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ORIGINAL PAPER

Dehydration of Fermented Isobutanol for the Production of Renewable Chemicals and Fuels

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Abstract Fermented 2-methyl-1-propanol (isobutanol) can be used directly as a biofuel or can be catalytically dehydrated to 2-methylpropene (isobutylene), which serves as a platform molecule for synthesizing other fuels or chemicals. The dehydration reaction was studied over alumina catalysts to determine the impact of process conditions and model compound impurities from fermentation. No significant impurity effects were observed over short (8 h) timescales and dehydration was demonstrated at high conversion and with high selectivity to isobutylene.

Keywords 2-Methyl-1-butanol · Biofuel · Biobutanol · Isobutylene · Isooctene

1 Introduction

Recent advances in biotechnology and fermentor design have led to commercially viable processes that produce 2-methyl-1-propanol (isobutanol) in high yield without any significant byproducts [1]. This renewable isobutanol (obtained from fermentable biomass-derived sugars) can be used directly as an oxygenated blendstock for gasoline or as an industrial solvent. Dehydration of this isobutanol to 2-methylpropene (isobutylene) generates a versatile platform molecule that can be converted into a wide range of renewable fuels and chemical products using conventional petrochemical catalysis. For example, the isobutylene can be dimerized or etherified with renewable methanol or ethanol to form fully renewable gasoline blendstocks isooctene, MTBE, or ETBE [2]. The isobutylene can also be polymerized directly to form renewable butyl rubber [3] or further reacted to form renewable monomers such as methyl methacrylate [4] and terephthalic acid [5, 6] (Fig. 1).

Alcohol dehydration reactions over solid catalysts have been studied and reported in the literature since at least the early 1900s (for example, see [7] and [8]). Isobutanol is most typically dehydrated over mildly acidic gamma-alumina catalysts. However, isobutanol dehydration has been demonstrated over numerous catalysts through the years, including inorganic acids, metal oxides, zeolites, acidic resins, and many more. Knoezinger et al. published a series of papers differentiating the dehydration rates of the various butanols and described the reaction mechanism on alumina catalysts with evidence from isotope substitution and surface IR measurements [9–12].

A key parameter in the dehydration of isobutanol is the selectivity to isobutylene. Several competing products can be observed in the dehydration of isobutanol. Macho et al. described the skeletal isomerization that can occur under dehydration conditions for the various butanols [13]. In the dehydration of isobutanol, the primary carbocation is initially formed. Since primary carbocations are the least stable type, most of the ions rearrange to form tertiary carbocations, which then deprotonate to form isobutylene. However, some of the primary carbocations undergo a methyl migration forming linear secondary carbocations, which deprotonate to form 1- or 2-butene. The competing reactions are shown in Fig. 2. In contrast to isobutanol, tert-butanol forms the tertiary carbocation directly, so very high purity isobutylene can be easily obtained.

For the products shown in Fig. 1, it is desirable to conduct the dehydration such that isobutylene selectivity is maximized. There are other applications where it might be

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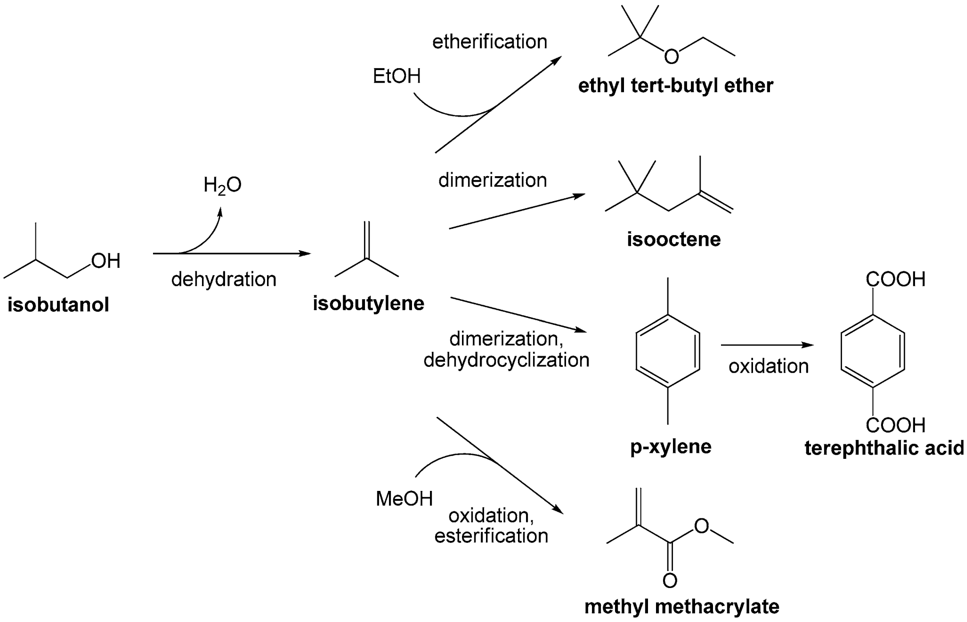

Fig. 1 A subset of fuel and chemicals that can be synthesized from isobutanol

desirable to generate higher concentrations of linear butenes. In these cases, a catalyst and conditions that push the mix of butenes toward the equilibrium composition shown in Fig. 3 are desired. (Note: equilibrium compositions were calculated with Aspen Plus using the Peng-Robinson physical property model).

Although isobutanol dehydration reactions over solid (primarily alumina) catalysts have been studied extensively, little work has focused on issues that are specific to fermented isobutanol. For example, fermented isobutanol is initially dilute in water and can be dried to whatever degree is desired. In the initial distillation, isobutanol and water form a low-boiling heterogeneous azeotrope, which, upon condensation, separates into an aqueous phase (~8.5 wt% isobutanol) and an organic phase (~15 wt% water). It may be more economical to use wet isobutanol recovered from the decanter (~15 wt% water) as feed for dehydration rather than drying it further with an additional distillation column.

Additionally, some impurities from the fermentation process may be different from byproducts present in petroleum-derived isobutanol. Several papers have been published that investigate water and impurity effects in dehydrating fermented ethanol [14–16]. They show that water improves catalyst stability and that aldehydes can negatively impact catalyst life in the case of ethanol dehydration. However, articles on dehydration of fermented isobutanol are not available.

The aim of this paper is to investigate issues relevant to dehydration of fermented isobutanol for downstream fuels and chemicals. These issues include the effects of temperature, pressure, water content, and fermentation impurities on conversion and selectivity to isobutylene.

2 Experimental Section

Commercial grade isobutanol was obtained from Industrial Chemical Company (Denver, CO) with a minimum purity of 99.5% (Note: Certificate of analysis showed 99.97% isobutanol). Using this high purity isobutanol as a base, typical classes of impurities were added individually to determine the impact on conversion and selectivity of the dehydration reaction as well as the fate of the impurity. Reagent grade quantities of the target impurities were obtained from Sigma-Aldrich.

Dehydration experiments were carried out in a gas-phase fixed bed catalytic reactor system as shown in Fig. 4.

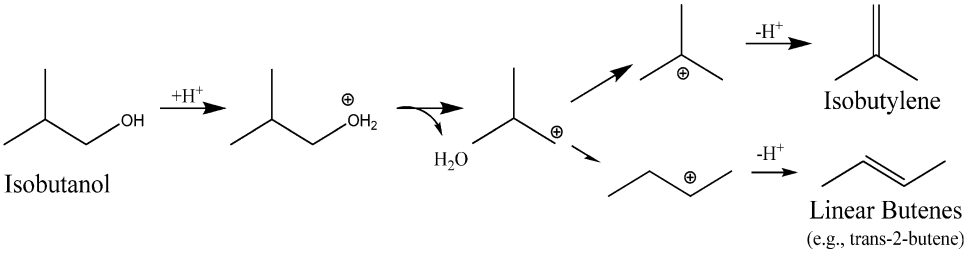

Fig. 2 Mechanism for dehydration of isobutanol to produce mixed butenes

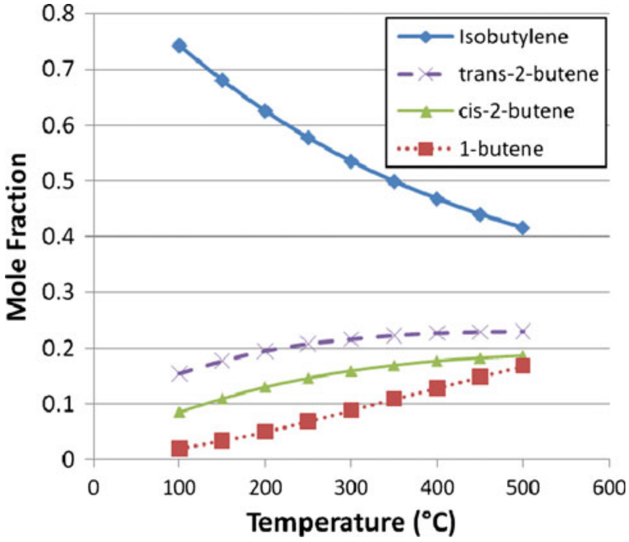

Fig. 3 Equilibrium composition of butene isomers

The primary components of the reactor system included a Series I HPLC pump (0.1–9.9 mL/min), mass flow controllers (Aalborg GFC model 0–500 sccm) for gaseous feed, an electrically heated preheater section instrumented with a type-K thermocouple immediately before the entrance to the main reactor, a 1/2″ O.D. × 17″ main reactor tube housed in a single zone tube furnace (ThermoScientific Lindberg/Blue M), an ice bath to quench reactor effluent, a back pressure regulator (Go model BP3), and a gas–liquid separator. The main reactor tube was loaded with 7.5 g of crushed catalyst particles in the middle of the tube, and glass beads were used to fill both ends of the reactor. This also ensured a uniform reactant temperature prior to contact with the catalyst.

In a typical experiment, nitrogen was fed through the reactor system at 100 sccm during heat up. The preheater and reactor system were heated to the desired reaction temperature (~250–400 °C). If the experiment was to be at a pressure greater than 1 atm, the back pressure regulator was adjusted to the appropriate pressure (0–75 psig). Once the system reached steady state (approximately 1 h), the feed pump was initiated and the nitrogen flow ceased. A typical feed rate of isobutanol was 0.78 mL min^{-1}, which resulted in a WHSV of 5 h^{-1}. The system was allowed to equilibrate for at least 30 min prior to any measurements.

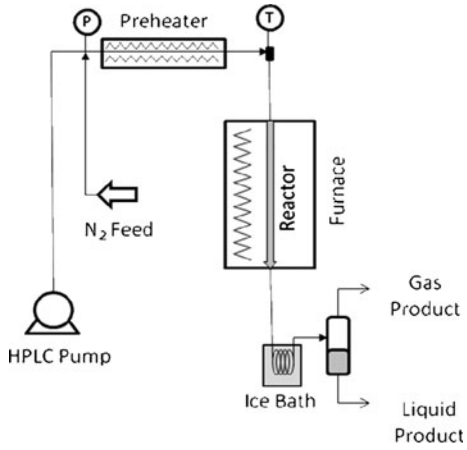

Fig. 4 Schematic of dehydration reactor system

Effluent from the reactor was cooled in an ice bath and the pressure was reduced to atmospheric. The product was separated into gas and liquid streams and each was analyzed separately. The gas flow rate was measured manually with a soap bubble flow meter 4–6 times over 30 min, and samples were captured in standard GC vials for analysis. Gas phase analysis was performed on an Agilent 7890 equipped with a Restek Rt-Alumina (PLOT) column (60 m × 0.32 mm I.D.) and an FID detector. The method was isothermal (70 °C) and all C_1–C_5 paraffins and olefins were resolved. The liquid effluent was collected in a graduated cylinder to measure liquid flow and also to quantify the fraction of aqueous and organic liquids when two liquid phases were present (above ~8.5 wt% isobutanol, as described above). Liquid samples were diluted with an internal standard and analyzed by GC-FID using an Agilent 5890 equipped with a ZB-FFAP column (30 m × 0.32 mm I.D. × 0.25 µm film). A subset of the samples were analyzed by GC–MS or derivatized with DNPH and analyzed by LC to quantify certain analytes.

In the cases of "high conversion", where a single aqueous liquid phase was present, conversion was calculated with the measured concentration of isobutanol in the liquid phase. In the cases of "low conversion", where two liquid phases (water-rich phase and isobutanol-rich phase) were present, two methods were used to estimate conversion. The relative volumes of the two liquid phases were used to calculate conversion and the flow rate of the gas-phase product was used to calculate conversion. Uncertainty is fairly high when conversion is less than ~98% and two liquid phases are present.

3 Results and Discussion

3.1 Catalyst Evaluation

A wide variety of catalysts were evaluated for the dehydration of isobutanol to produce isobutylene (or mixed butenes). Some of the more acidic catalysts, such as ZSM-5 zeolites, Y-type zeolites, and Amberlyst acidic resins, not only catalyzed the dehydration reaction but also catalyzed dimerization (or further oligomerization) of the butenes product. For the purposes of this paper, these catalysts are not included because the goal is to focus on the dehydration step to produce isobutylene or mixed butenes as a platform molecule that can be used to synthesize a wide variety of chemicals and fuels. Additionally, it was found that the conditions required for dehydration are not optimal for dimerization and result in isomers with inferior fuel/chemical properties to the ones obtained when the two reactions are carried out in series.

In this paper, data from experiments using two commercial gamma-alumina catalysts (denoted A & B), and two developmental catalysts (C & D) with low levels of silica to increase the acidity slightly, where catalyst D is the most acidic of the four catalysts, is reported. In each experiment, wet isobutanol (10 wt% water) was fed to the reactor system at atmospheric pressure and WHSV = 5 h^{-1} to determine the dehydration conversion and selectivity to isobutylene versus temperature (Figs. 5, 6). Note: Selectivity is defined as % of a given isomer in gas-phase C_4 products.

Catalyst A required the highest temperatures for good conversion and showed poor selectivity to isobutylene. The initial hypothesis was that catalysts requiring lower temperatures would minimize skeletal rearrangement and maximize isobutylene selectivity. However, catalyst D had the highest conversion at low temperatures, but was accompanied by the lowest selectivity to isobutylene of this group of catalysts. The low selectivity of catalyst D is attributed to the fact that the acidity of the catalyst facilitates both the dehydration as well as the skeletal isomerization. Catalysts B and C both showed a good combination of high conversion and good selectivity to isobutylene, with catalyst B showing the highest selectivity at all temperatures. For applications where maximal isobutylene is desired, catalyst B (BASF AL3996 4.5 mm cut rings) is preferred. On the other hand, some downstream applications prefer linear butenes and in those cases, catalyst D is the preferred dehydration catalyst.

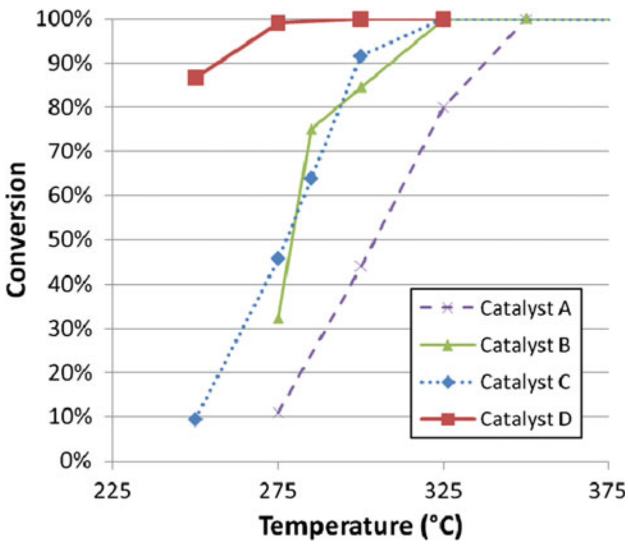

Fig. 5 Conversion of isobutanol versus temperature over four catalysts

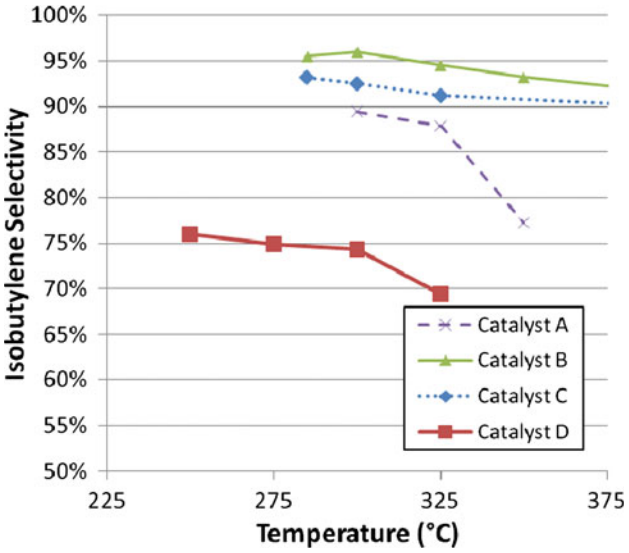

Fig. 6 Selectivity to isobutylene versus temperature

A typical chromatogram of the gas-phase product from the dehydration reactor is shown in Fig. 7. In this experiment, the selectivity to isobutylene was 95.1%, with 1.6% 1-butene, 0.5% trans-2-butene, and 1.9% cis-2-butene. For a series of measurements over an hour of operation, the selectivity to isobutylene varied by less than ±0.5%. This mixture is consistent with the kinetically limited carbocation rearrangement mechanism proposed by Macho, et al. and as discussed previously (Fig. 2). Additionally, a small amount of isobutane (0–1%) was observed. This may be due to some carbon deposition on the dehydration catalyst which liberated hydrogen that saturated a small fraction of the isobutylene (most likely on the metal surfaces of the reactor tube). Or, it may be due to the reaction of isobutylene with isobutanol to produce isobutane and isobutyraldehyde.

Additional experiments over a wide range of conditions showed that catalyst B most consistently produced the highest selectivity to isobutylene and showed a lower sensitivity to temperature fluctuations. Therefore, the remainder of this paper focuses on impacts of other parameters on dehydration of isobutanol over catalyst B.

3.2 Pressure Effect

Although lower pressure is favored for dehydration (1 mol → 2 mol), there may be practical benefits to carrying out the reaction at moderate pressures. For example, dimerization of isobutylene is typically carried out at high

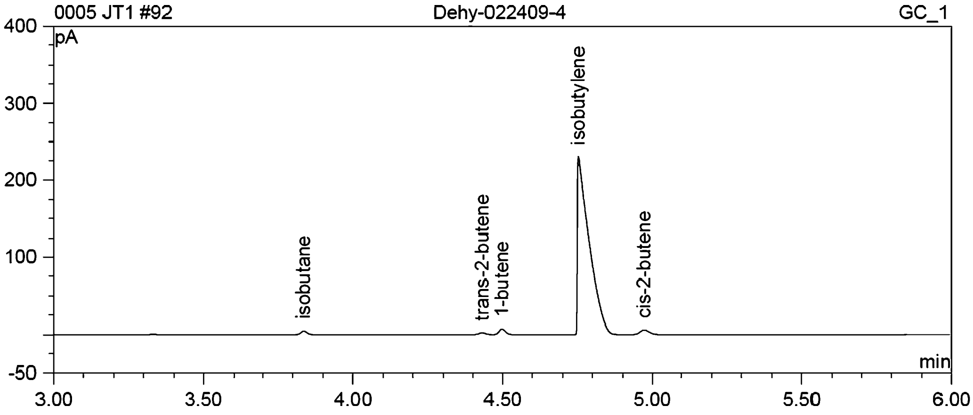

Fig. 7 Chromatogram showing composition of gas-phase mixed butene stream

Table 1 Impact of pressure on the isobutanol dehydration reaction

Run	Temperature (°C)	Pressure (psig)	Conversion[a] (%)	Isobutylene selectivity (%)
1	285	0	71–76	95.5
2	285	60	35–46	96.0
3	325	0	99.0	94.2
4	325	60	98.8	95.0

[a] Range of conversions reported for the experiments at 285 °C are estimated using the two methods described in the Sect. 2

pressures of 750–1000 psig. If the dehydration is carried out at atmospheric pressure, the gas-phase isobutylene is easily separated from the water and then must be compressed in order to condense it prior to pumping up to high pressures. On the other hand, at modest pressures of >45 psig, isobutylene and water can be separated in a decanter as two separate liquid phases and the isobutylene can be pumped directly up to high pressures. Since it is desirable to avoid using a compressor in these applications, it is important to understand how pressure affects the dehydration reaction.

Experiments were conducted at 285 °C to determine the effect of pressure at conditions where the reaction is not complete and also at 325 °C where high conversion is expected. Isobutanol with 1 wt% water was fed to the reactor at WHSV $= 5$ h^{-1} and pressures of 0 and 60 psig. The results are shown in Table 1. It is clear that pressure negatively affects the conversion at 285 °C and the lower conversion is accompanied by a slightly higher selectivity. However, at 325 °C, higher pressure does not significantly change conversion or selectivity. Therefore, it is feasible to run the dehydration with moderate pressure if process energy consumption benefits can be achieved.

3.3 Water Content

Isobutanol recovered from a fermentation process will most likely be dried to <1% water (as is typical for fuel grade ethanol) using a conventional beer still, decanter (for the heterogeneous azeotrope), and rectifier column in a modified ethanol facility. It may be economically beneficial to forgo some of the drying steps and feed wet isobutanol directly to a dehydration reactor. Therefore, experiments were conducted to determine the effect of isobutanol water content on conversion and selectivity in the dehydration reactor. In this set of experiments, catalyst B was used, the reactor pressure was 60 psig, and the feed rate was WHSV $= 2$ h^{-1}. Dry isobutanol was compared with isobutanol containing 1 wt% water and 15 wt% water (saturated). Experiments were carried out at 285 °C, where incomplete conversion is expected, and at 325 °C, where high conversions are observed. The results are shown in Table 2.

At 285 °C, the water content of the isobutanol negatively impacts the conversion in the dehydration reactor and causes a slight increase in isobutylene selectivity. However, at 325 °C, near-complete conversion is observed for all water contents and no significant change in selectivity is observed. Therefore, if the reactor is run at typical conditions where conversion is high, it is feasible that wet isobutanol can be used directly without the need for a rectifier column.

3.4 Effect of Impurities

Four experiments were conducted to determine the effects and fate of typical classes of fermentation impurities in the dehydration reactor. These impurities arise from metabolic

Table 2 Impact of isobutanol water content on dehydration reaction

Run	Feed water content	Temperature (°C)	Conversion[a] (%)	Isobutylene selectivity (%)
1	Dry	285	53–61	95.8
2	1 wt%	285	52–57	95.9
3	15 wt%	285	28–42	96.3
4	Dry	325	99.8	95.2
5	1 wt%	325	99.8	95.4
6	15 wt%	325	99.3	95.0

[a] Range of conversions reported for the experiments at 285 °C are estimated using the two methods described in the Sect. 2

Table 3 Impact of impurities spiked into isobutanol dehydration feed

Run	Feed	Iso-BuOH conversion (%)	Isobutylene selectivity (%)	Impurity conv. (%)
1	Iso-BuOH + 1 wt% H_2O	99.8	95.7	NA
2	Base + 1% isopentanol	99.7	95.8	99.9
3	Base + 1% ethanol	99.4	95.5	66
4	Base + 1% acetone	99.5	96.1	99.6
5	Base + 1% isobutyraldehyde	99.8	96.3	?

side reactions in the biocatalyst or small levels of contamination by other microorganisms. For this study, isopentanol, ethanol, acetone, and isobutyraldehyde were chosen as model impurities analogous to the fusel alcohol, acetone and acetaldehyde impurities typically found in ethanol fermentations [11]. Each impurity was prepared at 1 vol.% in isobutanol with 1 wt% water. The spiked levels were higher than those observed in fermentation product, but the intention was to exaggerate any effects by spiking at these high levels. (Note: the effects over long catalyst runs was not the intention of this study, but should be investigated). The isobutanol mixture was fed at a WHSV = 2 h^{-1} to the reactor that was maintained at 325 °C and 60 psig, and results are shown in Table 3.

It is clear from Table 3 that none of the impurities have a significant effect on the isobutanol dehydration reaction over short run times. The fate of the impurities is important to understand for downstream reactions. Isopentanol (3-methyl butanol) was dehydrated to form 3-methyl-1-butene and 2-methyl-2-butene. The two C_5 olefins would continue on with the isobutylene and likely be incorporated into the dimerization products downstream. Dehydrated ethanol formed ethylene, which would likely be unreactive in most downstream processes. Acetone formed stoichiometric quantities of propylene. It is not clear how the acetone is converted to propylene, but may be reduced with isobutanol to form isopropanol and isobutyraldehyde followed by the dehydration of isopropanol. Low levels of isopropanol were detected in the reactor effluent when acetone was present in the feed. Low levels of propylene would likely be incorporated in the dimerization reactor. Isobutyraldehyde did not result in any additional gas-phase products. We had problems quantifying the isobutyraldehyde, so conversion results are not reported. There was no obvious effect on catalyst performance over these timescales. Overall, the impurities spiked at these high levels did not demonstrate any immediate impacts on dehydration conversion or selectivity. It is feasible that there may be long-term impacts on catalyst life, such as those discussed for ethanol [9] [11], but these have not been tested at this time. Further work is required to evaluate long-term impacts.

4 Conclusions

Isobutanol can be dehydrated over commercial gamma-alumina catalysts at high conversion and with good selectivity to isobutylene. Water content and pressure both negatively affect conversion and selectivity, but good results can still be achieved at 325 °C, 0–60 psig, WHSV = 5 h^{-1} and up to 15 wt% water in the isobutanol feed. Typical classes of fermentation impurities investigated in this study did not negatively impact isobutanol dehydration. The fate of byproducts from these impurities would depend on the downstream processes. Further work is required to determine long-term effects of impurities or water content on dehydration catalyst life.

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investigated as a means to convert isobutanol into a wide range of renewable products.

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