

# **UNIVERSITY OF TWENTE.**

Faculty of Science and Technology

# Reaction pathways in the dehydration of propyleneglycol over scandium oxide catalyst

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### Preface

This report constitutes the MSc thesis of Dennis Tjeerdsma in the degree of Chemical Engineering at the University of Twente. The project was performed from May 2019 - April 2020. The project constitutes 45 ECTS credits and was carried out within the Catalytic Processes and Materials group at the University of Twente.

The project was executed under the supervision of dr. J.A. Faria and prof.dr.J.P.Lange. I wish to thank them for their support during this project. This project was completed in thanks due to their feedback and guidance. The assignment was made possible partly due to the work previously performed under the guidance of J.P.Lange. It was also made possible for me to show my work at NCCC 2020 through a poster, for which I am grateful.

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### Abstract

Biomass based chemicals are increasingly seen as an environmentally friendlier alternative to fossil fuels. As a result, propane polyols are becoming more widely available thanks to the deployment of bio-diesel plants. Propyleneglycol is a valuable chemical that can be upgraded by performing a dehydration to allyl alcohol and a subsequent oxidation reaction to acrylic acid. This route requires both catalyst and process optimization before coming industrially viable due to the limited yields achieved. The present research aims to develop a catalyst capable of reaching the selectivity and productivity required of an industrial catalyst.

This research studied the dehydration of propyleneglycol over scandium oxide catalysts based on the excellent selectivity shown in the similar 2,3-butanediol dehydration reaction. A continuous Plug Flow Reactor was used to study the kinetics and behavior of the system. Samples were analyzed using HPLC to determine the concentration of products in the liquid sample.

Our results show that under similar reaction conditions, the dehydration of propyleneglycol behaves significantly different when compared to 2,3-butanediol. Results suggest that the selectivity towards the unsaturated alcohol was lower for the propyleneglycol dehydration. It was determined that the dehydration towards the dehydration products follows first order behavior. The apparent activation barriers towards the main dehydration products were measured to be approximately 115kJ/mol. Significant selectivity to byproducts was measured over the scandium oxide catalyst. This study speculates on the fundamental reason for the discrepancy between dehydration reactions. It was calculated that the kinetic constant towards Propionaldehyde/Propanal was the highest with  $2.87\pm0.22s^{-1}$ .

Evaluation of the studied system reveals that the scandium oxide catalyst is not applicable in an industrial system. Additional work is required on improving the selectivity and reducing the total cost of the catalyst. The introduction of a support is an interesting area for further research. In addition, the fundamental difference between 2,3-butanediol and propyleneglycol remains speculation. An overview of the reported data is presented in Figure 1.



Figure 1: Overview of experimental data obtained in the present research (black squares) and highest reported value by Pramod et al.[1] (red triangles). Conversion - Yield parity line presented by black dotted line, selectivity target by blue dotted line

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#### Abbreviations

- **AA** Allyl Alcohol
- AC Acetone
- AcrA Acrylic acid
- 2,3-BDO 2,3-Butanediol
- °C Centigrade
- HAC Hydroxyacetone
- MEK Methyl Ethyl Ketone
- MFC Mass Flow Controller
- MPV Meerwein-Ponndorf-Verley
- $\mathbf{N}_2$  nitrogen
- PAL Propionaldehyde/Propanal
- PFD Process Flow Diagram
- PG Propyleneglycol
- POL 1-Propanol
- p.p. Percentage Point
- REO Rare Earth Oxide
- $\mathbf{Sc}_2\mathbf{O}_3$  scandium oxide
- TOS Time On Stream

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#### Chapter 1

## Introduction

In the current material driven world, oil is an important feedstock for a lot of monomer reactants, bulk and fine chemicals [2]. The value of these chemicals fluctuates with the crude oil price[2]. Together with environmental concerns and the energy transition, considerable research is being done to provide more sustainable feedstocks for these chemicals. Conventional petrochemical routes are considered to be unsustainable due to the dwindling supply of oil and environmental concerns. Alternative sources of energy have become more widely available in the form of solar, wind, hydro and geothermal power. Chemicals are another matter as biomass based processes are often unable to compete with conventional petroleum based processes. An increase in bio-based bulk and fine chemicals is essential due to declining carbon resources [3]. The selective valorization of bio-mass waste and residue to high value chemicals is a complex step due to the diverse amount of waste streams available. Typical waste streams consist of a mixture of these chemicals and thus make selective upgrading challenging. 12 platform molecules have been identified as molecules that could be valorized to high value chemicals derived from biomass [4].

 $CH_2 = CH - CH_3 + O_2 \xrightarrow{Catalyst} CH_2 = CH - CHO + H_2O$ Propylene Acrolein

$$CH_2 = CH - CHO + 1/2 O_2 \xrightarrow{Catalyst} CH_2 = CH - COOH$$
  
Acrylic Acid

Figure 1.1: Reaction scheme of propylene oxidation to AcrA[5]

AcrA is a high value chemical primarily used in the production of acrylates. Additionally, the polymerized structure of AcrA is increasingly used in flocculants and dispersants [6]. A derivative of AcrA, acrylic esters, are often found in paints, coatings, adhesives and binders [6]. AcrA is seen as a potentially favorable chemical due to the large market of AcrA (8Mt  $a^{-1}$ ) and high price (1600\$ - 2200\$ per ton) [2]. The main pathway for producing high grade AcrA is the oxidation of propene [6–8]. This reaction can be performed by applying a one or

two step process. The two step process typically has higher selectivity and conversion than the one step process [6]. The production of allylic compounds is one of the main industrial applications of propene [9]. The reaction scheme of propylene oxidation is presented in Figure 1.1.

Biobased processes to produce AcrA typically use fermentation or biomass-derived reactants [6]. One of the major pathways for producing AcrA is the formation of AcrA from glycerol. This requires a dehydration step, subsequently followed by an oxidation step [10]. The direct one step conversion of glycerol to AcrA results in low yields [11]. The two major pathways that have recently been studied are the dehydration of glycerol to acrolein and the deoxydehydration to AA [12]. The pathway through AA shows a high yield of 94.5% and the subsequent oxidation step to AcrA an equally promising yield of 92% [11].

One source of environmentally friendly chemicals might be biomass based chemicals [13]. Biodiesel is a potential alternate feedstock for fuels and bio-based chemicals. Biodiesel is mostly produced from vegetable oils and animal fats [14]. A primary alcohol is needed to perform the transesterification and esterification reactions required to produce biodiesel [14]. After the acid reactor, several separation steps are employed to separate the ester and glycerol. This separation is based on the density difference between the product ester and glycerol [14]. A mixture of polyols is produced as a byproduct in the production of biodiesel.[15]. These polyols are potential feedstocks for the valorization of high value chemicals. PG is one of the main by-products in the biodiesel production[14].

Another route through which PG can be produced is the hydrogenolysis of glucose [16, 17]. To produce this glucose, biomass sources such as starch[18, 19] and cellulose[20] are first converted to glucose. The conversion of starch or cellulose to glucose is essentially reducing the molecules into its chemical building blocks. The bonds between the monomers are cleaved, often using a  $H_2$  cofeed to saturate the bonds. The conversion of glucose to polyols is one step further in the hydrogenolysis reaction scheme. Continuing to supply  $H_2$  will further cleave the carbon bonds in the molecule, producing a mixture of alkanediols that can be valorized to high value chemicals.

AA can be produced through a variety of routes. Traditionally, AA is produced through hydrolysis of allyl chloride. Another industrially used route is the rearrangement of propyleneoxide to AA. Recently more sustainable routes have been investigated. A promising route seems to be the deoxydehydration of glycerol to AA. The reaction scheme for this route is presented in Figure 1.2.



Figure 1.2: Reaction scheme for the deoxydehydration of AcrA to AA[11]

This research investigates a recently discovered route of producing AA from PG. The production of AcrA from PG can be done through two different routes. One of the potential pathways is the oxidation of PG to lactic acid. The lactic acid is consecutively dehydrated to

produce AcrA. The second route switches the reaction steps, first dehydrating PG to AA and consecutively oxidizing to produce AcrA. Pramod et al. have studied the dehydration of PG to AA over K-doped  $ZrO_2$  catalyst. This research shows promising results with a 32% yield to AA[1]. In their research, Pramod et al. essentially destroy the acid sites on the surface by doping the catalyst in potassium. The surface character of the catalyst is now basic, killing

This research expands on the work of Pramod et al. by investigating the dehydration of PG over  $Sc_2O_3$  catalyst. The surface of this catalyst is not modified, so potentially more byproducts will be formed while performing this reaction.  $Sc_2O_3$  previously has shown high selectivity towards unsaturated alcohols. An example is the dehydration of 2,3-BDO to 3-buten-2-ol [21]. This research will investigate the reaction schemes occurring in the dehydration including consecutive reactions to heavy products, acetalization, ketonization and aldol condensation products.

all acid catalyzed reactions conventionally performed over the catalyst.

#### Chapter 2

# **Literature Review**

The valorization of PG to high value chemicals is an interesting study due to the increasing production of bio-diesel. This chapter will describe the relevant literature pertaining to the present research. PG dehydration to AA has only been studied by Pramod et al. [1]. The dehydration of PG to PAL is a more common research topic and will serve as the theoretical basis of this research combined with the dehydration of diols over Rare Earth Oxide (REO) catalysts. Main topics of this review will be the acid catalyzed dehydration of PG, the base catalyzed dehydration of PG, the acid catalyzed dehydration of related diols, the base catalyzed dehydration of related diols and the properties and structure of REO catalysts.

#### 2.1 Propyleneglycol dehydration

The dehydration of PG to PAL has been repeatedly studied by various authors. The reaction equation for this dehydration is simple. A water molecule is removed from the molecule by removing a hydroxide and hydrogen group from the molecule. A double bond is formed to stabilize the molecule. This dehydration reaction can have several products. One of the main products produced in current research is PAL [22]. A byproduct of this dehydration reaction is AC[22]. Acetalization and aldol retro addition can form heavier products under longer residence times and higher temperatures [1, 23]. An overview of the reactions observed in current literature is presented in Figure 4.19. At normal conditions (T = 298.15K, P = 1atm)  $H_2O$ , PG, AA, PAL and AC are all liquids.

The desired dehydration reaction is the dehydration of PG to AA. It is known that the dehydration of PG to PAL and AC occurs over acid sites [24]. The active sites for the dehydration to AA have not been investigated at this time.

#### 2.1.1 Acid catalyzed mechanisms

PAL and AC are the main side products produced in the dehydration of PG and are mainly produced over the acidic sites on the surface of the catalyst. In these reactions, a diol is converted into an aldehyde and ketone respectively. An aldehyde has a double bonded oxygen group on a terminal carbon atom while a ketone has a double bonded oxygen atom

on a non terminal carbon. The acid sites primarily used in this reaction are the Brønsted acid sites on the surface of the catalyst [22, 24, 25]. The reactions are given in the reaction equations below.



Figure 2.1: Reaction equation of PG dehydration to PAL



Figure 2.2: Reaction equation of PG dehydration to AC

As discussed before, these reactions primarily take place over the Brønsted acid sites on the catalyst. Zhang et al. have studied the reaction mechanism of these dehydration reactions over zeolite based catalysts and found a probable reaction mechanism for the dehydration of PG to PAL and AC. The mechanism proposed by Zhang et al. is presented in Figure 2.3.



Figure 2.3: Acid catalyzed dehydration mechanism of 1,2-propanediol [24]

In the proposed mechanism, the reactant molecule is first adsorbed to the surface of the catalyst. This dehydration mechanism is determined to be an E1 elimination scheme[24, 26]. One of the hydroxide groups is protonated by the hydrogen atom on the Brønsted acid site. A stable leaving group is created on the protonated hydroxide group. Water leaves the molecule producing a molecule with a carbenium ion on the corresponding carbon atom. A carbenium ion is characterized by its lack of electrons, creating an overall positive charge on the carbon atom. Due to the position of the hydroxide groups, 2 intermediates can be formed. In the first intermediate, the carbonium ion is positioned at a terminal carbon atom.

The second intermediate has the carbenium ion in the middle of the chain. Carbenium ions are stabilized by surrounding carbon groups donating part of their electron cloud to the carbenium ion, decreasing the electron positive charge of the ion. The molecule can rearrange itself to a more stable form, by rearranging the position of the hydroxide group and a hydrogen molecule. Depending on the position of the carbenium ion, the reaction further proceeds to produce AC or PAL. A hydride shift is performed to stabilize the carbon atom, at the same time the hydrogen atom leaves the hydroxide group regenerating the Brønsted acid site. A double bond is formed between the remaining oxygen atom and the corresponding carbon atom. The stable molecule desorbes from the catalyst surface.

Figure 2.3 shows the possibility of a rearrangement to a third intermediate. This intermediate results in the production of AA, and starts from 1,3-propanediol instead of PG. This rearrangement is unlikely to occur as a result of the rearrangement being a less stable molecule. However, with sufficient thermal energy input, reaction and rearrangement speed can be fast enough to produce AA using this mechanism [24].

Direct dehydration to PAL and AC are not the only reactions catalyzed by the acid sites on the catalyst surface. Zhang et al. have proposed a mechanism for the production of 2-ethyl-4-methyl-1,3-dioxolane [24].



Figure 2.4: Acid catalyzed mechanism to 2-ethyl-4-methyl-1,3-dioxolane[24]

The acid catalyzed reaction to 2-ethyl-4-methyl-1,3-dioxolane proceeds over the same Brønsted acid sites as the acid catalyzed dehydration reactions [24]. In this mechanism the hydrogen from the Brønsted acid site protonates the double bonded oxygen on the PAL molecule. The oxygen becomes positively charged and will take back one of the electrons shared in the double bond. At the same time, PG approaches on the other side of the molecule, donating one of its hydrogen atoms to regenerate the active site on the catalyst. The oxygen from which the hydrogen is donated, bonds to the carbon atom attached to the new hydroxide group. The hydroxide group is protonated to form water, a stable leaving group. After water leaves the molecule, the oxygen connecting the molecules forms a double bond with the PAL side of the molecule. This oxygen is now positively charged due to sharing electrons over too many bonds. The second hydroxide group on PG donates its hydrogen to regenerate the active site and takes one of the bonds from the positively charged oxygen.

It is investigated that the production of POL is produced over the same Brønsted acid sites as the dehydration and retro aldol condensation reactions [24, 27]. Peng et al. have tested the production of POL from PG over ZrNbO catalysts using various reactant and H-donor ratios. Using these experiments, the mechanism in Figure 2.5 was proposed.



M = Nb or Zr  $R_1, R_2 = Organic functional group$ 

Figure 2.5: Acid catalyzed conversion of PG to POL [27]

The first stage presented in this mechanism is the same as the dehydration mechanism to PAL in Figure 2.3. The proposed mechanism is a ligand exchange mechanism activating the carbonyl group on the molecule binding it to the metal surface of the catalyst. A hydride transfer takes place between the two molecules on the surface of the catalyst forming POL and Hydroxyacetone (HAC).

To summarize, the acid catalyzed mechanisms primarily proceed over Brønsted acid sites on the surface of the catalyst. These Brønsted acid sites protonate the hydroxide groups on the molecules to create a stable leaving group (water). A double bond is formed after the hydrogen is regenerated from a  $\alpha$ -hydrogen on the molecule.

#### **MPV** reduction

The Meerwein-Ponndorf-Verley (MPV) reduction reaction is a reaction mechanism in which aldehydes and ketones are reduced to their corresponding alcohols. This reaction requires a ketone or aldehyde to protonate the double bonded oxygen in the aforementioned molecules. Additionally, a hydrogen donor is required to donate the hydrogen to the aldehyde or ketone. This reaction is essentially a hydride transfer between two molecules. There have been several discussed pathways for the MPV reduction reaction. It is commonly agreed that the most likely pathway is the direct route [28]. An example of the mechanism is presented in Figure 2.6, this mechanism works for any aldehyde or ketone molecule by substituting the R1 and R2 rest groups with the appropriate carbon chains [29].



Figure 2.6: MPV reduction mechanism over ZrO<sub>2</sub> catalyst [29]

Maresz et al. describe the MPV mechanism over catalysts with zirconia, alumina, magnesium and boron active species [29]. In this mechanism, the carbonyl group acts as a hydrogen acceptor and the alcohol as a hydrogen donor. In the case of a primary alcohol, the corresponding unsaturated alcohol will be formed. The production of unsaturated alcohols is one of the main applications of the MPV reduction reaction [30]. The mechanism shows the coordination of the reactants on the same Lewis acid site. After adsorption, a sixmembered transition state ring is formed to shift the hydrogen. The formation of this ring is considered to be the rate limiting step. The hydrogen transfer is followed by the destruction of the base sites on the surface actively participate in the MPV reduction reaction [30, 31]. Komanoya et al. observed that the activity of this reaction is significantly enhanced by the close presence of the base sites on the surface of the ZrO<sub>2</sub> catalyst. The surface of the Sc<sub>2</sub>O<sub>3</sub> catalyst used in the present research is discussed extensively in section 2.3.2. In summary, Sc<sub>2</sub>O<sub>3</sub> has similar Lewis acid and base sites in close proximity, potentially allowing the MPV reduction reaction to proceed over the studied catalyst.

The mechanism described above can be applied to the aldehyde and ketone in the present research. This will lead to the corresponding reduced primary alcohol. The hydrogen donor in this system is PG, with two hydroxide groups that can donate their hydrogen to the aldehyde or ketone. One PG molecule undergoing MPV reduction twice seems unlikely as the resulting molecule, with two double bonded oxygen atoms, will be highly reactive and unstable. The reactions schemes with possible products are given in Figure 2.7 and Figure 2.8. In the case of PAL, HAC and POL are produced in a molar ratio of approximately 1:1. Similarly to PAL, 2-propanol and HAC will be produced in a 1:1 molar ratio in the MPV reduction reaction.



Figure 2.7: MPV reduction scheme for PAL with PG, hydride transfer by the secondary hydroxide



Figure 2.8: MPV reduction scheme for AC with PG, hydride transfer by the secondary hydroxide

In the Figures above, the secondary hydroxide group is used to illustrate the MPV reaction in the presently studied system. The primary hydroxide group can also provide the proton for the hydride transfer, resulting in the production of the corresponding alcohol in combination with lactaldehyde. No distinction can be made between HAC and lactaldehyde on the HPLC. For this research, HAC is considered to be the primary pathway.

#### 2.1.2 Base catalyzed mechanisms

Base catalyzed reactions of PG are fewer in number and are typically less active than their acid counterparts [32]. The only observed base catalyzed reaction is the dehydration of PG to AA by Pramod et al.[1]. In their paper they mention the etherification of PG. However, no evidence is provided for the formation of 2-(2-Hydroxypropoxy)-1-propanol. The reaction equation is presented in Figure 2.9.



Figure 2.9: Reaction equation of PG dehydration to AA

The dehydration mechanisms over base catalysts are known as E1cB elimination reactions[33]. In the E1cB reaction mechanism an acidic hydrogen on the molecule is bound to the base group on the catalyst [33]. This creates an anion, forcing the hydroxide group to leave the molecule. This mechanism is significantly different from the reaction mechanism over acid catalysts discussed in section 2.1.1. The active sites for the desired dehydration mechanism over  $Sc_2O_3$  is determined to be the point deficient oxygen sites [34]. The position of these sites will be discussed in section 2.3.2.

The basic sites on the surface are always accompanied by their acidic counterpart. As such, these acid counterparts are always present and the reactions described in section 2.1.1 will proceed in parallel with the desired dehydration reaction. It has been shown that

the dehydration of alcohol to their corresponding alkenes in base catalyzed reactions can be enhanced by their Lewis acid counterparts [35]. The mechanism described above is presented in Figure 2.10.



Figure 2.10: E1cB reaction mechanism of base catalyzed dehydration [33]

#### 2.1.3 Base catalyzed etherification

In the previous section, it is mentioned that Pramod et al. note the etherification of PG with itself, producing 2-(2-hydroxypropoxy)-1-propanol. The production of this ether is not unlikely as the etherification of glycerol has been shown to proceed over an acid-base pair [36]. The mechanism for the etherification of glycerol is presented in Figure 2.11.



Figure 2.11: Base catalyzed glycerol etherification [36]

In the base catalyzed etherification one of the hydroxide groups in the molecule is attacked by the basic oxygen on the catalyst surface. A proton is abstracted from the first molecule and adsorbed on the catalyst surface. The negatively charged oxygen on the first molecule attacks the terminal hydroxide group on the second glycerol molecule. The hydroxide group is adsorbed onto the surface and recombines with the adsorbed hydrogen to form water. At the same time, the negatively charged oxygen forms a covalent bond with the second molecule forming an ether bond.

#### 2.1.4 Dehydration of PG to AA

From the previous sections it is known that the primary pathway for PG is the dehydration is the formation of PAL. Pramod et al. have done a preliminary investigation on the dehydration

KOH loading	Conversion [mol%]	LA + HAC[%]	ACE[%]	AA[%]	PAL[%]	POL[%]	UNK[%]
0	83.9	20.3	1.7	4.3	12.6	36.9	24.2
0.1	78.4	25.3	1.4	4.1	13.7	25.7	29.8
0.5	27.1	12.0	0.6	4.4	2.9	19.3	60.9
1	25.7	7.1	0.0	5.5	0.0	9.9	77.5
3	27.2	1.5	0.0	4.5	0.0	2.6	91.3
5	19.2	2.2	1.8	9.6	0.0	4.1	82.4
10	8.8	0.0	0.0	23.4	0.0	0.0	76.6
HAP	16.3	28.9	0.0	8.0	0.0	27.4	35.7

Table 2.1: Influence of KOH loading on performance of  $ZrO_2$  catlalyst, T: 350° GHSV: 7183 LA: Lactaldehyde, HA: Hydroxyacetone, ACE: Acetone, AA: Allyl alcohol, PAL: Propanal, POL: 1-Propanol, UNK: unknowns, HAP: Hydroxyapatite (Ca/P = 1.56)

to AA [1]. This section will focus on discussing their observations and findings. Note that not all of the information discussed in this section is presented in the published paper. Some of the information is shared through the supplementary information attached to the paper. The supplementary information can be found in the same location as the published article.

In their research, a K-doped ZrO<sub>2</sub> catalyst is used to perform the dehydration reaction. The modification of the ZrO<sub>2</sub> catalyst is the key part of this research as it suggests the active sites involved in the desired dehydration reaction. The K-modified ZrO<sub>2</sub> catalyst is prepared by dissolving the desired amount potassium of in 20ml of water. The catalyst was added to the aqueous solution and stirred at room temperature for 2 hours. Water was evaporated from the solution at 100 °C for 2-4h and further dried in a vacuum over overnight. The doping of the catalyst in potassium significantly affects the surface properties of this catalyst. The following data is taken from the supplementary information provided by Pramod et al., the data is briefly discussed in the publication [1].

Pramod et al. observed a decrease in activity with increasing amounts of potassium doping. Vice versa, an increase in selectivity to AA was observed. As noted by Pramod et al., the increasing selectivity to AA indicates the poisoning of the acid sites on the catalyst surface. These sites are responsible for the dehydration to PAL, AC, MPV reduction, aldol condensation and acetalization reactions. Essentially, all acid catalyzed pathways to (heavy) (by)products are killed by the basification of the catalyst surface. Additionally, the basic properties of the surface will hinder the possibility of secondary isomerization of AA to PAL as it is suggested that isomerization of these species also takes place over the acid sites [32].

A preliminary study has been done on the reaction kinetics of the PG dehydration. Pramod et al. observed 1st order behavior for the dehydration of PG, regardless of the dilutions of the feed. The data supporting this behavior is presented in Figure 2.12. High



Figure 2.12: 1st order kinetic plot of PG dehydration over 10KZrO<sub>2</sub> at 400°C

conversion data (>90%) are excluded from this plot.

The behavior observed in Figure 2.12 is clear first order behavior. This is to be expected, as there is only 1 reactant in the dehydration of PG and there is no dissociation of this reactant on the surface to be the rate limiting step. In this dehydration reaction, PG adsorbs on the surface of the catalyst. On the surface the PG dissociates to water and the unsaturated alcohol (AA). As there are no other reactants or components involved, 1st order behavior is a logical order for the reaction. No change of order is observed in a diluted feed. The dilution of the feed introduces steam into the system. One would expect a detrimental effect in the activity of the catalyst. Water is one of the products and could thus reduce the formation of the dehydrated species by being present in the system. In addition, water could competitively adsorb on the catalyst surface reducing the amount of active sites available for the adsorption of PG.

Analyzing the actual behavior of the reaction in the presence of steam shows a different picture then described in the previous paragraph. Initially, when diluting the feed by 50% with water. A significant increase in activity was observed. This increase becomes more pronounced at higher conversion levels/longer contact times. When further diluting the feed, the reverse behavior was observed. The decrease in activity when moving from a 50vol% solution to a 25vol% solution of PG is a remarkable find as one would expect the activity to further increase. Pramod et al. attribute a similar effect on a promotion of the desorption of AcrA. However, there is no AcrA present in the currently discussed system. Pramod et al. refer here to the second discussed system, the oxidation of AA to AcrA. This behavior would suggest a similar promotional effect of steam on the desorption of AA from the catalyst surface up till certain molar concentrations of steam.

#### 2.2 Similar dehydration reactions

There have been a multitude of studies on the dehydration of terminal diols to homoallyl alcohols. The dehydration of 2,3-BDO is taken as a model reaction as this molecule closely resembles the molecular structure of PG. The dehydration of 1,4-butanediol over lanthanide based catalysts is studied by Igarashi et al.[37]. Lanthanide group catalysts are chemically similar to  $Sc_2O_3$ , making this research of interest for the PG dehydration reaction [38]. In contrast to PG and 2,3-BDO, 1,4-butanediol is a terminal diol and consequently has its hydroxide groups on the on the terminal carbon atoms. It is discovered that REO catalysts often are selectivity for a particular dehydration reaction depending on the molecule and desired product [21, 32, 39–42].

The REO catalysts often have the ability to dehydrate the unsaturated alcohol further. Wang et al. have studied the dehydration of 3-buten-1-ol over several REOs, including  $Sc_2O_3$  [43]. It is found that, given enough residence time,  $Sc_2O_3$  can further dehydrate the unsaturated alcohol to a diene. In addition, the effect of the ionic radius is studied for the dehydration of 3-buten-1-ol. It is observed that this effect is different for 3-buten-1-ol than for 2,3-BDO. This is most likely due to the difference in lengths between the hydroxide group in the molecules[41, 43].

#### 2.2.1 The dehydration of 2,3-BDO

There is a limited amount of information available on the dehydration of PG. Especially the base catalyzed dehydration to AA is a novel area of research. Systems with similar molecules and catalysts can serve as a reference for the present study. For the model systems, a selection of (terminal)diols and REO catalysts is made.

2,3-BDO has a similar molecular structure to PG. Both are alkanediols that can freely rotate due to the absence of double bonds in the molecules. The only difference between these molecules is the presence of an additional methyl group in the BDO. Similarly to PG, the desired main product of the dehydration reaction of BDO is an unsaturated alcohol. A ketone is formed as the main byproduct instead of an aldehyde as in the PG dehydration.

A multitude of studies have been performed on the dehydration of 2,3-BDO to 3-buten-2-ol. Duan et al. studied this dehydration reaction over various REOs and tries to correlate the properties of the REOs to the dehydration reactions occurring [41]. In their study, the influence of cationic radius of the metal in the crystalline structure, the crystalline structure itself and finally the calcination temperature at which the catalyst is prepared are considered. It is found that smaller ionic radii provide better selectivity towards the unsaturated alcohol. This behavior is attributed to the distance between the hydroxyl groups in the molecule being similar to the distances between the catalyst activity and selectivity towards the desired product. The increase in activity due to ionic radius is attributed to the distances in the molecule being more optimized for metal cations that are closer to each other. For the crystalline structure no explanation is provided, but it most likely has to do with the naturally occuring active sites on the various surfaces.

Multiple studies for several REOs have been done by the group and they have determined several reaction pathways for the dehydration of 2,3-BDO over REOs [44–49]. Based on these studies, a reaction mechanism was proposed for the dehydration of 2,3-BDO to 3-buten-2-ol over  $Sc_2O_3$  catalysts. The mechanism is presented in Figure 2.13.



Figure 2.13: Proposed mechanism for the dehydration of 2,3-butanediol over  $Sc_2O_3$  catalyst

The mechanism in Figure 2.13 show the dehydration mechanism for 2,3-BDO to 3-buten-2-ol over Sc<sub>2</sub>O<sub>3</sub> catalysts. The molecule is first adsorbed on two acid sites and one base site. In this case, the acid sites are the acidic metal cation sites and the base sites are the oxygen sites at the edge of the oxygen deficient point. The hydroxide groups are anchored to the acid site while the  $\beta$ -hydrogen is adsorbed to the base site. To produce the unsaturated alcohol, the hydroxide group and  $\beta$ -hydrogen are attacked at the same time. This way, water forms on the surface and the molecule desorbs to form the unsaturated alcohol. 2,3-BDO is a good molecule for this reaction as the molecule is symmetrical. There is no preference to which  $\beta$ -hydrogen is adsorbed to the base site as both hydroxide groups can be attacked to form the unsaturated alcohol. A logical conclusion from this would be that the model reaction is more active towards the production of the unsaturated alcohol. After the dissociation step, water is formed on the surface and the molecule desorbs from the acid site. At the same time, water desorbs from the surface into the gas phase. A double bond is formed in order to create a stable molecule. The active site is now regenerated for further reaction.

The behavior of 2,3-BDO to 3-buten-2-ol over CaO modified ZrO<sub>2</sub> catalysts is studied by Duan et al. [41]. CO<sub>2</sub>/NH<sub>3</sub> was added to the reactant stream to poison the base/acid sites respectively. A conversion and selectivity decrease due to CO<sub>2</sub> poisoning, strongly suggest that the dehydration reaction occurs over acid-base sites. The CaO is heterolinked into the monoclinic ZrO<sub>2</sub> surface[41]. This is suggested to generate new active sites on the catalyst surface. The study concluded that active sites of medium strength most likely act as the main active sites in the dehydration reaction [41]. However, Cheng et al. found that the acid site can also product 3-buten-2-ol as an intermediate before the complete dehydration to butadiene [50]. Ohtsuka et al. studied the dehydration of 2,3-BDO to 3-buten-2-ol over yttria-stabilized zirconia catalysts [51]. An increase in selectivity towards the unsaturated alcohol was found with increasing calcination temperature and yttria content. It is concluded that the dehydration mechanism most likely proceeds over the acid-base sites as previously discussed by Duan et al..

#### 2.2.2 Dehydration of diols to unsaturated alcohols over Sc<sub>2</sub>O<sub>3</sub>

This section provides an overview of the dehydration of several diols to unsaturated alcohols over  $Sc_2O_3$ . These components are all similar to the studied component and the previously described model reaction. The most studied form diol dehydration is the dehydration of terminal diols to their unsatured alcohol products. A focus is placed on the dehydration over  $Sc_2O_3$  catalyst as this is the catalyst of interest for this research. An overview of these reactions is presented in Table 2.2. This list is compiled from various sources. Notably, most of this data is provided by Sato et al. In this section, reasons for the differences between different chain lengths and hydroxide positions are speculated.

Diol	Temp [℃]	W/F	GHSV	Carrier gas	Conversion [%]	Selectivity [%]
2,3-butanediol	325	0.93	2761	N2	99	89
2,3-butanediol	325	0.93	2701	N2	99.9	85
2,3-butanediol	425	0.94	-	N2	100	1.9
1,2-butanediol	325	0.93	4801	H2	20	4
1,3-butanediol	325	0.05	-	N2	18.2	39.0
1,4-butanediol	350	0.17	-	N2	67.3	69
1,5-pentanediol	400	0.17	-	N2	63.3	75.5
1,6-hexanediol	350	1.39	1625	N2	47.8	40.7
1,7-heptanediol	350	1.39	1625	N2	42.3	59.6
1,8-octanediol	350	1.39	1625	N2	55.8	65
1,9-nonanediol	350	1.39	1625	N2	55.9	57.6
1,10-decanediol	350	1.39	1625	N2	59.7	74
1,12-dodecanediol	400	1.39	1625	N2	93.4	60.1

Table 2.2: Various diol dehydration reactions over  $Sc_2O_3$  compiled from several sources [1, 39, 44, 46, 49, 53–55]

A comparison of the different dehydration reactions of terminal diols is made difficult by the varying reaction conditions of the data. Often the reaction temperature and/or weight of catalyst varies for the reported data. Comparing the data of C6+ carbon dehydration is easier as this is reported by the same source [55]. No change in activity is observed for terminal diols with different carbon chains. The interaction between the hydroxyl groups is minimal on the long chain carbon, and will thus have little influence on the activity. From a thermo-dynamical point of view, it is expected that an increase in activity should be seen based on the gibbs free energy of the reaction according to Equation 2.1. The heat of adsorption (H) is determined to be independent of carbon chain length, and thus approximately equal for all the diols[56]. The entropy increases with decreasing chain length, making the gibbs free

energy of low chain diols more negative [56]. A lower energy state is always preferred and the system will go to this low energy state.

$$\Delta G_{aibbs} = \Delta H - T \Delta S \tag{2.1}$$

Selectivity seems to show a slight trend upwards with increasing carbon chain length. Error bars are not reported and it is thus hard to draw a conclusion from the presented data. This could be within the margin of error of the experiment. The selectivity is speculated to not change with carbon chain length as the hydroxide groups on the terminal carbon atoms have little influence on each other in long chain diols [55].

The data of short carbon chain dehydration reactions is more difficult to compare due to the significantly different reaction conditions of the studied systems. Optimal reaction temperature can vary between  $325 \,^{\circ}$ C to  $400 \,^{\circ}$ C. The catalyst weight to feed ratio has a similarly large range of  $0.05 - 1g_{cat} g_{feed}^{-1} h^{-1}$ . In general, it can be assumed that the conversion increases with both W/F and temperature. Instead of a general trend, a quantitative comparison has to be made between the different carbon chain lengths. If one analyzes the reaction conditions at 1,4-butanediol and 1,5-pentanediol, it is observed that the W/F is constant and the temperature drops. An increase of 4.0 Percentage Point (p.p.) is observed in reducing the carbon chain length. However, temperature decreases from  $400 \,^{\circ}$ C to  $350 \,^{\circ}$ C. The 4.0 p.p. increase could be a consequence of errors in the measurement. Error bars are not reported by Sato et al.[39], so this can not be verified. The decrease in temperature combined with the increase in conversion suggests a significant activity increase for short carbon chain lengths.

The behavior of different C4 diols is interesting as a significant difference in conversion and selectivity is observed. The desired product of the C4 diols depends on the considered diol. The temperature reduction from 350 ℃ and 325 ℃ and W/F reduction from 0.17 to 0.05 between 1,4-butanediol and 1,3-butanediol should be taken into account in this comparison. The conversion of 1,3-butanediol is significantly lower than the conversion of 1,4-butanediol. The temperature and W/F contribute a large amount of this reduction. It is not possible to conclude if any other factors might be contributing to this reduction. The selectivity is another matter, as a significant decrease of 30 p.p. towards the unsaturated alcohol can be observed. It should be noted that the main byproduct in both reactions is tetrahydrofuran. Possible explanations for this behavior can be the position of the hydroxide groups relative to each other. Hydroxide groups that are closer to each other will have more influence on each other. In addition, the difference in electronic structure between the molecules could explain the decreased selectivity. Finally there is the possibility of a different, more/less stable, intermediate in the dehydration reaction. In the terminal diol case, the hydroxide group is always on the terminal carbon atoms. Protonation of this hydroxide group will always result in a primary carbenium ion, which would most likely undergo rapid rearrangement to produce a more stable secondary carbenium ion.

The reaction conditions of 1,2-butanediol are again different from the previously mentioned cases. The reaction temperature of 1,2-butanediol is equal to 1,3-butanediol ( $325 \degree$ C). However, the W/F ratio of 1,2-butanediol is significantly higher then either 1,3-butanediol or 1,4-butanediol. Hydrogen is used as the carrier gas instead of nitrogen. 1,3-butanediol is the closest case to 1,2-butanediol, and will thus be used as a first comparison. The desired reaction product is different, as the desired product of 1,2-butanediol dehydration is 2-buten-1-ol. The only difference between the desired products is the position of the double bond. A similar conversion is observed, even though the catalyst to feed ratio is much higher for the 1,2-butanediol. This suggests that the activity for the 1,2-butanediol reaction is higher than for the 1,3-butanediol reaction. The  $\beta$ -hydrogen will be slightly more acidic due to the distance of the two hydroxide groups in 1,2-butanediol. This could be an explanation for the increased reactivity of 1,2-butanediol. Additionally, rearrangement to the correct intermediate product could be easier due to the proximity between the hydroxyl groups. If the terminal hydroxide group is removed, the resulting carbenium ion has a much easier time isomerizing the secondary form by shifting the hydroxide group one carbon instead of two carbons in the case of 1,3-butanediol. Selectivity to the desired product is significantly lower than the 1,3-butanediol dehydration reaction. A simple reason for this could be that the 2buten-1-ol molecule is much less stable than the 3-buten-2-ol molecule, due to the proximity of the double bond and the hydroxide group.

2,3-BDO is more comparable to the terminal diol cases than the 1,2-butanediol and 1,3butanediol. 2,3-BDO is also a symmetrical molecule, the only difference is the positions of the hydroxide groups being on the inner carbon atoms instead of the terminal carbon atoms. As these molecules can produce the desired unsaturated alcohol over both hydroxide groups and  $\beta$ -hydrogens, one would expect activity for these molecule to be twice as high as the 1,2-butanediol or 1,3-butanediol cases. Under similar reaction conditions, a temperature of 325 °C and a catalyst to feed ratio of 0.93, a much higher conversion is observed than for the 1,2-butanediol case. However, it is guite a challenge to draw conclusions from this comparison, as the contact time between catalyst and reactant components is higher. In addition, the activity of 100% makes it impossible to conclude if this is the maximum activity. The activity of 100% conceals the amount of the catalyst bed performing the reaction. Part of the bed could be inactive as the conversion is already at 100%. Additionally, the end of the bed could be performing consecutive reactions, influencing the selectivity of the reaction. In this case, the observed selectivity is high, so this is not an issue. However, it is guite remarkable that such a high selectivity is observed at conversions of 100%. In general, it can be concluded that the activity is higher for the 2,3-BDO system.

The 2,3-BDO cases are easier to compare as mostly the same reaction conditions are used. In two of the cases, temperature, catalyst to feed ratio, contact time and carrier gas are similar. This results in similar activity and selectivity, making a convincing case that these results are valid. However, a higher temperature ( $425^{\circ}$ C) case shows a selectivity of only 1.9%, suggesting the formation of heavies, coke or additional reaction products at higher temperatures.

#### 2.3 Catalyst properties

This section describes the (surface) properties of REO catalysts. Examples of these properties are the active sites on the surface and the acid-base strength of these properties.

#### 2.3.1 Acid-base properties of REO catalysts

REOs are a class of metals with interesting catalytic properties [38]. Often these materials are used as promoters or additives to metal and/or supported catalysts [21]. The structure of the REO depends on the ionic radius of the metal and the preparation of the metal oxide catalyst [38]. In opposition to most acid-base type catalysts, the REOs possess a basic surface character opposed to an acidic character [52].

REOs exhibit behavior known as polymorphism. This references to the ability of the REOs to change structure depending on the temperature applied to the REO [57]. Three crystalline structures have been discovered at temperatures under 2000 degrees Centigrade [57]. These types are designed as A, B and C. Typically the C type occurs at lower temperatures and a transition from  $C \rightarrow B \rightarrow A$  is observed with increasing temperature [57]. These crystalline forms are more commonly referred to as Hexagonal (A), Monoclinic (B) and Cubic Bixbyite (C). In addition to these basic types, a modified form of the Cubic Bixbyite form, Cubic Fluorite (Cf) is observed in a number of REOs [48]. The change of crystalline form results in a change in the surface properties of the metal oxides. Under the presence of high temperatures more stable crystalline forms start to dominate the shape of the metal oxides. The change of properties occurs due to the rearrangement of atoms in a more structured crystalline shape due to the high amount of energy supplied to the system and the harsh conditions in the system.

Due to these structural properties, the REOs are an interesting class of materials. The subtle differences in electronic and crystalline structure of the metals has an effects on the basicity and acidity of the surface [21]. An example of this behavior can be seen in the different crystalline structures. Oxygen vacancies are formed on the sites of the surface to generate an electronically neutral surface. Dehydration reactions are often performed over acid-base catalysts due to the mechanisms described in the previous sections. The to-be-used catalyst can be selected based on the results obtained from several acid-base catalyzed reactions. The catalyst will be selected based on the properties required to perform the reaction. The production of PAL and AC are undesirable. Thus, the catalyst should be selected as such that the production of these byproducts is reduced while the production of the aldehyde form and the production of the ketone form are the Brønsted and Lewis acid sites. A catalyst.

The influence of the acid site strength, basic strength, density and type of site on the dehydration of glycerol to acrolein is investigated by Chai et al. [58]. The authors have divided the catalysts into several groups depending on their acid-base strength. The first

group consists of catalysts with a basic character, for example, lanthanum oxide and cerium oxide. The second group represents catalysts with weak to medium acidic strength, group 3 consists of catalysts with strong acid sites. Finally, the acid sites in group 4 are of a very strong nature. The results of this research show clearly that there is a correlation between the acid strength of the catalyst and the selectivity towards acrolein. The base catalysts in group 1 show a low selectivity towards acrolein due to the lack of acid sites of sufficient strength on the surface of the catalyst. Selectivity towards acrolein increased with increasing strength in acid strength. However, it is observed that acidic sites that are too strong are subject to secondary reactions. Acrolein selectivity decreased and the formation of coke on the catalyst was observed, suggesting that the catalysts with the strong acidic groups produce other products besides acrolein. Additionally, a decrease in activity was observed for the group with very strong acidic sites [58].

To prevent the formation of PAL and AC over the catalyst, the amount of Brønsted and strength of Lewis acid sites on the surface of the catalyst should be limited. A catalyst with a basic surface character would be preferential to perform this reaction. Acid and base sites of medium strength would most likely perform best as they facilitate the abstraction of atoms while not being able to cleave carbon - carbon bonds.

#### **2.3.2** $Sc_2O_3$ surface

 $Sc_2O_3$  has a cubic bixbyite structure [39]. This means that there are naturally forming oxygen deficiencies on the surface of the catalyst. These are points where an oxygen atom is missing from the surface to balance the electron charge of the molecule [39]. The cubic bixbyite structure of indium oxide is presented in Figure 2.14, this structure is similar to  $Sc_2O_3$ .

Figure 2.14 shows the naturally occurring 222 facet on a cubic bixbyite surface. The 222 facet is the energetically most stable surface of a cubic bixbyite crystalline phase [48]. The oxygen defect points on the surface expose the metal cations underneath the layer of oxygen [48]. Due to this exposure, the metal cations become available as a catalytically active site. The oxygen atoms on the edge of the point deficient site become lighly basic due to the need for a neutral charge in the structure. Applying high temperatures to metal oxides will grow the most stable facet of the metal oxide [48]. As a result, the application of high calcination temperatures will create larger particles with smaller surface areas. The active sites are formed more often on this surface thanks to the growth of the 222 facet of the crystalline phase.


Figure 2.14: Cubic Bixbyite structure 222 facet with oxygen defect points [47]

# **Chapter 3**

# **Experimental**

This section will describe the experimental setup, experiments and analysis used in this research. The experimental setup will be described in detail to provide a context for the experiments, results and discussion. This chapter is divided in three sections describing the catalyst preparation, experimental procedure and analysis respectively.

# 3.1 Catalyst preparation

The catalyst is prepared according to the procedure developed by Sato et al.. In this procedure, the Sc<sub>2</sub>O<sub>3</sub> catalyst is bought in its oxide form at purity of 99.9%. The Sc<sub>2</sub>O<sub>3</sub> powder is calcined at 800 °C in N<sub>2</sub> (N<sub>2</sub> for 3 hours).

# 3.2 The experimental setup

A Process Flow Diagram (PFD) of the experimental setup is presented in Figure 3.1. The ISCO 500D syringe pump has its own reservoir into which the reactant solution is pumped before the experiment. These syringe pumps provide flowrates up till 204ml/min and have a 507ml reservoir. The accuracy on the set point of the flowrate is 0.5%. The liquid reactant enters the evaporator at the bottom. The dimensions of the evaporator are similar to the dimensions of the actual reactor tube. In the evaporator, the liquid reactant feed is evaporated to its gaseous form. A pressure sensor is present between the evaporator and reactor to monitor the reaction conditions in the system. Next to the pressure sensor, the carrier gas is injected into system. The carrier gas is injected at a different position than the reactant liquid to create a more stable system. The gas mixture enters the reactor at the top and is pushed downward by the pressure provided by the pump and carrier gas. This gas is directly taken from the N<sub>2</sub> network and controlled by a Brooks 5850S Smart Mass Flow Controller (MFC) that can provide a flow of 0-70ml/min N<sub>2</sub>. it should be noted that this MFC is originally calibrated for argon, which is why the specified range of 0-100ml/min is not met. The system is open at the outlet, guaranteeing an atmospheric pressure in the system. The downward flow of the gas mixture prevents the catalyst bed from fluidizing. The catalyst bed

is held in place by a very fine mesh of gauze. Gas can flow freely through this mesh though it induces a small pressure drop over the catalyst bed. The reactor tube has an internal diameter of 6mm and a straight length of 60cm. Around the reactor tube, three heaters and thermocouples control the temperature of the catalyst bed and reactor tube. The bend at the top of the tube is not accounted in this length. An additional pressure sensor is placed behind the reactor to safeguard the pressure conditions in the system. A condenser after the reactor tube condenses the gaseous components back to a liquid product. The liquid product samples can be extracted from a G/L separator for analysis on the High Pressure Liquid Chromatography(HPLC). The temperature of the tube in the glycol cooling system is approximately 5 °Centigrade (°C) The carrier gas is vented to the ventilation system while the liquid product is collected in a 500ml flask. The liquid product is weighed by a KERN KB 10000-1 balance.



Figure 3.1: Process Flow Diagram of Plug Flow Reactor setup

All experiments in this research were performed on the setup presented in Figure 3.1. A pure reactant feed was used for most of the experiments. In the case of a steam atmosphere, the reactant feed was diluted to the desired ratio of  $H_2O:PG:N_2$ . The MFC in this system was designed for argon gas, adding the requirement of a calibration curve for the gas flow rate through the system. The Brooks GF80/GF81 MFC at the end of the system monitors the amount of  $N_2$  leaving the system.

### 3.3 Analysis

Reactant and product samples were analyzed using HPLC to determine the concentration of the components. The HPLC consists of a Shimadzu LC-10A liquid controller and a RID-10A differential refractive detector. The Aminex HPX-87h column in operated under standard conditions with a mobile phase flowrate of 0.6ml/min, an oven temperature of 35 °C and a mobile phase of 5mM H<sub>2</sub>SO<sub>4</sub>. The retention time of the components was identified under a retention time of 60 minutes. No signal was found after a retention time of 30 minutes as such, a retention time of 30 minutes was used to determine the concentrations. A calibration curve was determined for each of the components simultaneously by injecting a known mixture of components into the HPLC. This slope of the calibration curve was determined in a range of 0.01 - 8 g/L for each of the components. The concentration of the components can be determined from the RID signal combined with the calibration curve according to equation 3.1. In this equation,  $x_{component}$  is the mass concentration of the component in the sample. The mass concentration of the sample taken from the experimental setup is found after adjusting for the dilution of the sample.

$$x_{component} = \frac{RID \ peak \ area}{response factor}$$
(3.1)

#### 3.3.1 Conversion, selectivity & yield

Conversion, selectivity and yield are the definitions used to quantify the results obtained from the HPLC. In this research, the conversion is determined from the amount of PG converted to (by)products in the sample. The definition of this conversion is given in equation 3.2. This definition is also applicable to the model reaction using the 2,3-BDO reactant.

$$Conversion = \left(1 - \left(\frac{M_{sample}}{M_0}\right)\right) * 100\%$$
(3.2)

In a similar manner, the yield is defined as the amount of mol product produced compared to the maximum amount of mol product that can be produced. The definition for the yield can be found in equation 3.3. This definition is also used for the model reaction after substitution of the components.

$$Yield = \frac{M_{product}}{M_{reactant,0}}$$
(3.3)

## 3.4 Equations

$$P * V = n * R * T \tag{3.4}$$

Ideal gas law, P = pressure [Pascal], V = volume[ $m^3$ ], n = amount of moles [mol], R = ideal gas constant[J mol<sup>-1</sup> K<sup>-1</sup>], T = temperature [K]. R is considered to be 8.314 for this research.

The equation is primarily used in the determination of the gas flow rates. All gas flow rates in the present research are calculated at standard conditions (T = 273.15K, P = 1 atm).

$$catalyst \ to \ feed \ ratio = \frac{W}{F} \tag{3.5}$$

Catalyst to feed ratio, W = weight of catalyst [g], F = Molar feed of reactant [mol  $h^{-1}$ ]

$$k = Ae \frac{-Ea}{RT}$$
(3.6)

Arrhenius equation, k = rate constant [s<sup>-1</sup>], A = pre-exponential factor, Ea = apparent activation energy [J mol<sup>-1</sup>], R = ideal gas constant[J mol<sup>-1</sup> K<sup>-1</sup>], T = temperature [K]

$$contact \ time[s] = \frac{catalyst \ volume[ml]}{Total \ gas \ flow \ rate[ml/s]}$$
(3.7)

## 3.5 Component properties

Compound	Tm [℃]	Tb [℃]	density [g ml <sup>-1</sup> ]	MW g mol <sup>-1</sup> ]	heat capacity [J mol <sup>-1</sup> K <sup>-1</sup> ]	Hvap [kJ mol <sup>-1</sup> ]	рКа
2,3-butanediol	19	183,6	0,987	90,122	173,6	63,2	14,9
Methyl Ethyl Ketone	-86,7	79,9	0,805	72,107	136,6	35,5	14,7
3-buten-2-ol	-94,3	97,1	0,838	72,107	120,4	40,1	-
propylene glycol	-42,9	188,9	1,04	76,1	135,5	66,5	-
allyl alcohol	-90,5	97,2	0,854	58,08	88,3	46,7	15,5
propanal	-80	46,3	0,81	58,08	88,4	31,9	-
acetone	-93,8	58	0,785	58,08	100,5	35	19,2
1-propanol	-126,5	98,1	0,803	60,096	149	49,3	16
hydroxyacetone	-38,3	145,6	1,06	74,08	110,8	42.0	-
water	0	100	0.997	18.02	75.2	40.8	7

Table 3.1: Physical and thermodynamic properties of the compounds in this research. Data compiled from various sources [59–61]

# 3.6 Process Safety

A Risk Inventory and Evaluation (RI&E) is performed in advance of conducting the experiments to ensure safety during the experiments. The RI&E accounts for explosion risks, toxicity of chemicals, cleaning and several other aspects of performing safe and accurate experiments. The RI&E goes in depth on the safety of the utilized setup. As such, this report will not elaborate on the safety in the system. The RI&E can be found in appendix G. 

# Chapter 4

# **Results and Discussion**

This chapter will describe the outcome of the characterization and testing of the  $Sc_2O_3$  catalyst. The characterization sections will be split in the various techniques used. The results of the catalytic and kinetic testing will be split based on the model and desired reaction. The results of the model reaction will be compared to the results obtained from literature while the results of the desired reaction will be compared to the results found over  $ZrO_2$  by Pramod et al.[1]

# 4.1 Characterization

The catalyst prepared in the present research is analyzed using Brunauer–Emmett–Teller (BET) adsorption and X-Ray Powder Diffraction (XRD). These characterization techniques are employed to determine the surface area of the synthesized catalyst and the phases occuring in this powder. It is mostly used as a means to verify that the synthesized catalyst is the desired catalyst.

#### **BET** adsorption

BET adsorption is applied using a Micromeritics TriStar Surface Area and Porosity analyzer. The specific catalyst surface area is determined by measuring the amount of adsorbate gas on the catalyst surface. A degas temperature of 300 °C is applied during the procedure. The surface area is consequently determined by fitting the measured data too a Langmuir adsorption model. This model is based on a monolayer adsorption on the catalyst surface. The theory of this model or BET will not be discussed in this research. The sample analyzed consists of a standard Sc<sub>2</sub>O<sub>3</sub> powder sample, mostly containing particles in the size of 0-45 $\mu$ m. Using this method, a surface area of 17.21m<sup>2</sup>/g is determined. Internal pore area is determined by the t-plot method, accounting for 3.46<sup>2</sup>/g of the total surface area. This confirms that most of the catalytic activity of the catalyst is going to be on the outside of the catalyst. The complete results of the BET surface area can be seen in appendix F.

#### XRD

The XRD pattern of the  $Sc_2O_3$  powder is measured using a Bruker D2 PHASER XRD. The pattern is determined between  $2\theta$  angles of 10° and 80°. The measured XRD pattern is presented in Figure 4.1.



Figure 4.1: XRD pattern for Sc<sub>2</sub>O<sub>3</sub> powder

The main crystalline phases are attached in the Figure above. The main crystalline peak is obtained at a  $2\theta$  of 30°. This is the peak of the 222 facet, confirming that the catalyst is synthesized as desired.

# 4.2 The model reaction

The model reaction was used to test the activity and selectivity of the  $Sc_2O_3$  catalyst. The results found in literature by Duan et al.[41] and Zeng et al.[53] are verified by performing the model reaction under similar reaction conditions as performed by the above mentioned authors. The temperature was kept constant at 325 °C. Liquid flow rate varied between the experiments in the presence and absence of steam, this will be discussed in the appropriate sections. The N<sub>2</sub> carrier gas flow rate is kept constant at 45ml/min. Due to the nature of the early sample taking in the setup it was opted to first use a diluted 2,3-BDO stream in order to ease the sampling. The early sampling point for the HPLC required approximately 5-6ml of liquid in the sampling point before samples were able to be taken. Thus, the dehydration of 2,3-BDO in the presence of steam will first be discussed.

#### 4.2.1 2,3-BDO dehydration in the presence of steam

The 2,3-BDO dehydration reaction was first tested in the presence of steam. Reasons for this being that the  $Sc_2O_3$  catalyst is expensive and using less of this catalyst is preferred. This made collecting samples from the HPLC sampling point significantly easier. 2,3-BDO was dissolved in water to a 5vol% solution and fed to the evaporator at a liquid flowrate of 6ml/h. The reactant mixture was evaporated at 160 °C after several evaporation performance tests. As one might imagine, the water in the liquid feed influences the atmosphere in which the reaction takes place. 95vol% of this liquid feed stream is water, having a significant effect on the partial pressure of reactant in the gas phase. Recalculating the feed to their molar stream will allow for the determination of the partial pressure of each component in the system. Table 4.1 presents the molar feeds of the different components. As one can see, the partial pressure of reactant in the gas phase is very low due to the high amount of water and N<sub>2</sub> present in the system.

Component	Flowrate [ml/h]	mass flow [g/h]	molar flow [mol/h]	Mol fraction gas phase
Water	5.7	5.6715	0.315	0.563
2,3-Butanediol	0.3	0.296	0.01	0.008
Nitrogen	2700	3.38	0.241	0.431

Table 4.1: Flowrates and molar fractions 2,3-BDO dehydration in the presence of steam

For this experiment, a catalyst weight of 0.4067g is used. Consequently, the catalyst to feed ratio during this experiment is  $123.9g_{cat} \text{ mol}_{2,3-BDO}^{-1} \text{ h}^{-1}$ . Duan et al. use a slightly lower catalyst to feed ratio of  $85.0g_{cat} \text{ mol}_{2,3-BDO}^{-1} \text{ h}^{-1}$ . It should be noted that Duan et al. use a pure 2,3-BDO feed, resulting in a much higher partial pressure of 2,3-BDO in the system. The volume of gas evaporated from the liquid is calculated according to the ideal gas law defined in equation 3.4. Both water and 2,3-BDO are considered in this calculation. For the described system, the volume of the evaporated liquid amounts to 9782 ml/h, significantly larger than the N<sub>2</sub> carrier gas flow. This is mostly due to the presence of water in the system, significantly contributing to the total amount of moles flowing through the system. Considering the density of Sc<sub>2</sub>O<sub>3</sub>, the bed volume occupied by the Sc<sub>2</sub>O<sub>3</sub> will be 1.544cm<sup>3</sup>. Note that the dilution of the bed is not accounted for, as only the contact between active catalyst and reactant is considered. The results of the experiment are presented in Figure 4.3.



Figure 4.2: Conversion and selectivity results of the 2,3-BDO dehydration in the presence of steam

The results of the first experiment are shown in Figure 4.3. The conversion, selectivity and yield are depicted on the y-axis in percentage [%]. The x-axis represents the Time On Stream (TOS) in hours. The conversion level of 2,3-BDO is represented by the black crosses in the graph. The 3-buten-2-ol selectivity, Methyl Ethyl Ketone (MEK) selectivity, unknown selectivity and 3-buten-2-ol yield are represented by the blue triangles, red dots, magenta downward triangles and yellow plus icons respectively. It can be observed that the conversion is high at approximately 95% carbon conversion. The conversion point at 2.5 hours seems to be slightly out of line with the other data points. This could be explained by an error in the measurement. Otherwise the conversion data is relatively constant over the reaction time of 6 hours. However, due to this high levels of conversion it is impossible to draw conclusions from this data. The stability or deactivation of the catalyst cannot be determined due to the high conversion. With high conversions, it is not possible to determine the amount of the catalyst bed used to perform the reaction. It could be that the first section of the bed is doing the measured reaction, and after deactivating a second part of the bed takes over, showing no deactivation in the measured reaction time. It is thus desired to do experiments at much lower conversion levels to gather more information on the reaction.

The selectivity levels to the different reaction products measured is constant over the reaction time. The selectivity to unknown products is defined as 100% - selectivity to the measured products. Interestingly, a low selectivity to the desired unsaturated alcohol (3-buten-2-ol) is observed. MEK is observed in larger amounts than expected compared to literature [44]. These results indicate that water is might be altering the surface of the catalyst or the reactions occurring in the system. In addition, a lot of unknown products are observed in this reaction. Due to the high conversion levels, it is hard to determine if the presence of

steam has an influence on the activity of the catalyst. These results are verified by redoing the experiment to confirm the obtained results. The results of the duplo experiment are presented in Figure 4.3



Figure 4.3: Duplo of conversion and selectivity results of the 2,3-BDO dehydration in the presence of steam

In these results, a similar conversion level is observed. This is to be expected as the activity of the catalyst is simply too high to decrease the conversion to acceptable levels at these flow rates and reaction condition. Selectivity to MEK and 3-buten-2-ol is comparable to the previously obtained results. Again, there is a high selectivity towards unknown products. The reproduction of this experiments confirms the initially observed results. It can thus be assumed that these experiments were performed correctly and are valid.

Interestingly, no decrease in activity is observed due to the introduction of steam in the system. One would expect that due to the decreased partial pressure of reactant, and the possibility of competitive adsorption, the activity of the catalyst for the dehydration reaction would decrease. One explanation could be the previously described usage of the bed. The selectivity towards the ketone and unknown products are remarkable as the PG dehydration towards AA studied by Pramod et al. do not show this behavior. As of yet there is no explanation for the observed behavior. It seems that water is killing the selectivity towards the desired product. There seems to be a promotion of the reaction to degradation products, possibly by adsorbing to the catalyst surface on the basic sites. A summary of the results obtained in the presence and absence of steam is presented in Section 4.2.2.

#### 4.2.2 2,3-BDO dehydration in the absence of steam

A similar experiment has been carried out in the absence of steam. In this case, an increase in total liquid flow is required to properly take samples for the HPLC. The 2,3-BDO flow rate is increased to 1ml/h to allow for sample collection. The volume fraction of water in the reactant feed is reduced to zero to remove the steam presence from the reaction. In addition, removing the presence of steam significantly increases the partial pressure of 2,3-BDO in the gas phase. The same weight of catalyst is used for this experiment. Consequently, the catalyst to feed ratio decreases as there are more moles of reactant in the feed. To be exact, the catalyst to feed ratio decreases to 37.1  $g_{cat} \mod_{2,3-BDO}^{-1} h^{-1}$ . The temperature, pressure and N<sub>2</sub> flow rates are kept at the same rate compared to the last experiment. The results of the experiment are presented in Figure 4.4.



Figure 4.4: Conversion and selectivity results of the 2,3-BDO dehydration in the absence of steam

In the Figure above one can observe the conversion and selectivity of the 2,3-BDO dehydration in the absence of steam. The conversion and selectivity are depicted on the y-axis while the TOS is represented on the x-axis. There are only 4 points instead of 5 due to the low liquid flow rate applied in this experiment. This resulted in the inability to take 5 samples on a single day. No 2,3-BDO was observed in the product sample over the full reaction time, even though the catalyst to feed ratio was significantly decreased. However, a direct comparison is not possible as one has to take into account the increased partial pressure of 2,3-BDO in the gas phase. This increased in partial pressure is accompanied by a higher diffusion rate of 2,3-BDO to the active sites on the catalyst surface. In addition, competitive adsorption effects between water and 2,3-BDO are less significant as only the water produced in the dehydration reactions are present in the system. This report neglects effects of competitive adsorption effects and desorption limitations of (by)products as there is no way to draw conclusions on these subjects from the measured data. Like the conversion data, the selectivity towards the main product and byproduct are constant over the reaction time. In fact, a very high selectivity towards the desired product is measured in this reaction. This is surprising as one can imagine that at high conversion there is a significant chance of (by)product(s) consecutively reacting. In section 2.1.1, it was discussed that the formation of heavy products, such as aldol condensation and acetalization, are very much concerns in these types of dehydration reactions. Yet, this behavior is not significantly observed in the current research, nor in the research conducted by Duan et al. The results from this section, section 4.2.1 and Duan et al.[41] are summarized in Table 4.2. There is the possibility of limited formation of heavy products based on the mass balances of the system.

Experiment	2,3-BDO conversion [%]	3B2Ol selectivity [%]	MEK selectivity [%]
Sato	96.6	72.1	7.5
Zeng	55	90	0
Presence of steam	89.4	9.56	25.58
Absence of steam	100	76.73	7.42

Table 4.2: Comparison of 2,3-BDO dehydration data compiled from the present research, Zeng et al.[53] and Duan et al.[41]

From Table 4.2 it can be observed that the results obtained in the absence of steam are very similar to the results obtained by Duan et al.. It can be concluded that the catalyst is performing as expected for the dehydration of 2,3-BDO. With this result in mind, the  $Sc_2O_3$  catalyst is applied to the PG dehydration.

### 4.3 PG dehydration to AA

This section will discuss the results of the dehydration of PG. The dehydration of PG to AA is performed over  $Sc_2O_3$  catalyst. It is decided to focus on the reaction in the absence of steam, due to the results obtained in section 4.2.1. Even though one could argue that the reaction can be performed in the presence of steam as described by Pramod et al. and in section 2.1.4.

#### 4.3.1 Confirmation of catalytic activity

 $Sc_2O_3$  is confirmed to be catalytically active by testing the reaction with an empty tube and a quartz bed similar to the catalyst bed used in the catalytic experiments. Similar reaction conditions were used in the initial studies as to replicate the model reaction as closely as possible. A notable difference is the increase in reactant flow rate from 1ml/h to 2ml/h. This allows for the collection of samples with lower TOS. In the initial experiments, the reaction temperature of 325 °C was used in combination with a catalyst weight of approximately 0.5g. The reactant flow is evaporated at 190 °C. The N<sub>2</sub> carrier gas flow rate was kept constant at 45ml/min. The catalyst bed is diluted to a catalyst fraction of 0.1 by using quartz (250-500 $\mu$ m). The quartz is confirmed to be inert by performing a blank test. In this blank test, the reactor is filled only with quartz. The rest of the conditions are kept constant. By considering the density of the quartz, it is calculated that the length of the bed with 0.5g of Sc<sub>2</sub>O<sub>3</sub> and a catalyst weight fraction of 0.1 is approximately 6.6mm in these reactors, this ensures that an adiabatic temperature configuration is applied and there are no hot spots in the reactor. The quartz bed in the blank experiments is kept at the same length for a fair comparison of the three different scenarios.

Beactor bed type	Information	PG conversion	Mass balance
neactor bed type	mormation	[%]	[%]
Empty tube	Х	0	N/A
Quartz bed	6mm quartz bed	0.056	-
	6.6mm bed		
diluted bed	0.5g	75.4	71.7
	catalyst fraction 0.1		

Table 4.3: Comparison between a typical PG dehydration catalytic test and comparable empty reactor tube and quartz bed diluent. Flows and conditions are constant over the experiments.  $T_{reaction}$ : 325°C, N<sub>2</sub> 45ml min<sup>-1</sup>, PG: 2ml h<sup>-1</sup>,  $T_{evap}$ : 190°C,  $P_{reaction}$ : 1atm,  $p_{PG}$ : 0.10atm

In Table 4.3 it can be seen that the empty reactor tube shows no conversion. This means that the wall of the reactor is not catalytically active in the PG dehydration reaction. It should be noted that for this comparison, one data point at similar conditions with  $Sc_2O_3$  catalyst is taken to perform a comparison and show the catalytic activity of the catalyst. In contrast to the empty reactor tube, a slight conversion is observed in a bed consisting only of quartz. It should be noted that no peaks are observed on the HPLC. It could be that the quartz inserts oxygen into the molecule for a reaction. Another explanation would be the introduction of a small amount of water in the system by the quartz. Errors in diluting the product sample could result in this discrepancy. The mass balance calculated for the diluted  $Sc_2O_3$  bed is calculated by determining the total mass of products and reactants in the product sample.

The diluted catalyst bed shows a much higher level of conversion at similar reaction conditions to the previously done blank tests. The conversion rises from 0.056% to 75.37%. The mass balance is worse compared to the blank samples as production of unknown byproducts takes place. These byproducts have not been identified and can thus not be counted in the mass balance. In general, it can be said that the experiment with the  $Sc_2O_3$  bed has significantly higher conversion of PG, and is thus catalytically active in this dehydration reaction.

#### 4.3.2 Influence of temperature on PG dehydration

The influence of changing the reaction temperature is investigated on the dehydration of PG. Specific attention is paid to the conversion, product distribution and yield of AA. The partial pressure of PG is constant in these experiments as the feed ratio of PG to N<sub>2</sub> does not change with changing reaction temperature. The N<sub>2</sub> flow rate is kept constant at a rate of 45ml min<sup>-1</sup>. Similarly, the liquid reactant flow rate is kept constant at a level of 2ml h<sup>-1</sup>. Based on the molar flow rates, the molar fraction of PG in the gas phase is calculated to be 0.10. Consequently, the partial pressure in of PG in the gas phase is approximately 0.10 atm.

For all of these experiments a catalyst weight of approximately 0.50g is used. A fresh catalyst bed is used for each experiment to ensure there are no influences by previous days of experiments. The bed is diluted to a catalyst fraction of 0.1 by diluting the bed with quartz particles ( $250-500\mu$ m). The catalyst to feed ratio for the experiments performed in this section is constant and calculated based on the aforementioned catalyst weight and flow rates. The catalyst to feed ratio for these experiments is calculated to be 18.3 g<sub>cat</sub> mol<sub>PG</sub>  $^{-1}$  h<sup>-1</sup>. This is a significantly lower catalyst to feed ratio then applied in the dehydration of 2,3-BDO. Comparing this value to the W/F applied in the study by Pramod et al.[1], again shows that in the present research a significantly lower W/F is applied. The conversion and product distribution are measured over a reaction temperature range of of 250 - 400 °C. The experimental results are presented in Figure 4.5.



Figure 4.5: Influence of reaction temperature on the conversion and product distribution of PG dehydration over  $Sc_2O_3$ .  $N_2$  45ml min<sup>-1</sup>, PG: 2ml h<sup>-1</sup>,  $T_{evap}$ : 190°C,  $P_{reaction}$ : 1atm,  $p_{PG}$ : 0.10atm

In Figure 4.5 the conversion, selectivity and yield are shown on the y-axis in percentage. The reaction temperature is depicted by the x-axis of the graph. The conversion of PG is calculated as the amount of carbon in known products. Similarly, the yield to AA is calculated based on the total amount of carbon in the product. Selectivities are calculated based on PG conversion and the yield towards the (by)products. Note that the formation of HAC is not included in this graph as at the time of measuring this was not included in the research. In general, selectivity towards HAC is slightly lower than the formation of POL It is chosen to present selectivities as it is easier to draw conclusions from this data. It should be noted that the selectivities include both the error in the PG conversion and the error in the yield of the (by)product. The conversion of PG and mass balance are depicted by the black diamonds and black triangles respectively. The trends in these data points are depicted by the solid black line and dotted black line respectively. The selectivity towards the different (by)products are represented by the various colors. AA, PAL, POL and AC are represented by dark blue, orange, grey and yellow respectively. Unknown products are depicted by cyan. The unknown products includes all the carbon not found in the identified products. Essentially this can be boiled down to 100 - (by)product selectivity.

The conversion of PG is observed to increase with reaction temperature from 250 - 325 °C. This result is to be expected as the reaction rate increases with reaction temperature as per the Arrhenius equation presented in equation 3.6. Interestingly, it can be seen that the conversion starts to decrease slightly when the reaction temperature is increased from 325 to 350 °C. This could indicate that there is some sort of equilibrium or that thermodynamic limitations are starting to arise at these levels of conversion. Adsorption limitations can start to limit the reaction as the reactants desorb before reacting. A further increase in reaction temperature leads to a significant decrease in conversion. After the experiment it was observed that the catalyst emerged from the reactor black. Suggesting that there is coke, and possibly heavy components forming on the surface of the catalyst. The coke will block the active sites on the catalyst surface, reducing the total reaction rate over that catalyst. It is expected that a further increase in reaction temperature will decrease the conversion of PG as the decomposition and formation of heavy products are accelerated. This behavior could be countered by decreasing the contact time between catalyst and reactant, reducing the amount of time the reactant and (by)products get to react in consecutive reactions.

The product distribution as a function of the temperature shows an interesting trend that is hard to explain directly. At the temperature of 250 °C, it can be seen that very few actual (by)product(s) are made. Selectivity towards known products is shown to be low at lower temperatures. An explanation for this could be that there is another unknown reaction is taking place that is dominating at the low temperature. Another explanation would be an issue in the desorption of (by)product(s) at lower temperature. These issue with desorption could result in the molecules on the surface consecutively reacting to other products. As the temperature increases, the reaction rate towards known products increases. At 325 °C, approximately 71% of the carbon entering the system as PG ends up in known components. The amount of carbon ending up in known products is significantly higher than at lower temperatures. Mass balance is generally better at lower temperatures as more carbon is accounted for in the reactant. It is most likely that the dehydration reactions are accelerated to such a degree that the system starts being dominated by these reactions, increasing the selectivity towards known products. The unknown products likely consist of the etherification

reaction at low temperature and the formation of heavy aldol condensation products at elevated temperatures. Even further increasing the temperature show an increase to unknown products likely due to the increasing decay of dehydration products to heavies in the product. This is usually observed in combination with deactivation of the catalyst, which is not seen in the present research.

It should be noted that additional peaks are observed on the HPLC. The total area of these peaks is observed to increase slightly with reaction temperature. HAC is included in these peaks and can be analyzed for further research. The response factor of the different products can be found in appendix E. An estimation to the concentration of unknown products can be made by utilizing this total surface area under the unknown peaks and considering the average response factor of C3 molecules in this study. Taking these peaks into account using the described method is not sufficient for full mass balance closure. The response factor for C6 etherification or C6+ heavy products would be significantly higher, resulting in higher concentrations for similar peak response factors. One would need to know the molecules being produced and the response factor of similar molecules to be able to properly estimate the concentrations of heavies obtained in the sample.

The yield of AA is seen to increase with increasing reaction temperature. A slight increase in selectivity with reaction temperature is observed for this dehydration reaction. However, the increased conversion has a more significant contribution to the increase in yield, as just more of the reactant is consumed in the reaction. Consequently, more of the AA is formed and an increase in selectivity towards AA is observed in this graph. At higher reaction temperatures, selectivity to AA decreases. This can be explained by AA degrading to consecutive products.

The data from the temperature range experiments is supplemented with experiments at higher temperatures and lower conversion. Measuring the activation barrier at low conversions limits the amount of consecutive reactions in the system. Based on this data, Arrhenius plots for the various dehydration reactions can be determined. The formation rate of the (by)products is taken as the activity of the catalyst. The formation rate of the several products should be equal to the disappearance rate of PG. This is not completely true as there are also degradation reactions taking place in this system. An attempt was made to determine the activation energies of the various dehydration reactions in the system through these Arrhenius plots. The Arrhenius plots for the formation of the various products is presented in Figure 4.6.

In Figure 4.6, the y-axis represents the disappearance rate of PG into the various dehydration products. The y-axis is on a natural logarithmic scale. On the x-axis, the temperature is represented in the form 1000/K [Kelvin]. The figure contains three different Arrhenius plots for PAL, AA and AC. The various components are represented by the black triangles, red diamonds and blue dots respectively. The formation of POL is added to the formation of PAL as POL is produced through PAL. It can be seen that the fitted linear lines closely fit the data points. The calculated disappearance rates to the various dehydration products are all measured at  $\leq$ 20% conversion. At high conversion levels, other phenomena such as equilibria between reactions and subsequent reactions start to play large roles, making this



Figure 4.6: Arrhenius plots for the various dehydration products occurring in the system measured at  $\leq$ 20% conversion

data unreliable for an apparent activation barrier determination.

From the slope of the linear fitted lines above, the activation energy of the various dehydration reactions can be determined. The error for this fit is determined by EXCELS LINEST function, which evaluates the error in the determined slope based on the presented data. The PAL fit seems to be the worst based on the R-squared of the fit. This is not unexpected as it is known from literature that PAL degrades to heavy products. Additionally, PAL can perform MPV-reduction with PG to produce POL and HAC. The issue with these subsequent reactions is that the rate of disappearance of PAL is also dependent on the reaction temperature. These reactions can respond differently to temperature and it is thus not guaranteed that this response will be proportionate. As AC is a more stable molecule, it is expected that this activation energy will resemble the actual value. However, the AA linear curve is a different matter. There is the potential for AA to isomerize to PAL and vice versa. The same arguments can be made here as for the fit of PAL. The energy barriers for the various dehydration reactions are reported in Table 4.4.

Product	Ea [kJ/mol]		
Allyl alcohol	127.8±15.1		
Propanal	115.6±13.8		
Acetone	114.8±10.1		

Table 4.4: Apparent activation barriers calculated from the linear fit presented in Figure 4.6 at  $\leq$  20% conversion.

The energy activation barrier results obtained from the Arrhenius plots in 4.6 do not raise any immediate concerns based on their values. The determination of the apparent activation barriers can only be done in a kinetic regime. In a mass transfer limited regime, the mass transfer limited step is measured instead of the kinetic rate limiting step. the The existence of internal mass transfer limitations can be theoretically predicted by utilizing the Weisz-Prater criterion. It is expected that there are no internal mass transfer limitations due to the nature of this catalyst. As a bulk metal oxide catalyst is used in this research, there are very little (if any at all) internal pores for internal mass transfer to occur in. Most of the active sites on these catalysts will be on the outside surface. The Weisz-Prater criterion is calculated based on typical values for a heterogeneous catalyst in a gas phase reaction in appendix C. As expected, it is predicted that no internal mass transfer limitations exist in the studied system. The presence of external mass transfer limitations are excluded experimentally in section 4.3.4. The product distribution at similar conversions is evaluated in Figure 4.7.



Figure 4.7: Product distribution of PG dehydration reaction at similar conversions and different temperatures.  $T_{reaction}$ : 250-325°C,  $N_2$  45ml min<sup>-1</sup>, PG: 2ml h<sup>-1</sup>,  $T_{evap}$ : 190°C,  $P_{reaction}$ : 1atm,  $p_{PG}$ : 0.10atm

Evaluating the product distribution observed in Figure 4.7 reveals interesting trends in the formation and disappearance rate of the (by)product(s). In the graph above, the red squares, blue diamonds, black dots, magenta triangles and yellow dots represent the conversion, selectivity to POL, selectivity to AA, selectivity to PAL and selectivity to AC respectively. The mass balance for each of the systems is  $\geq$ 90%. The selectivity towards AA shows a maximum, possibly due to etherification at low temperatures and rapid consecutive reaction at higher temperatures. PAL rapidly increases with temperature, also note the maximum of the POL curve. This large decrease in selectivity is not observed in HAC, raising questions to an additional pathway to HAC or consecutive reaction of POL.

by repeating the experiment.

#### 4.3.3 PG dehydration in the presence of steam

The presence of steam on the dehydration of PG is investigated by introducing water into the reactant solution. A similar catalyst to feed ratio is maintained by diluting the reactant stream with water and increasing the reactant flow. The reactant flow is respectively increased from 2ml/h to 8ml/h. The introduction of water in the system changes the molar composition of the gas phase to 0.69:0.06:0.25 (H<sub>2</sub>O:PG:N<sub>2</sub>). The reaction conditions are similar to the previously described experiments. Based on the results obtained in section 4.3.2 a reaction temperature of 325 °C is applied. Nitrogen flow is kept constant at a flow rate of 45ml/min. The evaporation temperature is adjusted to 167 °C to obtain the same molar fractions in the gas phase as in the original reactant mixture.



Figure 4.8: Product distribution of PG dehydration in presence/absence of steam

In Figure 4.8 the pure PG case and 75v% water case are compared. A decrease in the PG conversion is observed in the presence of steam. Pure PG and 75vol% water are represented by blue and orange respectively. A slight increase in selectivity towards the acid catalyzed reactions is observed with the increase in volumetric water content. No definitive conclusions can be drawn from the observed conversions due to the high level of conversion in both cases. The results suggest that the conversion decreases. In general an increase towards the acid catalyzed reactions is observed. This is possibly caused by the adsorption of water on the catalyst surface.

#### 4.3.4 External mass transfer limitations

Section 4.3.2 briefly mentions the concept of internal mass transfer limitations in a catalyst. However, there is also to possibility of external mass transfer limitations being present in catalytic systems. In the case of external mass transfer limitations, the molecules of reactant are too slow in diffusing to the surface of the catalyst, resulting in the reaction being limited by the diffusion of reactant to the surface of the catalyst. External mass transfer limitations are typically problems in liquid phase reactions as the diffusivity of reactant molecules through a liquid is much slower as through a gas. The molecules in a liquid are much more densely packed together compared to a gas, limiting the movement of reactant to the surface of the catalyst. Gas phase reactions are often not inhibited by external mass transfer limitations. Checking for external mass transfer limitations can be done by keeping a constant catalyst to feed ratio (space velocity) and adjusting the flow and amount of catalyst in proportional amounts. In the case of external mass transfer limitations, one would detect a decrease in conversion when decreasing the gas flow rate (and amount of catalyst weight). This is due to the contact between gas phase reactant and catalyst bed being too short, preventing the reactant molecule from reaching the active site on the surface.

It is determined if the system is affected by external mass transfer limitations by performing the experiment mentioned in the paragraph above over the complete range of the gas flow rates used in this research. By using the complete range of gas flow rates, it can be excluded that any of the experiments performed in this research are affected by external mass transfer limitations. The catalyst to feed ratio is approximately  $3.53g_{cat}$  mol<sub>PG</sub><sup>-1</sup> h<sup>-1</sup> N<sub>2</sub>.



Figure 4.9: Conversion determined for several gas flow rates, constant  $W/F = 3.53g_{cat} \text{ mol}_{PG} \ ^{-1} h^{-1} N_2$ : variable, PG: variable,  $T_{evap}$ : 190°C,  $P_{reaction}$ : 1atm,  $p_{PG}$ : 0.10atm

The results of the experiments described above are presented in Figure 4.9. The conversion is depicted on the y-axis, this axis is limited to 35% conversion as no higher values of conversion were observed. The total gas flow rate of vaporized reactant (PG and N<sub>2</sub> is depicted on the x-axis. The x-axis range from 2500-5300 ml/h as this is the range of flow rate

which this research experiments in. Unfortunately there are only three data points for this experiment due to time limitations. However, from this data it can be concluded that there are no external mass transfer limitations in the researched system. The conversion value is found to be approximately 29% at the mentioned catalyst to feed ratio. The conversions are determined by averaging the conversion of the experiment over a period of 5 hours (1 data point per hour). The error bars presented in the graph are determined as the standard deviation in the 5 hour averaged conversion data. As can be see in the graph, the conversion is constant over the entire gas flow range. It is concluded that there are no external mass transfer limitations present in the system.

#### 4.3.5 Kinetic study

Similarly to the temperature, one can determine the influence of contact time on the dehydration of PG to AA. This is affecting the catalyst to feed ratio or the space velocity of the system. A simple way to do this is to change the amount of catalyst in the system. Another way is to decrease or increase the gas flow rate over the catalyst. The N<sub>2</sub> flow rate has to be proportionally adjusted to maintain a constant partial pressure of reactant. Reaction orders can be determined by varying the partial pressure of reactant in the gas phase and measuring the conversion of reactant as a function of the partial pressure.

There are other ways to determine the order of a reaction. However, these ways require the assumption of a reaction order before testing for the order. These methods require knowledge about the reaction and its potential mechanisms. From literature it is known that the most likely mechanism for the dehydration of PG is similar to the mechanism for dehydration of 2,3-BDO. In this mechanism the main rate determining step is the adsorption of the reactant on the active sites. It is expected that the reaction will follow first order behavior based on the rate determining step of the 2,3-BDO dehydration. A first order kinetic plot can be generated by varying the contact time between catalyst and reactant. The natural logarithmic of the conversion is presented on the y-axis and the contact time on the x-axis. In a first order reaction, the resulting fit through the data points will show a linear dependence. The results of the various contact time experiments are shown in Figure 4.10. All other data measured at 325 ℃, including external mass transfer limitations, is considered in this plot.

In Figure 4.10 the conversions observed for various contact times are presented. The reaction temperature is kept constant at  $325 \,^{\circ}$ C. Similarly, the partial pressure of PG is constant in all the systems at 0.10atm. The data point in the top right, at almost 80% conversion is the average of the triplo measured experiment. The data for this experiment is available in appendix **??**.

As expected, it can be seen that conversion approaches 0 with contact time between catalyst and reactant approaching 0. The error in the measured conversion data is approximately 10% of the actual value. This is to be expected as the error is mostly dependent on the curves under the HPLC, and should thus be mostly consistent. In addition, error from dissolving the product sample in water to produce an HPLC grade sample is present in these data points. The first order kinetic plot can be generated by taking the natural logarithm of 1 -



Figure 4.10: Conversion determined for several space velocities, constant W/F = various,  $N_2$ : variable, PG: variable,  $T_{reaction}$ : 325°C,  $T_{evap}$ : 190°C,  $P_{reaction}$ : 1atm,  $p_{PG}$ : 0.10atm

conversion and plotting this against the contact time. The first order kinetic plot is presented in Figure 4.11.



Figure 4.11: First order kinetic plot for the dehydration of PG to AA,  $N_2$ : variable, PG: variable,  $T_{reaction}$ : 325°C,  $T_{evap}$ : 190°C,  $P_{reaction}$ : 1atm,  $p_{PG}$ : 0.10atm

The first order kinetic plot is shown in Figure 4.11. On the y-axis the natural logarithm of 1 - conversion is plotted against the contact time on the x-axis. Due to the logarithmic nature of the y-axis, a linear plot will be obtained for first order behavior. Conversions up to 30% are considered for this plot. A first order trend is observed for the dehydration of PG based on the fit and considering error bars in the system. Slight deviations in data can be attributed

to error in the experimental setup and preparation of the sample. As W/F increases, an increase in POL and decrease in PAL and AA is observed. The mass balance decreases from 92% to 70% due to an increase in side reactions. At very high conversion levels (75-80%), selectivity towards the desired products seems to increase. The reason for this is unknown. A duplo was conducted on this experiment and this yielded the same results. This behavior is illustrated in Figure 4.12. Please note that not all of the previously shown conversion data points are reported in the figure for the sake of clarity.



Figure 4.12: Product distribution various Catalyst to feed ratios, N<sub>2</sub>: variable, PG: variable, T<sub>reaction</sub>: 325°C, T<sub>evap</sub>: 190°C, P<sub>reaction</sub>: 1atm, p<sub>PG</sub>: 0.10atm

#### **Co-feeding of propanal**

An experiment with co-feeding PAL is done in order to determine the actual reactions taking place in this complex system. This experiment can be compared with the experiment with pure PG feed. The pure PG feed experiment will serve as a baseline for all of the co-feeding experiments. In this experiment the flow rate of liquid PG is kept constant at 1ml/h to obtain the same catalyst to reactant ratio as for the co-feed experiments. It should be noted that co-feeding with other products will be discussed in their respective sections. For all these experiments the following conditions are applied: N<sub>2</sub>: 45ml min<sup>-1</sup>, PG/product: 2 ml h<sup>-1</sup>, T<sub>reaction</sub>: 325 °C, T<sub>evap</sub>: 167 °C, P<sub>reaction</sub>: 1atm. As 50/50vol% solutions are used for these experiments, the total amount of moles will vary slightly depending on the performed experiment and co-fed reactants. In this case, the reactant feed consists of a ratio of PG:PAL

of 0.98:1. This is fairly close to 1:1 molar ratio but it should be kept in mind while analyzing the data that this ratio is not exactly 1:1. The results of the measurements are presented in Figure 4.13.



Figure 4.13: 50/50vol% feed of PG/PAL at the following conditions averaged over a period of 5h: N<sub>2</sub>: 45ml/min, PG/PAL: 2ml/h, T<sub>reaction</sub>: 325°C, T<sub>evap</sub>: 167°C, P<sub>reaction</sub>: 1atm.

The results of the co-feeding PAL are presented in Figure 4.13. The yields of the various (by)product(s) are represented by the various colors. Selectivity is not presented in this plot as the selectivity towards PAL is difficult to calculate as PAL is simultaneously a reactant and (by)product. Thus, it is decided to present only the conversion of the original reactant, PG, and yields of the various (by)product(s). The pure PG situation is presented by the left bar while the co-fed situation is shown on the right. It should be noted that the yield of the (by)product(s) is measured according to the standard HPLC procedure.

The conversion of PG is equal for both situations when considering the error in the measurements. A conversion of 37-39% is obtained for both cases with PG in the reactant feed. Based on this information, the discrepancy found in the blue bars is purely due to the reactant feed being a mixture. The yield towards AA and AC are found to remain constant in all situations, meaning that both are measured equally in all cases. This behavior is strange as one would expect the yield towards the other dehydration products to decrease with a decreasing concentration of PG. Since it has been shown that PG follows first order behavior in section 4.3.5. This behavior indicates that there are other pathways through which the dehydration products can be produced. A possible scenario is the isomerization of dehydration products to each other, or the reversibility of the reactions to the original reactant. Further investigation will indicate the pathways involved.

The yield towards PAL is discussed separately as this is the co-fed reactant and a product at the same time. Interestingly, the yield of PAL is lower than the initial concentration of PAL in the reactant mixture. Approximately 39% of PAL is converted to other products. Part of this PAL is converted to POL and HAC through MPV reduction reaction. An increase in the yield of these to byproducts in seen compared to the pure PG reactant feed. This increase is to be expected as there is more PAL in the system, increasing the rate of conversion to POL and HAC.

Surprisingly, the amount of carbon ending up in unknown products is lower than the pure PG case. It would be expected that more aldol condensation and cyclopentanone products are being formed in the PG/PAL mixture as compared to the pure PG feed. It is possible that the PAL is saturating the surface of the catalyst in competition with PG. The formation of these heavier products typically requires an additional reactant molecule such as PG or even HAC. The large amount of PAL on the surface could inhibit the adsorption of these other species on the surface. The constant conversion between the two experiments indicate that these reactions use different active sites on the catalyst surface. This is in agreement with the literature on the dehydration of 2,3-BDO dehydration.

#### Co-feeding of allyl alcohol

AA is co-fed in a similar way to PAL described in the previous section. All conditions are kept similar, except the catalyst to feed ratio of the co-fed product. This value is adjusted slightly as the total amount of moles on the 50/50vol% mixture is slightly different between the two reactants. The ratio of reactants in the feed is 1:0.93 (PG:AA). Consequently the vapor pressure of each component is slightly different than in the previous experiment. This should be considered accordingly in the obtained results. The results are averaged over a 5h experiment to determine the values presented in Figure 4.14.



*Figure 4.14: 50/50vol% feed of PG/AA at the following conditions averaged over a period of 5h:* N<sub>2</sub>: 45ml/min, *PG/AA: 2ml/h variable*, T<sub>reaction</sub>: 325°C, T<sub>evap</sub>: 167°C, P<sub>reaction</sub>: 1atm.

The conversion of PG and yields of the various (by)product(s) for the pure PG and co-fed AA case are presented in Figure 4.14. The catalyst to feed ratio of PG to catalyst is equal as in the co-feeding of PAL. The conversion of PG is observed to be equal in both cases. This confirms that the formation of AA is the reaction dominantly occurring over the base sites. A lower amount of AA is observed compared to the reactant feed of the experiment, indicating that AA consecutively reacts to byproduct(s). Coupled with the increase in PAL yield compared to the pure PG scenario this seems to indicate that AA readily isomerizes to the aldehyde form. The increase in POL yield in the PG/AA case seems to confirm an increase in reaction rate of the MPV reduction reaction when higher amounts of PAL are present in the system. Interestingly, the amount of carbon ending up in unknowns is again lower than under pure PG conditions. This could confirm the possibility of the active sites being blocked, preventing consecutive reactions. The pure AA case shows a more exaggerated version of the previously described behavior. The formation of PG is unlikely as this is only shown to proceed in the presence of acetic acid [62].

#### **Co-feeding of acetone**

A similar co-feeding experiment is performed with a 50/50vol% ratio of PG/AC. The reaction is performed under the same conditions as the previously describe co-feeding experiments.

In this case the PG:AC molar ratio in the feed is approximately 1:1,01. The results of the experiment are summarized in Figure 4.15.



*Figure 4.15: 50/50vol% feed of PG/AC at the following conditions averaged over a period of 5h:* N<sub>2</sub>: 45ml/min, *PG/AC: 2ml/h variable*, T<sub>reaction</sub>: 325°C, T<sub>evap</sub>: 167°C, P<sub>reaction</sub>: 1atm.

The result of the PG/AC co-feeding experiment are presented in Figure 4.15. An interesting observation is made in the conversion of PG in this case. A higher yield to PG than the reactant feed is observed due to a higher response of PG in the product mixture than in the reactant mixture. This result could indicate that the dehydration of AC is reversible over this catalyst. However, a more likely case is the formation of an aldol condensation product that shows up as PG on the HPLC. A large amount of AA and PAL is observed for the co-fed AC case. However, it is unlikely that isomerization of AC takes place as this would require rearranging a double bonded oxygen in the molecule. In addition to this, very few unknown products are formed in this reaction. This suggests that the active sites on the surface are filled, inhibiting consecutive reactions.

It is chemically unlikely that AC is hydrated to PG. Even if this reaction would occur, AC

would hydrate to 2,2-propanediol [63]. Coordinating both hydroxide groups on the C2 atom. This is observed in very low amounts and is considered negligible[63]. While it might be possible for a catalyst to perform this reaction, a more plausible explanation is that another reaction is taking place. There is the possibility of an aldol condensation product of AC with PG or even AC with itself, that shows up at the same position as PG on the HPLC. MS analysis can reveal the true cause of this observation.

#### Co-feeding of allyl alcohol and propanal

In the previous experiments it has been argued that there is the possibility of isormerization between different dehydration products. In addition, the possibility of reversibility is considered as a higher yield of PG is observed in the co-feeding of AC. The current section looks at a co-feeding of the two main dehydration products in an attempt to understand the reaction pathways occurring in the system. The reaction conditions applied in this system are similar to the previously discussed cases. AA and PAL are co-fed at a volumetric ratio of 50/50vol%. Consequently, the molar ratio in the reactant stream is 1:0.95AA:PAL. The results of this experiment are presented in Figure 4.16.



Figure 4.16: 50/50vol% feed of PAL/AA at the following conditions averaged over a period of 5h: N<sub>2</sub>: 45ml/min, AA/PAL: 2ml/h, T<sub>reaction</sub>: 325°C, T<sub>evap</sub>: 167°C, P<sub>reaction</sub>: 1atm.

The reactant feed of 50/50vol% AA/PAL shows a very interesting yield distribution to the various (by)product(s). The most remarkable aspect might be the formation of PG in this system. This indicates the reversibility of atleast one of the dehydration reactions. There are no known cases of PAL hydrating to PG. AA has been reported to hydrate to PG, but only in the presence of acetic acid [62]. As such, it is more likely that an unknown aldol condensation product forms that shows up as PG on the HPLC.

The second interesting observation in these results is the lack of POL + HAC. The inhibition of the MPV reduction reaction is most likely due to the lack of contact time between catalyst and feed. The inhibition of MPV reduction is because this requires PG to occur. The presence of POL in the product sample indicates atleast the presence of some PG in the system. Critically looking at the amount of moles of unknown product compared to the total amount of PG reveals that there are less moles of unknown product. Assuming one mole of water is formed for the formation of every mole of unknown product, the mole balance of the system cannot be justified. Considering a PG yield of 24.3% and an unknown products yield of 1.8%, an amount of moles of water of 8.64 millimol/h is missing from the balance. One possible explanation is the presence of water in the analytic solutions. PAL and AA have a purity of approximately 97wt% and 99wt% respectively, assuming the remaining percentage of the solutions is water, about 1.8 millimol of water is introduced in the system with the reactant feed. The amount of water in the reactant solution combined with the water formed through reactions to unknown products is about 2.34 millimol per hour. This means that approximately 4.5 millimol of water is missing from the balance. Another pathway through which water could be introduced to the system is the catalyst. However, this seems unlikely as the catalyst is treated at 400 °C for 16h before the experiment is started. If the error in the reaction system and analysis system is considered, the water missing in the mole balance is within margin of error. The measured error is seen to be approximately 10% of the measured value. For a PG yield of 24.3% this amount to 2.4%. Subtracting this value from the yield of PG and adding this to the unknown yield already results in only 3.1 millimoles missing. Due to the nature of the definition of unknown products (100% - measured products), it is not unthinkable that this error compounds and has a significant effect on the total amount of unknown products in the system. This can guickly add up to the total moles of water required. An unknown yield of 13.6% would be required to fully close this mole balance. This is a significant increase, so it cannot be ruled out that there is some other form of water introduced in the system. An increase of this magnitude seems unlikely. The formation of an unknown aldol condensation product that shows up as PG on the HPLC could be a plausible explanation for the behavior. It could even be that the samples had longer before analysis, partially reacting the molecules back to PG before analysis took place. Based on the previous sections it can be concluded that the presence and formation of PAL is undesirable.

#### Estimation of reaction constant

The present section attempts to estimate the rates towards the dehydration products and reactions between these products. The estimation of the reaction constants is performed



Figure 4.17: Simplified reaction scheme for the estimation of rates based on the results obtained during (co)feeding experiments

at low conversions to minimize the degradation of PAL to heavy products. A large amount of side reactions are observed in the complete system discussed in section 4.4. Dioxolane, cyclopentanones, etherification and heavy aldol condensation products are neglected in the present estimation, as these compounds are not quantifiably measured. The isomerization between PAL and AA is considered to be negligible at low conversions. Isomerization of AC to the other dehydration products is neglected because of the unlikely scenario of a double bonded oxygen rearranging itself on the molecule. The simplified scheme is presented in Figure 4.17. The calculated rates are based on the rates measured in the previous sections. The reversibility of the dehydration reactions is neglected as this is unlikely to occur and unlikely to have a significant effect on the determination at the conversions studied in this section. Most unknown products are considered to be derivatives from PAL. As POL is formed through PAL and HAC is active in the formation of cyclopentanones, the yield towards POL is added to the yield of PAL as the total reaction rate towards PAL.

The simplified reaction scheme in Figure 4.17 has considerably less reactions than the complete proposed reaction pathways. The reaction constants towards the major dehydration products will be estimated by plotting the yield towards the products versus contact time between catalyst and reactant. Conversions of PG up to 20% are considered for this estimation. Low conversions are applied to eliminate the activity of consecutive reactions. Intercept is set to 0,0 as the yield of the product should be 0 at 0 contact time. The reaction constants are determined in Figure 4.18 and summarized in Table 4.5. The errors in the linear trends are evaluated using EXCELS LINEST function using a 0,0 intercept.



Figure 4.18: Estimation of kinetic constants for the main dehydration pathways in PG dehydration.

Component	k [s <sup>-1</sup> ]		
Propanal	2.87±0.22		
Allyl alcohol	$1.12{\pm}0.12$		
Acetone	$0.064{\pm}0.061$		

Table 4.5: Determined reaction constants for the main dehydration products

With these results, it is confirmed that the reaction rate towards PAL is the fastest over this catalyst. Work has to be done to kill the reaction rate towards PAL while increasing/keeping the reaction rate towards AA.

## 4.4 Proposed reaction pathways

It is known from literature that PG and its dehydration products can perform several reactions. Based on the data obtained in the present research, it has been suggested that there are several reaction pathways in this system. The proposed reaction pathways are shown in Figure 4.19.



Figure 4.19: Proposed reaction pathways for the dehydration of PG over  $Sc_2O_3$  catalyst

The complete proposed reaction pathways are presented in Figure 4.19. Note that the formation of several unknown aldol condensation products of PG with AC The pathways starts at the center of the figure in the red circle. The acid catalyzed reactions are shown in the light red color while the base catalyzed reactions are in the blue regions. PG has been shown to dehydrate to all three potential dehydration products. It is difficult to draw a conclusion about the rate of the three different dehydration reactions compared to each other. It is however known that PAL is preferentially formed over AC in the catalyzed reaction. This is in line with the reaction mechanism determined Zhang et al. [24]. Interestingly, the experiments co-feeding with product(s) suggest the isomerization of AA and PAL to each other. As the pathway of formation for an additional aldol condensation reaction cannot be determined by the present research, it is left out of the pathway scheme. It should be noted that this most likely proceeds through AC.

The etherification of PG with itself is shown on the left hand side of the mechanism. No evidence was found for the etherification in this research. This reaction was included in the mechanism based on the observations and speculation of Pramod et al. [1]. The present research cannot exclude the formation of 2(2-hydroxypropoxy)1-1-propanol. Based on the carbon mass balance, there are still unknown products that have to be identified. There is also the possibility of the etherification product degrading to the desired product. This would mean the reaction pathway occurs but cannot be observed due to the formation of AA.

The formation of PAL is undesired in the studied system. This is not only because of the

formation of this byproduct. In addition, PAL serves as the basis for the pathways to several other byproducts. One of the main reaction pathway observed in this research is the MPV reduction of PAL and PG to POL and HAC. Hydrides are shifted from the diol to the aldehyde and produces a primary alcohol as the main product. In theory, ketones should also be able to perform MPV reduction reaction[29]. In this system, this would amount to the formation of 2-propanol and an additional product. 2-propanol is not observed on the HPLC, and it is thus concluded that this reaction pathway does not take place in the studied system. 2-ethyl-3-methyl-1,3-dioxolane can also be formed from a combination of PAL and PG. This proceeds over the Brønsted acid sites as described by Zhang et al.[24]. A similar reaction can occur over the Lewis acid sites by directly abstracting the hydroxide group from the molecule. It is generally thought that this is a reversible reaction that is pushed back to PAL by kinetics. Pramod et al. speculate and observe the formation of cyclopentanones over basic sites from PAL. No evidence for or against this pathway is observed in the present research. The final pathway through PAL is the formation of heavy products occur through aldol condensation reactions.

A significant amount of PAL is observed over the  $Sc_2O_3$  catalyst. As the  $Sc_2O_3$  surface lacks Brønsted acid sites, the dehydration reactions to the byproducts most likely proceed over the Lewis acid sites. In this mechanism, a hydroxide group is abstracted from the molecule by the electron accepting Lewis group. A positive carbenium intermediate is formed due to the abstraction of the hydroxide group. The following steps in the mechanism would process analogous to Figure 2.3. More research will reveal the actual dehydration mechanism. As the results show first order behavior, the most likely rate limiting step is the adsorption on the catalyst surface.

At the time of writing, it is unknown why the behavior of dehydration is significantly different between 2,3-BDO and PG. One of the explanations for this could be that there is the formation of a more stable intermediate in the PG dehydration reaction. If the terminal hydrogen is abstracted, a primary carbanion is formed, which is more stable than its secondary form in the 2,3-BDO dehydration. This could decrease the formation of the unsaturated alcohol. Another explanation could be the reactivity of the side-product. In 2,3-BDO dehydration, MEK is formed as the primary by-product. In general, ketones are much less reactive than the aldehyde formed in the PG dehydration. The actual reason for this phenomena has yet to be investigated.

#### 4.5 Industrial application

A PFD for the dehydration of PG to AA has already been proposed by Pramod et al. As such, this evaluation will not be reiterated in this research. Instead, the calculated industrial operating window will be applied in this research to test the viability of the  $Sc_2O_3$  catalyst. The PFD will change slightly due to the results obtained in this research. The PFD of this process is presented in Figure 4.20. Only the dehydration step is considered in this PFD as this is the step of interest for this research. An example of an industrial PFD for the




Figure 4.20: Industrial PFD for the dehydration of PG to AA in a plug flow reactor system

The PFD proposed in 4.20 is relatively simple as this only considers the major unit operations and neglects the consecutive oxidation step. In addition, a pure (>99wt%) PG feed stream is considered for this process. These conditions closely represents the system considered in this research. In this case, a simple plug flow reactor will be sufficient for the dehydration step. The industrial operating window determined by Pramod et al. is presented in Table 4.6, the corresponding values for the present research are also presented alongside the industrial requirements[1]. For this evaluation, the experiment yielding the higher selectivity towards AA is selected as the benchmark. The activity of the catalyst is based on the volume occupied by  $Sc_2O_3$  and the mass production of AA per hour following from the selectivity and conversion((10.4%).

	Unit	Target	PG dehydration
Selectivity	% theory	>85(>75)	29.18
Activity	$g_{prod} \: I_{reac} \: ^{-1} \: h \: ^{-1}$	>100	5762
Stability	Month	<24	1
Product concentration	wt%	>3	3.02

Table 4.6: Industrial operating window for the PG to AA as determined by Pramod et al.[1]

The criteria in Table 4.6 are self explanatory except for the stability. The stability is defined as the amount of time it takes for the catalyst to reach the 1000  $g_{product}$  per  $1g_{cat}$  threshold. A low number is thus preferred as all product made after this threshold is a bonus. The stability is thus directly linked to the activity of the catalyst. Based on the targets set by Pramod et al.[1], the catalyst meets all industrial targets except for selectivity towards AA.

The catalyst in its current form is not applicable as an industrial catalyst. The small size of the particles results in a very large pressure drop even over shallow beds. In the

first part of the Ergun equation, the pressure drop is proportional to the particle diameter squared. Consequently, very small sized particles have a very large increase in pressure drop. The  $Sc_2O_3$  active catalyst would have to be dispersed on a support and extruded into more favorable shapes. In addition, the powder form of the catalyst is likely not mechanically sufficient to support a large bed of particles.

## Chapter 5

## Conclusion

This research aimed to investigate the possibilities of  $Sc_2O_3$  as a dehydration catalyst in the dehydration PG to AA. In this investigation, special consideration is taken into the industrial viability of this process and the reaction pathways/mechanisms occurring in the system. At the time of writing,  $Sc_2O_3$  is not applicable as an industrial catalyst due to the relatively low selectivity towards the main product. A decline in reactant cost is expected as the product of PG increases with increasing biomass utilization. A lower selectivity towards AA will be required if reactant cost decreases, enabling the industrial applicability of this process. The  $Sc_2O_3$  catalyst meets the industrial requirements for productivity, stability and product concentration in product stream. It should be noted that the initial cost of the  $Sc_2O_3$  catalyst is not accounted for in this calculation. As  $Sc_2O_3$  is rare and expensive, this might be detrimental to the applicability of the investigated process.

The kinetics of the system were studied by varying the contact between reactant and catalyst. No external or internal mass transfer were observed in this research. The activation barriers of the three dehydration reaction were determined by measuring the formation rate of the three dehydration reactions and plotting the well known Arrhenius plot. All three dehydration activation barriers were determined to be approximately 115kJ/mol. The similarity is expected as the reactions are so similar in nature. The logarithmic consumption rate against contact time indicates that the consumption of PG follows first order behavior. Conversion of PG is observed to increase with contact time. The selectivity towards the desired product decreases with conversion as the components in the system get more time to consecutively react. In general, an increase in unknown products is observed with increasing conversion and contact time. It is determined that the reaction constant for the dehydration of PAL is the highest of the dehydration reactions.

In the co-feeding experiment, a wide variation of reactions is observed. The reaction pathways of the system are presented in Figure 4.19. Isomerization between AA and PAL is likely to occur in the system. The co-feeding experiments reveals the formation of an unknown aldol condensation product. As the likelihood of reversibility of these reactions is low.

In conclusion, the current research determines that the  $Sc_2O_3$  catalyst is currently not ready for industrial application. More research is needed to improve the selectivity of the

catalyst. The catalyst has to be dispersed on a support thanks to the small particle size of the powder. The complexity of the system demands a more thorough investigation before an industrial setting can be considered.

## Chapter 6

## Recommendations

In the current research a large focus is placed on determining the pathways in the reaction. This focus is placed as a result of the discrepancy between the model reaction and the dehydration of PG. It is observed that significantly more byproducts are formed in the case of the C3 molecule compared to the C4 molecule. This research briefly touched upon this subject and attempts to speculate possible causes for this behavior. The main cause of the difference between these molecules remains speculation at the time of writing. One possible explanation could be the stability of the ketone molecule formed in the model reaction compared to the aldehyde in the C3 reaction. The aldehyde is more reactive and will consecutively react to other products. A ketone will is more stable and as such will possible not show such behavior. This could influence the isomerization and and dehydration towards the ketone of the C4 product, resulting in the preferential formation of the unsaturated alcohol. Another possible explanation for this behavior was speculated to be the formation of a stable carbanion intermediate in the C3 dehydration. The abstraction of the hydrogen creates a relatively stable carbanion ion on the surface of the catalyst. The stable carbanion ion inhibits the formation of the unsaturated alcohol product. In comparison, the secondary carbanion ion in the C4 dehydration is less stable. More research in this topic could reveal the cause of this behavior and will help the scientific community understand these complex systems of dehydration reactions and metal oxide catalysts. Another explanation could be that the preferential pathway is through the secondary carbenium ion after abstraction of an hydroxide group.

The previous paragraph reveals a limitation in the present research. The reaction pathways have been described and determined, yet the actual mechanism of the desired reaction is only speculated based on the model reaction. There is no evidence of the proposed mechanism even though this is the most likely mechanism in the dehydration to AA. The mechanism is linked to the active sites utilized in the reaction. Temperature Programmed Desorption was unfortunately not available, so the amount of acid and base sites on the surface of the Sc<sub>2</sub>O<sub>3</sub> catalyst could not be determined. Additional work should be done on the determination of the actual mechanism of base catalyzed dehydration to the unsaturated alcohol. A better understanding of the mechanism could help improve the catalyst.

The selectivity of the reaction is the main reason why the process is currently not indus-

trially viable. Other problems are the cost of the  $Sc_2O_3$  catalyst and the cost of reactant compared to product. A decline in reactant price would solve most of these problems. However, this cannot be controlled and as such it is recommended to take a more pro-active approach in increasing the selectivity of the reaction. From the proposed reaction scheme it can be deduced that the formation of PAL is detrimental. Once PAL is formed, several more side reactions become available, killing the selectivity of the process. A key towards improving the selectivity is thus the prevention of PAL formation. PAL is formed over the acid sites on the catalyst. Consequently, to improve the selectivity, it is necessary to reduce the amount of acid sites or poison/destroy these sites to reduce the formation of PAL. Pramod et al. have shown the ability to poison the acid sites by doping the catalyst in potassium [1]. A similar modification could be performed on  $Sc_2O_3$ , making the surface of the  $Sc_2O_3$  more basic. The poisoning of the active sites kills the acid-catalyzed reactions.

The next issue is briefly mentioned in the previous paragraph, the cost of  $Sc_2O_3$  catalyst. Pure  $Sc_2O_3$  is relatively expensive at approximately  $250 \in$  per 5 gram. In bulk, this cost will be less, but it is still very expensive for an industrial catalyst. In addition, the powder form of the catalyst does not lend itself for industrial operation due to a large pressure drop with such small particles. As such, there are several options of reducing the cost of the catalyst in this system. One could look at the activity and selectivity of similar materials and replace  $Sc_2O_3$  for a cheaper material. Another option is the incorporation of a secondary metal into the crystalline structure of the  $Sc_2O_3$ . A cheaper material could be incorporated into the matrix without significantly affecting the properties of the catalyst. The  $Sc_2O_3$  can also be dispersed on a support, thereby changing the bulk of the material to be a cheaper support material instead of the expensive  $Sc_2O_3$ . The support has to be selected based on the desired dehydration reaction. For the dehydration to AA, a basic support, like magnesium oxide, will most likely perform best.

For the dehydration of 2,3-BDO a wide range of REO materials has been studied.  $Sc_2O_3$  has been selected based on the results from these studies. However, in the present study PG has been shown to behave differently in the dehydration reaction compared to 2,3-BDO. While the active sites are expected to be similar, the dehydration of PG might benefit from a slightly different ion radius compared to the 2,3-BDO mechanism.  $Sc_2O_3$  is determined to be the best for 2,3-BDO [21]. Other REO might perform better in the PG dehydration system. Such a research would be in line with trying to modify the  $Sc_2O_3$  surface and determine the actual mechanism in the PG dehydration. Indium and lutetium are shown to be promising metal oxide catalysts in dehydration of 2,3-BDO[44].

Another issue arises in the mass balances determined in this system. Especially in the initial experiments under different reaction temperatures the mass balance is often not closed. Particularly at higher temperatures the mass balances are poor in general. The formation of heavy products at this temperature starts to become very significant. This reduces the mass balance as the aldol condensation products and cyclopentanones are unidentified in the present research. Identifying these components and reanalyzing the system at higher temperatures might further improve selectivity and activity of the catalyst. This would work especially well in combination with the modification of the catalyst surface, as now the acid

catalyzed portions of the reaction pathways are inhibited.

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## Appendix A

## **Data experiments**

This appendix contains all the raw data reported in this research. Note that the data are time averaged over the experiment. The data is sorted by experiment, error is reported in appendix B. Please note that only the data used in this research are presented, any additional data can be obtained from the author on request. Mass balance data are equally averaged over the 5h reaction period, so reported values might differ from substracting

Temperature	PG conversion	AA sel	PAL sel	AC sel	POL sel	Mass balance
250	11.6	8.4	11.3	0.09	17.8	92,7
275	17,9	13,8	10,6	0,32	21,1	90,2
300	30,5	20,9	35,6	0,36	24,8	93,0
325	75,4	16.3	26.2	0.31	19.6	71.7
350	73,7	12,8	24,2	0,29	16,9	66,2
375	41,2	10,6	15,2	0,70	10,8	55,6
400	52,1	5,01	8,55	3,22	6,28	59,2

#### **Temperature range**

#### External mass transfer

Flowrate N <sub>2</sub>	Flowrate PG	Total	Conversion	conversion error	Cat weight
[ml/h]	[ml/h]	[ml/h]	[%]	[%]	[g]
2700	613.3	3313	28,6	3,56	0,0645
2160	306.7	2467	29,7	2,56	0,045
4200	920.0	5120	30,3	2,89	0,104

Temperature	Conversion	Sel AA	Sel PAL	Sel AC	Sel POL	Sel hac	Mass bal	Wcat	W/F
250	11.6	8.43	11.3	0.09	17.8	-	92.7	0.49	17.98
275	17.9	13.8	10.6	0.32	21.1	-	90.2	0.49	17.98
300	20.7	25.2	24.7	0.55	28.9	25.1	97.2	0.15	5.58
325	17.6	17.0	38.9	1.10	6.31	21.1	93.8	0.05	1.77

### Determination apparent activation barrier

## Triplo 325C

Experiment	AA sel	PAL sel	AC sel	POL sel	HAC sel	Mass balance	PG conversion
first	16.3	26.2	0.31	19.6	-	71.67	75.4
duplo	23.1	30.0	0.95	11.8	9.21	73.50	77.5
triplo	18.8	29.2	1.03	15.4	9.95	71.73	79.4

#### Presence of steam

vol% water	conversion	AA sel	PAL sel	AC sel	POL sel	AA yield	Mass balance
0	79.4	18.8	29.2	1.03	15.4	14.3	71.7
75	61,7	11.7	27.7	3.9	25.7	7.2	48.7

## **Conversion selectivity**

W/F	Conversion	AA sel	PAL sel	ACE sel	POL Sel
13.87	70.8	7.85	15.5	3.11	14.5
1.18	10.4	29.2	30.7	0.72	10.0
1.77	17.7	17.0	38.9	1.10	6.31
2.94	30.1	10.8	24.7	0.70	4.00
2.55	30.8	11.1	25.3	0.72	4.10
2.36	30.6	12.4	28.6	0.77	4.39
18.52	79.4	18.8	29.2	1.03	15.4
0.82	7.11	24.8	32.7	0.22	2.57
18.48	77.5	23.3	30.0	0.95	11.8
7.32	50.6	10.2	14.2	1.48	4.08

### **Co-feeding**

Experiment	PG yield	AA yield	PAL yield	ACE yield	POL yield	HAC yield	UNK yield
Pure PG	65,8	2,33	5,13	0,00	1,47	2,52	22,8
PG/AA	29,4	33,4	15,7	0,48	6,57	2,59	11,9
PG/PAL	26,7	2,74	30,9	0,06	6,90	9,67	23,0
PG/AC	55,7	11,5	7,17	20,3	2,17	3,17	0,00
PAL/AA	24,3	27,0	37,2	4,58	3,12	2,00	1,78
PAL	23,1	2,10	54,9	0,02	11,1	5,66	3,06
AA	8,21	54,0	21,9	0,07	6,13	1,52	8,21

## Appendix B

## **Raw Error data**

## **Temperature Range**

error conv	error AA	error pal	error ac	error pol	error hac
2.21	1.45	2.64	0.17	3.54	-
2.36	2.16	2.58	0.33	4.37	-
9.10	3.29	7.66	0.69	5.42	-
2.57	1.39	1.96	0.59	0.83	-
3.22	2.50	1.77	0.53	3.90	-
4.99	2.70	3.23	1.33	3.05	-
10.7	1.38	3.17	0.69	2.08	-

#### **Contact time**

Conversion	Conversion error	error AA	error pal	error ac	error pol	error HAC
37.9	5.00	2.70	3.23	1.33	3.05	-
33.5	9.10	3.29	7.66	0.69	5.42	-
77.5	2.31	2.11	7.98	0.33	1.75	0.64
11.6	2.21	1.45	2.63	0.17	3.54	-
17.9	2.36	2.16	2.58	0.33	4.37	-
79.4	2.57	1.39	1.96	0.59	0.83	-
70.8	6.51	1.31	2.21	0.58	2.92	-
10.4	2.31	3.79	1.12	0.15	0.01	0.01
17.7	3.86	2.72	7.32	14.00	1.87	-
30.1	5.28	1.22	3.36	0.34	0.69	-
30.8	2.21	1.77	4.76	0.31	1.22	-
30.6	3.99	1.22	3.36	0.34	0.69	-
7.11	0.99	1.00	2.64	0.00	0.59	0.02
50.6	4.89	0.33	0.10	0.01	0.00	

## W/F selectivity

W/F	Conversion	AA error	PAL error	ACE error	POL error
13.87	70.8	1.31	2.21	0.579	2.923
1.178	10.4	3.79	1.12	0.148	0.008
1.767	17.7	2.72	7.32	0.483	1.874
2.945	30.1	1.215	3.36	0.336	0.695
2.551	30.8	1.77	4.76	0.314	1.219
2.360	30.6	1.22	3.36	0.336	0.695
18.521	75.4	1.39	1.39	1.96	0.830
0.823	7.11	1.00	2.64	0.000	0.594
18.481	77.5	2.11	7.98	0.328	1.748
7.316	50.6	0.326	0.096	0.013	0.001

## Determination apparent activation barrier

error conv	error AA	error pal	error ac	error pol	error hac
2.21	1.45	2.63	0.17	3.54	0.00
2.36	2.16	2.58	0.62	4.37	0.00
2.21	4.56	4.68	1.00	6.38	3.65
3.86	2.72	7.32	0.48	1.87	2.56

## Triplo 325C

Experiment	PG conversion	error conv	error AA	error pal	error ac	error pol	error hac
first	75.4	2.57	1.39	1.96	0.59	0.83	-
duplo	77.5	3.13	2.11	7.98	0.33	1.75	0.76
triplo	79.4	1.99	4.07	7.30	0.27	4.36	1.14

### **Co-feeding**

PG error	AA error	PAL error	ACE error	POL error	HAC error
3.71	0.69	1.33	0.00	0.33	0.56
3.79	3.47	3.23	0.07	0.89	0.14
3.17	0.48	2.12	0.02	1.53	2.30
3.89	0.54	1.71	3.31	0.53	0.61
1.85	2.32	5.06	0.09	0.29	0.31
5.23	0.67	8.38	0.02	1.80	1.24
1.08	6.74	7.23	0.04	0.72	0.37

## Appendix C

## Weisz-Prater estimation

In the main sections of the report the possibility of internal mass transfer diffusion limitations is briefly discussed. While tests were performed to eliminate external mass transfer limitations from the system, no such thing was done for the internal mass transfer limitations. The main reason for not executing these tests, such as varying the particle size, is that the present research works primarily with a bulk metal oxide catalyst. These types of catalysts have few pores and rely on the active sides on the outside of the catalyst. The high applied calcination temperature of 800 °C almost guarantees that few pores are present in these catalysts. The BET surface area measurement confirm this.

For the sake of completeness, and to eliminate any possibility of internal mass transfer limitations, the Weisz-Prater criterion is calculated for the tested  $Sc_2O_3$  catalyst. The Weisz-Prater criterion compares the rate of the reaction compared to the diffusivity of the molecule. Consequently, it follows that for a Weisz-Prater criterion of  $\leq 1$ , there are no internal limitations, as the terms for the reaction rate is in the numerator of the equation. The Weisz-Prater criterion will thus be  $\leq 1$  if the reaction rate is faster than the internal diffusion rate. Vice versa, the value will be greater than 1 if internal diffusion dominates the system. The Weisz-Prater criterion is presented in Equation C.1.

$$N_{W-P} = \frac{R r_p^2}{C_s D_{eff}}$$
(C.1)

In the Weisz-Prater criterion, the Weisz-Prater number is represented  $N_{W-P}$ , the reaction rate in [mol m<sup>-3</sup> <sub>cat</sub> s<sup>-1</sup> by R, the radius of the catalyst particle in [m] by r<sub>p</sub>, the concentration of reactant on the catalyst surface in [mol m<sup>-3</sup>] by C<sub>s</sub> and the effective diffusion rate of the reactant in the internal pores by D<sub>eff</sub> respectively. The effective diffusion rate can be calculated according to Equation C.2.

$$D_{eff} = \frac{D \epsilon}{\tau} \tag{C.2}$$

The effective diffusion rate can be calculated by multiplying the diffusion rate of the reactant in the gas by the porosity of the catalyst and consecutively dividing by the tortuosity of the catalyst. In the present study, the diffusion rate of PG in  $N_2$ , the tortuosity of the catalyst, the porosity of the catalyst and the concentration of reactant at the catalyst surface are unknown. The diffusion rate of PG in  $N_2$  at the reaction temperature could not be found in literature. As an approximation, the diffusion rate at ambient conditions is used in the calculation of the Weisz-Prater criterion. The values used and calculated in the calculation of the Weisz-Prater number are presented in Table C.1.

Parameter	(calculated)Value	Units
Cs	18,9487006	mol m $^{-3}$
eps	0,33	
tau	4	
D	8,79E-02	$m^2 \: s^{-1}$
Deff	7,25E-03	$m^2 \: s^{-1}$
Cs	18,9487006	mol m $^{-3}$
rp	4,50E-05	m
rate	14,21	mol m $^{-3}$ $_{cat}$ s $^{-1}$
Weisz-Prater	2,09E-07	

Table C.1: Parameters and values for calculation of Weisz-Prater criterion

As can be seen from Table C.1, the calculated Weisz-Prater number is lower than 1 for the worst case scenario of particle size. This result indicates that there are no internal mass transfer limitations present.

## Appendix D

## **Calibration of Mass Flow Controllers**

The MFCs in this research originally not being calibrated for  $N_2$ . To be able to properly use these MFCs in the present research, a calibration will have to be done for each of the MFCs. This way, the proper  $N_2$  flow can be applied to the system. The calibration is done by using an X external flow meter to measure the actual amount of  $N_2$  injected in the system at certain MFC settings.



Figure D.1: Calibration lines for the MFCs used in the present research

In the Figure above the calibration curves of the 2 utilized MFCs is shown. The linear equations are based on the setpoint from the initial MFC. This way, the setpoint for this MFC can be entered in the equation and the actual flow rate can easily be calculated. Similarly, one can solve the setpoint for the desired flow rate.

## Appendix E

## **HPLC** calibration

The product samples are analyzed using HPLC. To measure the actual concentration in the product sample, the peak are of the peak belonging to the specific compound, is converted using a response factor. The response factor for each of the components is presented in this appendix. Using these response factors, the concentration of the components can be determined according to Section 3.3.

#### Model reaction calibration

The calibration curves for the model reaction are presented in the Figures below.



Figure E.1: Calibration curve BDO



Figure E.2: Calibration curve 3-buten-2-ol



Figure E.3: Calibration curve MEK

#### Main reaction calibration

The calibration curves for the main reaction are presented in the Figures below.



Figure E.4: Calibration curve AA



Figure E.5: Calibration curve PG



Figure E.6: Calibration curve AC



Figure E.7: Calibration curve HAC

Appendix F

# **BET adsorption**

Full	Report S	Set
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TriStar 3000 V6.04 A	Unit 1 Port 2	Seri	ial #: 1341	Page 1
Sample: BM-180220 Operator: B20006 Submitter: Dennis/Jim File: C:\WIN300	) my 0\DATA\2020-020.SMP			
Started: 20/02/2020 8:3 Completed: 20/02/2020 12: Report Time: 20/02/2020 12: Warm Free Space: 8.7488 cm <sup>3</sup> Mea Equilibration Interval: 10 s Sample Density: 1.000 g/cm <sup>3</sup>	7:28PM Ana 50:08PM Anal 52:32PM asured C Low A	Ilysis Adsorptive: ysis Bath Temp.: Sample Mass: Cold Free Space: / Pressure Dose: utomatic Degas:	N2 77.350 K 0.0917 g 25.8621 cm <sup>3</sup> Measure None Yes	ed

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage 1 2	Soak Temperature 90 300	(°C) Ram	np Rate (°C/min) 10 10	Soak	Time (min) 60 6000		
Isotherm Tabular Report							
Relative Pressure (P/P	Absolute o) Pressure (mmHg)	Quantity Adsorbed (cm <sup>3</sup> /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)			
0.01010050 0.03339176 0.06811440 0.0797823 0.09981345 0.19971522 0.13973316 0.15971522 0.1796699 0.19964125 0.2498055 0.29918944 0.3983763 0.34917283 0.39833763 0.4486622 0.49855313 0.54835085 0.59822047 0.64791994 0.69782865 0.74741337 0.79707665 0.81887660 0.84761065 0.877233776 0.8965889 0.9237067 0.9448899 0.97240083 0.98076944 0.98075556 0.99348715 0.99348715	09      7.67870        30      25.38528        31      51.78212        34      60.65213        354      75.87996        39      91.05762        38      106.22692        39      121.41713        36      151.76828        36      156.58643        36      255.43982        34      203.19379        36      378.99432        31      416.84860        77      454.75723        32      442.53629        36      378.99432        31      416.84860        32      644.32542        36      378.99432        31      416.84860        32      643.1984        33      605.91522        33      605.91522        39      63.11884        36      663.11884        36      663.11884        36      663.11884        36      749.90033        33      755.14624        33      745.99033 <t< td=""><td>3.0464 3.5030 3.8254 3.9237 4.0753 4.2210 4.3604 4.4998 4.6425 4.7874 5.1316 5.4935 5.8660 6.2356 6.6068 6.9758 7.3564 7.7616 8.2526 8.8448 9.6290 10.7206 11.3767 12.6124 14.2304 17.0086 24.2874 33.1420 47.6982 52.2900 57.0390 62.4706 59.1247</td><td>00:46 00:50 00:53 00:55 00:57 00:59 01:01 01:05 01:05 01:07 01:09 01:11 01:14 01:14 01:16 01:18 01:22 01:24 01:22 01:24 01:22 01:24 01:28 01:30 01:35 01:37 01:39 01:42 01:42 01:42 01:55 02:03 02:16 02:22 02:28 02:28 02:38</td><td>760.23431</td><td></td></t<>	3.0464 3.5030 3.8254 3.9237 4.0753 4.2210 4.3604 4.4998 4.6425 4.7874 5.1316 5.4935 5.8660 6.2356 6.6068 6.9758 7.3564 7.7616 8.2526 8.8448 9.6290 10.7206 11.3767 12.6124 14.2304 17.0086 24.2874 33.1420 47.6982 52.2900 57.0390 62.4706 59.1247	00:46 00:50 00:53 00:55 00:57 00:59 01:01 01:05 01:05 01:07 01:09 01:11 01:14 01:14 01:16 01:18 01:22 01:24 01:22 01:24 01:22 01:24 01:28 01:30 01:35 01:37 01:39 01:42 01:42 01:42 01:55 02:03 02:16 02:22 02:28 02:28 02:38	760.23431			
0.97183988 0.95387424 0.93004510 0.90454416	36      738.68109        48      725.02081        50      706.90875        57      687.52600	55.5661 48.3199 39.5066 31.4123	02:43 02:47 02:50 02:58 03:06	760.08008			
TriStar 3000 V6.04 A	Unit 1 Port 2	Seria	al #: 1341	Page 2			
--	---	--	---	--------			
Sample: BM-18 Operator: B2000 Submitter: Dennis File: C:\WIN	0220 6 /Jimmy I3000\DATA\2020-020	.SMP					
Started: 20/02/2020 Completed: 20/02/2020 Report Time: 20/02/2020 Warm Free Space: 8.7488 cm <sup>3</sup> Equilibration Interval: 10 s Sample Density: 1.000 g/cm	8:37:28PM 12:50:08PM 12:52:32PM Measured	Analysis Adsorptive: Analysis Bath Temp.: Sample Mass: Cold Free Space: Low Pressure Dose: Automatic Degas:	N2 77.350 K 0.0917 g 25.8621 cm <sup>3</sup> Measured None Yes	d			

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep 1 2	: Stage	Soak Temperature 90 300	e (°C) Ran	np Rate (°C/min) 10 10	Soak	Time (min) 60 6000
		Isot	herm Tabular Re	port		
	Relative Pressure (P/Po	Absolute ) Pressure (mmHg)	Quantity Adsorbed (cm <sup>3</sup> /g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)	
	0.88097904	9 669.61462	24.3962	03:14		
	0.85425167	9 649.29968	17.4103	03:21		
	0.82552802	7 627.46741	13.3571	03:26		
	0.80484458	9 611.74634	11.8896	03:29		
	0.73289533	4 557.05914	9.4973	03:33		
	0.68420316	4 520.04919	8.6607	03:35		
	0.63360272	2 481.58881	8.0081	03:37		
	0.60132643	5 457.05624	7.6690	03:39		
	0.55180387	3 419.41513	7.2243	03:41		
	0.50167640	3 381.31424	6.8297	03:43		
	0.45162040	1 343.26767	6.4212	03:45		
	0.40145988	7 305.14166	6.0570	03:47		
	0.35132141	6 267.03241	5.6932	03:49		
	0.30119392	7 228.93150	5.3216	03:51		
	0.25106093	6 190.82642	4.9576	03:54		
	0.20092242	5 152.71713	4.6187	03:56		
	0.15057496	1 114.44903	4.2934	03:58		
	0.10061244	9 76.47352	3.9742	04:00		
	0.05009449	6 38.07583	3.5964	04:03		
	0.02995000	8 22.76440	3.3739	04:06		
	0.01005299	6 7.64108	2.9541	04:11		



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TriStar 3000 V6.04 AUnit 1 Port 2Serial #: 1341Page 4Sample:BM-180220<br/>Operator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:B20006<br/>Submitter:Deperator:Deperator:B20006<br/>Submitter:Deperator:Depe

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000

**BET Surface Area Report** BET Surface Area: 17.2052 ± 0.0435 m<sup>2</sup>/g Slope: 0.250902 ± 0.000633 g/cm<sup>3</sup> STP Y-Intercept: 0.002115 ± 0.000087 g/cm<sup>3</sup> STP C: 119.655133 Qm: 3.9523 cm<sup>3</sup>/g STP Correlation Coefficient: 0.9999809 Molecular Cross-Sectional Area: 0.1620 nm<sup>2</sup> Relative Quantity 1/[Q(Po/P - 1)] Pressure (P/Po) Adsorbed (cm<sup>3</sup>/g STP) 0.068114401 0.079782314 0.019107 0.022097 3.8254 3.9237 0.099813454 4.0753 0.027208 0.119778739 0.139733168 4.2210 4.3604 0.032238 0.042240 0.047177 0.159715229 4.4998 0.179669916 4.6425 0.199641256 4.7874 0.052104

Full Report Set							
TriStar 3000 V6.04 A	Unit 1 Port 2	Seria	al #: 1341	Page 5			
Sample Operator Submitter File	: BM-180220 : B20006 : Dennis/Jimmy : C:\WIN3000\DATA\2020-020.	SMP					
Started: 20, Completed: 20, Report Time: 20, Warm Free Space: 8.7 Equilibration Interval: 10 Sample Density: 1.0	(02/2020 8:37:28PM (02/2020 12:50:08PM (02/2020 12:52:32PM (488 cm <sup>3</sup> Measured s 000 g/cm <sup>3</sup>	Analysis Adsorptive: Analysis Bath Temp.: Sample Mass: Cold Free Space: Low Pressure Dose: Automatic Degas:	N2 77.350 K 0.0917 g 25.8621 cm <sup>3</sup> Measured None Yes				
Comments: start degas:1802	22020-14:48 end degas:200220	)20-8:35 weight loss aft	er degassing 8,4%				



TriStar 3000 V6.04 AUnit 1 Port 2Serial #: 1341Page 6Sample:BM-180220<br/>Operator:B20006<br/>Submitter:December 20006<br/>December 2000/DATA/2020-020.SMPSubmitter:December 2000/DATA/2020-020.SMPStarted:20/02/2020 8:37:28PM<br/>Completed:Analysis Adsorptive:N2<br/>Analysis Bath Temp.:77.350 K<br/>Sample Mass:0.0917 g<br/>Cold Free Space:25.8621 cm³ Measured<br/>Low Pressure Dose:None<br/>Automatic Degas:Yes

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000

Langmuir Surface Area Report

Langmuir Surface Area: 23.8821 ± 0.5650 m²/g Slope: 0.182279 ± 0.004312 g/cm³ STP Y-Intercept: 4.584259 ± 0.452588 mmHg·g/cm³ STP b: 0.039762 1/mmHg Qm: 5.4861 cm³/g STP Correlation Coefficient: 0.998325 Molecular Cross-Sectional Area: 0.1620 nm<sup>2</sup> Pressure Quantity P/Q (mmHg·g/cm<sup>3</sup> STP) (mmHg) Adsorbed (cm<sup>3</sup>/g STP) 51.78212 60.65213 13.536 15.458 3.8254 3.9237 75.87996 4.0753 18.619 4.2210 4.3604 21.573 24.362 26.983 91.05762 106.22692 121.41713 4.4998 29.421 31.702 136.58643 4.6425 151.76828 4.7874

Full Report Set					
TriStar 3000 V6.04 A	Unit 1	Port 2	Serial #: 1341	Page 7	
Sample: BM-18022 Operator: B20006 Submitter: Dennis/Jir File: C:\WIN30 Started: 20/02/2020 12 Report Time: 20/02/2020 12 Report Time: 20/02/2020 12 Warm Free Space: 8.7488 cm <sup>3</sup> Me Equilibration Interval: 10 s Sample Density: 1.000 g/cm <sup>3</sup>	20 nmy 00\DATA\2 37:28PM :50:08PM :52:32PM easured	020-020	SMP Analysis Adsorptive: N2 Analysis Bath Temp.: 77.350 K Sample Mass: 0.0917 g Cold Free Space: 25.8621 cm <sup>3</sup> Measured Low Pressure Dose: None Automatic Degas: Yes	i	

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000



Langmuir Surface Area Plot

TriStar 3000 V6.04 AUnit 1 Port 2Serial #: 1341Page 8Sample:BM-180220<br/>Operator:B20006<br/>Submitter:Densis/Jimmy<br/>File:Completed: 20/02/2020 8:37:28PMAnalysis Adsorptive:N2Started:20/02/2020 8:37:28PM<br/>Completed:Analysis Adsorptive:N2Analysis Bath Temp.:77.350 KReport Time:20/02/2020 12:50:08PM<br/>Report Time:Analysis Bath Temp.:77.350 KSample Mass:0.0917 gWarm Free Space:8.7488 cm³ Measured<br/>Sample Density:Cold Free Space:25.8621 cm³ MeasuredLow Pressure Dose:NoneSample Density:1.000 g/cm³Automatic Degas:YesYesYes

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep:	Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1		90	10	60
2		300	10	6000

 $\label{eq:constraint} \begin{array}{l} \mbox{t-Plot Report} \\ \mbox{Micropore Volume: } 0.001885 \mbox{ cm}^3/g \mbox{STP} \\ \mbox{Micropore Area: } 3.4606 \mbox{m}^2/g \\ \mbox{External Surface Area: } 13.7446 \mbox{m}^2/g \\ \mbox{Slope: } 0.888580 \pm 0.013249 \mbox{ cm}^3/g \mbox{Å STP} \\ \mbox{Slope: } 0.888580 \pm 0.013249 \mbox{ cm}^3/g \mbox{Å STP} \\ \mbox{Y-Intercept: } 1.218444 \pm 0.089733 \mbox{ cm}^3/g \mbox{STP} \\ \mbox{Correlation Coefficient: } 0.999556 \\ \mbox{Surface Area Correction Factor: } 1.000 \\ \mbox{Density Conversion Factor: } 0.0015468 \\ \mbox{Total Surface Area (BET): } 17.2052 \mbox{m}^2/g \\ \mbox{Thickness Range: } 5.5000 \mbox{Å to } 8.0000 \mbox{\AA} \\ \mbox{Thickness Equation: Harkins and Jura} \\ \mbox{t = [ 13.99 / ( 0.034 - \log(P/P0) ) ] ^ 0.5 \\ \end{array}$ 

Relative Pressure (P/Po)	Statistical Thickness (Å)	Quantity Adsorbed (cm <sup>3</sup> /g STP)
0.010100509	2.6254	3.0464
0.033391780	3.0435	3.5030
0.068114401	3.4133	3.8254
0.079782314	3.5153	3.9237
0.099813454	3.6769	4.0753
0.119778739	3.8262	4.2210
0.139733168	3.9676	4.3604
0.159715229	4.1039	4.4998
0.179669916	4.2364	4.6425
0.199641256	4.3665	4.7874
0.248980545	4.6833	5.1316
0.299189446	5.0069	5.4935
0.349172836	5.3381	5.8660
0.398837634	5.6828	6.2356
0.448662219	6.0511	6.6068
0.498553136	6.4499	6.9758
0.548350891	6.8872	7.3564
0.598220477	7.3761	7.7616
0.647919942	7.9298	8.2526

107

Full Report Set						
TriStar 3000 V6.04 A	Unit 1	Port 2	Seri	ial #: 1341	Page 9	
Sample: BM-180220 Operator: B20006 Submitter: Dennis/Jimmy File: C:\WIN30001 Started: 20/02/2020 8:37:2 Completed: 20/02/2020 12:50 Report Time: 20/02/2020 12:52 Warm Free Space: 8.7488 cm <sup>3</sup> Measu Equilibration Interval: 10 s Sample Density: 1.000 g/cm <sup>3</sup>	/ DATA\2 28PM :08PM :32PM ured	020-020.	SMP Analysis Adsorptive: Analysis Bath Temp.: Sample Mass: Cold Free Space: Low Pressure Dose: Automatic Degas:	N2 77.350 K 0.0917 g 25.8621 cm <sup>3</sup> Measured None Yes		

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%



TriStar 3000 V6.04 /	A Unit 1	Port 2	Serial #: 1341	Page 10
Samp Operat Submitt F	ole: BM-180220 or: B20006 er: Dennis/Jimmy ile: C:\WIN3000\DATA\2	020-020.SMP		
Started: 2 Completed: 2 Report Time: 2 Warm Free Space: 8 Equilibration Interval: 2 Sample Density: 2	20/02/2020 8:37:28PM 20/02/2020 12:50:08PM 20/02/2020 12:52:32PM 3.7488 cm <sup>3</sup> Measured 10 s 1.000 g/cm <sup>3</sup>	Analysis Adsor Analysis Bath T Sample I Cold Free S Low Pressure Automatic D	ptive: N2 emp.: 77.350 K Mass: 0.0917 g pace: 25.8621 cm <sup>3</sup> Mea Dose: None legas: Yes	sured

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000



#### BJH Adsorption dV/dlog(w) Pore Volume

		Full Report Set		
TriStar 3000 V6.04 A	Unit 1	Port 2	Serial #: 134	1 Page 11
Sample Operator Submitter File	:: BM-180220 :: B20006 :: Dennis/Jimmy :: C:\WIN3000\DATA\2	020-020.SMP		
Started: 20. Completed: 20 Report Time: 20 Warm Free Space: 8.7 Equilibration Interval: 10 Sample Density: 1.0	/02/2020 8:37:28PM /02/2020 12:50:08PM /02/2020 12:52:32PM 7488 cm <sup>3</sup> Measured s 000 g/cm <sup>3</sup>	Analysis Analysis Sa Cold Low Pre Autor	Adsorptive: N2 Bath Temp.: 77.350 ample Mass: 0.0917 Free Space: 25.8621 issure Dose: None natic Degas: Yes	K g cm³ Measured

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000



## 110

TriStar 3000 V6.04 A	Unit 1 Port 2	Seria	al #: 1341	Page 12
Sample: BM-1 Operator: B200 Submitter: Denn File: C:\W	80220 06 iis/Jimmy IN3000\DATA\2020-020	).SMP		
Started: 20/02/202 Completed: 20/02/202 Report Time: 20/02/202 Warm Free Space: 8.7488 cr Equilibration Interval: 10 s Sample Density: 1.000 g/c	20 8:37:28PM 20 12:50:08PM 20 12:52:32PM n <sup>3</sup> Measured m <sup>3</sup>	Analysis Adsorptive: Analysis Bath Temp.: Sample Mass: Cold Free Space: Low Pressure Dose: Automatic Degas:	N2 77.350 K 0.0917 g 25.8621 cm <sup>3</sup> Measured None Yes	1

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000



BJH Desorption dV/dlog(w) Pore Volume

Full Report Set					
TriStar 3000 V6.04 A	Unit 1	Port 2	Seri	ial #: 1341	Page 13
Sample: BM-180220 Operator: B20006 Submitter: Dennis/Jimmy File: C:\WIN3000\E Started: 20/02/2020 8:37:2 Completed: 20/02/2020 12:50: Report Time: 20/02/2020 12:52: Warm Free Space: 8.7488 cm³ Measu Equilibration Interval: 10 s Sample Density: 1.000 g/cm³	/ DATA\2 8PM 08PM 32PM Jred	020-020	0.SMP Analysis Adsorptive: Analysis Bath Temp.: Sample Mass: Cold Free Space: Low Pressure Dose: Automatic Degas:	N2 77.350 K 0.0917 g 25.8621 cm <sup>3</sup> Measured None Yes	

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Stage	Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000



TriStar 3000 V6.04 A

Unit 1 Port 2

Serial #: 1341

Page 14

Sample: BM-180220 Operator: B20006 Submitter: Dennis/Jimmy File: C:\WIN3000\DATA\2020-020.SMP

Comments: start degas:18022020-14:48 end degas:20022020-8:35 weight loss after degassing 8,4%

Sample Prep: Sta	ge Soak Temperature (°C)	Ramp Rate (°C/min)	Soak Time (min)
1	90	10	60
2	300	10	6000

#### Summary Report

Surface Area

BET Surface Area: 17.2052 m<sup>2</sup>/g

Langmuir Surface Area: 23.8821 m<sup>2</sup>/g

t-Plot Micropore Area: 3.4606 m²/g

t-Plot External Surface Area: 13.7446 m²/g

BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 16.0310 m²/g

BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 19.5302 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 715.846 Å width at P/Po = 0.972400839: 0.073780 cm<sup>3</sup>/g

t-Plot micropore volume: 0.001885 cm3/g

BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.095870 cm³/g

BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.096709 cm³/g \_\_\_\_\_

Appendix G

# **Risk and inventory evaluation**

## **Risk Inventory & Evaluation**

Catalytic testing of dehydration of propylene glycol over scandium oxide based catalysts

Dennis Tjeerdsma

## Overview of research and involved persons

#### Type of document

Internal "RI&E Experimental set-up"

Period

Starting date of building set-up:	July 2019
Starting date research:	August 2019
End date research:	February 2020

#### Involved responsible persons who did participate in the HAZOP study

	Name	Phone	Signature
Research group	Catalytic Processes & Materials	3033	
Responsible person			
Supervisor	Jimmy Faria	7115	
AMC Research group	Ing. B. Geerdink	2417	
Group Leader	Prof.dr.L. Lefferts	5410	

Type of research

Graduation research

#### Name of set-up/experiment/project

Catalytic dehydration of 1,2-propanediol to allyl alcohol over scandium oxide based catalysts

#### Research data

P <sub>max</sub> :	1 bar
T <sub>max</sub> :	425C

Type of compounds: Flammable, toxic, corrosive, environmental hazard, irritating

Type of research: Catalytic testing

#### Location of the set-up Laboratory ME309 Box 05

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 Appendix D: Chemical information

## 1 Research project description

#### 1.1 Motivation

The energy business in the world is shifting as a result of climate change. With the shift, comes an increasing demand for green sources of carbon and energy. One source of green carbon is the production of biodiesel from biomass. In this process, glycerol is formed as a byproduct. Additionally, a mixture of polyols can be produced from other feedstocks such as starch or sugar syrup. As a result, Propylene Glycol (PG) is becoming more available in the near future. One way of using PG, is to upgrade the molecule to Acrylic Acid (AcrA). In the past, the PG was oxidized to lactic acid, which was consecutively dehydrated to form Acrylic Acid. Pramod et al propose a dehydration of PG to Allylic Alcohol (AA), followed by an oxidation step to produce AcrA. The oxidation step for this process has been studied and shows promising results. The dehydration of PG still requires a catalyst with sufficient activity and selectivity towards AA. This research will study the applicability and kinetics of scandium-oxide based catalysts in the dehydration of PG to AA.

#### 1.2 Process & experimental setup



Figure 1, Process Flow Diagram of the experimental setup

Propylene glycol dissolved in water is pumped from the feed vessel to the heater at a rate of approximately 1ml/h (depending on the W/F ratio). Additionally, a carrier gas is fed to the heater at a rate of 40-80 ml/min. This carrier gas is used to adjust the GHSV of the system. The flow will be heated up to 325 degrees centigrade which evaporates the propylene glycol and water. Before the propylene glycol pump is activated, the catalyst in the reactor tube will be preheated by the carrier gas. The reactant flow will flow over the preheated catalyst bed (ID = 6mm, length = , +-500mg catalyst). There is no need for any pressure control as a system at atmospheric pressures is desired. The product flow is cooled down by water to condense propylene glycol, allyl alcohol and water

from the vapor stream. A glycol cold trap is placed before the micro gas chromatograph so no water can enter the GC. The liquid + gas product flow is led to a glass vessel where the liquid and gas phase are separated. At the cold trap, there is a sampling point to take liquid sample for the HPLC. The liquid phase is collected in the flask while the gas phase is vented over the ventilation system.

1.2.1 Reaction pathways main reaction

The project research is mostly concerning the dehydration of 1,2-propanediol to allyl alcohol. The following reactions and side reactions can take place in this dehydration process.

- C3H8O2(g) -> C3H6O(g)[Allyl Alcohol] + H2O(g)
- C3H8O2(g) -> C3H6O(g)[Acetone] + H2O(g)
- C3H8O2(g) -> C3H6O(g)[Propionaldehyde] + H2O(g)

#### 1.2.2 Reaction pathways model reaction

- C4H10O2(g) -> C4H8O(g)[3-buten-2-oll] + H2O(g)
- C4H10O2(g) -> C4H8O(g)[Acetoin] + H2O(g)
- C4H10O2(g) -> C4H8O(g)[Methyl Ethyl Ketonel] + H2O(g)

#### 1.3 Manual

#### 1.3.1 Preparation of catalyst

Sc2O3 catalyst can be prepared by wet impregnation method from scandium nitrate solution. 300 ml of the precipitant solution (ammonia water) is dripped into 300 ml of scandium nitrate solution in water (0.1mol/l) at 80 degrees centigrade under stirring. The suspension is filtered after stirring for 1 hour using suction filtration. The cake is washed 5 times before being rinsed using anhydrous alcohol. The precipitate is dried with n2 gas at room temperature overnight. The precipitate is crushed with a mortar and pestle and consecutively calcined at 800 degrees centigrade.

Additionally, to simulate the model reaction and do the first investigations of the dehydration of propylene glycol a scandium oxide powder from Sigma Aldrich will be used. This scandium oxide will be calcined in air at 800 degrees centigrade for 3 hours. The scandium oxide can then be used as is.

#### 1.3.2 Preparation of propylene glycol reactant solution

In case of a propylene glycol - water mixture, to study for example the behavior of the reaction in a steam atmosphere, the appropriate amount of propylene glycol will be mixed in water to dilute the propylene glycol to the desired degree. This is to be determined further before conducting the experiments. Early experiments will be performed using pure propylene glycol.

#### 1.3.3 Characterization of components

The characterization of the solutions is done using High Pressure Liquid Chromatography(HPLC). For this purpose, calibration curves have to be made to be able to properly characterize the components.

The solutions for the HPLC calibration curves are made using standard analytical stock solution of the components. The three stock solutions are mixed using equivalent molar ratios. This mother solution will be diluted to prepare 5 standard solutions. The analytical stock solutions can be used to identify the peaks. The calibration curves are generated using the area under the different peaks. It is important to dilute the solution to such a degree that the expected concentrations in the liquid phase fall within the calibration region

#### 1.4 Preparation activities

- Turn on the cooling device of GC 1 day before performing an experiment. The GC cannot be used unless the cooling device is on and the temperature inside the cooler is low enough. This is to prevent water from entering the GC.
- Check the thermocouples of the reactor and the heater
- Check that all connections are closed (L/G separator, Gas outlet) so no gas leakage can occur, flush with nitrogen to check a closing of the mass balance.
- Turn bakeout-method of GC off if turned on
- Connect GC to L/G separator
- Sign in to the HPLC user list before the experiment so the samples taken from the L/G separator can be analyzed during the experiment
- Check eluent level of the HPLC. Method uses approximately 300ml/8h

#### 1.5 During activities

#### 1.5.1 Set up

• Check if the temperature in the cooling system is low enough

- Place the to be tested catalyst in the reactor tube and insert the reactor tube inside the furnace.
- Heat the heater and reactor the the desired temperature
- Enter the flow rate of the carrier gas and open the valve
- Preheat the catalyst bed with the carrier gas and check to make sure all equipment is working. Check if there is no leakage by reading the gas flow rate on the mass flow meter in the in and outlet of the stream.
- If necessary, connect the GC for online analysis.

#### 1.5.2 Experimental run

- Set the pump for the propylene glycol to the desired flow rate
- Collect samples for HPLC every 30 minutes to check the stability of the system, follow the safety
  regulations for the appropriate chemicals

#### 1.5.3 Post activities

- Replace the reactant with water to flush the system
- Turn of the pump of the water tank and close the valves to shut down the "reactant" feed
- Flush the system with inert nitrogen gas to remove remaining compounds from the system
- Set the mass flow controller for the carrier gas to 0 and close the valve
- Turn off the heating elements and let the system cool down
- Disconnect the GC and set to bakeout if water was detected

#### 1.6 Cleaning

Before removing the reactor from the system, flush the system with water to remove any reactants and products present in the system. Take note to flush enough water to completely remove any compounds from the G/L separator. Flush the system with inert nitrogen to remove any residual compounds.

Clean the reactor by removing the catalyst and flush the reactor using water to remove any residual traces of reactants/products. No residual traces of reactants or products should be found in the system if the proper shut down procedure is followed.

#### 1.7 Emergency shutdown procedure

- Close the box and hit the emergency shutdown button to stop all heating and pumping in the system.
- Turn off the HPLC pump

#### 2 Risk Inventory and Evaluation Overview

This chapter presents an overview of different aspects that have an influence on the safety of the experimental work:

#### 2.1 Used chemicals

The following chemicals will be used:

Water, 1,2-propanediol, allyl alcohol, acetone, propionaldehyde, 2,3-butanediol, 3-buten-2-ol, methyl ethyl ketone, 3-hydroxy-2-butanone, 1-propanol, N2

#### 2.2 Safety precautions concerning the toxicity and hazards of chemicals used

Flammable chemicals should be stored in flammable cabinets and handled in working fume hoods. Goggles should be worn at all times while conducting experiments. Chemicals shall not be inhaled nor swallowed.

Propylene glycol, allyl alcohol, propionaldehyde, 1-propanol, 2,3butanediol, 3-buten-2-ol, acetoin and butanone are either toxic or irritant and should only be handled using a laboratory coat, safety glasses, closed shoes, long trousers and PVC/neoprene gloves.

assificati	ine on schei	mes	'S D	etwee
IARC	GHS	NTP	ACGIH	EU
Group 1	Cat. 1A	Known	A1	Cat. 1
Group 2A	Cat. 1B	Reasonably suspected	A2	Cat. 2
Group 2B	Cat. 2		A3	Cat. 3
Group 3			A4	
Group 4			A5	

In the worst case scenario, all of the propylene glycol is converted to allyl alcohol, and the allyl alcohol is exposed to the air for a significant period of time combined with a non functioning ventilation system in the box. In this case, considering a molar weight of 58.08 g/mol and a vapour pressure of 26.7mbar at 25

degrees centigrade. The concentration of allyl alcohol in the open air of the box will be 62.56 g/m3. This far exceeds the limit value of 4.8mg/m3. As such, adequate ventilation should <u>always</u> be present while working with this reaction. Additionally, keep the box as closed as possible to prevent any leaked allyl alcohol from spreading through the laboratory. In addition, checking the system for leaks by flushing with nitrogen before an experiment should prevent any allyl alcohol from coming in contact with open air. The allyl alcohol will be collected in the glass vessel from which it can be disposed safely in a fume hood.

#### 2.3 Safety regulations

As far as we know all valid safety regulations have been consulted and followed.

#### 2.4 Operation

1. The manual, containing the subjects:

- Preparation activities,
- Performing experiments,
- Sampling,
- Cleaning,
- Emergency shutdown procedure

## 2.5 Testing

The set-up is tested at high pressure in the HDL conform the regulations (see an).

#### 2.6 Maintenance and reparations of the set-up

- 1) Qualified personnel of the Science and Technology Department will do maintenance and eventual reparations of the set-up.
- 2) Before any reparations, the cleaning procedure described in the operational manual should be performed.
- 3) After any significant reparation, an adequate testing of the set-up will be done.
- 4) If changes are made on the set-up, the change will be documented and presented in this document.

#### 2.7 Documentation

Available documentation:

- 1) A copy of this report "Risk Inventory & Evaluation: Catalytic testing of dehydration of propylene glycol over scandium oxide based catalysts
  - The manual including the emergency shutdown procedure
  - Flowsheet of the set-up
  - HAZOP
- 2) Information sheet experiment

### 3 Organization of the place of work

#### 3.1 Ergonomics

- 1) Work space dimensions are: 200 cm x 200 cm x 200 cm.
- 2) The set-up is built in a metal frame.
- 3) General requirements:
  - laboratory ME309 has 2 main entrances and 2 escape routes
  - daylight can reach the work space through the windows
  - adequate neon light is installed at the ceiling
  - floors do fulfil the requirements
  - ventilation of the work space is provided
  - there are no sources of noise and vibrations in close proximity of the work space
  - there are several grounded electrical power connections (several mono-phase and one three-phase connection)
  - the source of warm and cold water is provided in the laboratory.

#### 3.2 Technical requirements

- 1) The set-up is placed in a separate, adequately ventilated box, provided with sliding doors, within ME309.
- 2) Operation of the set-up is clear and the set-up is well accessible.

#### 3.3 Safety measures

- 1) During the experimental work, personal protection is provided by:
  - safety glasses
  - adequate protection gloves
  - lab coat
- 2) A lexane plate shields the reaction vessel.
- Adequate ventilation (from the roof and point ventilation) is provided to prevent accumulation of gases (carbon dioxide) and vapours (toluene) inside the working space.
- 4) Pressure vessel is shielded by furnace

#### 3.4 Safety requirements

- 1) The following safety items are provided in or close to the work place:
  - fire alarm in the corridor
  - phone near door ME309R
  - fire extinguishers
  - two escape paths for the case of emergency
  - first aid kit in office ME309
  - eye shower near the main entrance
  - emergency shower above the main entrance
- 2) Safety signs
  - the up-to-date lab info card
  - signs: "safety glasses required", "no fire"
  - no additional indications concerning the dangerous situations
  - **no** indications concerning the escape routes
  - indications about who to inform in the case of an accident
  - no indications on the presence or absence of people

• indications about location of the First Aid Kit and safety showers

## 3.5 Skilled personnel

There are several skilled persons present at the site able to:

- 1) perform any reparation on the set-up,
- 2) repair electrical connections,
- 3) give technical assistance.

## 4 HAZOP (Hazard and Operability) study

The HAZOP study has been performed in the form of a discussion c.q. brainstorm-session by the involved persons. The HAZOP study consists of analyzing potential deviations of the process parameters. Table 2 the results.

Kennen Devietien Dessibl	Como								
Table 2. Analysis of the process parameter deviations									

d	Deviation	Possible causes	consequences	Action required
More	Pressure	Plugging in tubing/reactor	Failure of fittings (>250 bar)	Stop experiment Stop carrier gas flow
			Failure of vessel (>250 bar)	Stop reactant flow Clean system
		Malfunction of	No	Stop experiment
		manometer	consequences	Replace manometer
Less	Pressure	Pump reversal	No consequences - check valve prevents back flow	Stop experiment Shut down system
		Fittings not tightened properly	Leakage of toxic vapours	Stop the experiment Shut down system Ensure ventilation is working properly Wait for the toxic fumes to be removed by the ventilation system Tighten fittings to appropriate levels
More	Flow (heater/reactor)	MFC malfunction	No consequences	Stop experiment Close gas net valves Turn off MFC Repair/replace MFC
		Pump malfunction	No consequences	Stop experiment Turn off Pump Close pump valves

				Repair pump		
Less	Flow	Partial plugging	No	Stop experiment		
	(heater/reactor)		consequences	Shut down system		
				Clean system		
No	Flow	MFC Failure	No	Stop the experiment		
			consequences	Shut down system		
				Close the valve		
				Repair/replace MFC		
		Pump Failure	No	Close valves		
			consequences	Shut down system		
				repair		
		Plugging of	Pressure	Stop carrier gas flow		
		sep	failure of	Stop reactant flow		
			fittings/vessel(> 250bar)	Clean system		
		Plugging of gas inlet	No	Stop the experiment		
			consequences	Close inlet valve		
				Clean tubing		
		Partial Plugging of gas inlet	No			
		Province	consequences	Close inlet valve		
				Clean tubing		
More	Temperature	Heat source	Failure of	Remove heat source		
				Reduce heater		
			(>450C)	temperatures		
			-	Increase water cooling		
		(glycol)	Gas chromatograph	Stop experiment		
			poisoning	Disconnect gas chromatograph		
				Repair cooling system		
				Set gas chromatograph to bakeout		
		Cooling failure (H2O)	Reactants and	Stop experiment		

			products over ventilation system	Shut down set up Repair water cooling system
		Temperature probe malfunction	No consequences	Replace temperature probe
Less	Temperature	Temperature probe malfunction	No consequences	Replace temperature probe
		Heater (tube or reactor) malfunction	No consequences	Repair heating system of heating tube/reactor
No	Sampling flow	Plugging of sampling syringe	No consequences	Replace sampling syringe Clean syringe and sampling tube









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#### Appendix B: Information card main reaction

Durat Yes /	ion exp NO	eriment:	INFO	RMA <sup>.</sup>	TIONCAF		т	Valid until:February 2	2020				
React	ion/So	t of experiment	: (delete the	e symbol	s that are NOT a	pplicable and	l also this text	)	Risk-aspects	Y *)	Min/ma	x	
			•						*) tic	k if relevar	nt		
/	$\sim$		$\sim$	<b>^</b>	$\mathbf{\wedge}$				Pressure/vacuüm 1 atm				
				K V	PR	High/low temperature	•	425 C					
$\leq$		<b>( ()</b>	Moving parts										
C4H1 C3H8	002 -> 02 -> (	C4H8O + H2O (r 3H6O + H2O	model react	ion)	•				For carcinogenic and re phrase 340,350,360, all whether replacing the si alternative is possible. I additional risk assessm	protoxic su ways shou ubstance v Because of ent (RI&E)	ubstances, H Id be consid with a less h f the health r has to be m	H- ered armful risks, an nade.	
Am	ount					HAZAR	RE 🗄 JS S	UBSTANCES					
<mark>gr</mark> .	mol	Name				Vap.press (mbar)	Limit value (mg/m <sup>3</sup> )	H-phrase: nr + meanin	9.			Waste- cat.	
~10	0.13	1,2-propanediol			57-55-6	0.107	30	H319 - causes serious ey	e irritation + H315 - causes skir	irritation		3	
~10(	0.13		107-18-6 30.4 4.8 H225-flammable louid and vapour + H331-Toxic II inhaled + H311-Toxic In contact							xic in contact	3		
max)	1( <u>ma</u> x)	Allyl alcohol						with skin + H400-Very tox cause respiratory irritation	with skin + H400-Very toxic to aquatic life + H319-Serious eye irritation + H335-May cause respiratory irritation + H315-Skin irritation + H301-toxic if swallowed				
~10( max)	0.13 1( <u>ma</u> x)	Acetone			67-64-1	240	2420	H225-flammable liquid ar H319- serious eye imitatio	H225-fammable (guid and vapour+ H336-May cause drowsiness or dizziness + H319- serious evol inflation				
~10( max)	0.13 1(ma x)	Propionaldehyde			123-38-6	337	12.1	H225-flammable liquid an respiratory irritation + H3*	H225-flammable liquid and vapour + H319-Serious eye initiation + H335-May cause respiratory initiation + H315-Skin initiation				
~10(	0.13	1-propanol			71-23-8	28	1723	H225-Highly flammable lik	quid and vapour + H336-May c	ause drowsin	ess and	3	
max)	1( <u>ma</u> x)							dizziness + H318-Causes	serious eye damage				
~200 mg	1.45 E-3	Scandiumoxide			12060-08-1		30	•					
		E construction and		1.0	l at an and a second				Landardan an dara an abb				
Mama		Experiment	er VGI	N-C	Lab-supervisor	Sarety meas	ures: rinse eye	s with water for severa	minutes, on rinse on skil	n contact,	contact phys	sician on	
Name		Tjeerdsma	Gee	ert Irdink	Jimmy Faria	skin contact,	remove dotni	ig/snoes, don't lorce vo	mit on ingestion.				
Tol In	tern:	_	401	7	534897115	Long trouser	s closed shoe	s ab coat and safety g s, chemical PVC/neopr	ene doves				
. ci. iii	in an		421		001001110		a) <u>anada</u> anad						
Signal	ture <sup>1)</sup> :					first aid: Fire	exinguisher ne	earest exit, see safety					
1)Here	with I c	eclare that I infor	med myself	in a prop	er way about all	cleaning spil	ls: designated	waste container					
the as	pects o	f this experiment	and that I h	ave taker	all the								
neces	sary m	easures to work s	safely accord	ting the n	les of the UT.								
Lab-s	upervis	or is only relevan	t for the facu	iltyTNW.		I							

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#### **Risk Inventory & Evaluation**

Yes /	NO exp	periment: IN	FORM/	TIONCAR	D EXP	ERIMEN	T	Valid until:February	2020		
Reac	tion/So	rt of experiment: (de	ete the symb	ols that are NOT ap	plicable an	d also this te	xt)	Risk-aspects	Y *)	Min/m	
								*) tic	k if relevar	nt	
	<u>~</u>	$\wedge$	~	~				Pressure/vacu üm	~~~	1 atm	
			AV.	PR				High/low temperature	•	425 C	
<	. >	<b>( //) X</b> 2%5,	$\times$ $\mathbb{T}_2$ >	<≛ &>				Moving parts			
	•⁄	$( \rightarrow )$		$\mathbf{X}$				Electricity			
C4H1	002 ->	C4H8O + H2O	•	•				For carcinogenic and re phrase 340,350,360, al whether replacing the s alternative is possible, additional risk assessm	eprotoxic s ways shou ubstance Because o ient (RI&E)	ubstances Id be con with a less f the heal has to be	
Am	ount				HAZA	RL ± JS	SUBSTANCE	S			
<del>gr</del> .	mol	Name		CAS-nr	Vap.press (mbar)	Limit value (mg/m <sup>3</sup> )	H-phrase: nr + mea	aning			
~10	0.11	2,3-butanediol		513-85-9	0.23	-	H319 - causes seriou	319 - causes serious eye irritation + H315 - causes skin irritation			
~10( max)	0.11 1(ma x)	3-buten-2-ol		598-32-3	67	-	H225-flammable liqui contact with skin + H damage + H335-Res	H225-flammable liquid and vapour + H301-toxic if swallowed + H311-Toxic in contact with skin + H411-Toxic b aquatic + H315-skin imitation + H318-Serious eye damage + H335-Respiratory imitation + H332-harmful if inhaled			
~10( max)	0.11 1(ma x)	3-hydroxy-2-butanone/	acetoin	513-86-0	4	-	H226-flammable liqui causes skin irritation	226-flammable liquid and vapour + H319-causes serious sys irritation + H315- auses skin irritation			
~10( max)	0.11 1(ma x)	Methyl ethyl ketone/but	anon	78-93-3	95	600	H226-flammable liquid and vapour + H319-causes serious eye initation + H336- May cause drowsness or dicaness				
~200 mg	1.45 E-3	Scandiumoxide		12060-08-1	-	30	-				
		Experimenter	VGM-C	Lab-supervisor	Safety mea	sures: rinse e	ves with water for sev	eral minutes, on rinse on ski	in contact.	contact o	
Name	e.	Dennis Tjeerdsma	Bert Geerdink	Jimmy Faria	skin contac	t, remove cloth	ning/shoes, don't force	e vomit on ingestion.			
Tel. Ir	ntern:		4217	534897115	Long trouse	ers, closed sho	es, chemical PVC/ne	oprene gloves			
Signa	ture <sup>1)</sup> :				first aid: Fire exinguisher nearest exit, see safety						
<sup>1)</sup> Here the as neces	with I c spects c isary m	leclare that I informed of this experiment and easures to work safely	myself in a pro that I have tak according the	oper way about all en all the rules of the UT.	cleaning sp	ills: designate	t waste container				

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#### **Risk Inventory & Evaluation**

Appendix D: Chemical information												
	Chemwatch	TEEL-1	IARC	H phrases	5		P phrase:	5		Hazard pictograms		
Chemical Name	Hazard Alert Code		Carcinogenic		Suppl. statement	Prevention	Response	Storage	Disposal			
Water	0	-	-	-	-	-	-	-	-			
1,2-Propanediol	2	30mg/ m3	-	H315, H319	N/A	P280	P305 + P338 + P351 P313 + P337 P302 + P352 P313 + P332	N/A	N/A	N/A		
Aliyi Alcohol	4	unkno wn	-	H225, H331, H311, H400, H319, H335, H315, H301	N/A	P210, P270, P217, P280	P301 + 310, P330, P370 + P378, P302 + P352	P403 + P235, P405	P501			
Propionaldehyd	3	unkno wn	-	H225, H315, H335, H319	N/A	P210, P271, P240, P241	P370 + P378, P305 + P351 + P338, P312, P337 + P313	P403 + P235, P405	P501			
1-propanol	3	unkno wn	-	H225, H319, H336	EUH01 9	P210, P271, P240, P241	P370 + P378, P305 + P351 + P338, P312, P337 + P313	P403 + P235, P405	P501			
Scandiumoxide	1	30mg/ m3	-	N/A	N/A	N/A	N/A	N/A	N/A	N/A		
2,3-butanediol	2	Unkno wn	-	Н315, Н335, Н319	N/A	P271 P261 P280	P305+P351+P3 38 P312 P337 + P313 P302+P352	P405 P403+P2 33	P501			
## **Risk Inventory & Evaluation**

3-buten-2-ol	3	0.087p pm	-	H225, H301, H311, H411, H315, H318, H335, H332	N/A	P210, P270, P271, P280	P301+ P310, P305+P351+P3 38, P330 P370+P378	P401+P2 35, P405	P501	
3-hydroxy-2- butanon/acetoin	2	Unkno wn	-	H226, H319, H315	N/A	P210, P233, P240, P241	P370+P378, P305+P351+P3 38, P337+P313, P302+P352	P403+P2 35	P501	()
Methyl Ethyl Ketone/butanone	3	Unkno wn	-	H225, H319, H336	EUH06 6	P210, P270, P241, P240	P370+P378, P305+P351+P3 38, P337+P313, P312	P403+P2 35, P405	P501	