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Screening of catalysts and operating conditions for the high yield production of isosorbide from sorbitol dehydration

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Abstract. Isosorbide (ISB), one of the important sorbitol (SL) anhydrides, can be produced through sequential intra-molecular dehydration of sorbitol derived from renewable biomass resources. Its rigid structure has granted the ISB a wide application in the polymer industries. Conventionally, acidic catalyst in liquid phase was used in the SL dehydration process. This homogeneous catalysed reaction gave low ISB yield and required additional downstream processes for catalyst separation. In the present study, a few types of catalysts were screened for sorbitol dehydration at a mild condition. Amberlyst 36 outperformed the other catalysts and resulted the highest SL anhydride selectivity of 86%. The effects of nitrogen purging and catalyst pre-treatment to the reaction performance were also investigated. The purging system did not significantly affect the SL conversion and selectivity of the desired products. The used of dried Amberlyst 36 exhibited a positive impact by increasing the SL conversion and SL anhydride selectivity to 67% and 98% respectively.

1. Introduction

The emerging of bio-based economy from petro-economy requires the use of biomass-derived chemicals as building blocks for the manufacturing of materials to maintain the standard of living. This worldwide trend attributes to the increasing industrial importance of sorbitol (SL) which was identified by US Department of Energy as one of the top sustainable carbohydrate based platform chemicals [1]. Isosorbide (ISB), one of the SL anhydrides is of equal importance to SL. The chiral centre and rigid molecular structure have caused the unique characteristics of ISB that enable its wide application in the industries of pharmaceutical, cosmetics, and polymer [2][3]. In particular for polyester production, the use of ISB as monomer can improve the glass transition temperature, transparency and mechanical performance of polyester products [4].

Sequential intra-molecular dehydration of SL produces several types of sorbitan (SN) and ISB [5]. The previous studies discovered that 1,4 sorbitan (SN) and ISB are the major products during SL dehydration while the other components are in traces amount [6][7]. The SL dehydration process requires an acidic catalyst to increase the reactivity of the SL molecule. A strong acidic catalyst is preferable in comparison to the weak acidic catalyst to avoid the formation of unwanted by-products like coke and humins [8-10].



Traditionally, strong mineral acid (HCl , H_2SO_4 and H_3PO_4) and organic acid (p-toluene sulfonic acid) are widely used in the industry for dehydration due to its high activity [11-13]. The batch-wise SL dehydration processes were carried out under normal atmospheric pressure, elevated pressure, and microwave assisted condition using sulphuric acid (H_2SO_4) as catalyst. A considerably high yield of ISB was recorded as 77%, 90%, and 80% for the respective process [11][14][15]. In spite of this, the use of H_2SO_4 gives rise to the severe drawbacks such as equipment corrosion and additional downstream separation processes which may add extra capital and operating cost [13][16]. This recurring problem has geared the dehydration catalysis towards a green and sustainable heterogeneous catalytic system.

Many solid acidic catalysts (zeolite, metal phosphate, tungstophosphoric acid supported on metal oxides, sulphated metal, and sulfonic acid resin) have been adopted in the SL dehydration for ISB synthesis [1][4][8][14-21]. Among these catalysts, the SL dehydration catalysed by zeolite attained the highest ISB yield (81%) under mild operating conditions. Nevertheless, the pronounced performance of zeolite was achieved at the expense of high catalyst loading that causing industrial impracticability [22]. In addition, zeolite type catalyst also deactivated due to the structure distortion during the reaction [23]. Comparatively, sulfonic acid resins (Purolite CT269, P-SO₃H, and Amberlyst 35) were proven as the more stable catalyst that could give equally high SL conversion and ISB yield during the SL dehydration process [14][15][17]. Alternatively, a substantial amount of Bronsted acid sites required by the SL dehydration can also be provided by the sulfonic acid resin [2].

In the present work, Amberlyst 36 (AM 36) was evaluated as a catalyst for dehydration of SL to ISB using batch reactor at mild conditions. The effect of nitrogen purging and catalyst pretreatment were investigated.

2. Materials and methods

2.1. Chemicals

Sorbitol (97%, Aldrich) and Amberlyst 36 (Acros) were the reactant and catalyst respectively for the dehydration reaction, whereas isosorbide (Dianhydro-D-Glucitol, 98%, Santa Cruz) and 1,4 sorbitan (1,4-anhydro-D-Sorbitol, 97%, TRC) were used as the standard for gas chromatography (GC) analysis. Pyridine (99.5%, Merck), Chlorotrimethylsilane (99%, Merck) and 1,1,1,3,3,3 hexamethyldisilazane (98%, Merck) were used to pre-treat samples through silylation for gas chromatography analysis. All these chemicals were used as received without further purifications.

2.2 Sorbitol dehydration reaction

The sorbitol (SL) dehydration experimental studies were performed in a 500 ml 3-necked round bottom flask placed in a rotamantle equipped with temperature controller as shown in Figure 1. The flask was connected to a Liebig condenser circulated with hot oil (110 °C) to condense SL. The Liebig condenser was connected to a Dean-Stark apparatus attached with Graham condenser to condense the water vapour formed during the reaction. SL was first melted in the flask before it was further heated up to the desired reaction temperature. Then the catalyst was introduced to start the reaction. Throughout the reaction duration, samples were withdrawn at desired time interval. Prior to storage and GC analysis, the samples were cooled in the ice bath to cease the reaction. All experimental were repeated twice to ensure the reproducibility

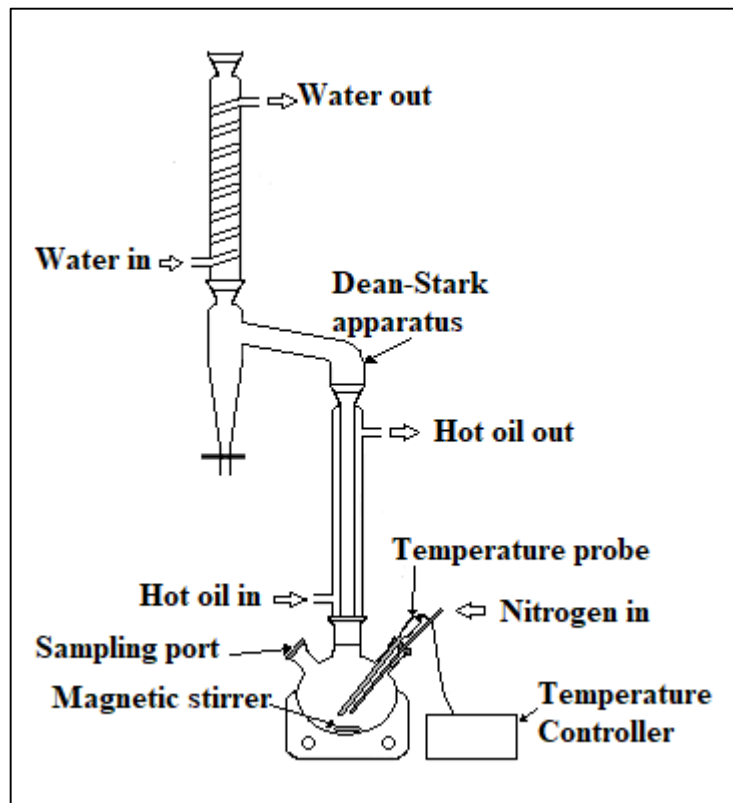


Figure 1: Experimental setup for SL dehydration

2.3 Gas chromatography analysis

The sample comprised of SL, 1,4 sorbitan (ST) and isosorbide (ISB) were analysed using gas chromatography equipped with flame ionisation detector GC-FID. The sample was pre-treated using silylation method to increase its volatility before GC analysis. 50 mg of sample was diluted in 3 ml of pyridine. Under vigorous stirring, 0.4 ml of hexamethyldisilazane and 0.3 ml of chlorotrimethylsilane were added consecutively. The sample was stirred for 30 sec before it was left for 15 minutes to complete the reaction. All samples were filtered and injected into GC-FID installed with CP-TAP column (25 m length x 0.25 mm i.d. x 0.1 μ m film thickness). The oven temperature was ramped at 8 $^{\circ}$ C/min from 100 $^{\circ}$ C to 350 $^{\circ}$ C, holding time of 7 min with carrier gas flow rate of 0.1 ml/min. Whereas, the detector and injector temperature were set at 250 $^{\circ}$ C and 380 $^{\circ}$ C respectively. The split ratio was 10:1 and the carrier gas was helium.

The SL conversion, ST yield, ISB yield, and SL anhydride selectivity were calculated using equation (1) to (4) respectively.

$$\text{SL conversion} = \frac{\text{mol SL}_i - \text{mol SL}_t}{\text{mol SL}_i} \times 100 \quad (1)$$

$$\text{ST yield} = \frac{\text{mol ST}_t}{\text{mol SL}_i} \times 100 \quad (2)$$

$$\text{ISB yield} = \frac{\text{mol ISB}_t}{\text{mol SL}_i} \times 100 \quad (3)$$

$$\text{SL anhydride selectivity} = \frac{\text{ST}_i \text{ yield} + \text{ISB}_i \text{ yield}}{\text{SL}_i \text{ conversion}} \quad (4)$$

where i is initial and t is a certain time instant.

3. Results and discussion

3.1 Catalyst screening

A blank run was performed for the non-catalysed SL dehydration at 140 °C for 4 hours. No SL conversion was detected, supporting the necessity of using catalyst to activate the hydroxyl molecules in the SL before it could dehydrate. This finding was in line with the outcome of the blank run carried out by Cubo et al. [24] at 150 °C for 24 h. Metal and resin based catalysts were screened in the present study. Despite the drawbacks of homogeneous catalyst, sulphuric acid was used to catalyse the SL dehydration for the comparison of its catalytic activity with heterogeneous catalysts. As anticipated, sulphuric acid shows outstanding activity as indicated by the highest SL conversion attained (>99%) in Figure 2. Nevertheless, the selectivity of the SL anhydrides like ST and ISB was only 30% in the SL dehydration catalysed by sulphuric acid. The corresponding yield of ST and ISB were 4% and 26% respectively. More than 60% of the converted SL has turned to the side product humins that causes the unwanted dark brown colour of final product. The extremely fast exothermic reaction attributed to the sulphuric acid has led to the unwanted carbonization. Among all the heterogeneous catalysts, AM 36 has shown its superior activity in catalysing the SL dehydration, validating the preference of Bronsted type of acidic catalyst in SL dehydration [25]. Although the SL conversion attained was only approximately 36%, the selectivity of SL anhydrides was 86%.

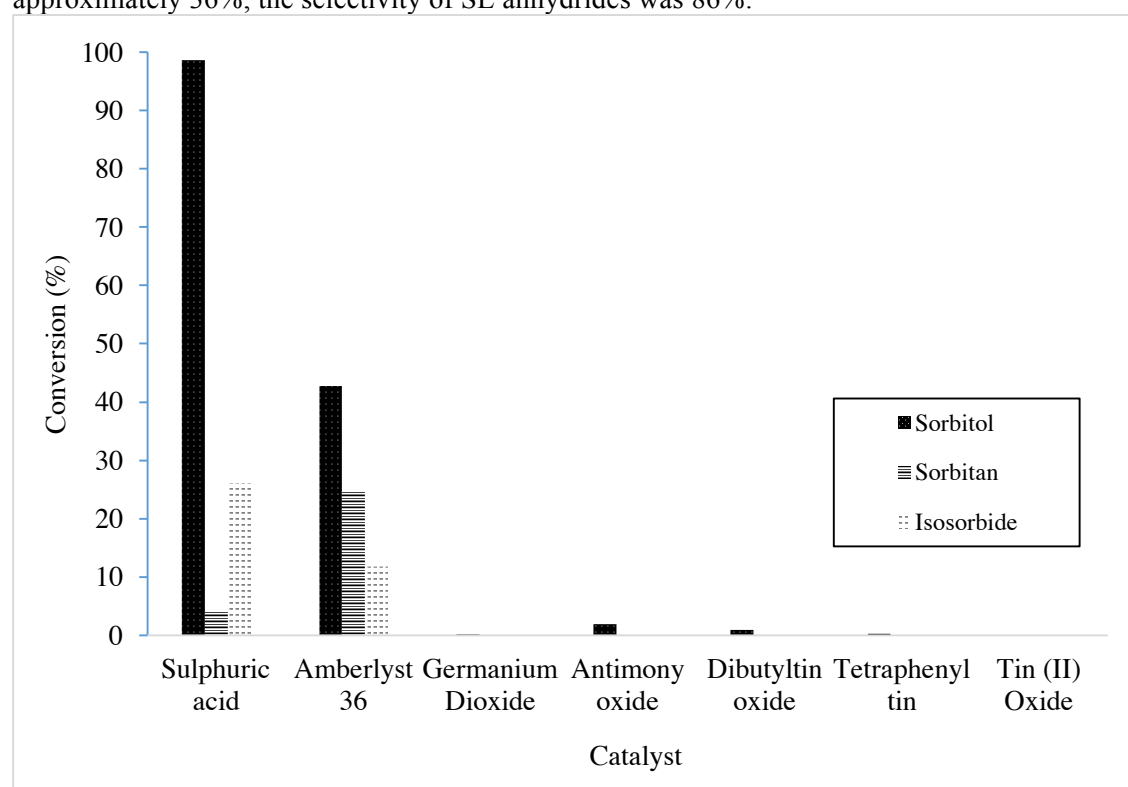


Figure 2. Catalyst screening for the SL dehydration at stirring speed of 300 rpm, temperature of 140 °C and catalyst loading of 1 wt% for 4 h.

3.2 Effect of nitrogen purging

The present work carried out the SL dehydration with and without continuous purging of nitrogen (N₂). It was reported that N₂ could displace oxygen in the reaction mixture to minimize the occurrence of side reactions including polymerisation of SL and its anhydrides [12][23][17][18][25]. In addition, the continuous N₂ purging is also expected to help in removing the water during the reaction in order to increase the conversion. Contrary to the literature, Figure 3 shows that the reaction performance of SL dehydration without N₂ flow was identical to the one achieved in the reaction with N₂ flow for 4 h. The

polymerisation of SL anhydrides was negligible as evidenced by the SL anhydride selectivity near 100% with ISB selectivity of 44% (as shown in Figure 4) in the reaction without N₂ purging. Considering the insignificant effect of N₂ purging to the reaction performance, SL dehydration in the subsequent studies was carried out without continuous flow of N₂.

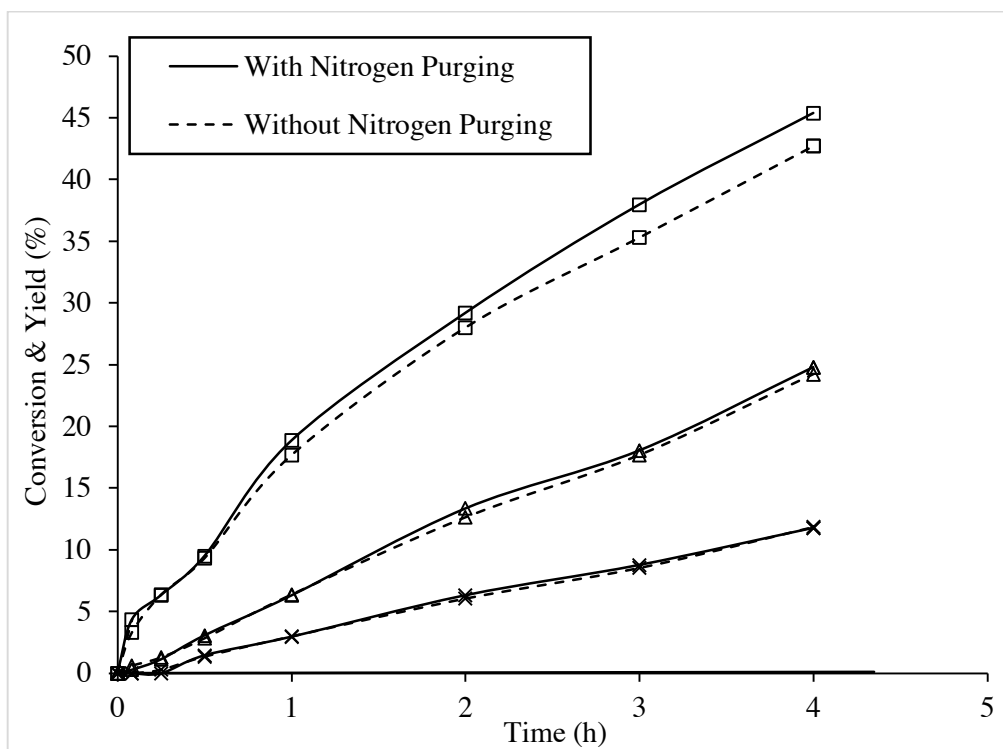


Figure 3. SL dehydration at stirring speed of 300 rpm, temperature of 140 °C, catalyst loading (AM 36) of 1 wt% and reaction time of 4 h with and without nitrogen purging system. (□) SL conversion, (Δ) ST yield and (x) ISB yield.

3.3 Catalyst pre-treatment

The raw AM 36 contains large amount of water. Typically, a simple drying process is required to remove water that could form hydrated protons ($\text{H}_3\text{O}^+-\text{SO}_3^-$) with the sulfonic acid group to prevent SL molecules from accessing the active sites [13]. As displayed in Figure 4, the SL conversion attained in the SL dehydration catalysed by pre-treated AM 36 is 20% higher than the one obtained in the reaction using untreated AM 36 as catalyst. In addition, the selectivity of SL anhydrides was also increased from 86% to 98% when the catalyst was dried before it was being used. The water presents in the un-pretreated AM36 can act as Lewis acid due to a lone pair of electrons in the water molecules. These Lewis acid sites were proven to give lower ISB selectivity in comparison to Bronsted acid catalyst in the SL dehydration reaction [13][18].

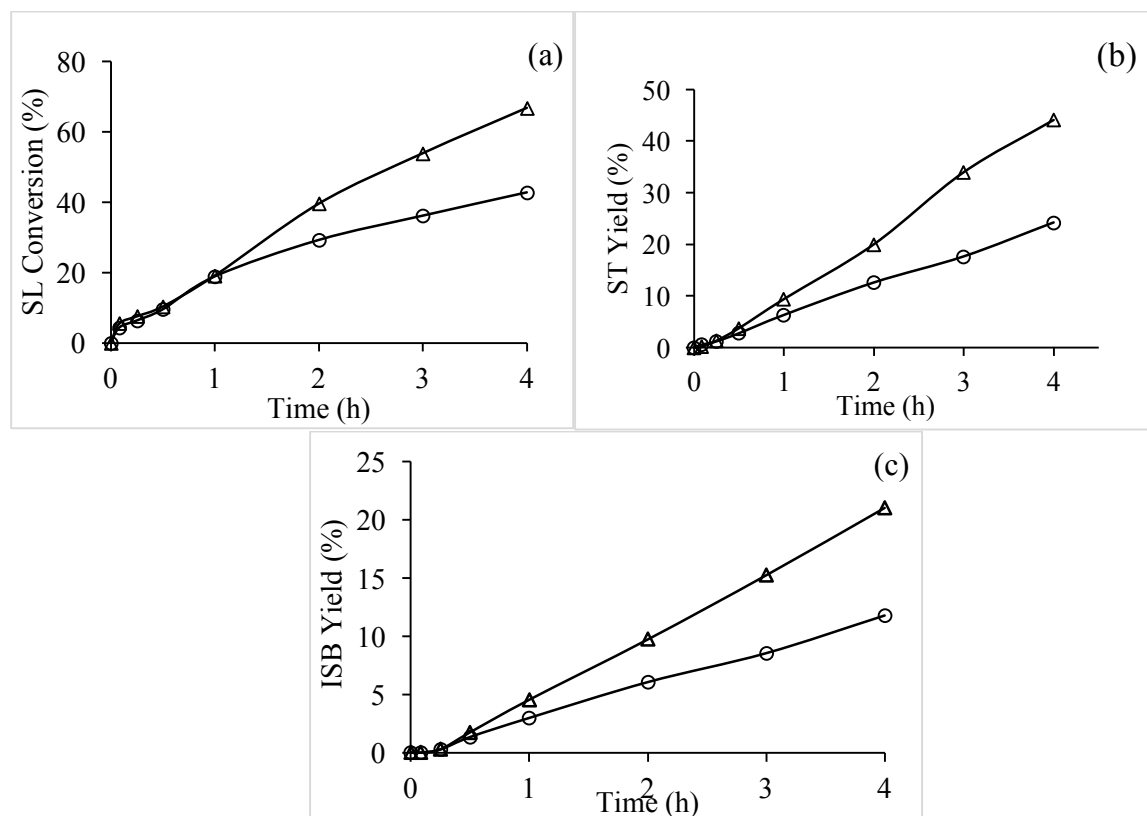


Figure 4. SL dehydration catalyzed by un-pretreated and pretreated AM 36 at the stirring speed of 300 rpm, temperature of 140 °C, catalyst loading of 1 wt% and reaction time of 4h. (Δ) Pre-treatment, (○) without pre-treatment.

4. Conclusion

High SL conversion and SL anhydride selectivity were achieved in the SL dehydration catalysed by AM 36 under a mild operating condition. Maximum SL conversion of 67% was attained with the corresponding SL anhydride selectivity of 98% in the reaction catalysed by 1 wt% of catalyst under the reaction temperature of 140°C and the stirring speed of 300 rpm for 4 h. The continuous nitrogen purging throughout the process was confirmed not affecting the reaction performance. On the other hand, the use of pre-treated AM 36 was proven to increase the SL conversion for approximately 56% with a resultant SL anhydride selectivity of nearly 100%. The positive impact of using the dried AM 36 was attributed to the absence of water molecules that acted as the obstacles to prevent SL from accessing the active sites and Lewis acid that promoted other side reactions rather than ISB formation.

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