CONDENSED PHASE CONVERSION OF BIOETHANOL TO 1-BUTANOL AND HIGHER ALCOHOLS

By

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ABSTRACT

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Higher alcohols are important chemical feedstocks as well as potential fuels. With the recent surge in bioethanol production, it would be advantageous to convert bioethanol to butanol and higher alcohols. Results by various authors for a wide range of reaction conditions are presented. For butanol specifically, the highest yields have been obtained with hydroxyapatite, hydrotalcite and alumina-supported nickel catalysts. The literature shows it is a challenge to convert ethanol to butanol, since no one has achieved butanol yields higher than ~30%.

In this research project, attention is focused on alumina-supported nickel, since it is robust, stable, and well suited for condensed phase ethanol Guerbet chemistry. Catalyst screening of different compositions was performed and higher alcohol selectivities were analyzed. The 8%Ni/8%La-Al₂O₃ was proven to produce over 80% selectivity to higher alcohols at 50% ethanol conversion. The impacts of water removal on target alcohol yield with the 8Ni/8La catalyst were investigated in a batch reactor. Removing water decreased selectivity to CH₄ and CO₂ from 15% without water removal to 8% with water removal.

Preliminary kinetics of 1-butanol and 1-hexanol formation were investigated by looking at initial rates of their formation at 215°C, 230°C, and 239°C. Runs with ethanol/acetaldehyde/H₂ were performed to investigate the steps of the ethanol Guerbet reaction mechanism. Runs completed at 150°C and 200°C were modeled and rate constants were determined for acetaldehyde hydrogenation, acetaldehyde condensation, and butyraldehyde hydrogenation. It was found ethanol dehydrogenation is in equilibrium and is the rate limiting step of the ethanol Guerbet mechanism. The activation energy for ethanol dehydrogenation was calculated to be 150 KJ/mol. Therefore, the effect of H_2 on a neat ethanol run was examined and found to have little effect on ethanol conversion rate. Ethanol conversion rates were the same due to the side reaction of H_2 with ethanol to CH_4 and water, which offsets the negative effect of hydrogen on acetaldehyde formation rate. The presence of excess H_2 was found to decrease 1-butanol and 1-hexanol formation rates.

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Dedicated to my parents, loving wife, and beautiful daughter Avery

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1 Literature Review and Background

1.1 Introduction

With the recent increase in demand for renewable fuels, there has been a surge in ethanol production to meet that demand. There are markets that could capitalize on this increased ethanol production. One such market would require this ethanol to be converted to butanol and higher alcohols. In fact, higher alcohols have energy values close to gasoline, making them better than ethanol for fuels (Table 1-1) [1]. Higher alcohols also have broad applications in the commercial chemical industry. Tsuchida et al. [2] reports, "n-Butanol is an important chemical feedstock used as a solvent and in polymer materials such as butyl acrylate and butyl methacrylate." Therefore, 1-butanol and higher alcohols have a higher market value than ethanol [3]. My research project will focus on butanol production from ethanol, but alcohols higher than 1-butanol can also be produced.

Table 1-1 Lower heating values are presented higher alcohols in MJ/L. The solubilities of the alcohols in water, and solubilities of water in the alcohols are also shown.

		Solubility (wt % at 20°C)	
	LHV (MJ/L)	of H_2O	in $H_2O^{[4]}$
Ethanol	21.1	100	100
1-Butanol	26.8	20.1	7.8
1-Hexanol	29.3	7.2	0.58
2-Ethyl-1-Butanol	29.9	4.6	0.43
1-Octanol	31.0		0.06
2-Ethyl-1-Hexanol	31.3	2.6	0.10
Gasoline	32.5 ^[1]		

The current method for producing 1-butanol is the oxo process, which uses petroleum as the feedstock [2]. With the oxo process, 1-butanol is produced from the hydroformylation of propylene [5]. A rhodium complex is used to combine hydrogen and carbon monoxide with propylene to form butryaldehyde (Figure 1-1).



Figure 1-1 Mechanism for the oxo process [5].

Butyraldehyde is hydrogenated downstream to produce 1-butanol. The oxo process is complicated, requires high energy input, and is costly [2]. Consequently, 1-butanol prices fluctuate because of fluctuating propylene prices; these price fluctuations are a direct result of fluctuating oil prices. A greener process needs to be realized, which would directly convert ethanol to 1-butanol. Not only would it be attractive to convert ethanol to 1-butanol from an environmental standpoint, but it may prove to be more attractive economically. Ethanol technologies, whether ethanol is being produced from starches or cellulose, are constantly evolving. Ethanol prices always have the opportunity to go down, while oil prices will most likely increase with time. Carbon-carbon coupling of alcohols is commonly regarded as the Guerbet reaction [2, 6-9]. This was first discovered by Guerbet in the late 19th century; Guerbet performed his



Figure 1-2 Reaction tree for the ethanol Guerbet reaction system.

reaction of ethanol to 1-butanol, but with little yield [10]. In the Guerbet reaction, ethanol is oxidized to acetaldehyde, the acetaldehyde undergoes an aldol condensation to crotonaldehyde, and then the crotonaldehyde is hydrogenated to 1-butanol [11]. One molecule of water is formed for every molecule of 1-butanol formed. The formed 1-butanol can then react with itself and ethanol to form 1-hexanol, 2-ethyl-1-butanol, 2-ethyl-1-hexanol and other higher alcohols. A Guerbet reaction tree is shown in Figure 1-2, which shows the aldol condensation mechanisms for these higher alcohol reactions. Some of the literature supports the Guerbet mechanism [2, 12, 13], and some of the literature supports a simpler proton abstraction mechanism [11, 14, 15].

In proton abstraction, a proton is extracted from the beta-carbon of one ethanol molecule which produces a nucleophile that attacks another ethanol molecule [11]. The coupled product



Figure 1-3 Hypothesized proton abstraction mechanism [11].

dehydrates to form 1-butanol and water (Figure 1-3). Experiments by Ndou, Yang C., and Yang K.W. with acetaldehyde support this mechanism [11, 14, 15]. It will be shown though that the literature more strongly supports the Guerbet mechanism [2, 13, 16].

Various researchers have made attempts to convert ethanol to 1-butanol over the past 80 years and have obtained moderate ethanol conversion percentages and moderate 1-butanol selectivities [2, 9, 11, 15, 17-20]. Others have used ethanol as a limiting reagent with methanol and/or propanol to attain moderate to high ethanol conversion percentages [3, 8, 21-23]. Of all reaction conditions, catalyst choice is the most important parameter. A heterogeneous catalyst is primarily looked at to keep process costs down. Many have used pure MgO or mixed with other basic cations as a solid-base catalyst for this reaction [9, 11, 12, 18-20, 22, 23]. Alkali cation zeolites have also been used for this reaction [14]. The most recent literature describes using partially decomposed hydrotalcites, hydroxyapatites, and alumina-supported nickel, which have produced the highest 1-butanol yields thus far [2, 15, 16, 18].

1.2 Economics and Energy Yield

Historically the price of 1-butanol has been roughly three times higher than the price of ethanol [1]. This makes it attractive to convert ethanol to 1-butanol if 1-butanol yields are high and the cost of production is minimal. Profit return (%) was calculated based on assuming two ethanol cost percentages (60% and 70%):

$Return \% = \frac{(P.Frac)(Butanol Sales+C6 Alcohol Sales)-Ethanol Cost}{Ethanol Cost} 100\%$

Where *P. Frac* is the ethanol cost fraction. The ethanol cost fraction represents the fraction of total production cost that is from cost of the raw ethanol feed. The other fraction represents processing cost. Higher alcohol yields were determined at target returns of 15% and 30%. At 70% ethanol cost percentage, it would take 82% higher alcohols yield to obtain 15% return. To achieve 30% return it would take 93% higher alcohol yield. As processing cost increases, higher alcohol yield also has to increase to achieve a return. In fact, at 60% ethanol cost, 30% return is not possible at 100% higher alcohol yield. A 15% return can be achieved at 95% higher alcohol yield.



Figure 1-4 Economics are shown for converting ethanol to 1-butanol and 1-hexanol. Ethanol was set as 70% and 60% cost of total production. Ethanol conversion is set at 100%. Prices from icispricing.com for ethanol and products were: ethanol (\$0.38 /lb), 1-butanol (\$0.97 /lb), 1-heanol (\$0.97 /lb).

Energy yield of converting ethanol to 1-butanol was calculated based on assuming 100% conversion of ethanol to 1-butanol. Two molecules of ethanol produce one molecule of 1butanol and one molecule of water. The lower heating value (LHV) for ethanol is 1278 kJ/mol and the LHV for 1-butanol is 2,509 kJ/mol [24]. The theoretical maximum energy yield is:

Energy Yield% =
$$\frac{LHV_{1-BuOH}}{2 * LHV_{EtOH}} * 100\% = \frac{2509}{2 * 1278} * 100\% = 98\%$$

Despite losing one mole of hydrogen to water, 1-butanol retains most of the energy from ethanol with 98% energy yield.

1.3 Early Patents

In U.S. patent 2,971,033 Farrar [17] discusses the condensation of ethanol over a catalyst consisting of potassium carbonate, magnesium oxide, and copper chromite. Reactions were carried out in an autoclave with pressures between 900-1000psi. Farrar had an ethanol

conversion of 32.5% at a temperature of 227°C and a pressure of 950 PSI. The selectivity to 1butanol was 47%.

In U.S. patent 1,910,582 [9] a process is described by Wibaut for converting ethanol to 1butanol over a magnesium oxide catalyst in a batch reactor. Wibaut states temperatures around 325°C and pressures around 450-1500 psi are favorable for ethanol conversion to 1-butanol. In all of the experiments described in the invention, ethanol was only in the vapor phase. At 275°C and a pressure of 1470 PSI, 26.8% ethanol conversion and 34% selectivity to 1-butanol was obtained. In U.S. patent 1,992,480, [20] Otto describes using magnesium oxide, copper oxide, chromium oxide, and silver oxide to convert ethanol to 1-butanol. Hydrogen was used as a carrier gas in a flow reactor. Ethanol conversion was 60% and 1-butanol selectivity was 16% at 260°C and 1300PSI.

1.4 MgO, Mixed Oxide, and Hydroxyapatite Catalysts

Ndou et al. [11] investigated various solid base catalysts for the conversion of ethanol to 1-butanol and found magnesium oxide to produce the best results in a vertical, fixed bed reactor. Nitrogen was used as the carrier gas and reactions were performed at atmospheric pressure. Ethanol was fed into the reactor at a relatively high temperature of 475°C. Though ethanol conversion was at 56%, 1-butanol selectivity was minimal at 18%. When pure acetaldehyde was passed over MgO, less 1-butanol was produced than when pure ethanol was passed over MgO.

Researchers have recently hypothesized MgO itself is not active enough to accomplish high 1-butanol formation rates [7, 13, 25]. Cosimo et al. [25] describes how formation rates of 1-butanol and isobutanol are slower than dehydrogenation reactions because acid-base surface properties are important and specific surface atom arrangements are needed to adsorb adjacent species. A strongly basic catalyst has to be tailored to improve high alcohol yields by

incorporating a specific type and amount of acid sites; the atoms of the catalyst also have to be arranged in a way that enables the maximum amount of aldol condensations to take place. Gines et al. [7] illustrated this concept by incorporating copper and potassium into a MgCeOx catalyst. Gines postulates copper increases aldol condensation by recombining hydrogen atoms to form hydrogen gas, which hydrogenates aldol species after they have coupled. Copper also prevents aldol species from hydrogenating back to ethanol molecules, which decreases ethanol conversion.

Marcu et al. [19] looked at combinations of Cu-Mg-Al mixed oxide catalysts and achieved low ethanol conversion percentages with moderate 1-butanol selectivities. Contrary to Ndou and Yang, C., Marcu had significant acetaldehyde selectivities, thereby contributing to the Guerbet mechanism. It was also shown that water had a negative impact on catalyst activity. When the reaction was carried out at 100 hours, the selectivity to 1-butanol was 80% and the ethanol conversion was 9%.

Marcu recently published a paper in 2013 [26] where they describe substituting Pd, Ag, Mn, Fe, Cu, Sm, and Yb as a component in their layered double hydroxide (LDH) precursor to their Mg-Al mixed oxide catalysts. They found a Pd-Mg-Al catalyst to have the highest 1butanol selectivity at 73%, but ethanol conversion was low at 4%. The Pd-Mg-Al catalyst was also found to have relatively strong basicity, but low acidity when compared with other mixed oxide catalysts in the study. The addition of water significantly decreased 1-butanol selectivity to 48%, with an increase of selectivity towards C_6 , C_8 acetals and acetaldehyde.

Tsuchida et al. [2] have shown that a nonstoichiometric hydroxyapatite (HAP) catalyst, which is a calcium phosphate compound ($Ca_5(PO_4)_3OH$), had the best 1-butanol yields when compared with various alkali oxides. Like Marcu, Tsuchida's data supported the Guerbet

mechanism on both HAP and MgO. At 300°C, the 1-butanol selectivity increased and acetaldehyde selectivity decreased as the contact time increased over HAP. Tsuchida hypothesized HAP is better at trapping molecular hydrogen than MgO, which allows more aldol condensations take place. Tsuchida's ideas agree with the ideas presented by Gines.

Tsuchida achieved significantly higher yields in US patent 6,323,383 using a CaCe/P catalyst [12]. Results were also obtained with other metals substituted for Ce. Tsuchida has achieved 1-butanol yield of 26.9%. Kourtakis et al. have also achieved significant 1-butanol yields [18, 27-29]. In U.S. patent 7,700,810, Kourtakis et al. [18] discussed the conversion of ethanol to 1-butanol over a hydrotalcite catalyst. Hydrotalcites are classified under a broad range of materials called layered double hydroxides (LDH's) [18]. The general formula of a LDH is $(M^{2+}_{1-x}M^{3+}_x(OH)_2)(A^{n-}_{x/n})\cdot yH_2O$ where M^{2+} is any divalent cation (Mg²⁺ for a hydrotalcite), M^{3+} is any trivalent cation, and A^{n-} is any anion [18]. As LDH's are heated they decompose to mixed oxides [18].

In this specific patent the hydrotalcite had the formula (Mg.753Al₂₄₇(OH)₂)(OH⁻ .247).(.5H₂O). Kourtakis reports partially decomposing their hydrotalcite catalyst before employing it in the conversion of ethanol to 1-butanol. Kourtakis also used similar hydrotalcites with different interlayer anions in U.S. patents 7,700,810; 7,700,811; 7,700,812; and 7,807,857 [18, 27-29]. Reaction data for these patents are summarized in Table 1-2 under the last three digits of each patent. Not only has Kourtakis done extensive work with partially decomposed hydrotalcites, they also have a patent application using lanthanum stabilized aluminum supported basic oxides [30]. Selectivity towards alcohols reached a maximum at 50% at 22% conversion with a 33.5 wt% K₂O/La-Al₂O₃ catalyst.

Patent	810	811	812	857
Reactor Type	Packed bed	Packed Bed, S.S	Packed Bed S.S	Packed Bed,
	S.S.			S.S.
Catalyst	(Mg.753Al.247	[(Mg.75Al.25(OH)	[Mg.75Al.25(OH)2	Ca.13[Al.987La.01
	$(OH)_{2}(OH^{-})$	2)(CO ₃][(CoEDTA ⁴⁻) ²⁻	$_{3}][CO_{3}^{2}] \text{ or } O^{2}$
	.247).(.5H ₂ O)	.125)].yH2O[CuC	}.44OH ⁻]1.63
		O ₃] _{.013}	(.56)2].yH2O	
Temp. (°C)	300	400	350	400
Pressure (psi)	14.7-3000	14.7-3000	14.7-3000	14.7-3000
Carrier gas	N ₂	N ₂	N ₂	N ₂
Etoh Conv. (%)	44.1	30.1	36.3	30
1-Butanol Sel. (%)	44.6	52.7	38.5	35
1-Butanol Yield (%)	19.7	15.9	14	10.5

Table 1-2 Reaction conditions, conversion percentages, and selectivities are reported for the conversion of ethanol to 1-butanol for Kourtakis [18, 27-29].

Building on the work of Tsuchida, Ogo et al. [31, 32] investigated substituting strontium for calcium in the hydroxyapatite structure. They also investigated substituting vanadium as vanadate, which replaces phosphate in hydroxyapatite. Their highest 1-butanol selectivity of 81% was obtained using a Sr-P hydroxyapatite in the vapor phase at 8% conversion at 300°C. This was higher than the previous selectivities by Tsuchida with a Ca-P hydroxyapatite. Like Tsuchida, the conversion is still too low to make the process practical. If higher conversions are achieved, 1-butanol selectivity will likely drop significantly. Tsuchida demonstrated this when they made biogasoline from ethanol [16]. They had 64% conversion at a high temperature (>400°C) but many components were made such as C_6 , C_8 alcohols, hydrocarbons, and some aromatics.

Carvalho et al. [33] suggested that there was disagreement among the authors over how the physiochemical properties of Mg-Al mixed oxide catalysts related to 1-butanol formation. Therefore, Carvalho investigated these properties of a typical Mg-Al mixed for 1-butanol production from ethanol. Carvalho found adjacent acid and medium strength base sites are needed to produce the intermediates needed for 1-butanol production, as well as accomplish the condensation. These pairs of acid/base sites are important, but strong base sites are not needed and there does not have to be a special atom arrangement in the catalyst, as others have suggested.

1.5 Homogeneous Catalysis

Homogenous catalysts were developed for the oxo process but also have been used for ethanol Guerbet chemistry. Koda et al. [34] used an iridium complex, dppp ligand, 1,7 octadiene, and sodium ethoxide at 120°C for 15 hours. They achieved 58% selectivity to 1butanol at 38% ethanol conversion. Other products formed were 2-ethyl-1-butanol, n-hexanol, 2-ethyl-1-hexanol, and n-octanol, which is characteristic of the Guerbet reaction mechanism. The temperature used was much lower (<100°C) than others in the literature. However, the iridium complex and ligand must be separated, which might not be economical at a large scale. Also, if sodium ethoxide and octadiene are required for the reaction, additional separation steps will be required.

Considering the costs and complications associated with homogeneous ethanol Guerbet reactions, it would make more sense to use an active heterogeneous catalyst that can obtain the same 1-butanol yield. However, at the 2013 Spring ACS meeting, Wass et al. [35] presented a high butanol selectivity of 95% with a ruthenium diphosphine catalyst. This is a significant selectivity that no one has presented in the literature to this date. In their paper published in Angewandte Chemie, they reported 82% 1-butanol selectivity at 34% ethanol conversion [36]. The concentration of the ruthenium was 0.1 mol % with 0.1 mol % ligand. There was also 5 mol% sodium ethoxide used as a base catalyst. Reactions were performed at 150°C.

1.6 Condensed phase reactions

Most of the literature has been concerned with Guerbet reactions in the vapor phase. Riitonen et al looked at γ -Al₂O₃-supported metal catalysts in a batch reactor at 250°C and pressures up to 100 bar.[37] Ethanol conversion and 1-butanol selectivity reached maximum values of 25% and 80%, respectively. The same authors then carried out continuous liquid-phase ethanol conversion to 1-butanol at 240°C and 70 bar.[38] With continuous operation, 1-butanol selectivity was 70% with a commercial Ni/ γ -Al₂O₃ catalyst and ethanol conversion was between 10 and 30%. Cobalt supported on γ -Al₂O₃ produced the highest ethanol conversion. Ghaziaskar et al achieved 35% ethanol conversion and 83% C₄+ alcohol selectivity at 250°C and 176 bar with 8% Ni/ γ -Al₂O₃.[39]

1.7 Alumina-Supported-Nickel Catalysts

Yang, K.W. et al. [15] studied ethanol condensation over alumina-supported metal catalysts and obtained results that agreed with Ndou and Yang, C. An 8%Ni/γAl₂O₃ catalyst was found to be the most effective at producing 1-butanol with 64.3% selectivity at 19.1% conversion. Selectivity to acetaldehyde, butyraldehdye, and ethyl acetate was 6%, 4%, and 3% respectively. No further characterization was carried out over these side products with time. These experiments were vapor phase reactions at 200°C. When acetaldehyde was passed over the alumina catalyst, less 1-butanol was produced than when pure ethanol was reacted over the alumina catalysts. The addition of crotonaldehdye also decreased 1-butanol formation.

Yang, K.W. was the first to report ethanol Guerbet reactions with an aluminum-supported nickel catalyst. Supported Ni catalysts have been used extensively for ethanol steam reforming reactions [40-43]. Nickel is becoming desirable as an effective ethanol Guerbet catalyst. Riittonen et al. [37] surveyed Ni and other metals supported on alumina in a batch reactor system at 250°C and autogeneous pressure. Nickel was found to be most active over platinum, silver, and gold. Highest 1-butanol selectivity reached was 80% at 20% conversion after 24 hours run time. While selectivity was high, ethanol conversion was too low for the long run time. Riittonen also investigated hydrogen addition and found a decreasing 1-butanol formation rate with increasing initial hydrogen pressure. Water removal was briefly examined by placing molecular sieves directly in the reactor. Ethanol conversion increased from 20% to 30%, but no further characterization or studies on water removal were performed.

Ghaziaskar et al. [39] performed ethanol Guerbet reactions to 1-butanol and 1-hexanol at 250° C in a continuous reactor. Sub and super critical ethanol reactions were investigated. The 8% Ni/ γ -Al₂O₃ catalyst first described by Yang, K.W. was used. Temperature was varied from 135-300°C with weight hourly space velocities varied from 6.4-15.6 h⁻¹. Conversion reached a maximum at 35% with 62% and 21% selectivity towards 1-butanol and 1-hexanol respectively. Other products in the reaction were acetaldehyde, butyraldehdye, ethyl acetate and 2-pentanone. Increasing the reaction pressure increased conversion by increasing the concentration and residence time.

1.8 Ethanol Reaction with Methanol

In U.S. patent 5,095,156 Radlowski [23] compared the conversion of methanol/ethanol mixtures over neat MgO, alumina-MgO, and charcoal-MgO. Copper, stainless steel, and quartz reactors were also investigated. A stainless steel reactor utilizing a charcoal MgO catalyst produced the best conversion percentages, but had high selectivities towards CO/CO₂.

Olson et al. [3] has shown that high conversions of ethanol and high selectivities of 2methyl-1-propanol could be obtained by using MgO-loaded carbon catalysts. It is apparent from Radlowski and Olson that carbon may be a significant factor in the Guerbet reaction of ethanol

and methanol. Reactions were done at 360°C in a continuous reactor at atmospheric pressure. Nitrogen was the carrier gas with a methanol/ethanol ratio of 7. Conversion for ethanol was 100% with 30% methanol conversion. There was 90% selectivity to 2-methyl-1-propanol.

In U.S. patent 5,559, 275 Barger [21] describes the conversion of methanol and ethanol to higher branched oxygenates by using a catalyst consisting of zinc, magnesium, zirconia, titanium, manganese, chromium, and lanthanide oxides. Much like Radlowski, the catalyst gave high conversion percentages, but also high selectivities towards CO/CO_2 . In patent 4,935,538, Budge et al. [44] achieved high C_6 aldol species yields from propanol. The procedure involved impregnating a United catalyst with cesium nitrate and bismuth nitrate, which helped improve yields.

Ueda et al. [8] explains a process for converting methanol and ethanol to higher alcohols using MgO. Ueda reported moderate conversions (60%) of ethanol, but 29% and 46% selectivity to n-propanol and 2-methyl-1-propanol respectively. The 2-methyl-1propanol was produced from formed n-propanol reacting with excess methanol, which is characteristic of the Guerbet mechanism. A continuous fixed bed quartz reactor was used for catalyst evaluation. Reactions were at 390°C and atmospheric pressure.

1.9 Research Objectives

1.9.1 Develop Efficient, Condensed Phase Alcohol Condensation Process Using Neat Ethanol

The literature predominantly reports ethanol Guerbet chemistry in the vapor phase at relatively high temperatures (>300°C). In this research project a condensed phase reaction process will be developed in a batch reactor to convert ethanol to higher alcohols. Lowering the reaction temperature will minimize side reactions and lower energy costs. Longer contact times are another advantage to liquid phase reactions, thereby increasing conversion. Running at the

needed higher pressures will also increase local gas phase concentrations and improve mass transfer.

1.9.2 Identify Robust, Stable Catalyst Compositions

This research will primarily focus on using heterogeneous catalysts to convert ethanol to 1-butanol. Many researchers have utilized hydrotalcite/LDH derived Mg-Al mixed oxides as well as hydroxyapatites to catalyze butanol production from ethanol. Mixed oxides are advantageous in that they contain the acid/base pairs necessary for aldol condensations to take place as well as the basicity required to perform ethanol dehydrogenation and butyraldehyde hydrogenation. This functionality can be replicated by a more stable and active aluminasupported nickel catalyst. Nickel metal provides dehydrogenation/hydrogenation functionality, while the specific acid sites on the gamma alumina work in conjunction with the nickel to perform the aldol condensation step in the Guerbet mechanism. Therefore, various nickel catalysts will be screened using lanthanum oxide to modify the acidity/basicity ratio to maximize target alcohol yield. Nickel content will be moderated to minimize ethanol decomposition.

1.9.3 Expand Understanding of Ethanol Guerbet Reaction Mechanism

There is disagreement in the literature on the mechanism for the ethanol to 1-butanol reaction. Some believe ethanol dehydrates and directly dimerizes to 1-butanol while others believe ethanol proceeds via an acetaldehyde intermediate as described by the Guerbet mechanism. Side products such as acetaldehyde, butyraldehyde and higher branched alcohols would support the Guerbet mechanism. One would not expect to see the presence of branched higher alcohols if ethanol directly dehydrates to 1-butanol. Reaction samples will be carefully analyzed for these intermediates and quantified in this research project to improve understanding of the ethanol Guerbet reaction

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2 Catalyst Screening

2.1 Introduction

The continuing trend in U.S. policy toward production of renewable fuels has led to the maturation of corn ethanol production and the recent emergence of commercial cellulosic ethanol production. In addition to being a biofuel, ethanol is a valuable chemical feed stock that could penetrate existing markets as its production increases. One such market is the production of 1-butanol and higher alcohols. These alcohols have broad applications in the commercial chemical industry as feed stocks and components for solvents, consumer goods, and materials [1]. As fuels, higher alcohols have energy values closer to gasoline than ethanol and have lower affinity for water, making them superior as fuel components to ethanol, as was shown in chapter 1 (Table 1-1)[2]. It is no surprise, therefore, that 1-butanol and higher alcohols have higher market value than ethanol [3].

The current method for producing 1-butanol is the oxo process, in which petroleumderived propylene[1] is hydroformylated (CO + H_2) over a homogeneous rhodium catalyst to form butryaldehyde, which is then hydrogenated to produce 1-butanol. The oxo process is complicated, requires high energy input, and is costly[1], and butanol prices fluctuate with propylene prices.

The direct conversion of ethanol to 1-butanol would be a renewable, environmentally "green" process that could become more attractive economically than the oxo process. Ethanol production technologies, whether utilizing sugar cane, starches, or cellulose, are constantly becoming more efficient and less expensive. Hence, ethanol prices will continue to decline over time, while oil (and propylene) prices will almost inevitably increase.

Reactions involving carbon-carbon coupling of alcohols are commonly regarded as Guerbet reactions [4-7]. Guerbet first reported the reaction of ethanol to butanol in the late 19th century, but achieved only a low yield [8] In the Guerbet reaction, ethanol is oxidized to acetaldehyde; acetaldehyde undergoes an aldol condensation to crotonaldehyde, and then the crotonaldehyde is hydrogenated to 1-butanol [9]. One molecule of water is formed for every molecule of butanol formed. The formed butanol can then react with itself or with ethanol to form 1-hexanol, 2-ethyl-1-butanol, 2-ethyl-1-hexanol, and other higher alcohols. It is noted that some literature supports this aldol condensation (Guerbet) mechanism, [1, 10-12] while other authors support a simpler proton abstraction mechanism [9, 13, 14]. In proton abstraction, a proton is extracted from the beta-carbon of one ethanol molecule, which produces a nucleophile that attacks another ethanol molecule [9]. The coupled product dehydrates to form 1-butanol and water.

Many researchers have converted ethanol to 1-butanol in the vapor phase at relatively high temperatures (>300°C), achieving ethanol conversions of 7-80% and 1-butanol selectivities of 10-70% [1, 7, 9, 11, 14-27]. Others have used ethanol as a limiting reagent with methanol and/or propanol to attain moderate to high ethanol conversion [3, 6, 21, 28, 29]. Catalyst composition is the most important factor in higher alcohol yields - many studies used MgO in pure form or mixed with other basic oxides as a solid base catalyst for this reaction [6, 7, 9, 15, 20, 21, 24, 29]. Alkali cation-exchanged zeolites have also been used [13]. The most recent literature describes partially decomposed hydrotalcites, hydroxyapatites, and γ -Al₂O₃ -supported nickel, which have produced the highest 1-butanol yields thus far [10, 14, 17].

Few researchers have performed ethanol Guerbet reactions in the condensed phase. Riitonen et al looked at γ -Al₂O₃-supported metal catalysts in a batch reactor at 250°C and pressures up to 100 bar [30]. Ethanol conversion and 1-butanol selectivity reached maximum values of 25% and 80%, respectively. The same authors then carried out continuous liquid-phase ethanol conversion to 1-butanol at 240°C and 70 bar [25]. With continuous operation, 1-butanol selectivity was 70% with a commercial Ni/ γ -Al₂O₃ catalyst and ethanol conversion was between 10 and 30%. Cobalt supported on γ -Al₂O₃ produced the highest ethanol conversion. Ghaziaskar et al achieved 35% ethanol conversion and 83% C₄+ alcohol selectivity at 250°C and 176 bar with 8% Ni/ γ -Al₂O₃ [16]. Although heterogeneous catalysts have been most widely studied, Wass et al. claimed 95% selectivity to 1-butanol with a homogeneous ruthenium diphosphine catalyst [31].

Mixed oxides, such as Mg_xAlO_{y} , contain weak Lewis acid-strong Bronstead base site pairs necessary for ethanol dehydrogenation, aldol condensation, and butyraldehyde hydrogenation [5, 32]. This functionality can be replicated by a more stable and active γ -Al₂O₃ supported nickel catalyst. This was first demonstrated by Yang et al, who used an 8wt% Ni/ γ -Al₂O₃ to achieve a vapor phase ethanol conversion of 19% with 64% selectivity to 1-butanol [14]. The nickel metal provides dehydrogenation/hydrogenation functionality, while the acid/base sites on the γ -Al₂O₃ work in conjunction with the nickel to perform the aldol condensation step in the Guerbet mechanism [5, 32].

The high selectivity achieved with nickel on γ -Al₂O₃ catalyst makes it a good starting point for this work, which investigates modification of the nickel catalyst with lanthanum oxide for condensed-phase ethanol Guerbet reactions. It is hypothesized that lanthanum will inhibit side reactions by adding basicity to the γ -Al₂O₃. Liquid phase processing is intrinsically preferable to the vapor phase route, as it involves smaller reaction vessels for the same throughput and saves energy by not requiring feed vaporization.

2.2 Experimental

2.2.1 Materials and Catalyst Preparation

Ni(NO₃)₂·6H₂O (Reagent Grade, Jade Scientific), and La(NO₃)₂·6H₂O (99%, Fluka) were used as catalyst precursors. The supports used include 1/8" x 1/8" γ -Al₂O₃ cylindrical extrudates (Johnson Matthey) and 1/16" diameter γ -Al₂O₃ spheres (Strem Chemical). Anhydrous ethanol (Koptec, 200 proof) was used as the initial reactor charge. The catalysts prepared (identifier) were 8 wt% Ni/ γ -Al₂O₃ (8Ni/Al), 10 wt% Ni/ γ -Al₂O₃ (10Ni/Al), 8 wt% Ni/7 wt% La₂O₃- γ -Al₂O₃ (8Ni/7La-Al), 14 wt% La₂O₃- γ -Al₂O₃ (14La-Al), 8 wt% Ni/9 wt% La₂O₃- γ -Al₂O₃ (8Ni/9La-Al), and 8 wt% Ni/ 10 wt% CeO₂ - γ -Al₂O₃ (8Ni/10Ce-Al).

Nickel catalysts supported on γ -Al₂O₃ were prepared by incipient wetness impregnation of γ -Al₂O₃ using a pre-determined quantity of solution to fill the γ -Al₂O₃ pore volume. The catalysts (30 g per batch) were dried at 130°C for 18 hours and then reduced at 525°C and 1 atm in a tubular flow reactor for 20 hours in 35 ml (STP) H₂/min. Nickel catalysts modified with La₂O₃ were prepared in the same fashion as above, except that La(NO₃)₃ was deposited first by incipient wetness impregnation of the γ -Al₂O₃ support followed by drying at 130°C for 18 hours, and calcining at 600°C for 20 hours in 35 ml/min N₂ flow. This assured there was La₂O₃ on the γ -Al₂O₃ surface before the impregnation of the other metals.

Most of the catalysts for screening studies were prepared on 1/8" extrudates, which were crushed into smaller particles (0.3-0.8 mm) before use. Several later catalysts were prepared on 1/16" γ -Al₂O₃ spheres and used without crushing in batch reactions.

2.2.2 Catalyst Characterization

Acid and base site densities on prepared catalysts were measured with a Micromeritics Autochem II chemisorption analyzer. Ammonia and CO₂ were used for acid and base site adsorption, respectively. After loading and establishing a stable baseline, catalysts were degassed by ramping the temperature to 600°C at 10°C/min under helium and holding at 600°C for 60 minutes. Outgassed samples were cooled to 25°C at 10°C/min and held for 10 minutes. Ammonia or CO_2 was then passed across the catalyst at a flow of 50 ml/min for 30 minutes. Gas flow was then changed to helium (50 ml/min) for 90 minutes to remove weakly bound gases. Desorption of CO_2 or ammonia was carried out by ramping temperature to 600°C at 10 °C/min and holding at 600°C for 30 minutes.

BET surface area measurements were done by nitrogen adsorption at 78K with Micormeritics ASAP 2010. Before analysis, samples were degassed in the degas port of the instrument at 120°C for 24 hr.

2.2.3 Batch Reaction Studies

Ethanol Guerbet reactions were performed in a 300ml Parr reactor (Model 4842, Parr Instruments, Chicago, Illinois) with reaction times between two and ten hours. Typically, 110 g of pure ethanol (or the desired feed mixture) was placed into the reactor along with the desired amount of catalyst. The reactor was purged with nitrogen and sealed with 0.1MPa of nitrogen overpressure. The reactions were carried out at autogeneous pressure.

The Parr reactor uses an Omega 1/8" stainless steel Type J thermocouple which was calibrated with the boiling points at 745 mm Hg absolute pressure of water (99.45°C), 1,2 propylene glycol 187.0°C), and ethyl nonanoate (226°C) [33]. The controller measured a temperature of 98°C for water, 185°C for 1,2 propylene glycol, and 225°C for ethyl nonanoate. Based on these results, a correction of $+1^{\circ}$ C was applied to the temperature measured during experiment. This correction was included when comparing experimental results with results obtained from phase equilibrium modeling using the SR-Polar equation of state.

Pressure measurements for all reactions used a pressure gauge on the reactor head. The pressure gauge had increments of 50 psi for pressures up to 3000 psig. The accuracy of this gauge was checked with a large 10 psi increment dial test gauge. To measure pressures in the range of reaction conditions, the reactor was evacuated to 14 torr and then filled with ethanol. Ethanol vapor pressure was measured from 190°C to 230°C, accounting for the reactor temperature correction mentioned above. The dial test gauge consistently read $1.5 \pm 0.5\%$ (5-10 $\pm 2-3$ psi) above the ethanol vapor pressure calculated from Antoine's equation[33] and the reactor head gauge consistently read $2.8 \pm 1.5\%$ (10-20 ± 10 psi) below the calculated ethanol vapor pressure. A check of the effect of this error on product yields and selectivities from experiment showed less than a one percentage point difference in selectivity in the worst case, so no correction to measured pressure was invoked in analysis of the experiments.

Initial catalyst screening experiments were performed at a catalyst loading of 0.093 g catalyst/g ethanol, a 280 rpm stir rate, and 230°C reaction temperature with only the final reaction mixture analyzed. In all later experiments, however, concentration profiles of key species over time were established by withdrawing liquid samples periodically from the reaction phase via a dip tube into an evacuated 1/8" x 8" stainless steel sample tube with a valve at each end to isolate the liquid sample from the reaction vessel. The sample tube was vented after isolating and the liquid sample was subjected to analysis by gas chromatography. Reactor pressure was monitored during reaction and after cooling at the end of reaction to aid in determining product compositions and quantities of gas formed. The quantity of gas produced in reaction was determined by weighing the entire cooled reactor with contents both before and after depressurization; the gas exhausted during depressurization was collected in a gas bag and analyzed by gas chromatography.

Liquid phase reaction samples were diluted 10-fold in acetonitrile and then analyzed on a Varian 450 gas chromatograph configured with a DB wax column (30 m x 0.53 mm ID, 1.0 µm film) and TCD detection. The temperature program for GC separation of liquid samples was to hold at 40°C for 2 min, ramp to 150°C at 10 °C/min, ramp to 250°C at 30°C/min, and then hold at 250°C for 2.00 min. Chromatographic response factors were determined by injecting calibration samples; in later experiments butyl hexanoate was used as an internal standard to improve analytical accuracy. A sample chromatogram is shown in Figure 2-1. The full component analysis is provided in Table A2-1, in Appendix A.

Liquid sample analysis was then changed to a 30 meter sol gel wax column with FID detection and split injection starting with run 02-29TLJ092013 on September 30th, 2013. This enabled better separation of components off the column. A split injector was used with a split ratio of 100:1. The temperature program was also changed to holding for 4 minutes at 37°C, ramp to 90°C at 10°C/min, hold at 90°C for 3 minutes, ramp to 150°C at 10 °C/min, ramp to 230°C at 30 °C/min, and then hold at 230°C for 2 minutes. A sample chromatogram is shown in Figure 2-2. A detailed component table for this run can be found in Appendix A, Table A2-2.

Gas phase samples collected during depressurization at the end of experiment were analyzed on a Varian 3300 gas chromatograph with 60/80 Carboxen-1000 column (15 ft x 1/8" SS, 2.1mm ID) and argon carrier gas. The temperature program for GC separation of gas samples was to hold at 40°C for 2.0 min, ramp to 250°C at 20 °C/min, and hold at 250°C for 5.0 min. A calibration gas mixture containing 2.0 vol% each of CO, CH₄, and CO₂, along with 100% CO₂ and 100% CH₄, were used to develop response factors for the gas analysis.



Figure 2-1 Sample chromatogram of liquid sample at end of run for run 79TLJ022812 using TCD detection. All alcohol peaks and water peak are resolved. A more detailed sample analysis is shown in **Error! Reference source ot found.** of Appendix A.



Figure 2-2 Sample chromatogram is shown for run 02-36TLJ101713 using FID detection. The sample was injected on a sol gel wax column with FID detector. A more detailed sample analysis is shown in **Error! Reference source ot found.** of Appendix A.

Chromatographic data were entered into an Excel spreadsheet where calculations of species mass fractions in each liquid sample were carried out. This information was then incorporated into the thermodynamic modeling of the reaction system as described below, ultimately leading to determination of ethanol conversion and product selectivities.

2.3 Results and Discussion

2.3.1 Catalyst Characterization

Catalysts used in reaction studies were subject to measurement of BET surface area via N₂ adsorption, acid site density via NH₃ chemisorption, and basic site density via CO₂ chemisorption. Results are presented in Table 6; profiles from temperature programmed desorption (TPD) experiments are given in Figure 5 for both NH₃ and CO₂. NH₃ desorption from γ -Al₂O₃ characterizes weak (35-150°C), medium (150-300°C), and strong (300-600°C) acid sites, and CO₂ desorption from γ -Al₂O₃ gives information on weak (35-150°C), medium (150-300°C), and strong (300-600°C) acid sites. These temperature ranges for relative base and acid site strengths have been assigned in prior work.[12]

Temperature programmed desorption results in Table 2-1 show that total acid site density is relatively constant on the several catalysts examined, although the distribution of acid site strengths shifts toward weaker acidity with addition of La₂O₃ to γ -Al₂O₃. Basic site concentration measured by CO₂ adsorption (Figure 10), in contrast, shows the expected strong increase upon addition of La₂O₃, with a concurrent shift from weaker (35-150°C) to stronger (> 150°C) basic sites at higher temperatures.

	Acid	Sites (µm	ol g ⁻¹)		Basic Sites (µmol g ⁻¹)				Surface Area
Catalyst	Weak	Medium	Strong	Total	Weak	Medium	Strong	Total	BET (m ² /g)
γ-Al ₂ O ₃	188	238	167	593	61	32	2	95	153
8Ni/Al	173	232	284	688	84	51	7	142	152
9 La-Al	185	295	114	594	120	146	49	315	145
8Ni/9La-Al	190	260	125	575	98	126	61	285	124

Table 2-1 Acid and base site densities from CO₂ and NH₃ chemisorption.

2.3.2 Catalytic Reactions

Analysis of reaction equilibria shows that all reactions are favorable except for dehydrogenation of ethanol to acetaldehyde, for which the equilibrium constant at reaction conditions is ~0.1 (see Supplementary Information). The SR-Polar equation of state has been applied to all reactions carried out and reported in this study. A typical experiment carried out at 230°C with 8Ni/Al catalyst is analyzed here to illustrate application of the model. In this run, samples were taken at ten time points. Ethanol conversion, product selectivities, and carbon recoveries were calculated after application of the SR-Polar equation to each time point (Table 2-2). The carbon recovery was greater than 95% for all time points. The 1-butanol selectivity starts low at 6%, but increases to a maximum of 51%. The selectivity towards CH_4 and CO_2 is high early in the reaction (<60 min), levels out, and then increase again at 600 minutes.

Initial experiments with Ni/Al₂O₃ and Ni/La₂O₃ /Al₂O₃ catalysts were carried out at 230°C, autogeneous pressure, and a catalyst loading of 0.093 g catalyst/g ethanol. In all reactions, the SR-Polar model was applied to most accurately characterize ethanol conversion and product selectivities. Initial results, shown in Table 2-3, show that 8 wt% Ni on γ -Al₂O₃ is

an active catalyst for the ethanol Guerbet reaction. For a 10 hour reaction at 230°C, 46% ethanol

conversion was achieved, higher than the conversion achieved by Yang, [14] with

Time (min)	0	20	40	60	120	180	240	300	664	1344
Ethanol (conv. %)	2.7	4.2	6.5	7.9	8.9	11.8	14.8	16.4	25.3	41.0
1-Butanol	5.8	11.5	15.5	21.2	34.7	42.4	46.0	51.6	52.4	47.5
1-Hexanol	0.5	0.0	0.6	1.1	2.2	3.6	4.5	5.5	7.0	7.9
CH_4	4.5	11.1	10.5	10.9	10.1	9.1	8.3	7.6	10.0	14.2
CO_2	0.9	2.2	2.1	2.2	2.0	1.8	1.7	1.5	2.0	2.9
2-Ethyl-1-Butanol	0.0	0.0	0.0	0.0	0.5	0.9	1.4	1.7	2.6	3.6
1-Octanol	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	1.0
2-Ethyl-1-Hexanol	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.7
Diethyl Ether	2.3	3.0	4.4	4.5	6.1	5.4	4.8	4.4	3.2	2.0
Ethyl Acetate	36.8	35.5	22.5	16.8	14.1	9.7	7.4	6.6	4.7	2.6
Acetaldehyde	16.4	14.4	10.4	8.4	7.7	4.4	4.7	4.2	2.5	1.2
Butyraldehyde	0.0	1.5	1.8	1.8	1.9	1.8	1.7	1.6	1.2	0.6
Unidentified	0.0	0.0	25.4	28.7	15.2	24.1	17.4	11.2	11.2	11.6
Carbon Recov. (%)	99.1	99.1	97.9	97.4	98.2	97.5	97.3	98.2	97.8	95.1

Table 2-2. Product selectivities are provided along with ethanol conversion and total carbon recoveries.

 Unidentified selectivity is based on total unidentified peak area using 1-hexanol response factor.

46% selectivity to 1-butanol and 13% selectivity to C_6 + alcohols. Total higher alcohols include 1-butanol, 2-ethyl-1-butanol, 1-hexanol, 1-octanol, 2-ethyl-1-hexanol, and 1-decanol. Methane was the major byproduct gas (20% selectivity), with minor amounts of carbon monoxide and carbon dioxide. Other products include acetaldehyde, ethyl acetate, and diethyl ether.

These results are consistent with the carbon-carbon bond cleaving capability of nickel metal and the acidity of γ -Al₂O₃. Increasing the Ni content to 10 wt% lowered overall alcohol selectivity because of increased ethanol decomposition to gases and possible steam reforming reactions.

Catalyst	HA Sel. (%)	Conv. (%)	HA Yield (%)
8Ni-Al	57	46	26
10Ni-Al	47	52	24
8Ni/7La-Al	65	50	33
14La-Al	67	16	11
8Ni/9La-Al	71	55	39
8Ni/10Ce-Al	71	50	35

Table 2-3 Preliminary catalyst screening experiments at 230°C, autogeneous pressure, 0.093 g cat/ g EtOH, and 10 hr run time. HA = higher (C_4 - C_8) alcohols.

To moderate the acidity of the γ -Al₂O₃ support, lanthanum oxide (La₂O₃) was chosen as a catalyst modifier since it has been shown to have promoting effects on supported nickel catalysts.[34, 35] Alkali earth metal oxides supported by La₂O₃-stabilized γ -Al₂O₃[36, 37] have also been used for ethanol conversion to butanol.

Addition of La_2O_3 to γ -Al₂O₃ did not directly improve 1-butanol selectivity, but it did improve the overall total higher alcohol yield. Interestingly, the highest 1-butanol selectivity was achieved with 14 wt% La_2O_3/γ -Al₂O₃ material, but this catalyst had very low activity. The catalyst screening showed 8 wt% Ni/9 wt% La_2O_3/γ -Al₂O₃ to be a preferred catalyst, since it gave the highest total higher alcohol (HA) yield of 38% at 57% ethanol conversion.

A set of experiments was performed at 230° C using 1/16" γ -Al₂O₃ support and 0.04 g catalyst/g ethanol catalyst loading to establish concentration profiles of product species over the course of reaction. Selectivities to the various products are plotted in Figure 2-3 for nickel catalyst with and without added lanthanum oxide.



Figure 2-3 Selectivities for 1-butanol, C_6 + alcohols, acetaldehyde, ethyl acetate, and diethyl ether for 8Ni/Al and 8Ni/9La-Al catalysts at 230°C and 0.04 g cat/g EtOH loading.

For the 8 wt% Ni/ γ -Al₂O₃, catalyst, initial selectivity is directed toward acetaldehyde, and ethyl acetate formation, with 1-butanol selectivity increasing gradually to 50% at 20% ethanol conversion. The addition of lanthanum oxide to the catalyst remarkably decreases acid-catalyzed ethyl acetate and diethyl ether formation, increases ethanol conversion, and essentially doubles 1hexanol selectivity. Because no acetic acid is observed, it is assumed ethyl acetate is a product of the Tischenko reaction of acetaldehyde[38]. Ethyl acetate formation rate is initially rapid and quickly declines to zero - this is likely indicative of a conditioning period of the catalyst, as calculations show the equilibrium constant of ethyl acetate formation from acetaldehyde is large (~800). APPENDIX

APPENDIX

A.1: Sample component tables for TCD and FID for GC analysis

Table A2-1 Components are identified from GC-MS for run 79TLJ022812 on DB wax column with TCD detector. GC-MS analysis was performed at the mass spec facility at MSU. Components with (*) identified by GC-MS and (**) indicates component was hidden and/or could not be located on chromatogram.

		Peak
Retention Time (min)	Chemical ID	Area
0.92	Dietheylether	10101
1.10	Acetaldehyde	67549
2.08	Butyraldehyde	27243
2.20	Ethyl Acetate	197058
2.87	Ethanol	3741478
**	2-Pentanone*	**
**	2-Ethyl-Butanal*	**
**	Decane*	**
4.25	Ethyl Butyrate*	52692
**	3-Hexanone*	**
4.64	Water	2801538
4.71	Butyl Acetate	89989
4.84	Undecane	22841
5.49	2-pentyl methoxyacetate*	117297
5.91	1-Butanol	2489708
6.35	2-Heptanone*	54781
6.86	Butyl Butyrate*	48488
7.08	Ethyl Hexanoate*	16763
7.64	Hexyl Acetate*	22306
7.83	4-Heptanol*	13899
8.2	2-ethyl-1-butanol	386047
8.41	4-nonanone*	24286
8.83	1-Hexanol	649619
9.15	2-ethylhexyl acetate*	4584
9.26	2-nonanone*	13771
9.55	Hexyl Butyrate*	16069
9.82	Ethyl octanoate*	4722
10.56	2-ethyl-1-hexanol	140734
11.01	2-nonanol*	2716
11.1	Unidentified	24675
11.41	1-octanol	161617
12.21	2-undecanone*	16622
12.89	Unidentifed	33246

Table A2-1 (cont'd)

	Total Unidentified	97804	
14 40	2-ethyl-1-dodecanol*	8046	
14.21	2-butyl-1-octanol*	5292	
13.60	Unidentified	39883	

Table A2-2 Components are identified for run 02-36TLJ101713. The sample was analyzed with a sol gel wax column and FID detection. Component with (*) is internal standard.

Retention Time		Peak
(min)	Chemical ID	Area
2.10	Dietheylether	2485
2.30	Acetaldehyde	7539
2.77	Unidentifed	1747
2.95	Unidentified	3321
3.57	Butyraldehyde	2122
3.73	Ethyl Acetate	4338
3.86	Acetal	1881
3.52	Ethanol	169829
5.38	Unidentified	6354
6.57	Crotonaldehyde	2498
7.30	Unidentifed	3582
8.23	Unidentified	2125
8.30	4-Heptanone	3451
8.66	1-Butanol	172274
9.34	2-Ethylhexanal	2263
10.00	Hexenal	1744
11.16	Unidentified	1155
12.01	2-ethyl-1-butanol	32484
12.55	Unidentified	1155
13.19	1-Hexanol	55153
14.57	Butyl Hexanoate*	94096
16.00	2-ethyl-1-hexanol	12968
16.72	Unidentified	2749
17.12	1-octanol	14665
18.60	Unidentifed	1024
18.87	Unidentified	3100
19.56	1-Decanol	3700
	Total Unidentified	19958



A.2: Response factors for reaction products of the ethanol Guerbet reaction

Figure A2-1 TCD response factors for ethanol, 1-butanol, ethyl acetate, and C₆ + alcohols.



Figure A2-2 TCD response factors for acetaldehyde, butyraldehyde, C₄+ esters, 4-heptanone, and 1-decanol.



Figure A2-3 TCD response factors for 1-butanol and C_6 + alcohols with butyl hexanoate internal standard.



Figure A2-4 FID response factors for ethyl acetate, diethyl ether, 1-butanol, and C_6 + alcohols with butyl hexanoate internal standard.



Figure A2-5 FID response factors for 4-heptanone, acetaldehyde, butyraldehyde, and C_6 + aldehydes.

A.3: CO2 chemisorption plot



Figure A2-6 CO₂ TPD profiles γ -alumina and γ -alumina- supported catalysts.



A.4: NH3 chemisorption plot

Figure A2-7 NH₃ TPD profiles γ -alumina and γ -alumina- supported catalysts.

A.5: Example BET surface area plot



Figure A2-8 Sample BET surface area plot for $8Ni/9La_2O_3-\gamma$ -alumina catalyst.

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3 VLE Modeling

3.1 Introduction

The phase equilibria for near critical ethanol Guerbet reactions with or without gas byproduct reactions have not been characterized in the literature. Alumina-supported nickel catalysts have shown to produce significant amounts of methane and carbon dioxide. The goal of the ethanol Guerbet reaction is to convert ethanol to 1-butanol and higher alcohols, therefore it is important to understand the roles of CH_4 and CO_2 . Ethanol can be cleaved to CH4 and CO2according to:

$$C_2 H_5 OH \to \frac{1}{2} CO_2 + \frac{3}{2} CH_4$$
 (3-1)

The CH4/CO₂ ratio has been found to be 3-5 in my ethanol Guerbet system with nickel catalysts.

Reactions are typically done at 230°C and autogeneous pressure. Pressures can be anywhere from 5 MPa to 14 MPa. At these conditions, there can be significant quantities of CH4 and CO2 in the liquid phase, while there can be significant quantities of ethanol, water, and butanol in the vapor phase. In order to do accurate computations of higher alcohol formation kinetics, selectivities, and ethanol conversion, the vapor liquid equilibria (VLE) of the ethanol Guerbet system needs to be quantified. Currently, no one has characterized and modeled the ethanol Guerbet system.

Because of the polar nature of alcohols and water, the system is not ideal. The reaction mixture is also near supercritical, since the critical temperature of ethanol is 241°C and the critical pressure of ethanol is 6.3 MPa [1]. Consequently, an equation of state model is needed in order to predict higher alcohol VLE at these conditions. Equations of state (EOS) account for the volume of the molecules as well as the interactions between molecules. EOS models are also

more suited for predicting P-V-T behavior of pure components and mixtures at near-critical to supercritical conditions.

After initial screening of models, the SR-Polar model in Aspen plus was chosen to model the VLE in the ethanol Guerbet system. Pure component vapor pressure data from the NIST data engine in Aspen was used for checking vapor pressure predictions. Binary data from NIST was also regressed to obtain binary constants used in the SR-Polar model. Volume translation constants were also applied in the SR-Polar EOS for better prediction of liquid densities. The final model was then used to model the 6-component system comprised of CH₄, CO₂, ethanol, 1butanol, 1-hexanol, and water. Other minor components are grouped with ethanol or 1-hexanol in the model according to their volatility.

3.2 Thermodynamic Modeling of Reaction

3.2.1 SR Polar EOS

The Peng-Robinson-Wong-Sandler (PRWS), predictive Soave-Redlich-Kwong (PSRK), and Schwartzentruber-Renon (SR-Polar) equations of state were chosen for initial model screening. These EOS's are known for accurate prediction of vapor pressures due to their incorporation of the acentric (ω) factor with the critical point (T_c, P_c) [2]. For the PRWS, three alpha functions were tested, standard PR alpha, Boston-Mathias, and Schwartzentruber. The PRWS and PSRK equations of state had the lowest average error of the three EOS's (Figure 3-1) at 2.1%. Results with other alpha functions for PRWS are shown in Table 3-1. It was decided to use the Schwartzentruber-Renon- (SR)-Polar EOS because it offers the advantage of a temperature dependent molar volume translation parameter. The SR-Polar EOS is also recommended for highly non-ideal systems at high temperatures and pressures. This is needed since predictions of liquid phase density for pure components with an equation of state deviate from experimental data at the near critical region [2].



Figure 3-1 Experimental vapor pressure data is compared with predicted vapor pressure by Peng Robinson and SR Polar [3].

Table 3-1 Comparison of error in vapor pressure calculated by PRWS, PSRK, and SR-Polar. PRWS- α_1 denotes standard PR, PRWS- α_2 denotes Boston Mathias, and PRWS- α_3 denotes Schwartszentruber [3].

		PRWS-			SR-
	$PRWS-\alpha_1$	α2	$PRWS-\alpha_3$	PSRK	Polar
Ethanol	1.3	1.1	12.5	0.9	0.9
1-Butanol	15.5	0.8	0.9	1.0	0.8
1-Hexanol	35.9	6.2	5.7	5.9	7.2
Water	4.9	0.4	0.4	0.4	0.5
Average Abs % error	14.4	2.1	4.9	2.1	2.4

Initial screening of several equations of state led to the selection of the Schwartzentruber-

Renon (SR)-Polar equation of state (EOS) to characterize vapor and liquid phases during batch reactor operation. Accurate prediction of liquid and vapor phase densities is important in the current application, but is generally challenging with an equation of state in the near-critical region [2]. The SR-Polar EOS was chosen because it offers the advantage of a temperature dependent molar volume translation parameter to best predict densities, and is recommended for non-ideal systems at high temperatures and pressures.

The SR Polar EOS was developed by Schwartzentruber and Renon in 1989.[4] It is a Soave-Redlich-Kwong (SRK) type equation of state. The SR-Polar EOS, including volume translation, is

$$P = \frac{RT}{V_m + c - b} - \frac{a}{(V_m + c)(V_m + b)}$$
(3-2)

The species included in the SR-Polar EOS model of the reaction system are ethanol, 1-butanol, 1-hexanol, water, CH_4 , and CO_2 , with the ratio of CH_4 : CO_2 determined by GC analysis of vented gas at the end of reaction. In reality, the reaction liquid phase contains minor amounts of other species including acetaldehyde, ethyl acetate, diethyl ether, and longer chain alcohols, aldehydes, and esters. For phase equilibrium modeling purposes, these components are combined with one

Component	Modeled Component
Ethanol	Ethanol
1-Butanol	1-Butanol
1-Hexanol	1-Hexanol
H_2O	H_2O
2-Ethyl-1-Butanol	1-Hexanol
1-Octanol	1-Hexanol
2-Ethyl-1-Hexanol	1-Hexanol
Diethyl Ether	Ethanol
Ethyl Acetate	Ethanol
Acetaldehyde	Ethanol
Butyraldehyde	Ethanol

 Table 3-2
 Grouping of observed species into modeled components.

of the species mentioned above according to volatility. The groupings are given in Table 2 below; unidentified peaks in sample chromatograms were assigned the response factor for 1-hexanol for calculation purposes, and any unaccounted carbon was assigned as 1-hexanol for

modeling and then subsequently removed to calculate yields based on the model results. Once compositions of the modeled components were established, their mole fractions were recalculated according to experimental results to give the modeled quantities of all species observed in Table 3-2.

3.2.2 Parameter Estimation

The SR-Polar EOS utilizes quadratic mixing rules for the attractive parameter *a* and the repulsive parameter *b*:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} (a_i a_j)^{1/2} x_i x_j [1 - k_{a,ij} - l_{ij} (x_i - x_j)]$$
(3-3)

$$b = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{b_i + b_j}{2} x_i x_j (1 - k_{b,ij})$$
(3-4)

where

$$k_{a,ij} = k_{a,ij}^0 + k_{a,ij}^1 T + k_{a,ij}^2 / T$$
(3-5)

$$l_{ij} = l_{ij}^0 + l_{ij}^1 T + l_{ij}^2 / T$$
(3-6)

For all binary pairs, $k_{b,ij}$ was set to zero and l_{ij} was set to zero except for the water/1-

butanol binary pair. The binary parameter in Eq. (3-5) was chosen to be constant, $(k_{a,ij}=k_{a,ij}^0)$ for ethanol/CO₂, and 1-butanol/CO₂. The binary pairs ethanol/1-butanol, and ethanol/water used $k_{a,ij}=k_{a,ij}^0+k_{a,ij}^2/T$. The water/1-butanol binary pair used $k_{a,ij}=k_{a,ij}^0+k_{a,ij}^2/T$ and $l_{ij}=l_{ij}^0+l_{ij}^2/T$. Ethanol/CH₄ and water/CO₂ were the only binary pairs that used a linear temperature dependence of $k_{a,ij}$.

Values of the $k_{a,ij}$ and l_{ij} parameters were regressed from experimental data in the AspenPlus database; parameters for the ethanol/CH₄ binary pair were later adjusted to better

describe the experimental results. Values of the regressed parameters are summarized in Table 3-3. For binary pairs where experimental data were not available, parameters were estimated using UNIFAC or Hayden-O'Connell models. It can be seen in Figure 3-2 that adjusting $k_{a,ij}$ for ethanol/CH₄ binary increased experimental error with respect to the literature data. The error is larger with respect to the literature data, because the model was calibrated to our experimental data, as discussed in section 3.2.4. The reactor configuration for reactions was used for VLE model calibration.

Binary	ka,ij0	ka,ij1	ka,ij2	lij0	lij2	Abs. Avg. Err. % (T. range)	Ref
EtOH/CO ₂ *	-0.100					40.3 (304 K-453 K)	[5-7]
EtOH/1-BuOH	0.047		-15.249			1.0 (323 K-403 K)	[8]
EtOH/Water	-0.004		-33.871			3.3 (298 K-473 K)	[9, 10]
1-BuOH/CO2	0.078					24.9 (313 K-430 K)	[11-13]
1-BuOH/Water	0.131		-81.051	0.211	58.836	1.5 (323 K-403 K)	[8]
EtOH/CH ₄ *	-2.362	0.0047				38.4 (398 K-498 K)	[14]
Water/CO ₂	-0.261	0.0006				20.6 (383 K-523 K)	[15]

Table 3-3 Binary parameters for the ethanol Guerbet system.

* The ethanol/CH₄ and ethanol/CO₂ binary parameters were adjusted to our experimental data. The avg. error % was 18% with fitted Aspen NIST data for ethanol/CH₄, but increased to 38% with parameter adjustment. The avg. error % was 6.5% with fitted Aspen NIST data for ethanol/CO₂, but increased to 40% with parameter adjustment.



Figure 3-2 Predicted hase equilibria for ethanol-CH4 is shown with the regressed, temperature dependent ka,EtOH-CH4 and with the ka,EtOH-CH4 adjusted to fit our validation experiments [14].

The pure component parameters for the SR-Polar EOS are defined by:

$$a_i = \frac{1}{9(2^{1/3} - 1)} \frac{(RT_{ci})^2 \alpha_i}{P_{ci}}$$
(3-7)

$$b_i = \frac{2^{1/3} - 1}{3} \frac{RT_{ci}}{P_{ci}}$$
(3-8)

The value of α_i at subcritical temperature is described by the extended Mathias equation (3-9); in the supercritical region the equation to determine α_i is known as the Boston-Mathias extrapolation (3-10).[16] For alcohols and water, T_{ri} is less than 1 and α_i is defined as:

$$\alpha_{i} = \left[1 + m\left(1 - T_{ri}^{\frac{1}{2}}\right) - p_{1,i}(1 - T_{ri})\left(1 + p_{2,i}T_{ri} + p_{3,i}T_{ri}^{2}\right)\right]^{2} \quad \text{when } T_{ri} < 1$$
(3-9)

For CH₄ and CO₂, T_{ri} is greater than 1 and α_i is defined as:

$$\alpha_i = e^{2[c_{\alpha i} \left(1 - T_{ri}^{d_i}\right)]} \quad \text{when } T_{ri} > 1$$
(3-10)

with

$$c_{\alpha i} = 1 - 1/d_i \tag{3-11}$$

$$d_i = 1 + \frac{m_i}{2} - p_{1,i} \left(1 + p_{2,i} + p_{3,i} \right)$$
(3-12)

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \tag{3-13}$$

The parameter ω_i is the acentric factor. For the polar components present in the ethanol Guerbet system, $p_{1,i}$, $p_{2,i}$, and $p_{3,i}$ are estimated by the Antoine equation.[16]

The SR-Polar EOS offers a temperature-dependent volume translation parameter c for the purpose of accurately predicting densities with a linear mixing rule:

$$c = \sum_{i} x_i c_i \tag{3-14}$$

Volume translation does not affect VLE composition calculations but does affect fugacity values.[16] For alcohols and water, $T_{ri} < 1$; therefore the pure component volume translation parameter c_i for these components is defined by:

$$c_i = c_{0i} + \frac{c_{1i}}{1 - T/T_{ci} + C_{2i}} \quad \text{(for } T_r < 1\text{)}$$

Table 3-4 Volume translation constants are listed for alcohols, water, methane, and CO2. The (*) indicates translation constant was fit to binary with ethanol and not pure component data [3].

Component	c _{0i} (m³/kmol)	c _{1i} (m³/kmol)	c _{2i} (m³/kmol)	Avg. Abs Error (%)
Ethanol	7.00E-03	2.50E-03	4.50E-02	3.8
1-Butanol	7.00E-03	2.60E-03	3.00E-03	0.6
1-Hexanol	1.10E-02	3.00E-03		0.8
Water	5.00E-03	7.97E-04		1.5
Methane*	-1.20E-01			
CO2*	-3.00E-02			

Values of $c_{0,i}$, $c_{1,i}$, and $c_{2,i}$ were regressed from pure liquid density data in the AspenPlus database. For CH₄ and CO₂, $T_{ri} > 1$ and $c_{0,i}$ was regressed from binary ethanol/CH₄ and ethanol/CO₂ liquid densities at conditions close to those of reaction (with $c_{1,i}$ and $c_{2,i}$ set to zero). Values of all regressed volume translation parameters are given in Table S3 of Supplementary Information.



Figure 3-3 SR-Polar translated density predictions are compared with experimental data [3, 14].

3.2.3 Applying SR-Polar EOS to Batch Experiments

The SR-Polar EOS is applied to batch Guerbet chemistry experiments to determine compositions and quantities of both vapor and liquid phases. This is done by interfacing the

AspenPlus V8.2 process simulator with Microsoft Excel 2013 via the AspenPlus Properties Addin in Excel. AspenPlus flash operations using TVFlash, particularly to identify bubble and dew point pressures at reaction temperature, are performed in Excel as described below after the Properties Backup (.aprbkp) file with SR-Polar binary constants and parameters is loaded into the Excel workbook.

When a liquid phase sample taken during reaction is vented to atmospheric pressure, dissolved gases flash out; consequently, the GC analysis of the remaining material reflects only the composition of the condensable portion of the liquid phase at reaction conditions. Starting with this composition, a mixture of $CO_2 + CH_4$ with a fixed molar ratio (x_{CH4}/x_{CO2}) is added to the GC-determined liquid composition using AspenPlus TVFlash (maintaining $\Sigma x_i = 1$) until the bubble pressure of the combined mixture equals the measured reactor pressure at the point the sample was taken. Once this has been done, the compositions, molecular weights, and densities of liquid and vapor phases at reaction conditions are defined. Because the total mass of the reaction mixture (m_T) is tracked during reaction, and the total mixture volume is constrained by the reactor volume (V_R), the number of moles of vapor n_V (and consequently moles of liquid n_L) in the reactor can be determined by combining Eq. (3-16) and (3-17) to give Eq. (3-18).

$$m_T = n_L M_L + n_V M_V \tag{3-16}$$

.....

$$V_R = \frac{n_L}{\rho_L} + \frac{n_V}{\rho_V} \tag{3-17}$$

$$n_V = \frac{V_R \rho_L M_L \rho_V - m_T \rho_V}{\rho_L M_L - \rho_V M_V}$$
(3-18)

Once vapor and liquid quantities and compositions are defined, the overall composition (z_i) of the reaction mixture is calculated for the time of sampling:

$$z_i = \frac{n_L x_i + n_V y_i}{n_{tot}} \tag{3-19}$$

where n_{tot} is the sum of n_V and n_L . Once this is done, the ratio of liquid-phase CH₄ to CO₂ mole fractions (x_{CH4}/x_{CO2}) chosen for the TVFlash calculation is then varied and that calculation is repeated until the calculated overall gas composition ratio (z_{CH4}/z_{CO2}) matches the overall experimental (z_{CH4}/z_{CO2}) ratio determined by GC analysis. A flowsheet for applying the SR-Polar model is shown in Figure 3-5.

The calculation of ethanol conversion and product selectivities and yields are then finally calculated by the following equations:

Selectivity to Species
$$i(\%) = \left(\frac{\text{moles C in product species } i}{\text{moles C in reacted ethanol}}\right) \ge 100\%$$
 (3-20)

Ethanol Conversion
$$\% = (1 - \frac{\text{moles of ethanol in product}}{\text{moles of initial ethanol charged}}) \times 100\%$$
 (3-21)

$$Yield of Species i (\%) = (\frac{Selectivity \%}{100\%}) (Converison \%)$$
(3-22)



Figure 3-4 Phase equilibria is shown for a binary, but fixed xi, yi, ρ L,and ρ v at a specific bubble pressure also apply to multi-component mixtures.


Figure 3-5 Flowsheet for SR-Polar model application to reaction data.

3.2.4 Model Validation and Parameter Adjustment

The phase equilibrium model using the SR-Polar EOS for the batch reactor was validated by conducting control experiments in which known quantities of the modeled components were placed into the Parr reactor and the reactor pressure was measured at reaction temperature. Two validation experiments were conducted at 230°C: one simulating high ethanol conversion (49%) and the other low ethanol conversion (22%). For these experiments and all subsequent applications of the SR-Polar EOS, a volume of 328 ml for the Parr batch reactor was used. A known liquid mixture of ethanol, 1-butanol, 1-hexanol, and water was first added to the reactor, which was sealed and then weighed. The reactor atmosphere was purged with CO_2 and pressurized to give the desired amount of CO_2 , and then weighed to verify the mass of CO_2 added. The gas inlet was then purged with CH_4 , connected to the reactor, and pressurized to a pressure higher than the reactor pressure to prevent backfilling. Methane was then added by monitoring pressure change, and then the reactor was finally weighed again to determine the mass of CH_4 added. The reactor was heated to reaction conditions, reactor pressure was recorded, and liquid samples were taken to determine composition. The SR-Polar EOS was then applied as described in the above section to calculate quantity, composition, and density of liquid and vapor phases in the reactor.

Experimental compositions and total calculated gas quantities for the validation experiment are shown in Table 3-5. The SR-polar EOS was found to underpredict total gas quantity at the simulated higher conversion; closer inspection of the results revealed that CH₄ solubility in the liquid phase was underpredicted when using the binary parameters regressed from experimental data. The binary VLE parameters were therefore further checked by performing experiments with just ethanol-CH₄ and ethanol-CO₂ binary mixtures in the batch reactor. Known quantities of the binary mixtures were heated to 215°C and 225°C, and pressure was recorded. The bubble pressure calculation was performed using TVFlash in AspenPlus for each of the binaries by adjusting $k_{a \cdot EtOH-CH4}^{0}$ and $k_{a \cdot EtOH-CO2}^{0}$ until the predicated gas error was minimized. At temperatures higher than 225°C, the binary bubble pressure calculation in AspenPlus did not converge because of the proximity to the ethanol critical point. For experimental temperatures up to 225°C, the best agreement between experimental and predicted quantities of ethanol and CH₄ in the reactor was obtained by adjusting the ethanol/CH₄ binary interaction parameter from $k_{a,EtOH-CH4} = 0.0030T-1.1945$ to $k_{a,EtOH-CH4} = 0.0047T-2.3619$ (T in K). Similarly, the best agreement with the ethanol/CO₂ binary experiment was obtained by adjusting the constant $k_{a,EtOH-CO2,0}$ from +0.1 to -0.1. These corrections resulted in the difference between predicted and actual CO₂ + CH₄ mass decreasing from 0.9 g to 0.6 g (with the total liquid species mass correspondingly adjusted in the other direction) for the high conversion experiment, while the difference between predicted and actual total CO₂ + CH₄ in the reactor for the low conversion experiment decreased from 0.4 g to 0.2 g (Table 3-5). With this correction, calculated overall reactor composition, ethanol conversion, and higher alcohol selectivities were within three percentage points of the experimental values in the validation experiments. The adjusted values of $k_{a,EtOH-CH4}$ and $k_{a,EtOH-CO2}$ were therefore used in all subsequent applications of the SR-Polar EOS to reaction studies.

	Overall mole fraction (z _i)				
	High Conversion		Low Conversion		
Component	Experimental	Predicted	Experimental	Predicted	
Ethanol	0.465	0.469	0.770	0.788	
1-Butanol	0.098	0.097	0.077	0.067	
1-Hexanol	0.045	0.041	0.013	0.010	
H_2O	0.202	0.215	0.101	0.099	
CH_4	0.133	0.126	0.023	0.022	
CO_2	0.056	0.053	0.016	0.014	
Total Mass of Species (g)	107.0	107.0	84.2	84.2	
Observed Pressure (psia)	1565	1565	800	800	
Liquid Species Mass (g)	95.1	95.7	82.2	82.4	
$CH_4 + CO_2 Mass (g)$	11.9	11.3	2.0	1.8	
Ethanol Conversion	0.485	0.476	0.219	0.194	

Table 3-5 Comparison of predicted and experimental gas quantities in SR-Polar validation experiments at 230° C with adjusted ethanol/CH₄ and ethanol/CO₂ binary parameters.

3.2.5 Liquid and Vapor Densities

The SR-polar EOS gives insight into phase behavior not normally observed or accounted for in batch reaction studies. Most reactions here were carried out at 230°C, close to the critical temperature of ethanol (238°C). Under these conditions, the liquid phase is significantly expanded and the vapor phase density is high enough that a significant fraction of the reaction mixture is in the vapor phase. At 230°C, pure ethanol has a liquid phase density of 0.44 g/ml (Figure 3-6), slightly more than half its value at 25°C, and the reaction mixture at partial conversion (right-most picture in Figure 3-6) is similarly expanded. This liquid phase expansion



Figure 3-6 Liquid and vapor phase densities for pure ethanol at 25°C (left), pure ethanol at 230°C (center), and for the reaction mixture at 41% ethanol conversion (right).

has safety implications, in that if the reactor is initially filled with too much ethanol, the liquid phase will expand and fill the reactor head space as reaction temperature is approached, leading to reactor overpressure and possibly reactor failure. Further, solid catalyst is not as easily suspended in the low density liquid solution at reaction conditions, thus leading to possible inaccuracy in rate characterization unless vigorous mixing is ensured. The expanded liquid reaction phase also requires activity-based kinetic models, because of its highly non-idea nature.

3.2.6 Comparison of SR-Polar EOS analysis with conventional liquid phase analysis

Ethanol conversion and alcohol selectivities obtained with the SR-Polar model are compared here to results obtained by conventional analysis of the flashed liquid sample, as is typically done in batch reaction studies. In conventional liquid phase-only analysis, reactor contents are assumed to be all in the liquid phase, so with pure EtOH as the starting material, EtOH conversion (%) = 100 - (wt% EtOH in sample) and selectivity to n-butanol (%) = (2MW_{EtOH}/MW_{BuOH})(wt% BuOH in sample)/(EtOH conversion (%)). A similar calculation applies for other alcohols. Figure 3-7 and Figure 3-8 give the comparison between these conventional liquid-only values and those calculated using the SR-Polar model. The liquid-only analysis almost uniformly gives "better" results, but the results do not represent reality and are thus misleading. First, EtOH conversion (Figure 3-7) is essentially the same for both analyses, because the EtOH mole fractions in liquid and vapor phases in the SR-Polar model are coincidentally similar at reaction conditions. Butanol selectivity (Figure 3-7) and hexanol selectivity (Figure 3-8) appear three to seven percentage points higher than the SR-Polar model when calculated using conventional liquid phase analysis, because carbon going to gases (CO_2 + CH_4) is not considered and because these heavier species are almost entirely present in the liquid phase. Most importantly, the calculated carbon recoveries for both methods are above 95% (Figure 3-8) – for the conventional liquid phase analysis, this is a direct consequence of the erroneous assumption that all materials are in the liquid phase and is again a misleading result.



Figure 3-7 Comparison of EtOH conversion and 1-butanol selectivity for conventional liquid phase analysis and SR-Polar EOS analysis.



Figure 3-8 Comparison of C6 alcohol selectivity and carbon recovery for conventional liquid phase analysis and SR-Polar EOS analysis.

In condensed phase reaction systems where the liquid phase is significantly expanded (e.g. often near the critical point of the mixture), and where species of widely different relative volatility are formed, it is important to do a careful analysis of the reaction mixture to obtain representative results. In this system, 10-25% of the reactor contents exist in the vapor state at reaction conditions, and a substantial quantity of gases are formed that are not observed when only the liquid phase is analyzed. The SR-Polar model provides a tool with which a more realistic picture of the products formed in reaction can be characterized.

Along with a comparison of carbon recoveries between the liquid-phase only method and using the SR-Polar model, hydrogen and oxygen recoveries were also compared for the two methods. The hydrogen recovery decreases from 101% to 93% at end of run for the liquid-phase

only model (Table 3-6). Using the SR-Polar model raised the hydrogen recovery to 98% and above for all the samples. Contrary to the carbon and hydrogen recoveries, oxygen recovery was 2-3 percentage points above 100% for most of the run and was 99% at end of run for the liquid-phase only method. Applying the SR-Polar model had no real effect on oxygen recovery. It actually demonstrated an oxygen recovery at end of run that was one percentage point lower than the liquid-phase only method.

	Hydrogen Recov. (%)		Oxygen Recov. (%)	
Time (min)	Liq. Phase Only	SR-Polar Model	Liq. Phase Only	SR-Polar Model
0	101.0	99.8	102.7	101.4
20	99.8	99.6	101.7	101.4
40	99.5	99.5	101.7	101.6
60	98.9	99.6	101.1	101.6
120	98.2	99.0	99.9	100.3
240	97.8	98.8	100.0	100.4
300	97.1	98.3	99.3	99.8
600	97.4	99.2	100.4	100.4
1301	93.3	98.4	98.6	97.7

 Table 3-6
 Hydrogen and oxygen recoveries are compared for the liquid-phase only method and SR-Polar model.

3.2.7 Experimental Repeatability

Two runs with identical 8 wt% Ni/9 wt% La₂O₃ catalyst were performed to demonstrate experimental repeatability. The ethanol conversion and carbon recovery profiles for the two runs are similar (Figure 3-9). After 10 hours of run time, ethanol conversion is $32.6\% \pm 4.6$ percentage points and carbon recovery is $97.8\% \pm 0.01$ percentage points. The 1-butanol selectivity after 10 hours is $52.2\% \pm 1.2$ percentage points and C₆₊ alcohol selectivity was 14.5% ± 1.3 percentage points (Figure 3-10). The experimental pressure is virtually the same for the two runs, but begins to deviate slightly after 10 hours (Figure 3-11). At end of run, reactor pressure reached 11.4 MPag for run 1 and reached 14.1 MPag for run 2. Though the end of run

reactor pressure is different, the difference did not noticeably affect the gas selectivity (CH_4+CO_2) .



Figure 3-9 Ethanol conversion and carbon recovery are shown for two runs with identical catalyst at 230°C and 0.04 g cat/g EtOH loading.



Figure 3-10 Selectivity to 1-butanol and C_{6+} alcohols is shown for two runs with identical catalyst at 230°C and 0.04 g cat/g EtOH loading.



Figure 3-11 Experimental reactor pressure and gas selectivities are shown for two runs with identical catalyst at 230°C and 0.04 g cat/g EtOH loading.

3.3 Conclusions

The condensed phase Guerbet reaction of ethanol to 1-butanol and C_6 + higher alcohols was performed in a batch reactor with γ -Al₂O₃-supported nickel/lanthanum catalysts. An 8wt% Ni/9wt% La₂O₃/ γ -Al₂O₃ catalyst gave a total higher alcohol yield as high as 38%, and total higher alcohol selectivity exceeding 85%. Modifying γ -Al₂O₃ with La₂O₃ greatly reduced both formation of ethyl acetate via the Tischenko reaction of acetaldehyde and diethyl ether via the acid-catalyzed dehydration of ethanol. Lanthanum oxide addition leads to a two-fold increase in total base site density, and reduction in strength of the catalyst acid sites.

Applying the SR-Polar EOS to batch Guerbet reactions provides a more rigorous analysis of reaction than conventional liquid phase sampling. The SR-Polar EOS accurately predicts higher alcohol vapor-liquid equilibria, liquid and vapor phase densities, and total quantity of gases produced in reaction. Although the ethanol conversion profile calculated using the SR-Polar EOS is virtually the same as with liquid-phase-only sampling, the product yields and selectivities are more accurately represented because species partitioning between liquid and vapor phases are more accurately modeled. Finally, the ability of the SR-Polar EOS to predict liquid expansion is advantageous in safely designing future ethanol Guerbet reactions at near critical conditions. APPENDIX

APPENDIX

B.1: Regressed binary data



Figure B3-1 Isothermal VLE data for ethanol-1-butanol at 323K, including SR-Polar prediction from regressed parameters [8].



Figure B3-2 Isothermal VLE data for ethanol-1-butanol at 403K, including SR-Polar prediction from regressed parameters [8].



Figure B3-3 Isothermal VLE data for ethanol-water at 298K, including SR-Polar prediction from regressed parameters [10].



Figure B3-4 Isothermal VLE data for ethanol-water at 348K, including SR-Polar prediction from regressed parameters [10].



Figure B3-5 Isothermal VLE data for ethanol-water at 473K, including SR-Polar prediction from regressed parameters [9].



Figure B3-6 Isothermal VLE data for ethanol-methane at 448K, including SR-Polar prediction from regressed parameters [14].



Figure B3-7 Isothermal VLE data for ethanol-methane at 498K, including SR-Polar prediction from regressed parameters [14].



Figure B3-8 Isothermal VLE data for ethanol-carbon dioxide at 304K, including SR-Polar prediction from regressed parameters [6].



Figure B3-9 Isothermal VLE data for ethanol-carbon dioxide at 353K, including SR-Polar prediction from regressed parameters [5].



Figure B3-10 Isothermal VLE data for ethanol-carbon dioxide at 453K, including SR-Polar prediction from regressed parameters [7].



Figure B3-11 Isothermal VLE data for 1-butanol-carbon dioxide at 313K, including SR-Polar prediction from regressed parameters [13].



Figure B3-12 Isothermal VLE data for 1-butanol-carbon dioxide at 393K, including SR-Polar prediction from regressed parameters [12].



Figure B3-13 Isothermal VLE data for 1-butanol-carbon dioxide at 430K, including SR-Polar prediction from regressed parameters [11].



Figure B3-14 Isothermal VLE data for 1-butanol-water at 323K, including SR-Polar prediction from regressed parameters [8].



Figure B3-15 Isothermal VLE data for 1-butanol-water at 383K, including SR-Polar prediction from regressed parameters [8].



Figure B3-16 Isothermal VLE data for 1-butanol-water at 403K, including SR-Polar prediction from regressed parameters [8].



Figure B3-17 Isothermal VLE data for carbon dioxide-water at 473K, including SR-Polar prediction from regressed parameters [15].



Figure B3-18 Isothermal VLE data for carbon dioxide-water at 523K, including SR-Polar prediction from regressed parameters [15].









Figure B3-20 SR-Polar liquid density prediction of 1-butanol with fitted density translation parameter [3].



Figure B3-21 SR-Polar liquid density prediction of 1-hexanol with fitted density translation parameter [3].



Figure B3-22 SR-Polar liquid density prediction of water with fitted density translation parameter [3].



Figure B3-23 SR-Polar liquid density prediction of ethanol-carbon dioxide with fitted density translation parameter [7].

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4 Impact of Water and its Removal on Ethanol Guerbet Reaction4.1 Introduction

In the context of the ethanol Guerbet reaction, few have investigated ethanol decomposition to CH₄, CO₂, CO, or H₂. Ethanol decomposition doesn't appear to occur with hydroxyapatite, MgO, or mixed oxide catalysts[1-4]. Wang et al do not report producing noncondensable gases with their 8wt% Ni/ γ -Al₂O₃ catalyst in a vapor phase reaction of ethanol at 200°C and atmospheric pressure [5]. Riittonen et al also performed reactions with γ -Al₂O₃supported Ni and other metals at 250°C and autogeneous pressure in a batch reactor [6]. They reported forming a gas product that was 2/3 H₂ and 1/3 CH₄. As they stated, Ni has been shown to cleave carbon-carbon bonds of ethanol [7]. The presence of water may play a role in these decomposition reactions.

Marcu et al first described the impact of water on 1-butanol production over a Cu-Mg-Al mixed oxide catalyst [8]. It was found when water was added to the reaction mixture, Lewis strong basic sites O^{2-} were converted to weaker Brønsted OH⁻ sites. They investigated the effect of water removal by taking the reaction mixture after running for certain period of time and drying it using MgSO₄ overnight. The reaction was resumed with fresh catalyst; an increase in ethanol conversion and 1-butanol selectivity was found when water was removed.

Riittonen et al also studied the effect of water; they suspected water could be playing a role in the hydrogen formation by way of steam reforming of ethanol. This was tested by adding 3 Å molecular sieves to the reactor prior to reaction. Ethanol conversion was increased from 20% to 30%. No further characterization was performed on gas production or mechanism. The resulting high H_2 concentration in their product gas was different from our reactions in that the primary components of our system were CH_4 and CO_2 . The amount of H_2 at the end of our

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reactions was ~ less than 5 mol%, indicating steam reforming isn't occurring at high ethanol conversion in our system. There also wasn't any CO in the product gas analysis which means the water gas shift reaction likely isn't occurring. In fact, the ratio of CH_4 to CO_2 is >3, which is in agreement with the ethanol decomposition reaction:

$$2C_2H_5OH \to 3CH_4 + CO_2 \tag{4-1}$$

This is an undesirable reaction due to two reasons; CH_4 and CO_2 are greenhouse gases and the price of methane is much cheaper than the price of ethanol. It was observed in all reactions that reactor pressure increased steadily with ethanol conversion. Though water isn't a reactant in this reaction equation, it was hypothesized increasing water concentration was promoting the decomposition reaction. Water concentration increases with conversion due to being a byproduct of the Guerbet reaction:

$$2C_2H_5OH \rightarrow 1\text{-}Butanol + H_2O \tag{4-2}$$

Steam reforming literature [9-12] has shown that water can react with EtOH to form H₂ and CO₂:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{4-3}$$

Interestingly though, this is more thermodynamically favorable at higher temperatures (>700K) [12]. The effect of water and its removal on the ethanol Guerbet reaction was studied.

4.2 Experimental

4.2.1 Materials

 $Ni(NO_3)_2 \cdot 6H_2O$ (Reagent Grade, Jade Scientific), was used as precursor to reduced metal and $La(NO_3)_2 \cdot 6H_2O$ (99%, Fluka) was used as precursor to the calcined oxide. The support used was 1/16" diameter γ -Al₂O₃ spheres (Strem Chemical). Anhydrous ethanol (Koptec, 200 proof) was used as the initial reactor charge. The catalyst composition used in this study was 8 wt% Ni/9 wt% La_2O_3 - γ -Al₂O₃ (8Ni/9La-Al).

The nickel catalyst modified with La₂O₃ was prepared by first depositing La(NO₃)₃ by incipient wetness impregnation of the γ -Al₂O₃ support followed by drying at 130°C for 18 hours, and calcining at 600°C for 20 hours in 35 ml/min N₂ flow. This assured there was La₂O₃ on the γ -Al₂O₃ surface before the impregnation of the nickel. Nickel was then added by the same wetness technique using Ni(NO₃)₂ and dried at 130°C for 18 hours. The nickel was reduced at 450°C and 1 atm in a tubular flow reactor for 20 hours in 35 ml (STP) H₂/min.

4.2.2 Catalytic reactions with water addition

The effect of water on CH_4 and CO_2 yields was confirmed by performing reactions with different initial water concentration in a 300 ml Parr autoclave reactor. The water concentrations studied were 0, 5 and 10 weight %. Ethanol and/or mixtures with water were placed in the reactor with catalyst and the reactor was purged with 1 atm of nitrogen and sealed. Reactor pressure was autogeneous and liquid samples were taken at specific time intervals. Reactor pressure was measured with a head pressure gauge at each sampling interval. The reaction temperature was 230°C at 900 rpm stir rate and a 0.04 g catalyst/ g ethanol loading.

4.2.3 Catalytic reactions with water removal

A system was required that could effectively remove water at high temperatures (230°C) and high pressures (700-2000 PSIG), while not interfering with the 8Ni/8La catalyst. When a desiccant is placed directly into the reactor, there is a chance the desiccant will catalyze side reactions, such as ethanol dehydration to diethyl ether if an acidic desiccant like calcium sulfate or a molecular sieve is used. Dessicants also work more effectively at lower temperatures. A

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water drying loop outside the reactor was devised to eliminate any potential for this issue to occur (Figure 4-1).



Figure 4-1 Recirculation loop with drying bed is shown with attachments to a 300 ml Parr reactor. The loop includes a chiller that cools the mixture to \sim 40°C and a heater that heats it back up to \sim 220°C.

The water drying loop consisted of a cooling section that dropped the reaction temperature of 230°C down to 35°C-50°C with a 1/8" in 1/4" shell and tube heat exchanger, 10.5" in length. The reaction mixture had to be cooled down to this temperature since molecular sieves 3A have the highest adsorption rate and capacity at lower temperatures.[13] The cooled mixture was then fed into a magnetically driven, single piston reciprocating pump. A pump was needed that could perform recirculation at autogeneous pressures up to 2000 PSIG. The pump was designed by Seifried et al. and was published in Review of Scientific Instruments.[14] It was well suited for this application since all joints were 316 stainless steel Swagelok. A pump with rubber o-rings and seals may not have stood up to the pressures and temperatures of this reaction system. The pump (assembled by hand), shown in Figure 4-2, consisted of 1/4" OD stainless tubing with associatively sized union tees and check valves. The four check valves allowed liquid to flow in only one direction. The main piston chamber was comprised of a magnetic 416 stainless steel precision ground rod that was 5/16 OD and 13 cm in length. The piston sat inside a 1/2" OD x 20 cm SS316 smooth bore seamless tube. The piston was driven by the push-pull forces of two solenoids. The piston solenoids were controlled by an in-house built square wave generator.

The cooled reaction mixture was then pumped to the drying bed, which consisted of 5.5" long, 1" diameter schedule 80 SS pipe with an empty volume of 4 in³. The drying bed was filled with roughly 55 g of ~ 2mm molecular sieve extrudates. Runs were also performed with ~ 2mm beads. The bead shape versus extrudate shape had negligible impact on packing density. The reaction mixture was then heated close to reaction temperature (~220°C) with heat tape before being returned to the reactor. Samples were taken at intervals as done previously above.



Figure 4-2 Schematic is shown for the recirculating pump, taken from Seifried [14].Circulating pump body parts: (a) pump cylinder, (b) solenoids (S1 and S2), (c) reducing union, (d) union cross, (e) plug, (f) check valve, (g) union-tee, (h) needle valve, (i) tubing, (j) piston, and (k) compression spring.

The water removal studies involved three different runs. The first run was performed with no loop and pure ethanol. This was one of two control runs. The second control run used the recirculating loop with glass beads used in the dryer instead of molecular sieves. This control was to show if the recirculation loop itself had any influence on the reaction. The third run utilized the drying loop, starting with pure ethanol. The reaction temperature was 230°C at 900 rpm stir rate and a 0.04 g catalyst/ g ethanol loading.

4.2.4 Modeling reaction system with water removal

Since water was being removed during the reaction, the other components' mole fractions increased accordingly. This increase had to be accounted for in the conversion and selectivity calculations, because they are based on the total amount of moles left in the reactor system at time, t_i . The theoretical quantity of water formed up to t_i is calculated by:

$$n_{H20form,t_i} = (x_{Bu0H} + 2x_{C60H} + 3x_{C80H})(n_L + n_{loop})$$

$$+ (y_{Bu0H} + 2y_{C60H} + 3y_{C80H})(n_V)$$

$$(4-4)$$

The accumulated water up to t_i is calculated by:

$$n_{H2Oaccum,t_i} = x_{H2O} (n_L + n_{loop}) + y_{H2O} n_V$$
(4-5)

In a reaction with no water removal, the theoretical water formed can be checked with the water accumulated by the ratio:

$$H_20 \text{ formed ratio} = \frac{n_{H20form,t_i}}{n_{H20accum,t_i}}$$
(4-6)

Where $n_{H2Ocheck,ti} = 1$ for the case where water isn't removed. For the water removal runs, a material balance can first be performed on the entire reactor system, including the water removal loop. At each time interval samples and rinses are taken out of the reactor, so this is accounted for by:

$$m_{sys,t_i} = m_{sys,t_{i-1}} - m_{sample,t_i} - m_{waste,t_i}$$
(4-7)

Where,

 m_{sys,t_i} is the system mas at t_i m_{sample,t_i} is the sample mass

m_{waste,t_i} is the waste mass from rinsing

Ethanol that's in the recirculation loop isn't modeled by the SR-Polar EOS so this mass is subtracted from the system mass to get the reactor mass at t_i:

$$m_{R,t_i} = m_{sys,t_i} - n_{loop} M_L \tag{4-8}$$

Where, n_{loop} is the moles of reactant in the loop and M_L is the average molecular weight of the liquid phase. This is a first approximation of the reactor mass, since this doesn't account for

water taken out in this step of the calculation. As was done with no recirculation loop in the VLE studies, the mass of the reactor is combined with the reactor volume constraint to determine moles in the liquid and vapor phases:

$$m_{R,t_i} = n_L M_L + n_V M_V \tag{4-9}$$

$$V_R = \frac{n_L}{\rho_L} + \frac{n_V}{\rho_V} \tag{4-10}$$

$$n_V = \frac{V_R \rho_L M_L \rho_V - m_{R,t_i} \rho_V}{\rho_L M_L - \rho_V M_V}$$
(4-11)

With n_L and n_V determined, water formed in the interval from t_{i-1} to t_i can be determined by:

$$n_{H20,int.form,t_{i}} = (n_{H20,form,t_{i}} - n_{H20,form,t_{i-1}})$$
(4-12)

Water accumulated is calculated from:

$$n_{H20,int.accum,t_i} = (n_{H20,accum,t_i} - n_{H20,accum,t_{i-1}})$$
(4-13)

Water removed is found by subtracting water accumulated from water formed:

$$n_{H20,int.rem,t_i} = n_{H20,int.form,t_i} - n_{H20,int.accum,t_i}$$
(4-14)

(4 4 4)

The total quantity of water removed at t_i is found by summing all interval amounts of water removed back to t_0 :

$$n_{H20,tot.rem,t_i} = n_{H20,int.rem,t_i} + n_{H20,int.rem,t_i-1} + \cdots n_{H20,int.rem,t_0}$$
(4-15)

The system mass is a function of water removed; after the first result of water removed at t_i is determined, it is subtracted from the initial approximation of the system mass. Water formation, accumulation, and removal are recalculated based on the new values for n_L and n_V . When there is no difference between calculated and predicted water removed, the true amount of

water removed at t_i has been found. Product selectivities are based on total accumulated product at t_i , which includes samples and rinses:

$$\frac{a_k x_{k,t_i} (n_{L,t_i+} + n_{loop}) + a_k y_{k,t_i} n_{V,t_i} + \sum_{0}^{i} a_k x_{k,t_i} (n_{sample,t_i} + n_{waste,t_i})}{n_{EtOH_0} - x_{EtOH,t_i} (n_{L,t_i} + n_{loop}) - y_{EtOH,t_i} n_{V,t_i} - \sum_{0}^{i} x_{EtOH,t_i} (n_{sample,t_i} + n_{waste,t_i})}$$
(4-16)

Where *a* is the ratio of carbon atoms in the product divided by carbon atoms in ethanol. Ethanol conversion is calculated similarly by:

$$Conv_{t_{i}} = 1 - \frac{x_{EtOH,t_{i}}(n_{L,t_{i}} + n_{loop}) + y_{EtOH,t_{i}}n_{V,t_{i}} + \sum_{0}^{i} x_{EtOH,t_{i}}(n_{sample,t_{i}} + n_{waste,t_{i}})}{n_{EtOH_{0}}}$$
(4-17)

4.3 **Results and Discussion**

4.3.1 Water addition runs

It was found when starting with 0, 5, and 10 weight % water, the gas selectivity ($CH_4 + CO_2$) profiles were similar with time (Figure 4-3). Gas selectivity for the 10% water run was approximately 4-5 points higher than the other two. The gas selectivity profiles vs conversion were virtually identical; gas selectivity steadily increases to 15% at 50% ethanol conversion. It was observed gas selectivity gradually increased with increasing water concentration (Figure 4-4). For the 10% water run, gas selectivity hovered at 10% up to 13% water concentration, then increased 10 points to 20% selectivity when water concentration reached 17%.

The theoretical amount of water generated for the control runs was calculated using equation (4-4). The ratio of the theoretical water generated to total water measured was calculated (Figure 4-5). From 0-20% ethanol conversion, the 5% and 10% water runs are 0.90 to 0.95. The pure ethanol run deviated more from unity and was around 0.80. Since all three runs had ratios less than 1, this meant more water was measured than what could be accounted for. It was reasoned additional could be generated from the hydrogen reacting with ethanol:

$$2H_2 + EtOH \rightarrow 2CH_4 + H_2O \tag{4-18}$$

This agreed with experimental data because CH_4/CO_2 was typically between 3-5. The excess methane was then used to calculate additional water generated and included into the accounted water ratio. The results are plotted on the right plot in Figure 4-5. The correction helped shift the ratio closer to 0.9 and above for all runs.



Figure 4-3 Gas selectivity $(CH_4 + CO_2)$ is plotted vs time on the left and vs ethanol conversion on the right.



Figure 4-4 Gas selectivity is plotted vs water concentration on the left and 1-butanol, C_4 - C_8 alcohol selectivity is plotted vs conversion on the right.



Figure 4-5 Accounted water ratio is plotted vs ethanol conversion on the left and the accounted water ratio including a correction for water formed from formed CH_4 is plotted vs ethanol conversion on the right.

4.3.2 Water removal runs

Gas selectivites were found to be lower for the run with water removal than the run with no water removal (Figure 4-6). Interestingly, the run with glass beads (no drying) subsituted for the molecular sieves had an identical gas selectivty profile. For the run without water removal, gas selectivty starts at 25% at beginning of the run, jumps down to 10% at 40 minutes, and gradually increases to 15% at end of run. For the runs with water removal, gas selectivity is constant at 5% for most of run and rises to 8% at end of run. Higher alcohol selectivites are slightly higher for the run with water removal versus the run with no water removal. The higher alcohol selectivity for the run with glass beads (no drying). These results support water removal as a potential route to minimizing gas formation.



Figure 4-6 Gas selectivites are plotted vs time (top left) and vs ethanol conversion (top right). Higher alcohol selectivites are plotted vs time (bottom left) and vs ethanol conversion (bottom right).
Gas and higher alcohol selectivities are plotted vs water concentration in Figure 4-7. There's a distinct trend in gas selectivity increasing with increasing water concentration. It is currently unexplained why the run with glass beads in the drying bed had a lower gas selectivity profile than the run with molecular sieves. The data show the glass beads didn't remove water, with water content reaching a maximum of 12 wt%, which was close to the run with no water removal loop at 10 wt%. On the contrary, higher alcohol selectivity was noticeably higher for the water removal run than the run with glass beads at water concentrations less than 5 wt%. For all five runs shown in Figure 4-7, higher alcohol selectivity trends downward with increasing water concentration. Carbon recovers were greater than 95% for the run without the water removal loop and for the run with water removal (Table 4-1). The carbon recoveries for the run with glass beads were much lower, with the lowest being 88% at end of run.





Table 4-1 Ethanol conversion and carbon recoveries are shown for runs with and without the water removation	al loop
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No Loop			With Loop (Glass Beads)			With Loop (Dryer)		
Time (min)	Conv.	C. Rec.	Time (min)	Conv. (%)	C. Rec.	Time (min)	Conv.	C. Rec.
0	2	100	0	3	99	0	2	99
20	5	99	20	6	99	20	7	98
40	8	99	40	8	99	40	10	97
60	9	98	60	11	99	60	12	96

Table 4-1	(cont'd)
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120	14	97	120	15	98	120	18	96
180	17	98	180	18	98	180	22	95
240	20	97	240	21	98	240	24	95
300	23	97	327	25	98	300	27	95
626	31	96	639	33	98	622	39	92
1346	48	96	1369	46	97	1376	52	91

4.4 Conclusions

It was hypothesized removing water would minimize ethanol decomposition to CH_4 and CO_2 . The data supports this, with gas selectivity at 25% for the run starting with 10 wt% initial water concentration. For the run with water removal, gas selectivity stays at 5% at water concentrations up to 4 wt % and 40 % ethanol conversion. It is unclear why minimizing water content decreases ethanol decomposition, because water is not a reactant. Therfore, increasing water concentration must be affecting the catalyst surface. Water may be saturating condensation sites on the alumina, thereby promoting nickel metal sites for decomposition. It is also possible water is irreversibly converting γ -Al₂O₃ to boehmite, which lacks the catalytic abilities of γ -Al₂O₃.

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5 Investigation of the Ethanol Guerbet Reaction Mechanism

5.1 Introduction

In the condensed phase Guerbet reaction of ethanol to 1-butanol and higher alcohols, La₂O₃-modified γ -Al₂O₃ supported Ni has proven to be an active catalyst. Unfortunately, this activity is not only for dehydrogenation/hydrogenation and aldol condensation reactions. Competing reactions occur, such as the Tischenko reaction of acetaldehyde to ethyl acetate, etherification of ethanol to diethyl ether, ethanol decomposition to CH4 and CO2, and steam reforming reactions of ethanol. Modifying γ -Al₂O₃ with La₂O₃ has already been shown to decrease Tischenko and etherification reactions. There is yet need for understanding the ethanol Guerbet reaction so that selectivity to unwanted side products is minimized.

Much can be learned from breaking down the steps of the Guerbet reaction:

$$2EtOH \underset{-2H_2}{\longleftrightarrow} 2Acetaldehyde \underset{-H_2O}{\longleftrightarrow} Crotonaldehyde \underset{H_2}{\rightarrow} Butyraldehyde \underset{H_2}{\rightarrow} Butanol$$

Little has been presented in the literature on the relative reaction rates of these steps or if any of these reactions may be in chemical equilibrium, which may impact the 1-butanol formation rate. Enthalpies of reaction and Gibbs free energies of reaction have been calculated for Guerbet **Table 5-1** Gas phase enthalpies and free energies of formation (298 K) and equilibrium constants at 503 K [1].

	∆H ^o r (kJ/mol)	$\Delta \mathbf{G^{o}_{r}}$ (kJ/mol)	Ke ^V
Reaction	(298K)	(298K)	(503K)
<i>Ethanol</i> \rightarrow <i>Acetaldehyde</i> + H_2	60.67	34.71	8.21E-02
2 Acetaldehyde \rightarrow Crotonaldehyde + H ₂ O	-13.42	-6.57	2.27
$Crotonaldehyde + H_2 \rightarrow 1$ -Butyraldehyde	-103.00	-72.22	7.74E+05
1 -Butyraldehyde + $H_2 \rightarrow 1$ -Butanol	-67.60	-34.01	31.83
$2 Acetaldehyde \rightarrow Ethyl Acetate$	-112.09	-62.12	4.42E+03
2 Ethanol \rightarrow Diethyl Ether + H ₂ O	-38.88	-13.89	10.82
$2 E than ol \rightarrow 3 CH_4 + CO_2$	-163.26	-210.47	2.46E+26

reactions as well as observed side reactions (Table 5-1). It was determined that ethanol dehydrogenation to acetaldehyde in the vapor phase at 503 K has an equilibrium constant of 0.1. This reaction has the lowest equilibrium constant of all reactions in the Guerbet reaction system. The only other reaction with a low equilibrium constant is the aldol condensation of acetaldehyde, which has an equilibrium constant of 2.3. All other reactions are irreversible.

Reactions of ethanol and acetaldehyde with H_2 were probed to examine the kinetics and equilibrium of ethanol dehydrogenation in the liquid phase. Kinetics of acetaldehyde condensation and butyraldehyde hydrogenation were also examined. Pure ethanol reactions were performed with H_2 to determine if H_2 would slow down ethanol reaction rates.

5.2 Experimental

5.2.1 Materials

Ni(NO₃)₂·6H₂O (Reagent Grade, Jade Scientific), was used as precursor to reduced metal and La(NO₃)₂·6H₂O (99%, Fluka) was used as precursor to the calcined oxide. The support used was 1/16" diameter γ -Al₂O₃ spheres (Strem Chemical). Anhydrous ethanol (Koptec, 200 proof), acetaldehyde (Fluka, 99%), butyraldehyde (Fluka, 99%), and isobutyraldehyde (Aldrich, 98%) were used for ethanol and ethanol/mixed aldehyde reactions. Reactions of 80 mol% ethanol/20 mol% acetaldehyde were performed at 150°C and 200°C with 5.2 MPa initial charge of ultra pure H₂ (Airgas, 99.999%). Reaction of 51 mol% ethanol/49 mol% butyraldehyde was performed at 230°C. The catalyst composition used in this study was 8 wt% Ni/9 wt% La₂O₃- γ -Al₂O₃ (8Ni/9La-Al).

The nickel catalyst modified with La_2O_3 was prepared by first depositing $La(NO_3)_3$ by incipient wetness impregnation of the γ -Al₂O₃ support followed by drying at 130°C for 18 hours, and calcining at 600°C for 20 hours in 35 ml/min N₂ flow. This assured there was La_2O_3 on the γ -Al₂O₃ surface before the impregnation of the nickel. Nickel was then added by the same wetness technique using Ni(NO₃)₂ and dried at 130°C for 18 hours. The nickel was reduced at 450°C and 1 atm in a tubular flow reactor for 20 hours in 35 ml (STP) H_2 /min.

5.2.2 Ethanol/acetaldehyde/H₂ reactions

All reactions were performed in a 300 ml Parr autoclave reactor. A mixture of 80 mol% ethanol and 20 mol % acetaldehyde was made prior to starting the reaction. The ethanol/acetaldehyde mixture was placed in the reactor with catalyst at 0.04 g cat/g mixture loading. The reactor was purged with H₂, sealed, and then pressurized to 5.2 MPa with H₂. Reactor pressure was autogeneous and liquid samples were taken at specific time intervals. Reactor pressure was measured with a head pressure gauge at each sampling interval.

5.2.3 Ethanol/H₂ reactions

The same reactor used for ethanol/acetaldehyde/H₂ reactions was also used for ethanol/H₂ reactions. Two reactions were performed at 230°C and 0.04 g cat/g ethanol catalyst loading. In both runs the 8Ni/9La-Al catalyst was placed in the reactor, sealed, and purged with H₂ overpressure. The reactor was heated to 250°C for 20 hours to pre-reduce the catalyst. After the reactor cooled to ambient temperature, ethanol was fed to the reactor from a 150 ml charging vessel. For the control run, the H₂ atmosphere was purged and sealed with N₂ at 1 atm before reactor heat-up. For the run with H₂, the reactor was pressurized to 1.4 MPa H₂ before reactor heat-up.

5.3 **Results and Discussion**

5.3.1 Preliminary Initial Rate Kinetics for 1-Butanol and 1-Hexanol

The formation rates of 1-butanol and 1-hexanol were characterized at three different temperatures: 215°C, 230°C, and 239°C (Figure 5-1). A run was done at 239°C, since the



critical point of ethanol is at 241°C and it was desired to stay out of the supercritical regime.

Figure 5-1 Initial rate data for 1-butanol and 1-hexanol at 0.06 g cat/g EtOH loading.

Data points from the first hour of each run provided linear rates from which activation energies could be determined. Data were plotted for 0.06 and 0.03 g cat/g ethanol catalyst loadings. The activation energies for 1-butanol and 1-hexanol formation were calculated to be 52 KJ/mol and



Figure 5-2 Arrhenius plots are shown for 1-butanol and 1-hexanol at 0.03 and 0.06 g cat/g EtOH loading. 63 KJ/mol respectively from an Arrhenius plot for these rates (Figure 5-2). The activation energies were taken as averages for the two different catalyst loadings. For comparison, Tsuchida calculated activation energies of 61 KJ/mol and 70 KJ/mol for 1-butanol and 1-hexanol formation over hydroxyapatite catalysts [2].

5.3.2 Effect of Catalyst Loading

The effect of catalyst loading on 1-butanol and 1-hexanol formation rates was also examined (Figure 5-3). As expected, rates increased with increasing catalyst loading. For 1butanol, when the loading was doubled from 0.02 to 0.04 g cat/g EtOH, the rate increased by a factor of 1.9. When the loading was quadrupled from 0.02 to 0.08 g cat/g EtOH, the rate increased by a factor of 3.4. The rate increase may not have equaled a factor of 4 due to not all catalyst spheres being suspended in solution at the higher loading. The rate increase factors for 1hexanol were more closer to theoretical with 2.1 and 3.9 when doubling and quadrupling catalyst loading. This demonstrates that the reactions are carried out under a catalyzed, kinetic regime at the conditions used.



Figure 5-3 Initial reaction rates for 1-butanol and 1-hexanol formation at different catalyst loadings.



Figure 5-4 Selectivites for 1-butanol and 1-hexanol are plotted at different catalyst loadings.

The selectivity profiles were examined at the different loadings (Figure 5-4). It was found for both 1-butanol and 1-hexanol the selectivity increases with increasing catalyst loading. At 40 minutes the 1-butanol selectivity increased from 20% to 55% with the higher catalyst loading. At 60 minutes, the 1-hexanol selectivity increased from 4% to 12% with the higher catalyst loading. Ethanol conversion was calculated two ways (Figure 5-5). Conversion was first calculated based on reacted ethanol carbon determined from the ethanol concentration. Ethanol conversion was then calculated based on carbon equivalence in the liquid products. The ethanol conversion based on liquid products is lower than the ethanol conversion based on ethanol concentration. The explanation for this is that there are unaccounted gases in the conversion based on liquid products.

It can be seen from Figure 5-5 that the slopes for the different loadings are different for the two plots. The most noticeable difference is ethanol conversion for the 0.02 g cat/g EtOH



loading in the left plot. This shows a higher ethanol reaction rate for the 0.02 g cat/g EtOH

Figure 5-5 Plotted on left is ethanol conversion vs time, based on carbon in ethanol. Plotted on right is ethanol conversion vs time based on ethanol carbon equivalence in the liquid product.

loading than the 0.04 g cat/g EtOH loading. When looking at the conversion based on liquid products, the 0.02 g cat/g EtOH loading has the lowest ethanol reaction rate, as expected. The 0.04 g cat / g EtOH loading is a factor of 1.7 larger than the 0.02 g cat/g EtOH loading on the right plot, which is close to the theoretical factor of 2. As explained in the paragraph above, there were unaccounted gases in the liquid product. This means for the 0.02 g cat/g EtOH



Figure 5-6 Selectivities for 1-butanol and 1-hexanol are plotted vs conversion at different catalyst loadings. Ethanol conversion was determined from reacted ethanol carbon based on GC analysis of the liquid product.

	0.02	g cat/g	EtOH	0.04	0.04 g cat/g EtOH		0.08 g cat/g		EtOH
	EtOH	Prod.	C.	EtOH	Prod.	C.	EtOH	Prod.	C.
time (min)	Conv.	Conv	Recov.	Conv.	Conv.	Recov.	Conv.	Conv.	Recov.
0	2.8	0.3	97.6	3.5	0.4	96.9	0.2	0.6	100.4
20	4.6	0.9	96.3	4.5	1.9	97.4	5.2	3.2	98.0
40	6.3	2.3	96.0	4.1	3.8	99.8	8.6	6.8	98.2
60	7.2	3.4	96.2	6.1	5.7	99.7	10.9	9.7	98.9
120	6.6	6.0	99.4	11.0	9.5	98.5	15.7	14.8	99.1
180	11.0	8.2	97.3	16.6	12.5	96.0	22.5	19.6	97.2
240	14.9	10.1	95.2	19.3	15.7	96.3	28.4	23.8	95.6
300	16.9	12.0	95.0	23.4	18.5	95.1	42.1	34.3	92.8
360	15.8	14.0	98.2	25.9	20.9	95.2	68.5	49.8	83.2

Table 5-2 Ethanol conversion based on ethanol concentration and carbon in the products is shown for the different loading runs. Carbon recoveries are also shown for the different loadings. All values shown are percentages.

loading, the nickel catalyst may have been more active for ethanol decomposition. From both plots it can be seen ethanol conversion doesn't increase proportionally with increasing catalyst loading. VLE modeling demonstrated the liquid phase is significantly expanded; therefore it is possible not all catalyst particles were suspended at the higher catalyst loadings.

Selectivites to 1-butanol and 1-hexanol are plotted vs ethanol conversion in Figure 5-6. In both plots, selectivity to 1-butanol and 1-hexanol is lower at low ethanol conversion (~5%) for all catalyst loadings. In particular, 1-butanol selectivity is ~ 5 percentage points lower for the 0.02 g cat/ g EtOH loading at ethanol conversion below 15%. This is consistent with the catalyst being more active for gas selectivity at the low loading. Carbon recoveries are also lower for the 0.02 g cat/ g EtOH loading (Table 5-2). The higher loading catalysts may have had more oxidation; the nickel catalysts weren't pre-reduced in-situ. The selectivity to 1-butanol reaches a maximum of 60% at 15% ethanol conversion. In general it appears the catalyst goes through a condition period for all catalyst loadings; this explains the jump in higher alcohol selectivity at ethanol conversion less than 5%.

5.3.3 Kinetic modeling of ethanol/acetaldehdye/H₂ reactions

The formation of 1-butanol from ethanol likely proceeds by way of an acetaldehyde intermediate; this is considered the classical Guerbet route. The other intermediates involved in this mechanism are the aldol condensation product, crotonaldehyde, and the partial hydrogenated product of crotonaldedhye, butyraldehyde. The literature has not really focused on the kinetics of the intermediate reactions. Tsuchida et al proposed reactions steps for 1-butanol and C₆ + alcohol formation, but only considered overall reactions for their kinetic modeling [2]. For instance, the rate constant, k_1 , was found for the reaction, 2EtOH \rightarrow 1-BuOH + H₂O. A rate constant was also found for ethanol dehydrogenation to acetaldehyde, but no rate constants were found for acetaldehyde condensation or any aldehydic hydrogenations.

For the mixed ethanol/acetaldehyde with H₂ runs in this paper, we proposed the following reaction steps:

$$EtOH \stackrel{\kappa_1}{\underset{k_{-1}}{\leftarrow}} Acetaldehyde + H_2$$
(5-5-1)

$$2A cetaldehyde \xrightarrow{k_2} Crotonaldehyde + H_2O$$
(5-5-2)

$$Crotonaldehyde + H_2 \xrightarrow{\kappa_3} Butyraldehyde$$
 (5-5-3)

$$Butyraldehyde + H_2 \xrightarrow{k_4} 1 - Butanol$$
(5-5-4)

It was stated earlier that the equilibrium constant is ~ 0.1 for ethanol dehydrogenation (Reaction 5-1) in the vapor phase. Since acetaldehyde hydrogenation and not ethanol dehydrogenation was observed in the mixed ethanol/acetaldehyde runs, an equilibrium constant for Reaction 5-1 wasn't incorporated in the kinetic model. Hydrogenation of crotonaldehyde (Reaction 5-3) was very rapid, so it was assumed its net rate of formation was zero. These reactions were modeled in Polymath by the following differential equations:

$$\frac{d[EtOH]}{dt} = k_{-1}[AD]P_{H2}$$
(5-5-5)

$$\frac{d[AD]}{dt} = -k_{-1}[AD]P_{H2} - k_2[AD]^2$$
(5-5-6)

$$\frac{d[CAD]}{dt} = \frac{1}{2}k_2[AD]^2 - k_3[CAD]P_{H2} \approx 0$$
(5-5-7)

$$\frac{d[BAD]}{dt} = \frac{1}{2}k_2[AD]^2 - k_4[BAD]P_{H2}$$
(5-5-8)

$$\frac{d[BuOH]}{dt} = k_4[BAD]P_{H2}$$
(5-5-9)

$$\frac{d[H_2O]}{dt} = \frac{1}{2}k_2[AD]^2$$
(5-5-10)

$$\frac{d[P_{H_2}]}{dt} = \frac{V_l}{V_g} RT(-k_{-1}[AD]P_{H_2} - k_4[BAD]P_{H_2})$$
(5-5-11)

The concentrations in the rate equations have units of molarity and are represented by [*EtOH*] (ethanol), [*AD*] (acetaldehyde), [*CAD*] (crotonaldehyde), [*BAD*] (butyraldehyde), [*BuOH*] (1butanol), and [H_2O] (water). Hydrogen is quantified by partial pressure and has units of atmospheres. The variables V_l and V_g are the reactor liquid and gas volumes respectively. The ratio of V_l to V_g is multiplied by *RT* and used to convert [*AD*] and [*BAD*] to pressure. The solubility of H_2 is assumed to follow Henry's law based on data from Brunner et al [3]. Vapor liquid equilibria for the binary ethanol/ H_2 at 498 K is plotted in Figure 5-7. Rate constants $k_{.1}$, k_2 , and k_4 were adjusted until the desired fit was achieved of the model to the experimental data.

The following paragraphs describe the fit of the kinetic model to the experimental data at 150°C, 175°C and 200°C. Because the reaction begins with 20 mol % acetaldehyde, 1,1diethoxyethane formation from acetaldehyde and ethanol was observed. Diethoxy butane formation from butyraldehyde and ethanol was also observed. Since these products were minor (~0.10 M), they weren't incorporated in the kinetic model.



Figure 5-7 Vapor liquid equilibrium is shown for ethanol and H₂ at 498 K [3].



Figure 5-8 Modeled ethanol concentration at 150°C, 175°C and 200°C. Initial charge of 80 mol% ethanol, 20 mol% acetaldehyde with 0.04 g cat /g reactant loading.

150°C		175°C		200°C	
Modeled [EtOH]	% Error	Modeled [EtOH]	% Error	Modeled [EtOH]	% Error
14.3	-2.0	14.1	0.4	14.4	1.2
14.5	1.5	14.3	1.1	14.9	-0.7
14.6	3.0	14.5	0.9	15.0	1.5
14.7	1.9	14.7	0.2	15.1	0.2
14.8	3.7	14.7	-0.6	15.1	-1.2
15.0	3.6	14.8	-0.6	15.1	-1.4
15.3	1.7	14.9	-1.1		
15.3	1.3	14.9	-1.5		
15.4	0.3				

Table 5-3 Modeled ethanol concentrations with percent errors are shown at 150°C, 175°C, and 200°C.

The modeled rate equations fit the ethanol data well at 200°C, but not as well at 150°C (Table 5-3). Modeled data fits the 175°C run the best with absolute error less than 1% for most samples. Due to starting with an initial charge of hydrogen, acetaldehyde hydrogenation to ethanol was immediately observed in all runs. The ethanol concentration steadily increased from 14.2 M to a maximum of 15.3 M (Figure 5-8). There was some scatter for ethanol data points at time points less than 100 minutes (Figure 5-8). The acetaldehyde concentration started at 3.5M for all runs, but much of it reacted during the heat-up stage for both runs. The modeled rate equations fit the acetaldehyde consumption profiles well (Figure 5-9). Specifically, the modeled acetaldehyde concentration profiles fit better for the 150°C and 175°C runs (Table 5-4). Therefore, t_0 was for when the reaction reached steady reaction temperature. Reactions were modeled with the true acetaldehyde concentration at t_0 .

Consumption of butyraldehyde was observed in all runs, but its formation was only observed in the 150°C run between 0-50 minutes and observed in the 175°C run between 0-10 minutes (Figure 5-10). For the 150°C run, the rate equations modeled the formation of butyraldehyde well, and also modeled its consumption well from 50 minutes on to the end of the run (Table 5-5).



Figure 5-9 Modeled acetaldehyde concentration at 150°C, 175°C, and 200°C. Initial charge of 80 mol% ethanol, 20 mol% acetaldehyde with 0.04 g cat /g reactant loading.

150°C		175°C		200°C		
	Modeled [AD]	% Error	Modeled [AD]	% Error	Modeled [AD]	% Error
-	2.1	-7.0	1.2	-12	0.91	-22
	1.7	-15	0.7	-30	0.27	-63
	1.4	-19	0.5	-27	0.17	-49
	1.2	-22	0.2	-15	0.04	-61
	1.0	-14				
	0.6	-11				
	0.2	-17				

Table 5-4 Modeled acetaldehyde concentrations with percent errors are shown at 150°C, 175°C, and 200°C.



Figure 5-10 Modeled butyraldehyde concentration at 150°C, 175°C and 200°C. Initial charge of 80 mol% ethanol, 20 mol% acetaldehyde with 0.04 g cat /g reactant loading.

Time (min)

150°C		175°C		200°C		
Modeled [BAD]	% Error	Modeled [BAD]	% Error	Modeled [BAD]	% Error	
0.05	249	0.11	-8.2	0.28	-2.3	
0.15	158	0.15	-18	0.21	-12	
0.20	35	0.14	-29	0.16	16	
0.24	-8.0	0.08	-23	0.06	19	
0.25	-16					
0.23	-8.7					

Table 5-5 Modeled butyraldehyde concentrations with percent errors are shown at 150°C, 175°C, and 200°C.

Formation profiles for water and 1-butanol are shown in Figure 5-11. Water appears to form right away from 0-50 minutes, but its concentration remains constant at 0.9 M for the duration of the 150°C run, until it jumps to 1.2 M at the end. The water concentration was predicted the best for the 175°C run (Table 5-7). The run was modeled at the starting concentration of 2.5 M and since there is no rate equation accounting for water consumption, the model poorly predicted water concentration (Table 5-7). At 200°C, the water profile reaches 1.2

M sooner, but levels off at 1.2 M. At 150°C, 1-butanol concentration steadily increases to 0.4 M at end of run. The 1-butanol concentration at 175°C and 200°C follows a similar profile to water, with the concentration leveling off at 0.5 M after 50 minutes and 150 minutes of run time respectively. These observations can be explained by the acetaldehyde concentration profile. At 150°C, acetaldehyde isn't completely consumed until 300 minutes, while at 200°C it's completely consumed by 50 minutes. This is consistent with no condensation reactions taking place after 300 minutes at 150°C and no condensation reactions taking place after 50 minutes at 200°C.



Figure 5-11 Modeled 1-butanol and water concentration at 150°C, 175°C, and 200°C. Initial charge of 80 mol% ethanol, 20 mol% acetaldehyde with 0.04 g cat /g reactant loading.

Starting hydrogen partial pressure was calculated for all runs. The hydrogen partial pressure was also modeled (Figure 5-12). The experimental hydrogen partial pressure was calculated based on the quantity of hydrogen reacted. The number of moles of hydrogen reacted

were found by quantifying Guerbet hydrogenation activity. For instance, one mole of butyraldehyde is produced from one mole of H_2 hydrogenation (Reaction 5-3). One mole of 1butanol is produced from 2 moles of H_2 hydrogenation (Reaction 5-3 and Reaction 5-4). The initial hydrogen partial pressure was determined by multiplying the starting reactor pressure by the ratio of reaction temperature to room temperature.

150°C		175°C		200°C	
Modeled [BuOH]	% Error	Modeled [BuOH]	% Error	Modeled [BuOH]	% Error
0.02	31	0.04	56	0.07	-38
0.03	240	0.10	146	0.23	10
0.05	361	0.16	44	0.29	-12
0.08	299	0.25	9.2	0.39	-10
0.11	164	0.29	-11	0.45	-11
0.21	63	0.34	-5.9	0.45	-15
0.40	39	0.34	-6.3		
0.44	9.3	0.34	-7.1		
0.46	5.4				

Table 5-6 Modeled 1-butanol concentrations with percent errors are shown at 150°C, 175°C, and 200°C.

Table 5-7 Modeled water concentrations with percent errors are shown at 150°C, 175°C, and 200°C.

150°C		175°C		200°C		
Modeled [H ₂ O]	% Error	Modeled [H ₂ O]	% Error	Modeled [H ₂ O]	% Error	
0.41	13	0.53	4.4	0.97	4.5	
0.52	33	0.65	-2.5	1.07	21	
0.60	5	0.70	-25	1.08	8.3	
0.67	0	0.73	-2.5	1.08	6.9	
0.71	-2	0.74	-22	1.08	-1.2	
0.79	-10	0.74	-5.1	1.08	-5.3	
0.86	-11	0.74	-7.0			
0.87	-2	0.74	-4.9			
0.87	-25					

The modeled partial hydrogen pressure fits the experimental data well for the 175°C run and the 200°C run, particularly between 0-50 minutes run time (Table 5-8). For the 150°C run, the model doesn't fit as well from 0-50 minutes, but fits the data well from 200 minutes to end of run. The model may be overpredicting hydrogen consumption for hydrogenation reactions in the 150°C run.



Figure 5-12 Modeled hydrogen partial pressure at 150°C, 175°C, and 200°C. Initial charge of 80 mol% ethanol, 20 mol% acetaldehyde with 0.04 g cat /g reactant loading.

Table 5-8 Modeled partial pressures of hydrogen with percent errors are shown at 150°C, 175°C, and 200°C.

150°C		175°C		200°C		
Modeled PH ₂	% Error	Modeled PH ₂	% Error	Modeled PH ₂	% Error	
54.0	-2.6	72.5	40	53.1	-9.4	
50.3	-19	65.8	41	38.8	2.2	
47.2	-23	60.4	55	35.3	-13	
43.6	-18	54.4	86	30.1	0.3	
41.0	-25	51.4	133	27.7	26	
34.6	-27	48.3	153	27.6	37	
24.7	-23	47.6	187			
22.7	-18	47.4	222			
21.7	-3.0					

With the rate constants found at 150°C, 175°C and 200°C, approximate activation energies could be calculated with an Arrhenius plot (Figure 5-13). The activation energies and

frequency factors are shown in Table 5-9. The activation energy of acetaldehyde hydrogenation to ethanol is 69 KJ/mol. The activation energy of butyraldehyde to 1-butanol is 63 KJ/mol. The activation energy of acetaldehyde condensation to crotonaldehyde is 66 KJ/mol. Crotonaldehyde hydrogenation wasn't modeled since that reaction is so fast, the net rate of formation of crotonaldehyde is approximately zero.



Figure 5-13 Arrhenius plot is shown for the ethanol Guerbet reaction mechanism.

Table 5-9 Rate constants and activation energies are shown for ethanol/acetaldehyde runs at 150°C and 200°C.

	150°C	175 °C	200°C	E _a (KJ/mol)	Freq. Factor (Unit)
k_{-1} (atm ⁻¹ *min ⁻¹)	2.0E-04	4.5E-04	1.6E-03	68.6	5.8E+04 atm ⁻¹ *min ⁻¹
$k_2(L^*mol^{-1}*min^{-1})$	7.3E-03	2.5E-02	5.2E-02	65.6	9.7E+05 L*mol ⁻¹ *min ⁻¹
k_4 (atm ⁻¹ *min ⁻¹)	2.0E-04	7.0E-04	1.3E-03	62.6	1.2E+04 atm ⁻¹ *min ⁻¹

150°C		17	5°C	200°C	
AD Conv. (%)	C. Recov. (%)	AD Conv. (%)	C. Recov. (%)	AD Conv. (%)	C. Recov. (%)
37.1	99.7	62.4	91.7	67.4	96.0
43.5	97.0	70.1	91.7	79.3	99.2
50.3	96.1	81.5	91.9	90.7	95.9
58.3	97.5	92.0	91.8	96.9	96.9
67.9	95.5	98.1	92.0	99.7	97.5
80.3	95.1	99.7	92.8	99.7	97.7
92.8	96.7				
98.6	95.9				
98.6	97.3				

Table 5-10 Acetaldehyde conversion and carbon recoveries are shown for 20% acetaldehyde/80 % ethanol runs done at 150°C and 200°C. Ethanol conversion is not reported because ethanol was formed and not consumed. Catalyst loading was 0.04 g cat/g mixture.

i.

5.3.4 Effect of H2 on higher alcohol formation rate

It was found hydrogen had little effect on ethanol conversion and the ethanol concentration profile (Figure 5-14). From 100 to 300 minutes, ethanol conversion was 3 percentage points higher for the run without hydrogen. It was hypothesized starting with an initial hydrogen charge would slow down ethanol reaction rates due to ethanol dehydrogenation being an equilibrium limited reaction. A possible explanation for ethanol conversion rate being the same with and without H_2 is that while the presence of H_2 reversed ethanol dehydrogenation, it was offset by H_2 reacting with ethanol to produce CH_4 as described earlier:

$$2H_2 + EtOH \rightarrow 2CH_4 + H_2O \tag{5-12}$$

Evidence for this reaction is found in the water concentration profile (Figure 5-15). Though less water is being produced from condensation reactions in the run with H_2 , it is being produced by reaction (5-12). Therefore, the water concentration profiles for the two runs are virtually identical. Evidence of reaction (5-12) can also be seen in the carbon recoveries (based on liquid products) between the two runs (Table 5-11). For the run with no H_2 , carbon recovery is 98 %

or greater at up to 20 % ethanol conversion. For the run with H_2 , carbon recovery is 94-97 % at up to 17 % ethanol conversion. Since carbon recovery is only based on liquid products, this implies there was carbon lost to unaccounted gases.



Figure 5-14 Ethanol conversion and ethanol concentration are plotted for runs with and without hydrogen. Reaction temperature was 230°C with 0.04 g cat/g ethanol loading.



Figure 5-15 Water concentration is plotted vs time for the reactions with and without H_2 at 230°C and 0.04 g cat/g ethanol loading.

The 1-butanol and C_6 alcohol concentration profiles were different between the two runs, most notably for C_6 alcohols (Figure 5-16). At 200 minutes, the C_6 concentration was approximately a

factor of 4 more for the run without hydrogen, versus the one with hydrogen. The 1-butanol concentration was 1.25 times more for the run without hydrogen than the run with hydrogen at 200 minutes. The difference in 1-butanol and C_6 alcohol rates could also be seen in selectivity (Figure 5-17). Without hydrogen the 1-butanol selectivity is 60%+ and stays there during the **Table 5-11** Ethanol conversion (%) and carbon recoveries (%) are shown for runs with and without H₂. Carbon recoveries are based on liquid products only.

No H ₂		With H ₂		
EtOH Conv. (%)	C. Recov. (%)	EtOH Conv. (%)	C. Recov. (%)	
1.4	99.9	2.3	97.6	
3.7	99.7	2.6	98.1	
6.1	99.4	4.6	97.2	
8.2	99.5	7.6	95.5	
11.2	99.5	9.3	96.4	
16.5	98.2	13.5	95.6	
19.6	98.3	17.2	94.8	
28.2	95.0	27.7	93.2	

course of the entire run. With hydrogen present, 1-butanol selectivity didn't reach 60% until the end of the run. The C₆-OH selectivity without hydrogen present was double the run with hydrogen at a maximum of 16%.



Figure 5-16 Concentration of 1-butanol and C_6 alcohols are plotted for runs with and without hydrogen. Reaction temperature was 230°C with 0.04 g cat/g ethanol loading.



Figure 5-17 Selectivites of 1-butanol and C_6 alcohols are plotted for runs with and without hydrogen. Reaction temperature was 230°C with 0.04 g cat/g ethanol loading.

The ethanol conversion rate was nearly the same with and without H_2 due to the side reaction of H_2 with ethanol to CH_4 and water offsetting the negative effect of hydrogen on acetaldehyde formation rate. One would expect a higher CH_4/CO_2 ratio for the run with H_2 due to reaction (5-12). This is supported by GC analysis of the gas composition at end of the run. The CH_4/CO_2 ratio for the run with H_2 is 5.7 and for the run without H_2 is 4.5 (Table 5-12). Since the butanol and C_6 alcohol rates were lower with H_2 present, this is evidence of the ethanol dehydrogenation equilibrium limiting the reaction rate. Equations (5-5-1) and (5-5-2) demonstrate acetaldehyde is formed until equilibrium is achieved. The formed acetaldehyde than condenses to form crotonaldehyde. If the acetaldehyde condensation rate was the ratelimiting step in the

Table 5-12 Molar composition of gas phase at end of run is shown with CH_4/CO_2 ratio for the runs with and without H_2 .

	With H ₂	No H ₂
Run Time (min)	617	592
EtOH Conv. (%)	27.7	28.2
CH4 (mol %)	78.8	67.0
CO2 (mol %)	13.7	14.9
CH4/CO2	5.7	4.5

ethanol Guerbet reaction, then excess H_2 wouldn't slowdown 1-butanol and C_6 alcohol formation. Therefore, not only is ethanol dehydrogenation slower compared to acetaldehyde condensation, ethanol dehydrogenation is also equilibrium limited.

The undesired side reactions forming ethyl acetate and acetal (1,1-diethoxy ethane) were also compared for the runs with and without H_2 (Figure 5-18). It would be expected for ethyl acetate formation to be lower with H_2 , due to less acetaldehyde being available for the Tischenko reaction to occur. Ethyl acetate formation was found to be slightly lower with H_2 , but it was expected to be more noticeably lower. This may be connected with the formation of acetal:

$$2EtOH + Acetaldehyde \rightarrow Acetal + H_2O$$
(5-13)

Acetal formation for the H₂ run was approximately half that of the run without H₂ from beginning of run to 100 minutes. Both runs level off at 0.02 M. It is unclear why H₂ lowered acetal formation and not ethyl acetate formation. Ethyl acetate may form from direct dehydrogenation of two ethanol molecules over an 8 wt% Ni/9 Wt% La₂O₃- γ Al₂O₃ catalyst.



Figure 5-18 Concentration of ethyl acetate and acetal are plotted for runs with and without hydrogen. Reaction temperature was 230°C with 0.04 g cat/g ethanol loading.

5.3.5 Reaction of neat 1-butanol

Reactions with ethanol/acetaldehyde/H₂ helped explain the ethanol Guerbet mechanism,

but didn't offer information on butanol/butyraldehyde reactions. Aside from hydrogenation to 1-

butanol, other reactions of butyraldehyde are known to occur, due to the formation of C_6 and C_8 alcohols. It is not clear if the 1-butanol formed is ever dehydrogenated back to butyraldehyde. The data supports ethanol dehydrogenation as an equilibrium reaction, which limits the reaction rate of acetaldehyde to crotonaldehyde, and the subsequent hydrogenation to butyraldehyde and 1-butanol. The equilibrium constant for 1-butanol dehydrogenation in the gas phase is ~0.07 at 503 K. In the liquid phase the equilibrium constant is ~0.03 at 503 K. This implies that a run with pure 1-butanol would produce butyraldehyde at a small maximum concentration, much like acetaldehyde is produced in a neat ethanol run.

Data in Figure 5-19 from our neat 1-butanol run supports this hypothesis. Butyraldehyde concentration was higher than 2-ethyl-1-hexanol from 0 to 240 minutes, but reaches a maximum at 0.30 M. The Guerbet product from 1-butanol is the branched alcohol, 2-ethyl-1-hexanol. In



Figure 5-19 1-Butanol concentration is plotted 1-butanol concentration vs. time for the pure 1-butanol run at 230°C on the left. Butyraldehyde and 2-ethyl-hexanol concentrations are plotted vs time on right.

Table 5-13 Carbon recoveries and 1-butanol conversion are shown for the neat 1-butanol run at 230°C.

Time (min)	Conversion (%)	Carbon Recovery (%)
15	2.9	98.4
60	5.4	97.1
120	8.2	95.2
180	9.4	94.9
240	11.9	93.2
546	18.1	88.5
1455	30.5	81.8

the run with pure 1-butanol at 230°C, 2-ethyl-1-hexanol was the major product (Figure 5-19). At 500 minutes, the 2-ethyl-1-hexanol concentration increased to 0.65 M. Similar to the neat ethanol runs, there was decomposition of 1-butanol to gases. The main product gas was propane, with small amounts of CH_4 and CO_2 . This can be seen in carbon recoveries based on carbon in condensable liquid product (Table 5-13). The carbon recovery decreased from 98% at 15 minutes to 82% at 1455 minutes.

Much like neat ethanol runs, there was decomposition of 1-butanol to gases. Interestingly, propane was the major gas product at 56% (Table 5-14). There was also 23% CO_2 and 13% CH_4 . The mole ratio of propane: CH_4 : CO_2 was 4.2:1:1.7, which indicates propane may be decomposing under the same mechanism as ethanol decomposition. The reaction for 1-butanol decomposition is:

$$2C_4H_9OH \to 2C_3H_8 + CH_4 + CO_2$$
(5-14)

The mole ratios of propane to CH_4 to CO_2 didn't align well with reaction 5-14, which would have mole ratios of 2:1:1 for propane: $CH_4:CO_2$. This means additional propane either came from hydrogenation of 1-butanol or it was a different mechanism.

Table 5-14 End of run gas analysis is shown for neat 1-butanol run at 230°C.

5.3.6 Reaction of ethanol/butyraldehyde

A reaction was performed with 51 mol% ethanol/49 mol% butyraldehyde at 230°C and 0.04 g cat/g ethanol loading to examine the hydrogen scavenging ability of butyraldehyde. Ethanol undergoes dehydrogenation, which leads to butyraldehyde hydrogenation to 1-butanol. Butyraldehyde readily undergoes condensation reactions to C_6 and C_8 aldehydes (Figure 5-20). Butyraldehdye is almost completely consumed by 500 minutes. Unsaturated aldehydes, hexenal and 2-ethyl-2-hexenal, form early during the run and decrease at approximately100 minutes due to hydrogenation reactions to the saturated aldehydes, hexanal and 2-ethyl-2-hexanal.



Figure 5-20 Ethanol and butyraldehyde concentration vs time is shown in the top left. 1-Butanol and 2-ethylhexanol concentration vs time is shown top right. Concentrations of higher aldehydes hexenal (HEN), hexanal (HAN), 2-ethyl-hexenal (2-E-HEN), and 2-ethyl-hexanal (2-E-HAN) are shown in bottom left. Initial rates for higher aldehydes and 1-butanol are shown in bottom right.

The concentration profiles of these aldehydes and their initial reaction rates are shown in Figure 5-20. The initial reaction rate of butyraldehdye was found to be -0.050 mol/L-min. The sum of 1-butanol, C_6 and C_8 aldehyde initial formation rates was found to be 0.034 mol/L-min. This indicates 1-butyralde is reacting to other products. There were many unidentified products in the liquid gas chromatogram (Figure 5-21). Gaseous products were also formed, but it was unclear whether they were formed from ethanol or butyraldehyde. Loss of carbon to these unidentified products and gases is quantified in Table 5-15.

An interesting comparison is made between the concentration profiles of 1-butanol and 2ethyl-1-hexanol in the top right of Figure 5-20. The 1-butanol concentration reaches a maximum of 1.2 M by 400 minutes. The 1-butanol concentration remains at 1.2 M from 400 minutes to the end of the run because it is either in thermodynamic equilibrium or its net rate of formation is zero. The net rate of formation of 1-butanol is zero after 400 minutes, since 2-ethyl-1-hexanol may be forming from butyraldehyde from 1-butanol dehydrogenation. What's interesting is that the 2-ethyl-1-hexanol concentration is much lower than 1-butanol up to 400 minutes, but steadily increases from 0.2 M at 400 minutes to 1.3 M at the end of the run.



Figure 5-21 Gas chromatogram for ethanol/butyraldehyde reaction at end of run. Unmarked peaks are unidentified peaks.

Time (min)	BAD Conv. (%)	EtOH Conv. (%)	Carbon Recov. (%)
0	4.6	3.5	107.1
20	22.8	5.2	105.2
40	37.9	8.9	101.9
60	50.1	14.2	97.4
120	64.9	15.8	92.9
180	78.5	23.4	85.1
240	86.7	33.3	78.0
300	90.5	38.9	74.5
627	94.3	49.0	69.8
1401	98.5	73.1	69.6

 Table 5-15
 Butyraldehyde conversion and ethanol conversions are shown.
 Carbon recoveries are also shown.

5.3.7 Reaction of ethanol/isobutyraldehyde

It was found in the previous sections ethanol dehydrogenation is in equilibrium. Since ethanol is in equilibrium with acetaldehyde and hydrogen, the concentration of acetaldehyde is small. This translates to a lower acetaldehyde condensation rate. By starting with a mixture of ethanol and isobutyraldehyde, the mixture is deficient in hydrogen. This deficiency in hydrogen was hypothesized to increase higher alcohol formation rates, and therefore ethanol reaction rate. When comparing the slope of the ethanol concentration curve for the neat ethanol run versus the EtOH/isobutyraldehye run, the slope is steeper at 10 M [EtOH] for the EtOH/isobutyraldehyde run (Figure 5-22). Theoretically, if isobutyraldehyde was an inert, the reaction rate would be the same for both runs at 10 M [EtOH]. This implies the H₂ deficiency is driving the ethanol dehydrogenation equilibrium to acetaldehyde and H₂.

Differences were observed in the acetaldehyde concentration profiles (Figure 5-22). Acetaldehyde reaches a maximum of 0.10 M for the neat ethanol run, while it reached as high as 0.27 M for the mixed aldehyde run. Since equilibrium is pushed forward from isobutyraldehyde uptaking H_2 , acetaldehyde is able to reach a higher equilibrium value. This was also observed with butyraldehyde (Figure 5-23). For the neat ethanol run, butyraldehyde reached a maximum of 0.04 M. Butyraldehyde increased to 0.14 M with isobutyraldehyde present, then decreased to 0.02 M at end of run. There wasn't an observed increase in 1-butanol rate for the mixed aldehyde run (Figure 5-23). This could be due to the competition for H_2 from isobutyraldehyde. The isobutyraldehyde concentration started out much larger than butyraldehyde, therefore this may be to blame for the poor 1-butanol formation rate.



Figure 5-22 Ethanol and acetaldehyde concentration profiles are shown for a neat ethanol run and for the mixed 70 mol% EtOH/30 mol % isobutyraldehyde run at 230°C and 0.04 g cat/g mixture loading.





Concentration profiles for isobutyraldehyde and isobutanol are shown in Figure 5-24. As

expected, isobutanol was formed from the dehydrogenation of ethanol and subsequent

hydrogenation of isobutyraldehdye to isobutanol. Isobutyraldehdye was not expected to undergo condensation reactions, but a significant amount of it was converted to unidentified products (Figure 5-25). Approxmately 1.5 M of isobutyraldehdye is accounted for in isobutanol. The remaining 3 M is presumed to be in the unidentified peaks at the end of the sample chromatogram.



Figure 5-24 Concentration profiles are shown for isobutyraldehyde and isobutanol for the mixed 70 mol % EtOH/30 mol % isobutyraldehyde run at 230°C and 0.04 g cat/g mixture loading.



Figure 5-25 Chromatogram is shown for end of run of 70 mol% EtOH/30 mol% isobutyraldehdye at 230°C and 0.04 g cat/g mixture loading.

5.4 Conclusions

Reactions of ethanol with acetaldehyde and H_2 were performed to probe the ethanol Guerbet mechanism. It was hypothesized the first step of this mechanism, ethanol dehydrogenation, is in equilibrium. Reactions performed at 150°C, 175°C and 200°C were modeled to determine rate constants and activation energies. Runs at 230°C with hydrogen and without hydrogen demonstrated the ethanol conversion rate was virtually the same. Higher alcohol production was less for the run with H_2 , confirming the presence of excess H_2 drove ethanol dehydrogenation backwards. Ethanol conversion rates were the same due to the side reaction of H_2 with ethanol to CH_4 and water, which offsets the negative effect of hydrogen on acetaldehyde formation rate. The CH_4/CO_2 ratio was expected to be higher for the run with H_2 , which was confirmed by gas chromatographic analysis of the gas product. APPENDIX
APPENDIX

C.1: Master reaction List

Table C5-1 Part 1 of the master reaction list is shown. Runs with (*) are preliminary continuous runs with ethanol flow rate in ml/min under starting reactor mass column.

Run ID	Starting Material	Start. R. Mass (g)	Catalyst
50TLJ122111	Ethanol	100.66	8Ni/γ-Al2O3
52TLJ010312	Ethanol	104.04	8Ni/γ-Al2O3
62TLJ011212	Ethanol	78.76	10Ni/γ-Al2O3
66TLJ012012	Ethanol	76.05	8Ni-2Cu/γ-Al2O3
68TLJ012412	Ethanol	80.7	8Ni-2Cu/3La2O3-Al2O3
71TLJ020112	Ethanol	91.65	8Ni/7La2O3γ-Al2O3
73TLJ020812	Ethanol	86.76	8Ni/14La2O3-γ-Al2O3
75TLJ021012	Ethanol	75.57	14La2O3/γ-Al2O3
77TLJ021912	Ethanol	85.9	8Ni/9La2O3-γ-Al2O3 Spheres
79TLJ022812	Ethanol	84.67	8Ni/9La2O3-γ-Al2O3 Spheres
80TLJ030512	Ethanol	86.76	8Ni/9La2O3-γ-Al2O3 Spheres
81TLJ030612	Ethanol	72.79	8Ni/10Ce2O3-γ-Al2O3 Spheres
82TLJ030812	Ethanol	128.77	8Ni/14La-γ-Al2O3 Spheres
83TLJ031512	Ethanol	103.86	8Ni/11La2O3-γAl2O3
86TLJ032212	Ethanol	100.69	8Ni/11La2O3-γAl2O3
91TLJ041012	Ethanol	93.59	8Ni/11La2O3-γAl2O3
92TLJ041212	Ethanol	109.6	8Ni/11La2O3-γAl2O3
112TLJ072412	Ethanol	0.4 ml/min*	8Ni-2Cu/γAl2O3
114TLJ072712	Ethanol	0.4 ml/min*	8Ni/γAl2O3
116TLJ080112	Ethanol	0.4 ml/min*	8Ni/11La2O3-γAl2O3
120TLJ081412	Ethanol	88.6	8Ni/9La2O3-γ-Al2O3
122TLJ081612	Ethanol	0.8 ml/min*	8Ni/9La2O3-7-Al2O3
124TLJ082112	Ethanol	0.4 ml/min*	8Ni/9La2O3-γ-Al2O3
136TLJ092512	Ethanol	110.48	8Ni/9La2O3-7-Al2O3
141TLJ101012	Ethanol	109.83	8Ni/9La2O3-γ-Al2O3
142TLJ101612	Ethanol	110.22	8Ni/9La2O3-γ-Al2O3
143TLJ102212	Ethanol	110.04	8Ni/9La2O3-γ-Al2O3
146TLJ110712	50 wt%EtOH/50 wt % Water	109.56	8Ni/9La2O3-y-Al2O3
147TLJ111212	50 wt%EtOH/50 wt % BuOH	108.26	8Ni/9La2O3-γ-Al2O3
149TLJ112712	1-Butanol	113.3	8Ni/9La2O3-7-Al2O3
2-04TLJ021413	Ethanol	151.12	8Ni/9La2O3-γ-Al2O3
2-05TLJ021913	Ethanol	160.34	8Ni/9La2O3-7-Al2O3
2-07TLJ022613	Ethanol	160.42	8Ni/9La2O3-γ-Al2O3
2-09TLJ032813	95 wt % EtOH/ 5wt % Water	111.13	8Ni/9La2O3-7-Al2O3
2-10TLJ041613	93 wt % EtOH/ 7wt % Water	112.99	8Ni/9La2O3-γ-Al2O3
2-11TLJ051413	90 wt % EtOH/ 10 wt % Water	111.34	8Ni/9La2O3-γ-Al2O3

Table C5-1	(cont'	d)
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02-14TLJ052313	1.6 mol EA 98.4 mol EtOH	112.52	8Ni/9La2O3-γ-Al2O3
02-17TLJ071013	Ethanol	112.19	8Ni/γ-Al2O4
02-19TLJ071713	Ethanol	112.49	8Ni/9La2O3-γ-Al2O3
02-21TLJ073113	Ethanol	111.53	8Ni/9La2O3-γ-Al2O3
02-22TLJ080613	Ethanol	112.7	8Ni/4La2O3-γ-Al2O3
02-24TLJ080813	Ethanol	112.59	8Ni/9La2O3-γ-Al2O3
02-26TLJ081513	Ethanol	112.6	8Ni/9La2O3-γ-Al2O3
02-27TLJ091013	97 EtOH 3 mol iBAD	113.73	8Ni/9La2O3-γ-Al2O3
02-28TLJ091613	70 mol EtOH/30 mol IBAD	110.37	8Ni/9La2O3-γ-Al2O3
02-29TLJ092013	80 mol EtOH/ 20 mol AD	111.65	8Ni/9La2O3-γ-Al2O3
02-30TLJ092413	51 mol EtOH 49 mol BAD	110.11	8Ni/9La2O3-γ-Al2O3
02-32TLJ100713	Ethanol	110.9	8Ni/9La2O3-γ-Al2O3
02-33TLJ100813	Ethanol	111.08	8Ni/9La2O3-γ-Al2O3
02-35TLJ101613	Ethanol	112.85	8Ni/9La2O3-γ-Al2O3
02-36TLJ101713	Ethanol	112.12	8Ni/9La2O3-γ-Al2O3
02-39TLJ110513	80 mol 2-EHAN 20 mol AD	113.59	8Ni/9La2O3-γ-Al2O3
02-40TLJ110813	80 mol EA 20 mol AD	110.27	8Ni/9La2O3-γ-Al2O3
02-67TLJ010715	1-Butanol	109.28	8Ni/9La2O3-γ-Al2O3
02-72TLJ021115	Ethanol	117.82	4Ni-4Cu/11La2O3-γ-Al2O3
02-73TLJ021815	Ethanol	108.68	4Ni/14La2O3-y-Al2O3
02-77TLJ051815	61 mol EtOH 39 mol H2O	109.24	8Ni/9La2O3-γ-Al2O3
02-83TLJ072115	80 mol EtOH/ 20 mol AD	98.22	8Ni/9La2O3-γ-Al2O3
02-85TLJ072315	80 mol EtOH/ 20 mol AD	98.31	8Ni/9La2O3-γ-Al2O3
02-86TLJ072815	90 mol EtOH 10 mol EA	99.62	8Ni/9La2O3-γ-Al2O3
02-87TLJ072915	60 mol ETOH 20/20 AD/BAD	99.91	8Ni/9La2O3-γ-Al2O3
02-89TLJ081015	Ethanol	113.3	8Ni/9La2O3-γ-Al2O3
2-90TLJ081215	Ethanol	111.8	8Ni/9La2O3-γ-Al2O3
2-99TLJ121615	80 mol EtOH/ 20 mol AD	98.83	8Ni/9La2O3-γ-Al2O3

Table C5-2 Part 2 of the master reaction list is shown. Runs with (*) are preliminary continuous runs with catalyst bed weight under g cat/g react. column.

		Meas. Disp	g cat/g	Т.	Run t.	Conv.
Run ID	Catalyst ID	(%)	react.	(°C)	(min)	(%)
50TLJ122111			0.093	230	600	46
52TLJ010312			0.125	210	1200	37
62TLJ011212			0.093	230	600	52
66TLJ012012			0.093	230	600	35
68TLJ012412			0.093	230	600	34
71TLJ020112			0.093	230	600	50
73TLJ020812			0.093	230	600	49
75TLJ021012			0.093	230	600	16
77TLJ021912			0.093	230	600	55
79TLJ022812			0.093	230	1320	72
80TLJ030512			0.093	200	600	26

Table C5-2 (cont'd)

81TLJ030612			0.093	230	600	50
82TLJ030812			0.093	230	240	35
83TLJ031512			0.04	200	120	7
86TLJ032212			0.033	210	140	8
91TLJ041012			0.033	230	90	13
92TLJ041212			0.033	220	90	11
112TLJ072412			15.03 g*	210	165	20
114TLJ072712			15.03 g*	210	225	23
116TLJ080112			12.58 g*	210	240	20
120TLJ081412			0.033	210	120	9
122TLJ081612			12.52 g*	210	225	17
124TLJ082112			12.50 g*	230	240	33
136TLJ092512			0.060	230	1608	67
141TLJ101012			0.060	215	1595	51
142TLJ101612			0.060	239	491	50
143TLJ102212	118TLJ080609		0.066	230	1409	67
146TLJ110712	118TLJ080610		0.060	230	558	11
147TLJ111212	118TLJ080611		0.060	230	1750	85
149TLJ112712	118TLJ080612		0.060	230	1340	45
2-04TLJ021413	155TLJ012303		0.040	230	1346	48
2-05TLJ021913	155TLJ012304		0.040	230	1574	52
2-07TLJ022613	155TLJ012305		0.040	230	1629	48
2-09TLJ032813	155TLJ012306		0.040	230	1297	48
2-10TLJ041613	155TLJ012307		0.040	230		
2-11TLJ051413	155TLJ012308		0.040	230	1410	41
02-14TLJ052313	155TLJ012313	2.09	0.04	230	1348	
02-17TLJ071013	02-16TLJ070813	9.68	0.04	230	1344	38
02-19TLJ071713	02-16TLJ070813		0.04	230	1301	43
02-21TLJ073113	02-16TLJ070813 (450C)	8.04	0.04	230	1340	52
02-22TLJ080613	02-20TLJ073013	6.44	0.04	230	1376	43
02-24TLJ080813	02-16TLJ070813 (450C)	8.04	0.04	230	1373	29
02-26TLJ081513	02-16TLJ070813 (450C)	8.04	0.13	200	1351	38
02-27TLJ091013	02-13TLJ052113	2.5	0.04	230	327	36
02-28TLJ091613	02-13TLJ052113	2.5	0.04	230	1328	53
02-29TLJ092013	02-13TLJ052113	2.5	0.04	230	495	21
02-30TLJ092413	02-13TLJ052113	2.5	0.04	230	1401	73
02-32TLJ100713	02-13TLJ052113	2.5	0.02	230	360	16
02-33TLJ100813	02-13TLJ052113	2.5	0.04	230	360	26
02-35TLJ101613	02-13TLJ052113	2.5	0.04	230	300	21
02-36TLJ101713	02-13TLJ052113	2.5	0.08	230	1416	68
02-39TLJ110513	02-13TLJ052113	2.5	0.04	230	189	98
02-40TLJ110813	02-37TLJ102913		0.04	230	260	89
02-67TLJ010715	02-37TLJ102913		0.04	230	1455	
02-72TLJ021115	02-69TLJ012315		0.04	230	1275	21
02-73TLJ021815	02-69TLJ012315-noCu		0.04	230	1305	41
02-77TLJ051815	02-37TLJ102913		0.04	230	530	
02-83TLJ072115	02-37TLJ102913		0.04	200	246	100
02-85TLJ072315	02-37TLJ102913		0.04	150	267	99
02-86TLJ072815	02-37TLJ102913		0.04	200	277	

Table C5-2 (cont'd)

02-87TLJ072915	02-37TLJ102913	0.04	120	566	
02-89TLJ081015	02-37TLJ102913	0.04	230	592	28
2-90TLJ081215	02-37TLJ102913	0.04	230	617	28
2-99TLJ121615	02-37TLJ102914	0.04	175	240	

Run ID	Hi 1-BuOH Sol (%)	End 1-BuOH Sel (%)	Gas Wt	Reaction Notes
50TL 1122111	111. 1-DuOII Sei (70)	End. 1-BuOII Sei (70)	22.56	Reaction Notes
52TL 1010312	48 55		19.44	
62TL 1011212	38		19.44	
66TL I012012	58		5	
68TLI012412	59		47	
71TLJ020112	47		11.5	
73TLJ020812	45		11.5	
75TLJ021012	55		0.7	
77TLJ021912	42		8.9	
79TLJ022812	32		25.4	
80TLJ030512	54		2.37	
81TLJ030612	47		6.9	
82TLJ030812	54		4.9	
83TLJ031512	57	57	0.6	
86TLJ032212	74	50		
91TLJ041012	45	45	0.5	
92TLJ041212	35	27	0.6	
112TLJ072412	57	57		Trickle bed run (continuous)
114TLJ072712	42	42		Trickle bed run (continuous)
116TLJ080112	47	47		Trickle bed run (continuous)
120TLJ081412	45.8	45.8		
122TLJ081612	46	46		Trickle bed run (continuous)
124TLJ082112	30	30		Trickle bed run (continuous)
136TLJ092512	62	40.5	17.5	
141TLJ101012	56	50.8	6.5	
142TLJ101612	56	49	9.2	
143TLJ102212	57.7	42.5	18.5	142TLJ101612
146TLJ110712	62	17	8.4	
147TLJ111212			21.2	Conversion for EtOH
149TLJ112712	54	54	14.1	2-Ethyl-1-Hexanol Selectivty shown
2-04TLJ021413	50	43	7.9	
2-05TLJ021913	54	43		With drying loop (molecular sieves)
2-07TLJ022613	50	44		With drying loop (glass beads)

Table C5-3	Part 3	of the	master	reaction	list.
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Table C5-3 (cont'd)

2-09TLJ032813	44	39	8.8	
2-10TLJ041613				
2-11TLJ051413	42	37	10.8	
02-14TLJ052313			6.7	
02-17TLJ071013	60	57	7.7	
02-19TLJ071713	64	58	12.9	
02-21TLJ073113	63	50	18.9	
02-22TLJ080613	61	55	6.0	
02-24TLJ080813	49	43	11.6	4.59g Na2CO3 added
02-26TLJ081513	50	41	6.8	Higher catalyst loading run
02-27TLJ091013			1.2	
02-28TLJ091613			8.1	
02-29TLJ092013			1.8	
02-30TLJ092413			16.1	
02-32TLJ100713	55	55	0.7	
02-33TLJ100813	56	51	1.3	
02-35TLJ101613	53	53	1.3	Catalyst ground into fine particls
02-36TLJ101713	61	41	17.8	
02-39TLJ110513			0.5	
02-40TLJ110813			0.3	
02-67TLJ010715			15.9	
02-72TLJ021115	72	72	2.8	
02-73TLJ021815	56	55	8.0	
02-77TLJ051815			7.7	
02-83TLJ072115			0.9	started with 750 PSIG H2
02-85TLJ072315			0.4	started with 750 PSIG H2
02-86TLJ072815			1.7	started with 750 PSIG H2
02-87TLJ072915			0.4	started with 1000 PSIG H2
02-89TLJ081015	67	58	5.0	control run with pre-reducing catalyst at 250C, purged with nitrogen
2-90TLJ081215	57	57	6.9	Control run, started with 200 psi H2
2-99TLJ121615				started with 750 PSIG H2
			•	-

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6 Summary and Recommendations for Future Work

6.1 Catalyst Screening

Initial catalyst screening with γ -alumina supported nickel catalysts demonstrated they were active catalysts for the liquid-phase conversion of ethanol to 1-butanol and higher alcohols at 230°C and autogeneous pressure in a 300 ml Parr reactor. Specifically, the optimum catalyst configuration was found to be 8 wt% Ni-9 wt% La- Al. Total higher alcohol selectivity reached over 80% at 50% ethanol conversion. Adding La₂O₃ to the γ -alumina increased basicity, which decreased the Tischenko reaction of acetaldehyde to ethyl acetate and also decreased the etherification of ethanol to diethyl ether. This was confirmed with CO₂ TPD, which demonstrated a 2-fold increase of base sites when adding La₂O₃. Nickel is active for carboncarbon bond cleavage though and the decomposition of ethanol to CH₄ and CO₂ was overserved.

6.2 VLE Modeling

In the catalyst screening studies, CH_4 and CO_2 was usually observed at the end of each run. Gas samples weren't taken during intermediate points so a method was needed to quantify CH_4 and CO_2 in both the liquid and vapor phases. Due to the system being near the critical point of ethanol (241°C, 6.3 MPa) and having polar components, it was decided to use an equation of state to model the reactor. The SR-Polar equation of state was chosen because it offers accurate prediction of non-ideal mixtures and volume translation for better prediction of density. Accurate prediction of phase density is needed due to how expanded the liquid phase is.

Applying the SR-Polar EOS to batch Guerbet reactions provides a more rigorous analysis of reaction than conventional liquid phase sampling. The SR-Polar EOS accurately predicts higher alcohol vapor-liquid equilibria, liquid and vapor phase densities, and total quantity of gases produced in reaction. Although the ethanol conversion profile calculated using the SR- Polar EOS is virtually the same as with liquid-phase-only sampling, the product yields and selectivities are more accurately represented because species partitioning between liquid and vapor phases are more accurately modeled. Finally, the ability of the SR-Polar EOS to predict liquid expansion is advantageous in safely designing future ethanol Guerbet reactions at near critical conditions.

6.3 Impact of Water

It was hypothesized removing water would minimize ethanol decomposition to CH₄ and CO₂. The data supports this, with gas selectivity at 25% for the run starting with 10 wt% initial water concentration. For the run with water removal, gas selectivity stays at 5% at water concentrations up to 4 wt % and 40 % ethanol conversion. It is unclear why minimizing water content decreases ethanol decomposition, because water is not a reactant. Therefore, increasing water concentration must be affecting the catalyst surface. Water may be saturating condensation sites on the alumina, thereby promoting nickel metal sites for decomposition. It is also possible water is irreversibly converting γ -Al₂O₃ to boehmite, which lacks the catalytic abilities of γ -Al₂O₃.

6.4 Investigation of the Ethanol Guerbet Reaction Mechanism

Preliminary initial rate kinetics determined the reaction of ethanol to 1-butanol had an activation energy of 52 kJ/mol over a 8Ni/9La-Al catalyst. The activation energy for 1-hexanol formation was found to be 63 kJ/mol. The effect of catalyst loading was investigated and it was found the 1-butanol and 1-hexanol formation rates weren't directly proportional to catalyst loading. Reactions of ethanol with acetaldehyde and H₂ were performed to probe the ethanol Guerbet mechanism. Rate constants were found for acetaldehyde hydrogenation, acetaldehyde condensation, and butyraldehyde hydrogenation.

Runs at 230°C with hydrogen and without hydrogen demonstrated the ethanol conversion rate was the same. Carbon recoveries were lower for the run with H_2 , indicating carbon was lost to unaccounted non-condensable products. The primary component of these products was reasoned to be CH₄ from the reaction of H_2 with ethanol, which also produces water. The 1butanol and C₆ alcohol formation rates were found to be lower for the run with H_2 then the run without H_2 .

6.5 Recommendations for Future Work

6.5.1 Condensed-phase continuous reactions

The batch reactor has exclusively been used in this work for catalyst optimization, VLE modeling, reactor modification, and mechanism probing. Future work should look at performing condensed-phase reactions in a continuous reactor. Higher throughputs can be attained with continuous reactors. Condensed-phase continuous reactors, such as trickle bed reactors, offer the advantage of longer contact times. Preliminary testing was performed with a trickled bed reactor and the run conditions and results summary are shown in Table 6-1 and Table 6-2 respectively. **Table 6-1** Reaction conditions are shown for preliminary trickle bed reactions

Run ID	Catalyst	Temp. (°C)	Cat. Wt. (g)	EtOH (ml/min)
112TLJ072412	8Ni-2Cu/γAl2O3	210	15.03	0.4
114TLJ072712	8Ni/γAl2O3	210	15.03	0.4
116TLJ080112	8Ni/11La2O3-γAl2O3	210	12.58	0.4
122TLJ081612	8Ni/9La2O3-γAl2O3	210	12.52	0.8
124TLJ082112	8Ni/9La2O3-γAl2O3	230	12.5	0.4

Run ID	Time (min)	EtOH Conv. (%)	1-BuOH Sel. (%)
112TLJ072412	165	20	57
114TLJ072712	225	23	42
116TLJ080112	240	20	47
122TLJ081612	225	17	46
124TLJ082112	240	33	30

 Table 6-2 Results summary for preliminary trickle bed reactions.

It was found ethanol decomposition to CH_4 and CO_2 was hard to quantify due to the liquid sampling configuration. Ethanol conversion was also low compared to batch runs at 33%. Selectivty to 1-butanol was also low with a maximum of 57% for the run with nickel and copper. The data supports copper as a potential metal supplement to nickel to improve higher alcohol selectivity. Copper is not as rugged as nickel and was found to wear off the γ -alumina easily in batch reactions. It is recommended for both future continuous and batch runs to examine copper as a catalyst modifier.

Since γ -alumina-supported nickel catalysts are able to decompose ethanol to CH₄ and CO₂, the continuous reactor will need to have a sampling system to allow sampling both the liquid and vapor phases. Reactions are at high pressures (>5 MPa) so a backpressure regulator will be needed so that gas production can be quantified. When initial continuous testing runs were done with a trickle bed reactor, sample cylinders were pressurized with N₂ to match their pressure with reactor pressure. This caused gas samples to be diluted and CH₄/CO₂ composition couldn't be determined, and therefore quantified. Instead of sampling non-condensable product gases this way, reducing the reactor pressure to atmospheric with a back pressure regulator will enable appropriate gas phase sampling.

Gas production was correlated with increasing water concentration in the water studies section. The non-condensable gas composition at end of run indicates water isn't participating as

a reactant to reform ethanol to CH_4 and CO_2 . This means water must be affecting active sites on the 8 wt% Ni/9 wt% La₂O₃ catlyst. It is unclear if the water is converting γ -alumina to boehmite or converting strong Lewis sites to weaker Brønsted sites. During a continuous run this will need to be investigated by examining different sections of the catalyst bed. Ethanol conversion will be higher at the downstream end of the bed, therefore the catalyst would be different at the downstream end from the upstream end. For a given run it is recommended to sample catalyst from the top and sample catalyst from the bottom of the reactor. The crystal structure can be checked with x-ray diffraction and acid/base sites can be checked with NH₃/CO₂ chemisorption. Other molecules could be used for chemisorption to distinguish Lewis base sites from **B**rønsted sites.

6.5.2 Minimizing ethanol decomposition to CH₄ and CO₂

The catalyst configuration optimized in this work was 8 wt% Ni supported by γ -alumina, which was modified with 9 wt % La₂O₃. Modifying γ -alumina with La₂O₃ added basic sites, and therefore helped decreased undesired, acid-catalyzed side reactions. Nickel metal is highly active for cleaving carbon-carbon bonds though, which was observed in reactions with ethanol. Nickel easily decomposes ethanol to CH₄ and CO₂. Adding basic sites to the γ -alumina did not have an impact on this decomposition reaction. Future work should look at ways to modify the activity of nickel, without hurting its activity towards converting ethanol to 1-butanol and higher alcohols. Other metals, such as copper, could be added with nickel to reduce activity for cleaving carbon-carbon bonds.

Besides modifying the catalyst to minimize ethanol decomposition, modifying process conditions could help minimize ethanol decomposition. It is has already been shown decreasing water content decreases selectivity to gases. Another potential route to decreasing selectivity to gases is to utilize carbon monoxide and the water-gas shift reaction (WGSR):

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 (6-1)

The operating temperature (230°C) is low enough to favor CO_2 and H_2 formation. If the WGSR produces H_2 , it is likely the excess H_2 will decrease acetaldehyde concentration due to an equilibrium shift to ethanol. As was demonstrated in the ethanol/acetaldehyde/ H_2 runs, the excess H_2 decreased selectivity to 1-butanol and 1-hexanol. This would be from the potential reaction of the excess H_2 reacting with ethanol to produce CH_4 and water. If that were to happen, then adding CO to the reaction would not be beneficial. It is worth trying CO as a reducing reagent in a future reaction.