification of SL and AA was performed for 6 hours at a nominal condition with the reaction temperature of 140˚C, SL/AA molar ratio of 3:1, 0.5 wt% catalyst and stirring speed of 400 rpm. First, the reactants with designated SL/AA molar ratio were pre-heated individually to 120˚C. The reactants were then mixed and stirred at 400 rpm, making up a reaction mixture volume of 100 mL. The catalyst was added immediately after the mixing of the pre-heated reactants in the esterification reaction. The initial sample (at time of 0 hour) with a volume of 0.5 mL was withdrawn, cooled and kept for analysis. The sample was taken for every 15 minutes for the first hour and every 30 minutes for the subsequent hours. The experiments were repeated at various reaction temperature, SL/AA molar ratio and catalyst loading to investigate the effect of process parameter to the reaction performance.

The initial rate of reaction as shown on Eq. 1 was obtained through the differentiation of concentration of AA at time zero with the aid of Polymath Professional 6.0 polynomial regression analysis.

$$r_{AA0}=\left[\frac{dC_{AA}}{dt}\right]_{t=0} \tag{1}$$

where r_{AA0} is the initial reaction rate of AA in mol L^{-1} min^{-1}, C_{AA} is the concentration of AA in mol L^{-1} and t is time in minutes.

2.3 Determination of acid value

2.3.1 Preparation of KOH solution

One litre of 0.1 M potassium hydroxide (KOH) solution was prepared by dissolving 5.61 g of KOH with distilled water in 1 L volumetric flask. The prepared 0.1 M of KOH was standardized using potassium hydrogen phthalate (KHP) solution to determine the actual concentration of prepared KOH solution. KHP with the weight of 0.1 g was dissolved with 50mL of distilled water in a volumetric flask. Two to three drops of the indicator, phenolphthalein solution were added into the KHP solution. The KHP solution was titrated with KOH solution until pale pink colouration appeared. The amount of KOH solution was recorded and the actual concentration of KOH solution was determined using Eq. 2. The standardized 0.1 M KOH solution was then ready to be used for the AV titration.

$$\mathrm{M_{KOH}}=\frac{\mathrm{M_{KHP}}}{\mathrm{W_{KHP}V_{KOH}}} \tag{2}$$

where M_{KOH} is the actual concentration of KOH in mol L^{-1}, mL, M_{KHP} is the concentration of KHP in mol L^{-1}, W_{KHP} is the molecular weight of KHP in g mol^{-1} and V_{KOH} is the volume of KOH consumed during the titration in mL.

2.3.2 Titration method for acid value

Acid value (AV) titration method was used to quantify the free fatty acids presented in the product sample. AV is denoted as the amount of KOH in mg to neutralize 1 g of free fatty acid (FFA) or fat. The product sample (0.2-0.3 g) was weighed and dissolved in 50 mL of hot water (70 ˚C-80 ˚C) placed in a 250 mL conical flask. Two to three drops of phenolphthalein indicator were added and the mixture was well-shaked. The solution was titrated with 0.1 M KOH solution until pink colouration which persists for 30 s was observed. The volume of 0.1 M KOH titrant used was measured and AV was calculated by using Eq. 3. Subsequently, conversion of AA can be determined by using Eq. 4:

$$\mathrm{AV}=\frac{\mathrm{W_{KOH}\ V_{KOH}\ M_{KOH}}}{\mathrm{W}} \tag{3}$$

where W_{KOH} is the molecular weight of KOH in g mol^{-1}, V_{KOH} is the volume of KOH consumed in AV titration in mL and W is the weight of sample in g.

$$\mathrm{X}=\left(\frac{\mathrm{AV_t\text{-}AV_0}}{\mathrm{AV_0}}\right)\times 100\% \tag{4}$$

where X is conversion in %, AV_t is the acid value at particular time, AV_t and AV_O is the initial acid value at 0 hour.

2.4 Product colour grading using gardner liquid colour scale

Colour is an important indicator for the quality of sorbitol azelaic acid ester (SAAE). The Gardner liquid colour scale as specified in ASTM D1544 was used to grade the colour of the product sample. It is a single number colour scale for grading light transmitting scale samples with colour characteristics ranging from light yellow to brownish red. The scale numbered from 1 for the lightest to 18 for the darkest [14].

2.5 Kinetic study

The chemical equation for esterification of SL and AA catalyzed by GeO_2 is shown in Eq. 5.

$$\mathrm{C_6H_{16}O_4+C_6H_{16}O_6\leftrightarrow C_{15}H_{28}O_9+H_2O} \tag{5}$$

The reaction rate of AA, r_{AA} was determined by the differentiating the AA conversion with respect to time profile. Typically, the reaction mechanism of esterification can be elucidated using kinetic models such as Pseudohomogeneous (PH) model, Eley Rideal (ER) model and Langmuir Hinshelwood Hougen Watson (LHHW) model as shown in Eq. 6, 7 and 8, respectively [15].

$$\mathrm{r_{AA}}=\mathrm{k_f}\left(\mathrm{C_{AA}C_{SL}}\text{-}\frac{\mathrm{C_{SAAE}C_W}}{\mathrm{K_{eq}}}\right) \tag{6}$$

$$\mathrm{r_{AA}}=\frac{\mathrm{k_f}\left(\mathrm{C_{AA}C_{SL}}\text{-}\frac{\mathrm{C_{SAAE}C_W}}{\mathrm{K_{eq}}}\right)}{1+\mathrm{K_{AA}C_{AA}}+\mathrm{K_WC_W}} \tag{7}$$

$$r_{AA}=\frac{k_f\left(C_{AA}C_{SL}-\frac{C_{SAAE}C_W}{K_{eq}}\right)}{(1+K_{AA}C_{AA}+K_{SL}C_{SL}+K_{SAAE}C_{SAAE}+K_WC_W)^2} \tag{8}$$

where k_f is the forward rate constant, K_{eq} is the equilibrium constant obtained from the previous work [16], C_i is the concentration of component i, K_i is the adsorption constant for component i, the subscript of AA, SL, SAAE and W are azelaic acid, sorbitol, sorbitol azelaic acid ester and water respectively.

The kinetic models of PH, ER or LHHW were incorporated into the ordinary differential equations (ODE) derived from the mass balance equation of batch reactor. ODE solver in MATLAB, ode45 was then used to solve the ODE. The FMINCON function in the optimization toolbox of MATLAB was used to optimize the unknown kinetic parameters in the ODE while minimizing the objective function (the difference between the experimental and predicted conversion of AA). The model was evaluated based on the mean absolute relative error percentage between calculated concentration and experimental concentration (MAE) as shown in Eq. 9.

$$\mathrm{MAE}=\frac{\left|\sum \text{all data sample } \frac{X_{exp}-X_{calc}}{X_{exp}}\right|}{n_{sample}}\times 100\% \tag{9}$$

3. Results and discussion

3.1 Effect of temperature

The effect of reaction temperature was investigated by varying the temperature from 140°C to 220°C in the esterification. Reaction time, stirring speed and SL/AA molar ratio were fixed at 6 hours, 400 rpm and 3:1 respectively. Fig. 2 and Fig. 3 show that the AA conversion and initial reaction rate of AA increase with the reaction temperature. The AA conversion increased approximately 32.6% while the reaction rate increased 71.68% when the temperature rose from 140 °C to 220 °C. The collision between the reactants molecules becomes more violent at higher temperature, increasing the occurrence of collisions with sufficient energy to overcome the activation energy and initiate the reaction [17-18]. As consequence, higher AA conversion and initial rate of reaction can be obtained at an elevated temperature. Fig. 3 demonstrates that the initial rate of reaction increases averagely 40% with the temperature rise of 20°C. The rate of reaction was less sensitive to the reaction temperature, implying that the activation energy of AA esterified with SL reaction was low.

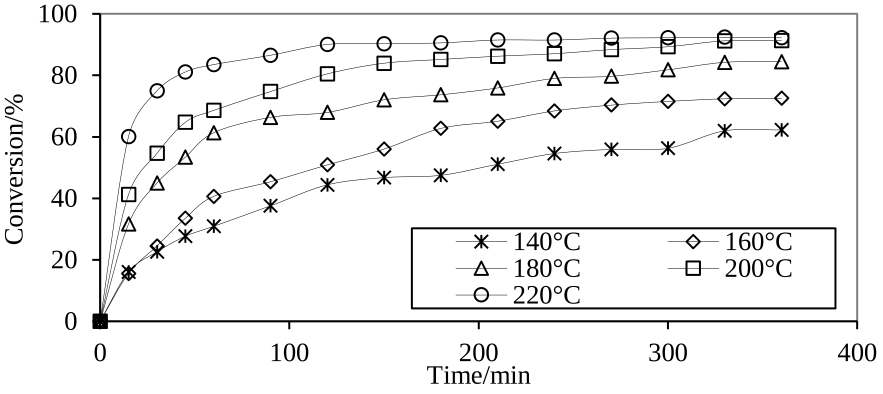


Figure 2. AA conversion profile for the reaction carried out for 6 hours at different reaction temperature. Reaction parameters: SL/AA molar ratio of 3:1, 0.5 wt% catalyst and stirring speed of 400rpm.

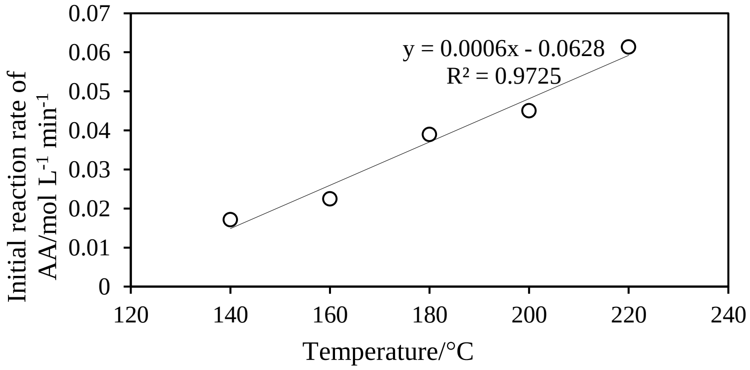


Figure 3. Initial reaction rate of AA at different temperature. Reaction parameters: SL/AA molar ratio of 3:1, 0.5 wt% catalyst and stirring speed of 400rpm

The reaction carried out at 200°C and 220°C achieved a similar AA conversion of about 92% after 6 hours of reaction. Despite the superior rate of reaction at 220°C, the product samples produced at 220°C was suffered with colour issues. Ideally, SAAE should be in transparent colour. A darker SAAE may be attributed to too high reaction temperature or impurities [19]. Fig. 4 compares the colour of the product samples produced at different reaction temperature with the Gardner colour scale. The colour of the product samples generated at reaction temperature of 220°C exceeded the Gardner scale laid between scales 1-18. Therefore, the reaction temperature of 200°C was chosen to be used in the subsequent experimental studies.

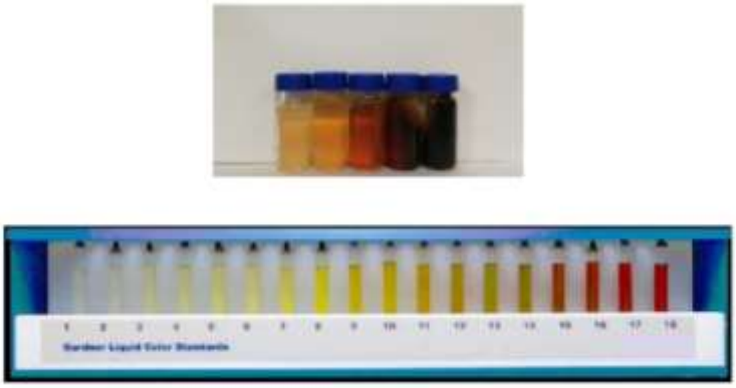


Figure 4. Colour of the product samples produced at different reaction temperature (from left 140°C, 160°C, 180°C, 200°C and 220°C) and Gardner scale model

3.2 Effect of molar ratio

The effect of SL/AA molar ratio was investigated by varying the molar ratio in excess SL (2:1, 3:1, 4:1, 5:1). The reaction was carried out for 6 hours at a reaction temperature of 200 °C, stirring speed of 400 rpm and catalyst loading of 0.5 wt%. Fig. 5 and Fig. 6 show that the AA conversion and initial rate of reaction carried out in the excess of SL.

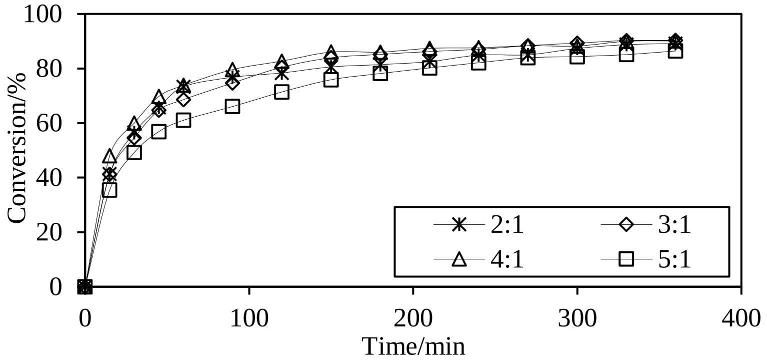


Figure 5. AA conversion profile for the reaction carried out for 6 hours at different SL/AA molar ratio. Reaction parameters: temperature of 200°C, 0.5 wt% catalyst and stirring speed of 400 rpm.

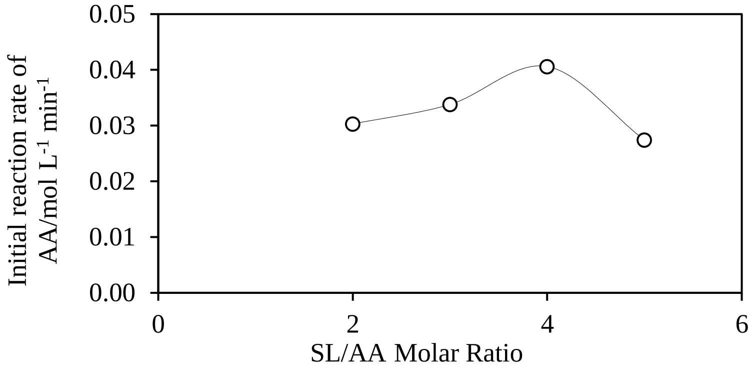


Figure 6. Initial reaction rate of AA at different SL/AA molar ratio. Reaction parameters: temperature of 200°C, 0.5 wt% catalyst and stirring speed of 400 rpm.

The reaction with the SL/AA molar ratio of 4:1 achieved an AA conversion of 80% within 1.5 hours. However, the duration required to achieve an identical AA conversion was doubled in the reaction carried out using SL/AA molar ratio of 2:1 because of its relatively low rate of reaction as shown in Fig. 6. The excess in SL could drive the esterification reaction equilibrium to product side [20-21] and hence expediting the reaction rate. Nevertheless, the higher conversion as anticipated based on Le Chatelier's Principle for the reaction with higher molar ratio of SL/AA, particularly for the SL/AA molar ratio of 5:1 was offset. The AA conversion and initial reaction rate at SL/AA molar ratio of 5:1 dropped to 86% and 0.0274 mol L^{-1} min^{-1} compared to 90% and 0.0406 mol L^{-1} min^{-1} at SL/AA molar ratio of 4:1. The hampering effect on AA conversion may be attributed to interruption of excess SL molecules to the access of AA molecules to the catalyst active sites. It is also worth to note that the reaction with over excessive of SL would require the more complex downstream separation processes which incur higher capital and maintenance costs [22]. Therefore, a SL/AA molar ratio of 4:1 was chosen in the following experimental studies to attain the effect of excess SL in increasing the rate of reaction and AA conversion.

3.3 Effect of catalyst loading

The esterification reaction of AA and SL at the best reaction temperature (200 °C), stirring speed (400 rpm) and SL/AA molar ratio (4:1) was carried out using 0 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt% of GeO_2 catalyst to verify the effect of catalyst. Fig. 7 reveals that the AA conversion increased by 25% in relative to the uncatalyzed reaction when 0.5 wt% GeO_2 was used to catalyze the reaction for 6 h. A further increase of the catalyst loading to 1.0wt% and 1.5 wt% resulted only negligible differences in the AA conversion achieved after 6 hours. In accordance to the findings of the AA conversion, AA initial rate of reaction shown on Fig. 8. The initial rate of reaction catalyzed by 0.5 wt% GeO_2 raised about 53% from 0.0186 mol L^{-1} min^{-1}, the initial rate obtained in the uncatalyzed reaction. However, the initial reaction rate started dropping when the catalyst loading increased to 1.0 wt% and 1.5 wt%, causing the initial rate of reaction of 0.0373 mol L^{-1} min^{-1} and 0.0346 mol L^{-1} min^{-1} respectively. The catalyst could accelerate the rate of reaction by lessening the activation energy. On the other hand, excessive catalyst would offset the advantages of the enhanced reaction rate by restricting the accessibility of the reactants to the active sites of catalysts [23-24]. The reaction catalyzed by 0.5 wt% of GeO_2 catalyst achieved the highest AA conversion of 90.10% and produced SAAE with the acid value of 11.82 mg of KOH/g of sample and Gardner colour grade of 17.

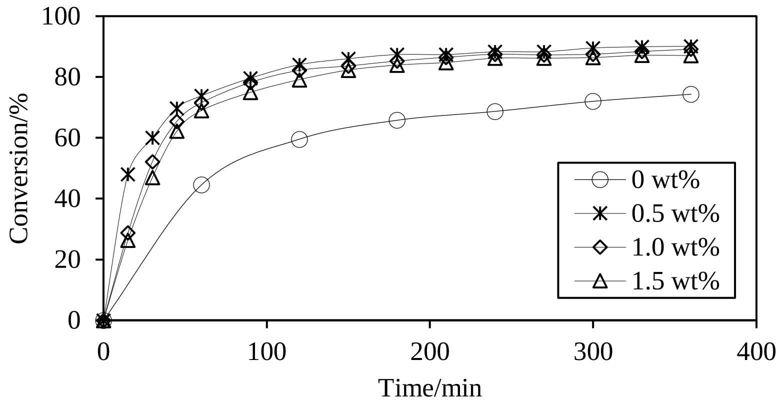


Figure 7. AA conversion profile for the reaction carried out for 6 hours at different catalyst loading. Reaction parameters: temperature of 200°C, SL/AA molar ratio of 4:1 and stirring speed of 400 rpm.

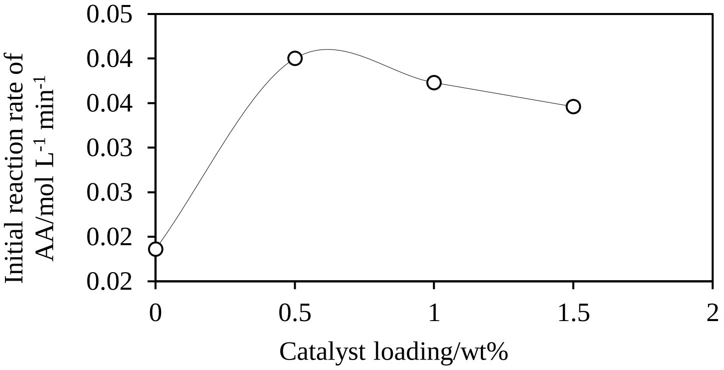


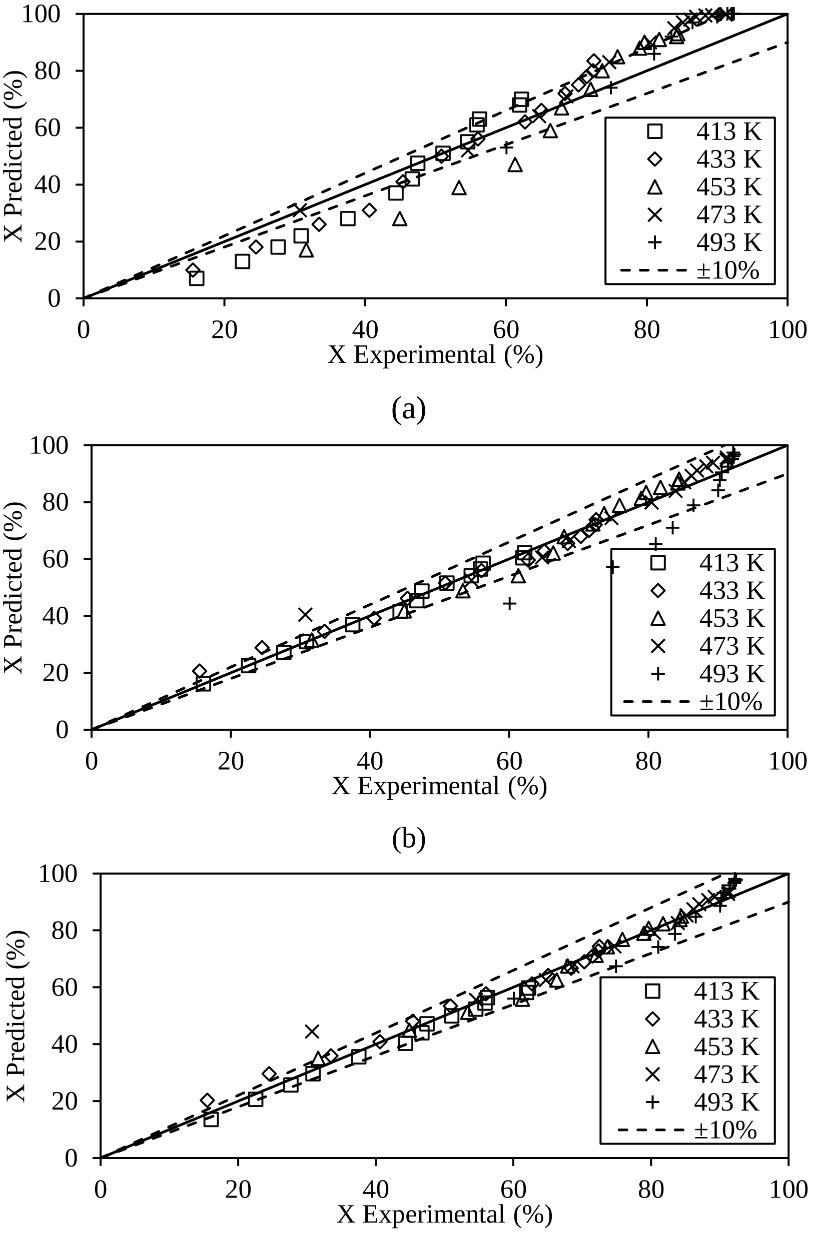
Figure 8. Initial reaction rate of AA at different catalyst loading. Reaction parameters: temperature of 200°C, SL/AA molar ratio of 4:1 and stirring speed of 400 rpm.

3.4 Kinetic modeling

The kinetic data obtained from the reaction study at various reaction temperatures was fitted with different kinetic models. Tab. 1 shows the kinetic parameters for each kinetic model while Fig. 9 demonstrates the parity plot comparing the experimental measured AA conversion and the predicted AA conversion. The data was best correlated to LHHW model as evidenced by the lowest mean absolute error (MAE) and a coefficient of determination, R^2 that was closest to one. An activation energy of 11.55 kJ/mol was determined through the Arrhenius plot shown in Fig. 10. The corresponding Arrhenius equation is given in Eq. 10.

$$k_f=6.49\times10^3\exp\left(-\frac{11554}{RT}\right) \tag{10}$$

A lower activation energy for the esterification reaction in the present study indicated the formation of SAAE was easier than the formation of sorbitol laureate though the esterification of SL with lauric acid catalysed by Para-Toluene Sulfonic Acid with activation energy of 50.8 kJ/mol [25].



(a)

(b)

(c)

Figure 9. Parity plot comparing the experimental measured X_{AA} with the predicted X_{AA} using (a) PH model, (b) ER model and (c) LHHW model.

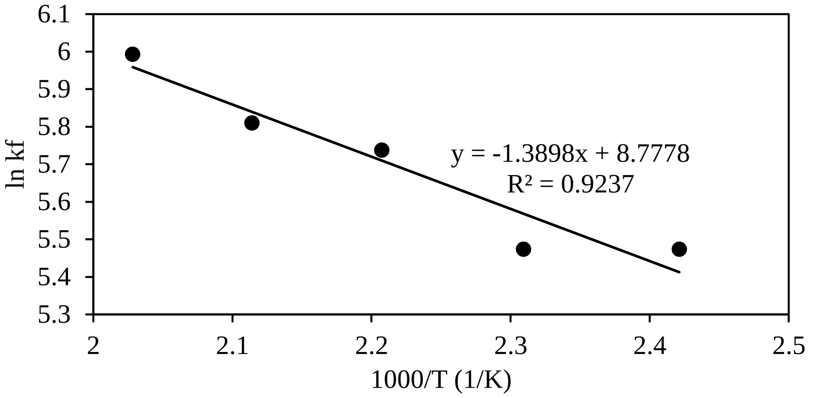


Figure 10. Arrhenius plot for the synthesis of SAAE at different reaction temperatures.

The esterification of SL with AA followed the LHHW mechanism in which the SL and AA molecules first chemisorbed on the side-by-side vacant active sites of the internal surface of GeO_2. The AA molecule then accepted proton from GeO_2. The protonated carbonyl group was then attacked by the adsorbed SL to form a surface tetrahedral intermediate which further decomposed to SAAE and water in adsorbed state. Finally, all the adsorbed molecules desorbed and the active sites were then unoccupied. Among all the chemical compounds, water has caused the highest adsorption equilibrium constant as shown in Tab. 1, implying that water is more prone to adsorption on the GeO_2 surface due to its higher polarity [26-28]. The adsorption constant as a function of temperature is shown in Eq. 11. The resulted ($-\Delta H_{is}$) for all the components as tabulated in Tab. 2 shows a typical adsorption process that released heat.

$$K_i=K_{iO}\exp\left(-\frac{\Delta H_{is}}{RT}\right) \tag{11}$$

where *i* is denoting *W, AA, SL* and *SAAE* and ($-\Delta H_{is}$) is the heat of adsorption.

Table 1. Kinetic parameters of the models used to fit experimental data.

Model	**Temperature (K)**	k_f **(L.mol^{-1} h^{-1})**	**MAE (%)**	K_{AA} **(L.mol^{-1})**	K_W **(L.mol^{-1})**	K_{SL} **(L.mol^{-1})**	K_{SA} **(L.mol^{-1})**	R^2
PH	413	0.03912	19.82	-	-	-	-	0.94
	433	0.06248	13.37	-	-	-	-	
	453	0.10965	16.42	-	-	-	-	
	473	0.25782	9.09	-	-	-	-	
	493	0.54609	8.12	-	-	-	-	
ER	413	19.02	1.65	12.26	801.03	-	-	0.97
	433	20.02	5.41	12.26	469.58	-	-	
	453	27.239	4.04	3.04×10^{-2}	294.76	-	-	
	473	29.353	5.03	1.66×10^{-4}	171.71	-	-	
	493	35.587	8.27	5.74×10^{-5}	164.22	-	-	
	413	238.28	4.98	15.97	80.22	0.993	5.36	0.99

LHHW	433	238.43	5.73	11.16	52.80	0.991	2.74
	453	310.47	2.45	4.51	48.51	0.500	1.68
	473	333.57	4.65	3.40	35.20	0.436	0.86
	493	400.71	4.64	1.64	28.40	0.331	0.44

Table 2. Heat of adsorption for all the components during the esterification of SL with AA.

Component i	***Heat of Adsorption, $-\Delta H_{is}$ (kJ mol^{-1})***
AA	-50.62
SL	-34.95
SAAE	-49.56
W	-17.27

4. Conclusion

The effect of reaction parameters on the esterification of SL and AA catalyzed by GeO_2 was investigated. The best operating condition for the process catalyzed by 0.5 wt% of GeO_2 was at reaction temperature of 200°C and SL/AA molar ratio of 4:1, achieving the highest AA conversion of 90.10%. The resultant SAAE product satisfied the specification of the polyester polyol for polyurethane production, with Gardner colour grade of 17 and acid value of 11.82 mg of KOH/g of sample. The esterification of SL with AA was well described by LHHW mechanism. The pre-exponential factor and activation energy were 6.49 x 10^3 L/mol.hr and 11.55 kJ/mol respectively.

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