CATALYST STUDIES ON THE CONVERSION OF BIOBASED INTERMEDIATES TO BIOBASED PRODUCTS

By

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ABSTRACT

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The goal of this work is to enhance the production of fuels and chemicals from fermentationderived materials via two routes. Route (a) focuses on Guerbet chemistry, the *n*-butanol production from ethanol; route (b) studies the production of acrylate esters from 2-acetoxypropanoic acid (APA) esters.

The catalytic condensation of ethanol to *n*-butanol and higher alcohols, known as the Guerbet reaction, has attracted more attention in recent years due to the commercial availability of ethanol as a bio-renewable feedstock. Among various catalysts considered for this process, none have obtained stable and economically affordable yields; alumina-supported metals have been less explored despite their promising primary results in the lower energy-demanding condensed-phase. Experiments on the continuous condensed-phase conversion of ethanol to *n*-butanol using Ni/La₂O₃/ γ -Al₂O₃ catalyst present a WHSV of >0.8 h⁻¹ and a temperature range of 210-250 °C as the ideal reaction conditions. Several nickel bimetallic catalysts have been employed to understand the behavior of these catalysts more effectively. Copper addition shifts the selectivity of the Guerbet products toward *n*-butanol rather than C₆+ alcohols, which is explained by the copper behavior reducing H₂ adsorption on the catalyst. Furthermore, the number of nickel atoms on the surface of the catalyst correlates directly with the performance of the Guerbet reaction, suggesting that the dehydrogenation of ethanol is the rate-limiting step of the reaction.

Among different catalysts and reaction conditions studied, the best results were obtained at the temperature of 250 °C and WHSV of 0.8 h⁻¹ using 1.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃ with 41% ethanol conversion and 74% C₄+ alcohols selectivity. Fusel alcohol Guerbet studies under the same conditions have resulted in 88% higher alcohols selectivity at 12% conversion. Preliminary kinetic modeling analysis for the isoamyl alcohol-ethanol mixtures shows that the ethanol self-condensation reaction has the highest rate constant among the self-condensation and cross-condensation reactions in the system.

Economic analysis for a first-generation facility producing 25 million gallons of *n*-butanol per year has been performed for several scenarios of catalytic performance and process configuration to investigate the viability of the commercial use of this catalyst. Results indicate that the *n*-butanol required selling price at 25% return on investment (ROI) can vary between \$1.30- \$1.60 per kg of *n*-butanol, which is reasonably competitive with the current *n*-butanol market price.

The highly selective production of 2-acetoxypropanoic acid (APA) from lactic acid and acetic acid through reactive distillation has motivated the study of the elimination reaction of APA esters to acrylate esters. Among different APA esters studied, the best results are obtained for those with no hydrogen on the β -carbon of the ester functionality. This hydrogen allows the elimination of the ester group as an alkene, leading to the production of highly reactive materials that can decompose to other side-products and reduce the desired products selectivity. The use of CO₂ as the diluent gas reduces the amount of carbon deposited on the surface of the contact material and maintains the rate of the elimination reaction in extended operation. Highest yields of 35% for butyl acrylate and 70% for methyl acrylate and benzyl acrylate at 550 °C and LHSV of 1.9 h⁻¹ have been achieved in this study.

Copyright by IMAN NEZAM 2019 This dissertation is dedicated to my wonderful parents and beloved wife Neda

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KEY TO SYMBOLS AND ABBREVIATIONS

D _p	particle diameter
ki	rate constant for species i
Κ	equilibrium constant
Х	reactant conversion
τ	superficial residence time
r _i	rate of formation of species i
С	concentration in mol/vol
Ea	activation energy
C _R	reactor cost
b	base reactor cost
Di	shell I.D.
p _{cm}	cost multiplier for O.D.
f_{cm}	cost multiplier for TEMA-type front head
r _{cm}	cost multiplier for TEMA-type rear head
CT	sum of base cost corrections for shell and tubes in the reactor
A _{ht}	surface area for heat transfer
Ei	escalation index (Chemical Engineering Plant Cost Index)
CTC	tray column cost
C _{bs}	base shell cost
C _{bt}	base tray cost
C_{pl}	base platforms and ladders cost
f_1	cost multiplier for column material
f_2	cost multiplier for column material
f_3	cost multiplier for tray type
f_4	cost multiplier for tray numbers
Ν	number of trays

W	vessel weight
L	column height
D	column diameter
T _b	head thickness
T _p	shell thickness
C _{SG}	steam generator cost
C_{bg}	base steam generator cost
Cc	air-cooled heat exchanger cost
S	reduced heat load
C _{ac}	air-cooled heat exchanger cost function
T_i	process inlet temperature
Ta	ambient temperature
Q	heat load
Che	other heat exchangers cost
CB	other heat exchangers base cost
A _{HE}	heat exchanger surface area
F _D	cost multiplier for the exchanger type
F _P	cost multiplier for the design-pressure
F _M	cost multiplier for the material of construction
C10	C ₁₀ alcohols
IA	isoamyl alcohol
APA	2-acetoxypropanoic acid
CS_i	calculated selectivity of species i based on GC results
CS_{ij}	calculated selectivity of species I with respect to reactant j based on GC results
$\mathbf{S}_{\mathbf{i}}$	total selectivity toward species i considering those molecules participated in other reactions
\mathbf{S}_{ij}	total selectivity toward species i with respect to reactant j considering those molecules participated in other reactions

1 Literature Review and Background

1.1 Introduction

Petroleum resources have always been the subject of serious concerns for depletion. According to a study made in 2017, by maintaining current production levels, the reservoirs of coal, natural gas, and oil resources will be depleted in 114, 53, and 51 years, respectively [1]. Furthermore, the role of fossil fuels in the current status of environmental sustainability has always been a controversial discussion. Some believe that regenerative and assimilative capacities should be considered while using non-renewable resources [2, 3]. Therefore, finding an alternative source of energy and commodities' starting material has been one of the most common challenges of researchers for decades. This alternative needs to be renewable, environmentally friendly, and efficiently produced to be considered as an appropriate option. The production of bioethanol (ethanol produced from bio-resources, C₂H₅OH) has been one of the significant achievements in this ongoing challenge. Being produced from the fermentation of sugar, starch, or cellulosic-based glucose [4], ethanol has been the most common substitute for engine fuels [5] and one of the primary starting materials for the production of commodities which are already being produced using petroleum-based resources.

Ethanol can be used as a starting material for the production of butanol (C_4H_9OH). Butanol has a wide range of applications in industry. Among them are its use as a chemical additive in the perfume industry, solvent in the paints and coatings industries, and extractant in the cosmetics and pharmaceuticals industry [6]. Moreover, butanol has some advantageous over ethanol as a fuel alternative. Chief among these are higher energy density, more resistance to water contamination, and no phase separation while mixing with gasoline. Also, butanol is more akin to gasoline

considering its chemical properties such as stoichiometric air-fuel ratio, heat of vaporization, research octane number, and motor octane number [7, 8].

1.2 Butanol Production Methods

1.2.1 Petrochemical Processes

Butanol is currently produced through petroleum-based methods. These methods are shown in Figure 1.1 [9] and are: (a) oxo synthesis, (b) Reppe synthesis, and (c) crotonaldehyde hydrogenation [10]. Among them, oxo synthesis is the most widely used process in the industry. In this process, first carbon monoxide and hydrogen are added to the carbon-carbon double bond of propylene in a hydroformylation process in the presence of various catalysts such as Co and Rh to produce butyraldehyde, and then butyraldehyde is hydrogenated to produce 1-butanol. The Reppe reaction is essentially the same as oxo synthesis except that this process involves low temperature (100 °C) and low pressures (5-20 bar) conditions that facilitate the direct formation of alcohols from the olefin. Crotonaldehyde hydrogenation was the preferred industrial process for 1-butanol conversion until the mid-1950s. This process involves three main steps including acetaldehyde condensation to acetadol in the presence of an alkaline catalyst, dehydration of acetadol by its acidification with acetic acid for the formation of crotonaldehyde, and finally hydrogenation of crotonaldehyde to 1-butanol in the presence of copper catalysts [10].

1.2.2 Fermentation Processes

Fermentation is one of the most common bio-based techniques for the production of butanol. There are two common fermentation methods used for the production of butanol. The first method, acetone-butanol-ethanol (ABE) fermentation, was discovered in 1911 by Strange Company & Graham Ltd. and a group of scientists [11]. In this method, hexose and pentose sugars are

fermented using *Clostridium acetobutylicum* to produce acetone, butanol, and ethanol in a standard 3:6:1 mass ratio, respectively [12].



Figure 1.1. Petroleum-based methods for the production of butanol. (a) oxo synthesis, (b) Reppe synthesis, and (c) crotonaldehyde hydrogenation [9]

There are a couple of issues involved with the ABE fermentation process. Among them are separation cost, low butanol titer, low yield, low productivity, and high cleaning costs resulting from potential bacteriophage invasion [13]. These challenges have been the subject of several studies during the past decade. Developed genetic engineering and pre-treatment processes have led to promising accomplishments in addressing some of these challenges. Indeed, the use of modified *Clostridium* strains has led to improved productivity of butanol compared to the other two main products [14]. Nevertheless, the most significant difficulties lay ahead when it comes to the separation costs and overall ABE yield [11].

1.2.3 Guerbet Process

The catalytic pathway for the production of bio-butanol from bio-ethanol is called the Guerbet reaction. The availability of ethanol at a large scale as one of the most prominent sources of bio-based carbon is one of the biggest motivations for butanol production through this process [15]. Guerbet was the first scientist who produced this process for the production of dimer alcohols from aliphatic alcohols with loss of one molecule of water [16]. While different mechanisms have been proposed for the production of 1-butanol from ethanol, the one which is accepted by most scientists is a three-step reaction involving dehydrogenation, aldol condensation, and hydrogenation [17]. This mechanism is explained in more depth in the next section.

There have been several studies for conducting Guerbet reaction with high ethanol conversion and selectivity to higher alcohols. These experiments were done in batch or continuous reactors with the use of heterogeneous and homogeneous catalysts at different reaction conditions [18-22]. Studying the proposed reaction mechanisms, reactor configurations, and catalyst structures used for obtaining higher product yields in previous similar studies will enhance the familiarity with the reaction system and improve the chance of finding an alternative process for the current petrochemical process used for butanol production.

1.3 Mechanisms Suggested for the Guerbet Reaction

1.3.1 Aldol Condensation

The primary mechanism accepted by most scientists for the Guerbet reaction is the indirect mechanism known as aldol condensation. This mechanism, shown in details in Figure 1.2, involves three main steps: ethanol dehydrogenation to acetaldehyde, acetaldehyde aldol condensation to crotonaldehyde, and crotonaldehyde hydrogenation to butanol [9]. The produced butanol can

participate in further Guerbet reactions with other alcohols to produce 1-hexanol, 2-ethyl-1butanol, 1-octanol, 2-ethyl-1-hexanol, etc. While dehydrogenation and hydrogenation steps require a metal catalyst to assist with hydrogen transfer, the aldol condensation step takes place in the presence of a support with both acid and base sites on it. Therefore, a multifunctional catalyst is required for conducting the reaction if the suggested mechanism is followed.



Figure 1.2. Reaction mechanism for the ethanol Guerbet reaction system [9]

Several observations support the proposed indirect mechanism. First, in most studies conducted on this reaction, the intermediate components for this mechanism are present as side-products [6, 9, 15, 18, 19, 23-26]. Second, Ogo et al. studied each intermediate component separately by

examining its reactivity at 300 °C and atmospheric pressure over hydroxyapatite (HAP) catalyst and observed high selectivity of the desired product in each experiment [24]. Third, Gines et al. studied the effect of adding labeled acetaldehyde to the feed and noticed improved butanol yield through the reaction of labeled carbon atoms [19]. Finally, the prerequisite for the aldol condensation step is the presence of a hydrogen atom on the α -carbon. Weizmann tested and approved this requirement through feeding different types of alcohols to the Guerbet reaction chamber [27]. All these evidence support the occurrence of this mechanism as the main one for butanol production from ethanol.

1.3.2 Direct Dehydration

The dimerization of two ethanol molecules, first proposed by Yang et al. in 1993 [28], is known is the direct dehydration mechanism for the Guerbet reaction. In this mechanism, as shown in Figure 1.3, a C-H bond in the β -position in the ethanol molecule is first activated and then condenses with another ethanol molecule to form butanol [17]. The most significant evidence for this mechanism is the lower activity of acetaldehyde compared to ethanol when fed to the reactor at reaction conditions [17, 28, 29]. However, the challenge with this mechanism is that all of the studies supporting it are conducted at high reaction temperatures (>350 °C) [26]. Under these conditions, even though selectivity to higher alcohols from acetaldehyde is lower than that from ethanol, the fact that higher alcohols are formed from acetaldehyde suggests that at high temperature the aldol condensation mechanism is still active.



Figure 1.3. Direct dehydration mechanism [17]

Scalbert et al. studied the Guerbet reaction using a non-metallic based catalyst (HAP) in the 350-410 °C temperature range and compared the reaction quotient (Q) to the thermodynamic equilibrium constant (K) for the two proposed mechanisms [29]. While the Q/K ratio for the indirect mechanism was in the order of magnitude of two to three, this ratio was well below one for the direct condensation mechanism, suggesting that the direct condensation is the primary mechanism at the studied temperatures. Even then, the authors discuss that at lower temperatures (not thermodynamically controlled conditions) and in the presence of metal-promoted catalysts (with the ability of the formation of surface hydrogen atoms), the dominating mechanism is the acetaldehyde aldol condensation reaction.

Based on the above discussions, one can claim that at high temperatures and over non-promoted oxides, the governing reaction mechanism is the direct dehydration reaction with the indirect aldol condensation mechanism occurring at slower rates. However, at lower temperatures and in the presence of metal-promoted supports, the accepted mechanism among most scientists is the indirect reaction.

1.4 Catalysts

1.4.1 Homogeneous catalysts

Homogeneous catalysts have shown significant potential for obtaining high conversion and selectivity for the Guerbet reaction. Typically, these catalysts involve a metal complex, a phosphine ligand, and a basic inorganic solution. The metal is responsible for hydrogen transfer in the hydrogenation and dehydrogenation steps, and the inorganic base is responsible for the aldol condensation. Due to the presence of the phosphine ligands, these catalysts are subject to degradation to phosphine oxides when exposed to air. The primary advantage of these catalysts is

their lower operating temperatures (<150 °C) compared to heterogeneous catalysts. Dowson et al. in 2013 were able to obtain 93% butanol selectivity and 22% ethanol conversion at 150 °C using ruthenium, bis(diphenylphosphanyl)methane ligand, and EtONa catalyst [30]. Same group was able to maintain the butanol selectivity at 31% ethanol conversion by upgrading the ligand to mixed-donor phosphine-amine (P-N) ligand [31].

Despite the high butanol selectivity obtained, one of the significant challenges involved in the homogeneous catalysts is the deactivation of catalyst due to the decomposition of the ligand. None of the studies mentioned above maintained their activity beyond 300 turnovers of the catalyst (moles of substrate reacted per mole of metal). Ligand decomposition is attributed to, but not limited to, inadequate water tolerance of the ligand [26]. Tseng et al. used an amide-derived N,N,N-Ru^{II} complex along with additional quantities of triphenylphosphine (PPh₃) to improve the TON to 530 with ethanol conversion of 53%; however, the butanol selectivity decreased to 78% [32]. Xie et al. were able to show this correlation between the TON and reaction selectivity more clearly [33]. Although they achieved the greatest TON of 18209 using acridine-based ruthenium pincer complexes at 150 °C, only 73% ethanol conversion and 60% butanol selectivity was obtained using this catalyst.

So far, the highest selectivity for the ethanol Guerbet reaction has been reported by Jones et al. [34]. They modified the iridium catalyst with nickel hydroxide at 150 °C and were able to obtain >99% butanol selectivity at 37% ethanol conversion and catalyst turnovers of 185. Despite the high butanol selectivity obtained, the stability of the catalyst is still the principal challenge in using this catalyst in industry. Other problems associated with this type of catalysts are separation costs and non-reusability of the catalyst.

1.4.2 MgO

Metal oxides are generally among popular heterogeneous catalysts for the Guerbet reaction because of the high alcohol selectivity they provide. They typically offer high basicity for the reaction environment, which is essential for the hydrogen exchange and condensation steps.

Ueda et al. studied several metal oxides for the continuous cross-condensation of methanol with ethanol in the vapor phase, and observed the best reaction performance with MgO as the catalyst [35]. Other metal oxides studied in their experiments were ZnO, CaO, and ZrO₂. They reported an ethanol conversion of 30% and selectivity of 80% to higher alcohols at 360 °C and atmospheric pressure for the MgO catalyst. The selectivity obtained was even higher when using C₃-C₅ alcohols as the second alcohol reacting with methanol [36]. MgO was also studied for the self-condensation reaction of alcohols. Ndou et al. investigated vapor-phase ethanol self-condensation over several metal oxides such as MgO, CaO, BaO, and γ -Al₂O₃ [17]. Optimal results were reported for MgO at 450 °C and 1 bar with 56% ethanol conversion and 19% selectivity to higher alcohols. The same group studied propanol self-condensation over MgO catalyst at similar reaction conditions and observed 28% conversion and 50% selectivity to 2-methyl pentanol. Adding H_2 to the reaction environment improved the selectivity to 70%. Among multiple researchers studying the MgO catalyst for the Guerbet reaction, there is consensus that the reaction has to happen at high temperatures and with vapor phase reactants. The minimum temperature used for a detectable activity of MgO as the catalyst for this reaction is 300 °C [15].

One of the methods to improve the performance of MgO in the Guerbet reaction was the addition of metals to the catalyst. However, the results were not very promising. Ueda et al. showed that the addition of transition metals to MgO typically maintained the rate of the dehydrogenation reaction, but inhibited the hydrogenation step [36]. Ndou et al. had a similar observation using alkaline earth and transition metals [17]. In both cases, the selectivity to higher alcohols was reduced two-fold or more. Besides, adding alkali metals increased the MgO catalyst basicity, leading to increased selectivity to the dehydrogenation products and decreased selectivity to the condensation products [37]. Olson et al. discovered that addition of nickel to activated carbon-supported MgO catalyst slightly improved the higher alcohols selectivity [38].

1.4.3 Mg-Al Mixed Oxides

Several researchers have addressed MgO as a catalyst that cannot solely provide all the functionalities required for the Guerbet mechanism [19, 23, 39]. Carvalho et al. claimed that adjacent acid and medium strength base sites are necessary for the dehydrogenation and condensation steps [40]. Di Cosimo et al. described the effect of Lewis acid sites on improving the rate of dehydrogenation reactions because of their enhanced hydrogen abstraction properties [23]. Tsuchida et al. compared a dominantly basic MgO catalyst with another catalyst with both acid and base sites on it and observed much higher selectivity to acetaldehyde and unsaturated alcohols in the reaction with MgO catalyst [39]. They justify this observation by stating that the acid sites have the capability of trapping the hydrogen molecules on the catalyst surface. Whereas on the MgO catalyst, H₂ is dissociated from the catalyst surface as a gas molecule.

Because of these catalytic requirements, several researchers have considered upgrading MgO catalyst using various metal oxides. Oxides of aluminum have been one of the most popular metal oxides that increase the acidity of the catalyst. Early in the 1930s, Fuchs et al. used a CuO/MgO/Al₂O₃ mixture for the vapor phase Guerbet reaction [41]. They were able to obtain 15% butanol selectivity and 56 % conversion at 260 °C in a fixed bed reactor. Generally, the most common way of obtaining a catalyst containing both magnesium and aluminum oxides is the calcination of hydrotalcite. Hydrotalcite is a basic layered double hydroxide (LDH) support with

Al positive charges neutralized between anionic hydroxide layers of Mg(OH)₂. Calcination of hydrotalcites leads to the collapsing of this structure and results in a mixture of Mg/Al oxides.

One of the advantages of using calcined hydrotalcite is to obtain an ideal number of acid and base sites on the catalyst, as the Mg/Al ratio can be adjusted as desired [15, 23, 42-47]. Di Cosimo et al. investigated different Mg/Al ratios for the Guerbet reaction and stated that 5>Mg/Al>1 is the ideal ratio [23, 42]. Higher Mg concentrations (more basicity) lowered the condensation reaction rate, and higher Al concentrations (more acidity) increased ethanol dehydration to ethylene and its coupling and dehydration to diethyl ether. Leon et al. confirmed this finding by stating that acid sites are responsible for the ethanol dehydration reaction to ethylene, limiting the selectivity of ethanol to higher alcohols [43, 44]. They also noted that at lower temperatures the basic sites are active for the condensation reaction, while acid sites are not active for dehydration reactions [45].

Another benefit of calcined hydrotalcite is the surface exchangeability of Mg and Al atoms with other metals to form other bi-metal or multi-metal mixtures. This characteristic has provided unique flexibility for this support. For instance, Leon et al. noticed that surface acidity can be reduced by replacing Al atoms with Fe, which leads to lower ethylene formation rates and increased desired products selectivity subsequently [44]. On the other hand, some researchers studied the effect of the addition of other metals by physically mixing them with calcined hydrotalcite. Carlini et al. mixed this catalyst with copper chromite for *i*-butanol production from methanol and *n*-propanol [46]. They were able to obtain 30% *n*-propanol conversion and almost complete iso-butanol selectivity at 200 °C and atmospheric pressure in the batch system. The same group tried to optimize this result using the impregnated Cu/Mg-Al mixed oxide, and were able to enhance the iso-butanol yield to 40% while maintaining complete selectivity [48]. They also

reported complete selectivity to iso-butanol and 80% *n*-propanol conversion with a vapor phase continuous reactor at 280 °C.

Carlini et al. reported that their results were exclusive to the addition of copper, and no optimization effect was observed by precipitating other dehydrogenating metals such as Ni, Pd, Ag, and Pt. Several other studies have confirmed the positive impact of copper addition on vapor phase ethanol dehydrogenation to desired intermediate products [49, 50]. A similar study made by Marcu et al. for the condensed phase Guerbet reaction showed the optimum loading of copper in calcined hydrotalcite to be between 5 wt% and 10 wt% for 9% ethanol conversion and 80% butanol selectivity [20]. Also, among various metals studied (Pd, Ag, Mn, Fe, Cu, Sm, and Yb), palladium had shown the best results, with 18% ethanol conversion 78% butanol selectivity at 300 °C and autogenous pressure [21]. According to this study, Pd-Mg-Al had stronger basicity and lower acidity compared to Cu-Mg-Al catalyst. However, other metal combinations, such as Sm-Mg-Al, that had stronger basicity and lower acidity than Pd catalyst, did not perform as well as this catalyst, confirming the importance of base/acid ratio in the catalytic condensation of ethanol. Zhang et al. obtained 70% *n*-butanol selectivity and 28% ethanol conversion for Pd-Mg-Al catalyst at 290 °C in a vapor phase batch reactor [51].

1.4.4 Hydroxyapatite (HAP)

Hydroxyapatite (HAP) or $Ca_{10}(PO_4)_6(OH)_2$ is a catalyst with both acid and base functionalities studied in several papers for the Guerbet reaction. The molar ratio of Ca/P can be controlled by adjusting the pH of the mixture solution while preparing the catalyst. This ratio corresponds to the base/acid sites on the catalyst surface. Tsuchida et al. found best butanol selectivity of 71% at 10% ethanol conversion for Ca/P molar ratio of 1.67, corresponding to a base/acid molar density ratio of 88 [39]. Hanspal et al. obtained 75% butanol selectivity and 24% acetaldehyde selectivity at only 7% conversion at 330 °C and atmospheric pressure in a fixed bed reactor [52]. They conducted an experiment at similar conditions using basic MgO catalyst and obtained 40% and 49% selectivity for butanol and acetaldehyde, respectively, at a lower catalyst activity. They explained this result by performing acid-base analyses on both catalysts and observing higher density of both base and weak acid sites on hydroxyapatite. Finally, they compared different acetaldehyde concentrations at the reactor exit, and observed a linear dependence of butanol formation on acetaldehyde concentration for MgO, and no specific relation between these two for the hydroxyapatite catalyst. This suggests that the vapor-phase acetaldehyde participates in butanol formation solely for the MgO catalyst [53].

Similar to the calcined hydrotalcite, one of the advantages of hydroxyapatite is its flexibility of substituting calcium, phosphorous, and hydroxide atoms with other atoms such as strontium, vanadium, and fluorine, respectively. Ogo et al. examined four catalysts using this method (Ca-P HAP, Sr-P HAP, Ca-V HAP, and Sr-V HAP) and observed the best results with the Sr-P HAP catalyst [24]. They were able to obtain 81% butanol selectivity at 8% conversion at 300 °C and atmospheric pressure in a fixed-bed continuous reactor. This group optimized these results by tuning the Sr/P molar ratio and were able to obtain 86% butanol selectivity at Sr/P molar ratio of 1.70 corresponding to base/acid molar density of 4.5. Although the conversion of ethanol was improved to 11% using this catalyst, it was still too low for considering this catalyst as an ideal one for the Guerbet reaction. Furthermore, this conversion was obtained at a relatively low WHSV of 0.35 h⁻¹, which indicates the high energy required to maintain the reaction conditions for a long time. Longer contact times also increase the chance of catalyst deactivation as a result of dimerization and polymerization of intermediate products such as acetaldehyde [26]. One of the methods of improving ethanol conversion while maintaining the WHSV in an acceptable range is

to increase the reaction temperature. However, this will lead to ethanol decomposition and sidereactions. For instance, Tsuchida et al. reported 76% ethanol conversion and 6% butanol selectivity at 450 °C [54]. Hanspal et al. recently studied the effect of cation and anion components on the performance of this catalyst by replacing Sr with Ca and OH⁻ with F⁻. They conducted their experiments at 633 K and atmospheric pressure in a fixed bed reactor and obtained most optimum results with HAP at 5% ethanol conversion and 72% butanol selectivity, which emphasizes the beneficial role of the hydroxyl group of HAP. Among different catalysts tested in this study, Sr-P HAP showed the highest rate of ethanol dehydrogenation to acetaldehyde (91% acetaldehyde selectivity), with a quite low coupling to butanol observed. Low butanol formation rate is assigned to the weak binding affinity for acetaldehyde on this catalyst. They also noticed that weaker base sites in HAP catalyst compared to MgO are responsible for reversible water adsorption on HAP, which enables the catalyst to stay active for the aldol condensation reaction at a higher rate [55]. Silvester et al. found the optimized ethanol conversion of 40% and 83% selectivity to butanol at the base/acid molar density ratio of 0.2 [56]. Similar to most of the other studies using this catalyst, this selectivity was obtained in the gas phase and high contact times.

1.4.5 Al₂O₃ Supported Catalysts

Metal-supported alumina is one of the more recent catalysts suggested for the Guerbet reaction. This alumina support contains both acid and base sites, and the addition of metal sites improves hydrogen transfer at the reaction conditions. Ndou et al. were one of the first research groups that studied this type of catalyst [17]. Using different alkali metals supported on alumina at 450 °C and atmospheric pressure, they were not able to obtain a selectivity of more than 4% for C₄ alcohols.

Previous studies on hydrotalcite-based catalysts had shown the ability of nickel to facilitate the Guerbet reaction at lower temperatures [57]. Yang et al. tested several metallic (Fe, Co, and Ni)

catalysts over γ -Al₂O₃ support; they obtained 19% ethanol conversion and 64% butanol selectivity at 200 °C and atmospheric pressure in a packed bed reactor using 8 wt% Ni/ γ -Al₂O₃ [58]. Other liquid side-products were acetaldehyde, butyraldehyde, and ethyl acetate. Fe/ γ -Al₂O₃ suppressed the activity of the reaction compared to the Ni/ γ -Al₂O₃ catalyst. Furthermore, Co/ γ -Al₂O₃ was as active as Ni/ γ -Al₂O₃; however, unlike nickel catalyst, ethyl acetate was the main product detected using cobalt. Finally, the same group studied different concentrations of nickel in the Ni/ γ -Al₂O₃ catalyst and obtained the highest butanol yield at 8 wt% nickel loading.

High pressure condensed phase reactions are popular conditions for the Guerbet reaction using alumina-supported catalysts. Ghaziaskar et al. studied the Guerbet reaction at different pressure (4-183 bar) and temperature (150-300 °C) ranges and were able to get C_{4+} selectivity as high as 83% at 35% ethanol conversion using 8 wt% Ni/γ-Al₂O₃ catalyst at 250 °C and 176 bar [8]. They claimed that the catalyst is active for at least 18 hours without any need for regeneration. Riittonen et al. conducted Guerbet experiments in a condensed phase batch reactor system at 250 °C and autogenous pressure using different metallic catalysts (Ni, Ru, Rh, Pd, Pt, Au, Ag) over γ -Al₂O₃ support [22]. Maximum butanol selectivity of 80% of liquid products at 25% ethanol conversion was reported for the 20.7 wt% Ni/y-Al₂O₃ at long contact times (24 hours). The second best performance was with the Pt catalyst. Later, the same group studied Ni, Co, and Cu catalysts over γ -Al₂O₃ in a condensed phase fixed bed reactor at 240 °C, 70 bar, and LHSV of 4.3 h⁻¹ [59]. While Co catalyst showed the highest activity (28% ethanol conversion), Ni provided the highest selectivity toward butanol (69% of liquid products). Cobalt results showed the highest selectivity toward ethyl acetate (83% of liquid products). Different copper loadings on γ -Al₂O₃ were also studied, and the results indicated that increasing Cu loading would inhibit the selectivity toward butanol, and introduce ethyl acetate as the main product. Due to the absence of qualitative and

quantitative analysis of gaseous products in these experiments, it is difficult to compare the selectivity results to similar studies.

Aside from ethanol reactions, Al₂O₃-supported metallic and bimetallic catalysts have also been used for the Guerbet reaction with other alcohols as the feed. Panchenko et al. compared the *n*-pentanol Guerbet reaction activity of different metallic catalysts (Pt, Pd, Ir, Ru, Rh) over different supports (C, Al₂O₃, TiO₂, CeO₂, ZrO₂) doped with different solid bases (NaOH, MgO, Al(OH)₃, Na₂CO₃, CaCO₃) in a condensed phase batch reactor at 180 °C and 10 bar [60]. Among the different catalysts studied, the highest conversion (12%) and selectivity (90%) to 2-propyl-1-heptanol was achieved using Pt/Al₂O₃ in the presence of aqueous NaOH solution. Hernandez et al. studied the Guerbet reaction of *n*-octanol using co-impregnated 10 mol% Ni/Cu (3/1)/Al₂O₃ at 225 °C and atmospheric pressure in a batch reactor [61]. They were able to obtain 95% *n*-octanol conversion and 75% C₁₆ alcohol selectivity after six hours of reaction. Although they suggested a new method for the preparation of this bimetallic catalyst, the classic wet impregnation of metal nitrates on the surface of the support resulted in the highest selectivity toward desired products.

Due to the importance of acid-base surface interactions in the Guerbet reaction, obtaining the right ratio and amount of these sites on the surface of the γ -Al₂O₃ support is a critical step in optimizing this catalyst. Ghaziaskar et al. showed that mixing basic Mn₂O₃/ γ -Al₂O₃ with Ni/ γ -Al₂O₃ resulted in superior activity compared to the Ni/ γ -Al₂O₃ catalyst [8]. A similar observation was made by Ogo et al. during their experiments with HAP catalyst [18]. Jordison et al. modified the base sites on the 8 wt% Ni/ γ -Al₂O₃ catalyst by impregnating different amounts of La₂O₃. They observed optimum ethanol conversion of 55% and C₄+ selectivity of 71% for the 8 wt% Ni/9 wt% La₂O₃/ γ -Al₂O₃ catalyst in a condensed phase batch reactor at 230 °C, autogenous pressure, and 10 hours of reaction time [9]. They noticed that the addition of La₂O₃ inhibited the rate of formation of ethyl

acetate produced by the reaction of acetaldehyde with ethanol. The biggest side-products in this system were gases such as CH_4 and CO_2 . The same authors studied the effect of water removal on the Guerbet reaction performance and were able to achieve 75% C_4 + selectivity and 50% ethanol conversion under similar reaction conditions and a water concentration of 5 wt% [25].

1.4.6 Other Catalysts

Similar to Al₂O₃, CeO₂ is a more recently used support for Guerbet reactions. This catalytic support is commonly incorporated with copper metal to enhance hydrogen transfer. In comparison with γ -Al₂O₃ supported catalysts, this catalyst gets activated at lower temperatures, with the drawback of being less selective to higher alcohols [26]. Earley et al., used the Cu-CeO₂ catalyst to achieve 67% ethanol conversion and 45% butanol selectivity at 260 °C and 100 bar pressure of CO₂ [62]. Jiang et al. impregnated copper on CeO₂/AC (activated carbon) surface and obtained up to 46% ethanol conversion and 42% butanol selectivity at 250 °C and 20 bar [63]. Both experiments were conducted in continuous reactors.

Activated carbon has also been used with other metals, metal oxides, and alkali metal salts for the Guerbet reaction. Onyestyak et al., obtained optimum results by modifying this support with nickel and KOH [64, 65]. A maximum higher alcohols yield of 62% at 350 °C and 21 bar was reported for this catalyst.

Mixed oxides have always been popular options for the Guerbet reaction. The use of Mg-Al mixed oxides has already been discussed in detail in previous sections. Gines et al. studied Mg/Ce oxides for the gas phase Guerbet reaction and observed the constructive effect of doping potassium for increasing the number of basic sites, and of impregnating copper for enhancing the hydrogen transfer steps [19]. Unfortunately, they did not report any conversion/selectivity for their experiments. Another mixed oxide used for this reaction is Mg/Zr mixed oxide. Regardless of the

disappointing catalytic performance of this material (8% ethanol conversion and 12% butanol selectivity), Kozlowski et al. showed the beneficial effect of adding sodium as the basic substrate to this catalyst [37].

Another catalyst reported for the vapor phase Guerbet reaction is alkali-zeolite catalysts. First introduced by Yang in 1993 [28], other scientists have since developed it further. Yang et al. studied various Rb-impregnated alkali-zeolite catalysts and found the optimum catalytic activity for Rb-LiX zeolite at 1 bar and 420 °C. Yoshioka et al. studied different catalysts for the ethanol Guerbet reaction at different pressures and temperatures and were able to obtain up to 12% butanol yield at 0.2 bar and 275 °C using Rb-Li ion-substituted zeolite catalyst [66]. Authors have not reported any conversion/selectivity results in this study.

1.5 Condensed Phase Reactions

The critical point that differentiates alumina-supported catalysts from other catalysts used for the Guerbet experiments is their activity at condensed phase conditions. Being able to run the Guerbet experiments at higher pressures and lower temperatures not only forces the reaction thermodynamically toward the production of the desired products, but also saves the cost and energy required for bringing the feed to the reaction conditions. Several studies have been conducted in recent years to improve the performance of the Guerbet reaction in the condensed phase using alumina-supported catalysts. These studies have been discussed in Section 1.4.5.

1.6 Continuous Reactors

Continuous reactors are generally favored in handling heterogeneous catalytic reactions. They are easier to set-up and control, more environmentally friendly, and subsequent product separations and catalyst regeneration can be achieved in a shorter time and lower cost compared to batch reactors [15, 67]. Moreover, continuous reactors are easy to scale-up, which is a big advantage for this type of process [8]. Wiles et al. discuss that besides quality, economical, and environmental advantages, safety perspectives are also superior in continuous reactors compared to batch processes, since heating systems and temperature control in these systems are more accurate [67].

All these mentioned benefits have made continuous processes more industrially relevant, especially for heterogeneous catalytic reactions. In Chapter 2 of this research, the continuous process for the catalytic Guerbet reaction has been optimized. In Chapter 3, the scale-up of this process has been studied and optimized in different aspects.

1.7 Nickel Bimetallic Catalyst

The mechanism of the Guerbet reaction has been discussed in Section 1.3. Hydrogen is a crucial component in the system, as it is involved in two steps of the reaction. As discussed earlier, metallic sites are responsible for hydrogen adsorption (desorption) on (from) the surface of the catalyst. Liberation of the molecular hydrogen produced in the dehydrogenation step from the surface of the metal to the reaction environment can desirably shift the first step of the reaction toward the formation of more acetaldehyde in one hand, and, on the other hand, create a challenge for the hydrogenation of the aldol condensation product (i.e. crotonaldehyde) toward the desired alcohol. Conversely, a strong hydrogen bond with the metal surface can restrain the hydrogenation of crotonaldehyde (and other aldol condensation products) to higher alcohols [68, 69]. Therefore, finding a balanced number and strength of metal-hydrogen bonds are the most critical challenges in obtaining an optimum selectivity for the Guerbet reaction. Furthermore, nickel is known for its strong capability of cracking the carbon-carbon bond present in ethanol, which leads to the decomposition of ethanol to gaseous side-products. Therefore, nickel-based bimetallic catalysts
are potential alternatives to investigate the possibility of improving the performance of the Guerbet reaction.

1.8 Objectives

1.8.1 Process and Catalyst Studies on the Guerbet Reaction

Experimental studies on the Guerbet reaction in this study divides into three main categories. These topics are discussed in detail in the following sections.

1.8.1.1 <u>Develop Ni/La₂O₃/γ-Al₂O₃ Catalyst in a Continuous Condensed Phase Reactor</u>

Jordison et al. [9, 25] have already studied Ni/La₂O₃/ γ -Al₂O₃ catalyst in batch reactors. However, no extensive work has been done so far for using this catalyst in a continuous reactor. Transitioning from batch to continuous reactors require a set of calculations to make sure that the starting point of experiments is in the right range of feed flow, reaction temperature, and catalyst quantity. Moreover, safety issues need to be considered and reviewed, since the operating process is different from the batch reaction.

Besides designing a continuous condensed phase process for the Guerbet reaction system, finding the ideal reactor configuration and operating conditions are the other objectives of this research. For this purpose, multiple reaction temperatures, feed flow rates, and catalyst compositions with different preparation conditions will be tested, and the optimum reaction conditions will be investigated. Multiple surface analyses will be obtained to address the catalytic observations made throughout the research. The results obtained from this section will be the basis of the studies conducted on bimetallic catalysts, as discussed in the next section.

1.8.1.2 Improve the Reaction Yield by Finding the Ideal Bimetallic Catalyst

Improving the rate of formation of higher alcohols compared to those of the side-reaction in the system is the primary objective of studying bimetallic catalysts. On the effect of the addition of second metal to nickel on hydrogen chemisorption and desorption, palladium and platinum are metals that are recognized to enhance this amount. Ni-Pt and Ni-Pd bimetallic catalysts show lower hydrogen desorption temperatures than the monometallic nickel, meaning that they form weaker hydrogen bond strengths compared to nickel [70-73]. Addition of copper to nickel could suppress the amount of hydrogen chemisorbed (desorbed) to (from) the surface of the catalyst, since copper is known as a metal that does not promote dissociative hydrogen adsorption [74]. Similar to copper, molybdenum and iron suppress the amount of hydrogen uptake of the nickel catalyst, and cobalt does not significantly change this amount [73, 75]. Copper and cobalt have also shown a weaker capability in cleaving the C-C bond compared to nickel. These two metals increase the resistance toward carbon nucleation and growth on the surface of the nickel-containing catalysts that could potentially help in inhibiting the decomposition of ethanol to gaseous side-products [76-78]. Finally, according to previous studies [59], one of the contributing factors in determining product selectivity is claimed to be the crystal structure of the metals. Therefore, adding a second metal could optimize the structure of the catalyst toward the production of more desired products. To cover as many varieties of catalyst optimization cases as possible, Cu, Co, Pd, Pt, Fe, and Mo bimetallic combination with Ni are examined in this study.

1.8.1.3 Understand the Mechanistic and Kinetic Behavior of the Reaction

As discussed earlier, the mechanism of the Guerbet reaction has been a controversial topic among researchers in the field. Ethanol multi-step conversion to acetaldehyde, crotonaldehyde, and finally butanol is the more accepted mechanism, while some researchers have not disregarded the direct dehydration of ethanol. In this study, we design and construct experiments to better understand the governing mechanism for the condensed-phase Guerbet reaction using the nickel-based La_2O_3/γ -Al₂O₃ catalysts.

Besides the mechanistic studies, other experiments have been performed to understand and predict the behavior of the reaction more accurately. For this purpose, experiments with the intermediate and final products as the feed of the reaction, along with the results obtained from surface analysis, are employed to discuss the rate-limiting step and activation energy for the reaction.

1.8.2 Techno-economic analysis of the industrial scale Guerbet reaction

A process concept is presented in which *n*-butanol and mixed C_{6} + alcohols are produced as saleable products; ethanol is recycled to achieve nearly 100% overall conversion and minor byproducts are burned to provide process energy. A process design is conducted using Aspen Plus V8.4 process simulation software, and economic analyses are carried out for several cases of ethanol conversion and alcohol selectivities. Several additional cases involving permutations of the base process configuration are also examined in attempts to improve process economics. At *n*-butanol selectivities achieved experimentally and for a facility producing 75 million kg *n*-butanol per year, the total capital costs, operating expenses, and the required *n*-butanol selling price for typical values of expected return on investment have been calculated [79].

1.8.3 Guerbet reaction studies of the Fusel Alcohols

Guerbet reactions were also conducted with fusel alcohols obtained from collaborating research groups in the project. Because the fusel alcohols obtained for these experiments contained approximately 5 wt% isoamyl alcohol (2-methyl-1-butanol, IA) in ethanol, reactions were carried out with blends of IA alcohol and ethanol of different compositions in order to better understand

reaction rates and selectivity to desired products. Reactions have been carried out in both batch autoclave reactor and in the continuous condensed-phase catalytic reactor.

1.8.4 Enhanced Acrylate Production from 2-Acetoxypropanoic Acid Esters

Acrylic acid and its esters are the starting materials for the production of polymers that are widely used in adhesives, paints, coatings, diapers, dispersants, etc. Acrylates are traditionally produced via a two-step propylene oxidation process, but recently their production from renewable feedstocks is receiving significant attention. Glycerol, 3-hydroxypropanoic acid, and lactic acid (2-hydroxypropanoic acid) have all been investigated as feed sources; of particular interest here is the formation and subsequent pyrolysis of 2-acetoxypropanoic acid esters (APA esters). Although this route has been known for a long time, our ability to achieve near-quantitative yields of APA and its esters from lactic acid and acetic acid via reactive distillation provides an incentive for further study of the pyrolysis step. Thus, reactor configurations and conditions for converting APA esters to acrylic acid esters in high yields have been examined and identified in this study [80].

2 Ethanol Guerbet Reaction

2.1 Introduction

Higher alcohols, such as *n*-butanol, can be produced via condensation of ethanol, also known as the Guerbet reactions. The availability of bioethanol is a major motivation for *n*-butanol production via this route [15]. Two possible reaction mechanisms for Guerbet reactions have been proposed: direct dehydration of the alcohols [17, 28, 81], and the more generally accepted three-step mechanism involving dehydrogenation, aldol condensation, and hydrogenation reactions. The latter is especially favored at lower reaction temperatures and over metal-containing catalysts [9, 15, 25].

Several heterogeneous and homogeneous catalytic systems have been proposed for Guerbet reactions. Heterogeneous catalysts are generally preferred due to lower separation costs and fewer environmental difficulties [15, 26]. Chief among these catalysts are MgO [17, 37, 38], multi-metal mixed oxides [21, 82, 83], hydroxyapatite [24, 29, 39, 84], alkali exchanged zeolites [28, 66], and alkaline activated carbon-supported catalysts [64, 65]. While most studies have failed to exceed a C_{4+} alcohol selectivity of 75% with ethanol conversions above 40%, there is consensus that an ideal acid-base balance is the key to the desired catalyst activity and higher alcohols selectivity.

Nickel metal supported on alumina has been recently introduced for the Guerbet reaction [8, 22, 59]. A significant property of this catalyst is its activity at lower temperatures (<250 °C), which not only allows the reaction to be run in the condensed phase at elevated pressures but also slows ethanol decomposition to undesired gaseous products such as CO₂ and CH₄. Jordison [9, 25] further improved conversion and selectivity of Ni/ γ -Al₂O₃ by adding La₂O₃ onto the support. This

modified catalyst gave a higher alcohol selectivity of 71% at an ethanol conversion of 55% in a stirred autoclave reactor at 230 °C and autogenous pressures.

In this chapter, we describe experiments conducted on the continuous condensed-phase Guerbet reaction. Several experiments have been performed to find the ideal reactor configuration and catalytic behavior of the Ni/La₂O₃/ γ -Al₂O₃ catalyst. Later, several catalysts of bimetallic combinations with nickel on the La₂O₃/ γ -Al₂O₃ support are studied to further optimize the catalytic performance of the reaction. Surface analysis and materials characterization techniques have been employed to assist with the catalytic studies. Finally, some experiments have been performed to assist with and confirm the proposed mechanism for the reaction.

2.2 Materials and Methods

2.2.1 Materials and Catalyst Preparation

Anhydrous ethanol (Koptec, 200 proof) was used as the feed in all experiments. In the monometallic experiments, Ni(NO₃)₂·6H₂O (99.999%, Aldrich) and La(NO₃)₃·6H₂O (>99%, Fluka) were used as catalyst precursors, and spherical 1.6mm diameter γ -Al₂O₃ (Strem Chemical) was used as the catalyst support. Three compositions of monometallic catalysts were prepared for this study: 8.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃, 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃, and 1.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃. The first composition of catalyst was prepared three different times with different impregnation and calcination times; that has affected the catalytic performance of the reaction. This will be discussed further in the following sections. Additionally, the first composition of the nickel catalyst (8.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃) was once made in big amounts (>500 g) to use for bimetallic catalyst preparation. This method of catalyst impregnation, named here as separate impregnation, assists with the integrity of the results while comparing different bimetallic mixtures with each other. In addition to the separate impregnation method, some catalysts were prepared by impregnating nickel and the second metal at the same time on the surface of the catalyst, named here as the co-impregnation method.

For the bimetallic experiments, Ni(NO₃)₂·6H₂O (99.999%, Aldrich), Cu(NO₃)₂·2.5H₂O (98%, Sigma-Aldrich), Co(NO₃)₂·6H₂O (98%, Sigma-Aldrich), Pd(NO₃)₂·xH₂O (40% Pd basis, Aldrich), Pt(NH₃)₄(NO₃)₂ (99.995%, Sigma-Aldrich), Fe(NO₃)·9H₂O (98+%, Sigma-Aldrich), NH₄·Mo₇O₂₄·4H₂O (81-83% MoO₃ basis, Sigma-Aldrich), and La(NO₃)₃·6H₂O (>99%, Fluka) were used as catalyst precursors. Catalysts were prepared using incipient wetness impregnation according to prior work [9]. To the alumina support, La₂O₃ was first impregnated by adding $La(NO_3)_3$ solution containing the desired quantity of lanthanum to the support in a quantity equal to the support pore volume, followed by drying at 130 °C for 20 h and calcination at 600 °C for 18 h in 50 ml/min N₂, to ensure the presence of La_2O_3 on the support surface. The same process was used for the addition of nickel and the second metal (starting with their aqueous starting material described above) to the La₂O₃/ γ -Al₂O₃ support, with an additional step of reducing metal oxides to the metal at 520 °C for 18 h using 50 ml/min H₂ at 1 atm. A complete description of the calculations and steps taken for the preparation of catalysts are described in Appendix A. All of the bimetallic catalysts in this study are prepared and reported on a weight basis. However, for simplicity, Table 2.1 shows the composition of metals in each of the bimetallic catalysts prepared in both mass and molar basis.

2.2.2 Reactor System

Reactions were performed in a 1.91 cm OD (1.57 cm ID) \times 76 cm length jacketed 316 stainless steel up-flow packed bed reactor with a 3 mm OD internal thermowell to measure the temperature profile in the reactor during the reaction. The reactor was heated with silicon oil using a Julabo

(Model SE-6) heating circulator, with the reaction temperature ranging from 170 °C to 250 °C. Silicon carbide (SiC, 20-50 mesh) was packed in the reactor inlet for preheating the feed, and stainless steel rod fillers were used on the top and bottom of the reactor to reduce the dead space inside the reactor. Figure 2.1 shows a schematic of the reactor system.

м		s %		Mole %						
IVI	Ni/M	Ni	Μ	Ni + M	La ₂ O ₃	Ni/M	Ni	Μ	Ni + M	La ₂ O ₃
-	-	8	-	-	9	-	13.9	-	-	2.8
Cu	2	7.7	3.8	11.5	8.7	2.2	13.1	6.0	19.1	2.7
Cu	20	8.0	0.4	8.4	9.0	22.7	13.6	0.6	14.2	2.7
Co	2	7.7	3.8	11.5	8.7	2.0	13.0	6.5	19.5	2.6
Pd	4	7.8	1.9	9.7	8.8	7.2	13.7	1.9	15.6	2.8
Pt	4	7.8	1.9	9.7	8.8	13.8	13.8	1.0	14.8	2.8
Fe	2	7.7	3.8	11.5	8.7	1.9	13.0	6.8	19.8	2.6
Mo	2	7.7	3.8	11.5	8.7	3.4	13.4	4.0	17.4	2.7

Table 2.1. Bimetallic catalyst compositions on a mass and molar basis. The balance is γ -Al₂O₃ in all cases. The data on the first row is for the 8.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃ catalyst that second metals are impregnated on. M is the second metal. Ni-Cu bimetallic is made in two different metal ratios.



Figure 2.1. Continuous flow reactor for ethanol conversion. (a - stainless steel rods; b - SiC packing for feed preheating; c - catalyst bed; d - thermowell; e - oil jacket)

Typically, 35 g of SiC and 29.9 g of catalyst supported on a quartz wool plug were placed in the reactor. The reactor was assembled and connected to the oil bath, and nitrogen gas was passed through the catalyst to purge air and ensure the absence of any leaks in the reactor system and connections. Then hydrogen gas was passed through the catalyst for 90 min after it reached the desired temperature to reduce surface nickel oxidized by exposure to air. A BioRad (Model 1350) liquid chromatography pump was used for dispensing liquid ethanol feed to the reactor. Liquid flow rates varied from 0.3 ml/min to 1.3 ml/min, corresponding to a weight hourly space velocity (WHSV) of 0.5-2.1 kg ethanol/kg catalyst/h. A pressure relief valve was connected to the reactor outlet. The reactor effluent was cooled to ambient temperature in a double pipe heat exchanger using building water as the coolant. A Tescom (Model 26-1764-24) back pressure regulator was used to control reactor pressure at 100 bar and reduce the effluent pressure to near atmospheric. Following pressure reduction, condensable products were recovered in collection vessels submerged in an ice bath (0 °C), and gaseous products that passed through the collection vessels were collected periodically in gas bags. Steady state was assumed to be achieved after 6-8 superficial residence times of feed materials through the reactor.

Initial experiments were conducted at the feed flow rate of 1.10 ml/min of ethanol at 230 °C using 29.9 grams of catalyst. This value was based on the observed conversion rate by Jordison et al. [9] in the batch reactor experiments using the same catalyst to give a reasonable conversion in the flow system. Details of the calculations of obtaining this number are available in Appendix B. The flow rate and temperature of the reaction were further modified in the later experiments to achieve optimum values of ethanol conversion and C_{4+} selectivity.

2.2.3 Analytical Methods

Liquid product samples were diluted 10-fold in acetonitrile and analyzed using a Varian 450 gas chromatograph (GC) with a flame ionization detector. A 30 m SolGel-Wax column (0.53 mm ID, 1 mm film thickness) was used with the following temperature program: initial temperature 37 °C for 4 min; ramp at 10 °C/min to 90 °C, and hold at 90 °C for 3 min; ramp at 10 °C/min to 150 °C; ramp at 30 °C/min to 230 °C and hold for 2 min. Butyl hexanoate 1% solution was used as an internal standard to improve the precision of the analytical calculations. Gas samples were analyzed using a Varian 3300 GC with a thermal conductivity detector. A 4.57 m 1.25 mm SS 60/80 Carboxen 1000 column (2.1 mm ID) was used with the following temperature program: initial temperature 35 °C for 5 min, then ramp at 20 °C/min to 225 °C.

The concentration of each species in the product mix was determined using response factors obtained from multi-point calibration curves. Response factors for unidentified components appearing in the chromatogram were taken as average values for species in close proximity to unidentified components. The calculated concentrations were entered into an in-house Excel spreadsheet to calculate ethanol conversion, product selectivity (mol ethanol to product/mol ethanol converted), product yield (mol ethanol to product/mol ethanol fed), and overall carbon recovery.

Karl Fischer titration was used to determine the water content in the feed and reaction products. Three titrations of each sample were employed to confirm the accuracy of the results.

2.2.4 Catalyst Characterization

Total (BET) surface area, pore volume, and pore diameter measurements were done using a Micromeritics ASAP 2010 Plus Physisorption apparatus with nitrogen adsorption at -195 °C. Prior to analysis, samples were degassed at 150 °C for 24 h.

Acid and base site densities and H₂ uptake of the catalysts were measured using Micromeritics Autochem II chemisorption analyzer. Ammonia and carbon dioxide temperature programmed desorption technique (TPD) were used for acid and base site density measurement, respectively. Catalysts were outgassed under helium flow by ramping the temperature at 10 °C/min to 600 °C and holding it at 600 °C for 60 minutes, followed by cooling the sample at 90 °C/min to 25 °C and holding it for 10 minutes. A 50 ml/min flow of ammonia or carbon dioxide was passed across the samples for 30 minutes at 25 °C. The physisorbed gases were cleaned by the 50 ml/min flow of helium at 25 °C for 180 minutes. Chemisorbed gases were desorbed by ramping the temperature at 10 °C/min to 600 °C and holding it at 600 °C for 180 minutes under the 50 ml/min flow of helium; the amount desorbed was measured by recording and integrating the derived intensity signal.

For measuring the hydrogen uptake, samples were outgassed by the flow of argon ramping at 10 $^{\circ}$ C/min to 600 $^{\circ}$ C and holding it at 600 $^{\circ}$ C for 60 minutes, followed by cooling it at 30 $^{\circ}$ C/min to 27 $^{\circ}$ C and holding it at 27 $^{\circ}$ C for 5 minutes. The hydrogen gas at the flow rate of 25 ml/min was passed across the catalysts at the same temperature for 120 minutes. Adsorbed hydrogen molecules were desorbed by 25 ml/min flow of argon ramping at 25 $^{\circ}$ C/min to 600 $^{\circ}$ C and holding it at 600 $^{\circ}$ C for 180 minutes. Desorption intensity signals were recorded and integrated for calculating the H₂ uptake of the catalysts.

The surface elemental distribution of the catalysts was monitored and measured via scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) using Carl Zeiss Variable Pressure SEM EVO LS25 at high vacuum mode. Although samples were sputter-coated with platinum to avoid their oxidation at room temperature before analysis, some oxidation was observed during the transition of the catalysts from preparation reactor to the sputter area.

This oxidation affected the SEM images quality, but not the molar ratios obtained from EDS analysis.

2.3 Experimental results

2.3.1 Control Experiments

Control experiments with La₂O₃/ γ -Al₂O₃ gave less than 2% ethanol conversion and less than 20% selectivity to desired condensation products, an indication that the metal-free support is inactive, and that Ni plays a key role in Guerbet reactions. Inert gas (N₂) and liquid (*t*-butanol) feeds were also fed to the reactor at typical reaction conditions (T= 230 °C, WHSV= 1.42 h⁻¹) to ensure that the mass balance closed to 100% and there was no leak in the system.

2.3.2 Nickel Monometallic Catalytic Experiments

Throughout the discussions on this chapter, all produced alcohols with more than six carbons are described as a single product denoted as C_{6+} alcohols. In most of the experiments, C_{6+} alcohols contain a similar product distribution. Figure 2.2 shows the typical molar distribution of C_{6+} alcohols in most of the experiments conducted.



Figure 2.2. Typical C_6 + *alcohols molar distribution. Negligible amounts of 1-decanol are also present.*

The overall material balance (=outlet flow/inlet flow \times 100) had a closure of 95%-101% in all of the experiments. Furthermore, carbon backbone recovery for most of the experiments was in the range of 94%-99%. This recovery is reported for each single experiment via the total reaction selectivity in Appendix D.3 and Appendix E.3. Finally, to assure that most of the water present in the system is the product of the Guerbet reaction, the theoretical amount of water formed in samples were calculated based on the stoichiometric conversion of the moles of higher alcohols and aldehydes. This value was divided by the water content from Karl Fischer titrations for some representative samples at different ethanol conversion ranges. For most of the cases, this ratio was in the range of 75%-85%. The difference could be due to the occurrence of water producing side-reaction, such as diethyl ether and methane production.

Reactor configuration for the 8.0 wt% Ni/4.5 wt% La_2O_3/γ -Al₂O₃ catalyst was studied to find the range of parameters at which this catalyst and similar ones demonstrate optimum performance for the Guerbet reaction. For this purpose, ethanol conversion and higher alcohols selectivity were studied at different temperatures and feed flow rates.

Figure 2.3 shows the performance of the Guerbet reaction at different temperatures. At the temperature of 210 °C, the maximum C₄+ alcohols selectivity of 71% is observed. Furthermore, ethanol conversion and gases selectivity increase with increasing temperature. Based on the ethanol conversion at different temperatures and assuming second order kinetics for the reaction, an activation energy was calculated for this catalyst. The activation energy obtained for the Guerbet reaction and the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst is around 121 kJ/mol. Details of the calculations are shown in Appendix C.



Figure 2.3. Temperature dependence of the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst for the Guerbet reaction (WHSV= 1.4 h⁻¹)

Next, the effect of feed flow rate on reaction performance at the temperature of 210 °C was studied. Weight hourly space velocity of the ethanol feed was calculated by dividing the mass flow rate of ethanol by the mass of the catalyst present in the reaction zone. As shown in Figure 2.4, at WHSV of 0.8 h⁻¹ and higher, the selectivity of C₄+ components stays around the maximum value of 73%. Moreover, the selectivity toward gaseous products and ethanol conversion decrease as WHSV increases. Thus, the optimum value for the WHSV is about 0.8 h⁻¹ for the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst.

Besides the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst, throughout the studies of the nickel monometallic catalyst several other nickel-based catalysts were made that varied by their nickel content, lanthanum content, preparation method, and metal dispersion. A detailed list of the experiments conducted on these catalysts, along with ethanol conversion and selectivity toward different products, are shown in Appendix D. For simplicity, these catalysts are labeled with

specific Roman numerals (i.e. Ni (I), Ni (II), etc.). Furthermore, Table 2.2 offers a representation of the performance of all of these nickel-based catalysts at a common experimental condition (T= 210 °C, WHSV= 1.42 h^{-1}) and other conditions with high product selectivity, along with the results of the surface analysis performed on them. Methane and ethyl acetate selectivity are also presented in the table as the key gaseous and liquid side-products formed. Other gases formed in reaction include CO, CO₂, CH₄, C₂H₆, and C₃H₈; other liquid byproducts were diethyl ether, acetaldehyde, butyraldehyde, and several unidentified components. The best experimental results obtained for the nickel monometallic catalysts belong to the 1.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃, with the C₄+ alcohols selectivity as high as 79% and the conversion of 22%, and the C₄+ alcohols selectivity as high as 74% and the conversion of 41%.



Figure 2.4. Weight hourly speed velocity (WHSV) dependence of the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst for the Guerbet reaction (T=210°C)

T WHSV		Conv.		Se	lectivit	y (%)		Acidic	Basic	H_2	
(°C)	(h ⁻¹)	(%)	C ₄ OH	C ₆ + OH	C ₄ + OH	CH_4	Ethyl Acetate	Sites (µmol/g)	Sites (µmol/g)	Chemisorbed (µmol/g)	
	Ni (I): 8.0 wt% Ni/4.5 wt% La ₂ O ₃ /γ-Al ₂ O ₃										
210	1.42	22	58	13	71	12	3	640	220	50	
230	1.42	42	46	13	59	18	0	040	220	30	
	Ni (II): 8.0 wt% Ni/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃										
210	1.42	28	52	15	68	12	2	590	320	73	
	Ni (III): 8.0 wt% Ni/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃										
210	1.42	8	60	13	73	6	1		550 300 11		
230	1.42	16	61	18	79	6	2	550 300		11	
250	1.42	30	54	18	72	8	2				
			Ni	(IV): 8.	0 wt%	Ni/9.0 v	wt% La ₂ C	O ₃ /γ-Al ₂ O ₃			
210	1.42	18	54	15	69	8	2	580	320	42	
	Ni (V): 1.0 wt% Ni/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃										
210	1.42	7	68	10	78	5	0		600 290		
230	0.79	22	58	20	79	6	1	(00		11	
250	0.79	41	51	23	74	8	1	000			
250	1.42	29	54	21	75	7	1				

Table 2.2. Comparison of the performance of different Ni/La₂O₃/ γ -Al₂O₃ catalysts and their surface characteristics.

Comparing the quantity of basic sites in different catalysts shows the direct effect of La_2O_3 loading on the basicity of the particles. Although the constructive effect of La_2O_3 presence on the selectivity to desired products has been discussed before [9], the results of this study do not reveal any correlation between the quantity of La_2O_3 and the performance of the catalyst.

Experimental results of catalysts with different nickel loadings at similar conditions show that the 1.0 wt% nickel catalyst has lower conversion than those with 8.0 wt% nickel, but less gas and liquid byproduct formation and overall higher selectivity to higher alcohol products. Furthermore, as discussed earlier for the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst (labeled as Ni (I)), for each

catalyst, as temperature increases or as space velocity decreases, ethanol conversion increases, selectivity to C_{4+} alcohols declines, and the quantity of gas and liquid byproducts formed increases.

The catalyst labeled as Ni (III) shows a lower ethanol conversion rate than the two other catalysts with the same composition (Ni (II) and Ni (IV)). The main cause for this observation is that this catalyst was made in large scales (~2 kg) for the nickel bimetallic experiments. This could affect the nickel particles during the calcination and reduction steps in two ways. First, nickel sintering or deactivation could occur during these large-scale exothermic processes in the areas with extremely high temperatures. Second, nitrogen and hydrogen diffusion through central catalytic particles could be interrupted by the surrounding particles, leading to inefficient and non-uniform calcination and reduction. These effects are further confirmed by measuring the hydrogen uptake of each of the catalysts, as shown in Table 2.2. The results indicate that the Nickel (III) catalyst has the lowest hydrogen uptake to nickel content ratio of all the catalysts. Considering that surface nickel atoms alone are responsible for the hydrogen adsorption, this observation justifies the correlation between the catalyst activity for the Guerbet reaction and the number of nickel sites on the catalyst surface. This will be further discussed in Section 2.3.4.

2.3.3 Nickel Bimetallic Catalytic Experiments

2.3.3.1 Experimental Discussion

Several metals (Cu, Co, Pd, Pt, Fe, and Mo) were impregnated on Ni catalyst as second metals in this study. As mentioned in previous sections, for consistency of the results, these metals were all impregnated to the 8.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃ catalyst labeled as Ni (III) that had been prepared in a large amount. A complete list of the experimental conditions of the bimetallic and nickel-free monometallic catalytic experiments with the selectivity toward different products are

reported in Appendix E. Among different catalysts studied at different experimental conditions, best results are for the co-impregnated 8.4 wt% (Ni/Cu 20/1)/9.0 wt% La₂O₃/ γ -Al₂O₃ catalyst with 74% C₄+ selectivity and 35% ethanol conversion at T= 250 °C and WHSV= 1.42 h⁻¹ and 78% C₄+ selectivity and 15% ethanol conversion at T= 230 °C and WHSV= 2.06 h⁻¹.

Table 2.3 compares the results of these bimetallic catalysts with the Ni (III) catalyst at a common experimental condition (T= 230 °C, WHSV= 1.42 h⁻¹) along with presenting results of the surface studies conducted on them. All of the catalysts that are reported in this table were prepared using the separate impregnation method. The Ni-Cu bimetallic catalyst shows an interesting behavior in having higher selectivity for butanol and lower selectivity toward longer chain alcohols (C_{6+}). This behavior could advantage processes that desire butanol as their main product since it produces more of this component. An example of this type of process is discussed in detail in Chapter 3. The Ni-Co bimetallic catalyst shows a substantial improvement in ethanol conversion, while the C_4 + activity is still in the 60%+ range. However, through analyzing other experimental conditions for this catalyst, not more than 66% C₄+ selectivity was achieved at conversions of more than 30%. These two bimetallic combinations are further studied based on their metal ratio, impregnation method, and monometallic behavior, which will be discussed later in this section. Other bimetallic combinations in Table 2.3 were not successful in either reducing the selectivity of one or more of the side-products or improving the selectivity/conversion of the desired components. However, in all those experiments, butanol was still the main product.

2.3.3.2 Surface Characterization

To get a better understanding of the trends observed for the bimetallic catalysts' performance, BET surface area analysis, NH₃, CO₂, and H₂ temperature programmed desorption (TPD) analysis were conducted on each catalyst. While the results of these studies are summarized in Table 2.3,

Appendix F shows the detailed profiles of CO₂, NH₃, and H₂ TPD for the Ni (III) catalyst and all of the bimetallic catalysts in Table 2.3. BET surface studies show that all of the catalysts are in the same range of available surface area (120-130 m²/g). Considering that the available BET surface area for both γ -Al₂O₃ and 9.0 wt% La₂O₃/ γ -Al₂O₃ supports are in the range of 140-150 m²/g, BET results from this table indicate that the metal particles impregnated on the surface of the support are mostly small enough not to cover the pores of the catalyst. Thus, they do not reduce the available surface area.

Table 2.3. Bimetallic catalysts experimental results and surface analysis comparison with the Ni (III) catalyst. Experiments are conducted at $T = 230^{\circ}C$ and $WHSV = 1.42 h^{-1}$ with ethanol as the feed. a: Ethyl Acetate b: Diethyl Ether. All bimetallic catalysts are prepared with the separate impregnation method.

Conv.	Selectivity (%)							BET	Acidic	Basic	H_2
(%)	C ₄ OH	C ₆ + OH	C ₄ + OH	CH ₄	CO_2	Eth. Ac. ^a	DEE ^b	area (m²/g)	Sites (µmol/g)	Sites (µmol/g)	Chemisorbed (µmol/g)
Ni (III): 8.0 wt% Ni/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃											
16	61	18	79	6	1	2	2	130	550	300	11
11.5 wt% (Ni/Cu 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃											
17	66	7	73	7	2	1	5	120	530	250	4
11.5 wt% (Ni/Co 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃											
33	43	23	66	7	2	1	0	120	540	330	13
				9.7 v	vt% (N	Ni/Pd 4	/1)/8.8 w	t% La ₂ C) ₃ /γ-Al ₂ O ₃		
20	53	14	67	5	1	1	7	120	600	390	21
	-	-		9.7 v	vt% (1	Ni/Pt 4/	/1)/8.8 w	t% La ₂ O) ₃ /γ-Al ₂ O ₃		
21	49	8	56	16	7	2	4	120	530	260	40
11.5 wt% (Ni/Fe 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃											
22	44	5	49	15	3	8	8	120	510	250	9
				11.5 v	vt% (1	Ni/Mo 2	2/1)/8.7 v	vt% La ₂	O ₃ /γ-Al ₂ O ₃		
9	51	2	54	3	0	14	1	120	590	110	3

 NH_3 and CO_2 TPD analysis demonstrate a correlation between selectivity toward the desired products and the base/acid ratio on the surface of the catalyst. This correlation, discussed

extensively in Chapter 1, has been previously acknowledged by many researchers [15, 23, 24, 39, 42-45, 56]; however, the reported base/acid ratio number seems to be varying based on the catalyst used and the operational conditions (phase, temperature, pressure, flow rate). In this study, the base/acid ratio for the Ni (III) catalyst is 0.6; as we deviate from this number in nickel bimetallic combinations, the selectivity toward C_{4+} alcohols declines. For instance, while this ratio for Ni-Cu bimetallic catalyst with the best performance among those studied is 0.5, for the Ni-Mo bimetallic catalyst, with the lowest C_{4+} alcohols selectivity, this number is 0.2. Nevertheless, the base/acid ratio is not the only factor determining the performance of the reaction; several other parameters such as base/acid site strength, metal dispersion on the catalyst surface, and hydrogenmetal bond strength need to be considered as well.

Trends obtained for the H_2 chemisorbed on the surface of the bimetallic catalysts in this study are in agreement with several papers in the literature [70-75]. Addition of copper to the nickel catalyst would lower the total amount hydrogen adsorbed on the surface of the catalyst since this catalyst does not promote hydrogen adsorption and is covering the surface of some of the available nickel metal sites [74]. This could justify why Ni-Cu bimetallic catalyst tends to produce more butanol rather than C₆+ alcohols. Having less available dissociated hydrogen on the surface of the metal not only will reduce the total selectivity of the Guerbet reactions, but also can preserve the produced butanol from further reacting into higher alcohols. A similar trend of hydrogen adsorption is observed for the addition of iron and molybdenum to the nickel catalyst. Cobalt addition, on the other hand, does not significantly promote or obstruct hydrogen adsorption on the surface of the catalyst. The difference observed in the performance of this catalyst compared to the nickel monometallic catalyst could be due to its different surface structure that promotes the production of side-products rather than higher alcohols [59]. Palladium and platinum addition have expectedly improved the hydrogen uptake of the catalyst drastically. These two metals are known for their strong ability to both adsorb and desorb hydrogen [70-73]. This explains the observed improvement in the activity of these catalysts. In addition, a decline in the selectivity toward C_{4+} alcohols is observed due to the strong metal-hydrogen bond formation that impedes the hydrogenation step and promotes the side-reactions. The strength of metal-hydrogen bonds can be assessed based on the H_2 TPD profiles that are presented in Figure F.3 in Appendix F.

Based on the assumption that all nickel, platinum, and palladium particles are capable of adsorbing H_2 , and that these particles are on the surface of the support without covering each other, metal dispersion and particle diameter can be calculated from the H_2 uptake results obtained. Calculations below, starting with the bulk metal density of each metal, describe the process performed for calculating these two quantities.

Atomic Volume
$$\left(\frac{m^3}{atom}\right) = \frac{1}{bulk \ metal \ density} \left(\frac{m^3}{g}\right) \times molecular \ weight \left(\frac{g}{mol}\right) \times 6.022 \times 10^{23} \left(\frac{mol}{atom}\right)$$

Assuming that bulk atoms are cubical with "a" being each edge's length, we can say that the atom volume is " a^{3} " with an exposed surface area of " a^{2} ". Therefore,

$$a = \frac{atomic \ volume}{atomic \ exposed \ surface \ area}$$
 Equation 2.1

where "*a*" is a property of the crystalline metal (2.22 for Ni, 2.45 for Pd, and 2.47 for Pt). Furthermore, considering that each mole of molecular hydrogen adsorbs onto two moles of metal, the bulk catalyst dispersion can be calculated using the amount of H_2 uptake. Note that for the bimetallic catalysts, the H_2 uptake by nickel is subtracted from the total H_2 uptake.

$$\begin{aligned} \text{Dispersion} &= H_2 \text{ uptake } \left(\frac{\text{mol } H_2}{\text{g catalyst}}\right) \times 2 \frac{\text{mol surface metal}}{\text{mol } H_2} \times \frac{1}{\text{metal } wt\%} \left(\frac{\text{g catalyst}}{\text{g metal}}\right) \\ &\times \text{MWmetal } \left(\frac{\text{g bulk metal}}{\text{mol bulk metal}}\right) = \frac{\text{surface exposed metal atoms}}{\text{bulk metal atoms}} \end{aligned}$$

Multiplying Equation 2.1 and Equation 2.2 with the assumptions we have uniform spherical catalyst particles with diameter "D" gives:

$$\frac{1}{a} \times Dispersion = \frac{metal \ particle \ surface \ area}{metal \ particle \ bulk \ volume} = \frac{\pi D^2}{1/_6 \pi D^3} = \frac{6}{D}$$
Equation 2.3

By performing the above calculations, the following equations will be derived for each one of the three metals. In addition, Table 2.4 represents the dispersion and the derived particle diameters for these metals. Results indicate that the second metals form significantly smaller particles and are more dispersed compared to the nickel particles.

$$D_p(\text{\AA})_{Nickel} \approx \frac{1330}{disp.(\%)}$$
 Equation 2.4

$$D_p(\text{\AA})_{Palladium} \approx \frac{1470}{disp.(\%)}$$
 Equation 2.5

$$D_p(\text{\AA})_{Platinum} \approx \frac{1480}{disp.(\%)}$$
 Equation 2.6

For understanding the distribution pattern of the components of the bimetallic catalysts, surface elemental analysis was conducted using Scanning Electron Microscopy (SEM) incorporated with Energy Dispersive Spectroscopy (EDS). Figure 2.5 shows a representative picture of the co-impregnated 11.5 wt% (Ni/Cu 2/1)/8.7 wt% La₂O₃/ γ -Al₂O₃ catalyst. Based on EDS results obtained at different regions of this catalyst, darker areas are rich in nickel and lighter areas are rich in copper. Nickel particles visible in this image are in the similar size range as the nickel particle diameter obtained based on the calculations described above.

Ni Dispersion (%)	Ni Particle D (nm)	2 nd Metal Dispersion (%)	2 nd Metal Particle D (nm)					
9.7 wt% (Ni/Pd 4/1)/8.8 wt% La ₂ O ₃ /γ-Al ₂ O ₃								
1.6	82.5	10.9	13.5					
9.7 wt% (Ni/Pt 4/1)/8.8 wt% La ₂ O ₃ /γ-Al ₂ O ₃								
1.6	82.5	57.7	2.7					

Table 2.4. Metal particle diameter and dispersion for the Ni-Pd and Ni-Pt bimetallic catalysts. Numbers are calculated based on the H_2 uptake.



Figure 2.5. SEM picture from the co-impregnated 11.5 wt% (Ni/Cu 2/1)/8.7 wt% La₂O₃/γ-Al₂O₃ catalyst.

Table 2.5 shows the surface elemental distribution of the components of the bimetallic catalysts and their comparison with the bulk molar percentages impregnated. La/Al and Ni/Al molar ratios are in close proximity with the bulk molar ratios, which supports the result obtained from BET studies indicating that lanthanum and nickel particles are not covering the pores. However, in most cases (except the Ni-Co bimetallic catalyst), the nickel to second metal ratio is smaller than the bulk ratio. This could be due to two main reasons. First, the second metal has formed smaller particle sizes compared to nickel particles, as suggested in the calculations performed for palladium and platinum particles, which increases its available surface area compared to nickel. Second, the second metal is covering the surface of nickel particles, as proposed for the Ni-Cu bimetallic catalyst, based on its decrease in H₂ uptake compared to the nickel monometallic catalyst.

La/Al (molar)		Ni/Al (molar)		Ni/M (molar)						
surface	bulk	surface	bulk	surface	bulk					
Ni (J	Ni (III): 8.0 wt% Ni/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃									
0.03	0.03	0.07	0.08	-	-					
11.5 wt% (Ni/Cu 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃										
0.03	0.03	0.09	0.08	2.12	2.2					
11.5	11.5 wt% (Ni/Co 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃									
0.04	0.03	0.11	0.08	3.06	2.0					
9.7	wt% (Ni	/Pd 4/1)/8.8	wt% La	a2O3/γ-Al2C)3					
0.02	0.03	0.09	0.08	1.03	7.3					
9.7	wt% (Ni	/Pt 4/1)/8.8	wt% La	a2O3/γ-Al2O	3					
0.04	0.03	0.07	0.08	4.29	13.3					
11.5	wt% (N	i/Fe 2/1)/8.7	7 wt% L	a2O3/γ-Al20)3					
0.04	0.03	0.08	0.08	0.86	1.9					
11.5	wt% (Ni	/Mo 2/1)/8.	7 wt% I	a_2O_3/γ -Al ₂	03					
0.03	0.03	0.07	0.08	2.04	3.3					

Table 2.5. Surface elemental analysis conducted on bimetallic catalysts using SEM/EDS.

2.3.3.3 <u>Ni-Cu and Ni-Co Detailed Experiments</u>

Since Ni-Cu and Ni-Co bimetallic catalysts showed some improvement in butanol selectivity and ethanol activity, respectively, these catalysts were subjected to further investigations to assess their potential for improving the overall performance of the Guerbet reaction. Ni-Cu bimetallic catalyst was tested at different metal ratios and impregnation methods. Besides, the monometallic copper catalyst was examined to better understand the trends observed for the Ni-Cu bimetallic catalyst. This study was performed on the cobalt monometallic catalyst as well. Table 2.6 represents the results of these studies.

Conversion $(0/)$	Selectivity (%)									
Conversion (%)	C ₄ OH	C ₆ + OH	C ₄ + OH	Ethyl Acetate	Gases					
Ni (III): 8.0 wt% Ni/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃										
16	61	18	79	2	11					
8.4 wt% (Ni/Cu 20/1)/9.0 wt% La ₂ O ₃ /γ-Al ₂ O ₃ (Co-Impregnation)										
18	65	11	76	3	12					
11.5 wt% (Ni/	11.5 wt% (Ni/Cu 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃ (Co-Impregnation)									
17	71	6	77	2	11					
11.5 wt% (Ni/Cu 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃ (Sep-Impregnation)										
11.5 wt% (Ni/C	u 2/1)/8.	7 wt% La	$_{2}O_{3}/\gamma$ -Al ₂ O	D ₃ (Sep-Impregr	nation)					
11.5 wt% (Ni/C 17	u 2/1)/8. 66	7 wt% La	2 O₃/γ-Al₂C 73)₃ (Sep-Impregn 1	nation) 13					
11.5 wt% (Ni/C 17	u 2/1)/8. 66 8.0 wt%	7 wt% La ₂ 7 Cu/9.0 wt	2 O 3/γ-Al2C 73 % La2O3/γ	D ₃ (Sep-Impregr 1 7-Al ₂ O ₃	nation) 13					
11.5 wt% (Ni/C 17 10	u 2/1)/8. 66 3.0 wt% 6	7 wt% La 7 Cu/9.0 wt 0	2 Ο 3/γ-Al2C 73 % La2O3/γ 6)₃ (Sep-Impreg 1 /-Al₂O₃ 62	13					
11.5 wt% (Ni/C 17 8 10 11.5 wt% (Ni/C	u 2/1)/8. 66 3.0 wt% 6 0 2/1)/8.	7 wt% La 7 Cu/9.0 wt 0 7 wt% La	2 O ₃ /γ-Al ₂ O 73 % La ₂ O ₃ /γ 6 2O ₃ /γ-Al ₂ O) ₃ (Sep-Impregr 1 /-Al ₂ O ₃ 62) ₃ (Sep-Impregr	13 5 nation)					
11.5 wt% (Ni/C 17 8 10 11.5 wt% (Ni/C 33	u 2/1)/8. 66 3.0 wt% 6 o 2/1)/8. 43	7 wt% La; 7 Cu/9.0 wt 0 7 wt% La; 23	2 Ο ₃ /γ-Al ₂ C 73 % La ₂ O ₃ /γ 6 2 Ο ₃ /γ-Al ₂ C 66) ₃ (Sep-Impregr 1 /-Al₂O₃ 62) ₃ (Sep-Impregr 2	nation) 13 5 nation) 16					
11.5 wt% (Ni/C 17 8 10 11.5 wt% (Ni/C 33 8	u 2/1)/8. 66 6 6 0 2/1)/8. 43 3.0 wt%	7 wt% La 7 Cu/9.0 wt 0 7 wt% La 23 Co/9.0 wt	2 O ₃ /γ-Al ₂ O 73 % La ₂ O ₃ /γ 6 2 O ₃ /γ-Al ₂ O 66 % La ₂ O ₃ /γ	3 (Sep-Impregn 1 7-Al ₂ O ₃ 62 03 (Sep-Impregn 2 7-Al ₂ O ₃	nation) 13 5 nation) 16					

Table 2.6. Different nickel, copper, and cobalt based catalysts studied. All results are at $T = 230 \,^{\circ}C$ and $WHSV = 1.42 \, h^{-1}$.

For the Ni-Cu experiments, the impregnation method does not significantly affect the experimental results. On the other hand, as the copper content increases in the bimetallic catalyst, the effect of shifting the selectivity toward butanol instead of C_6 + alcohols become more evident. Furthermore, lower catalyst activity at high copper loading is attributed to the formation of isolated CuO instead of the inverse spinel CuAl₂O₄ structure on the surface [58]. Moreover, the amount of gases formed in the monometallic copper catalyst is significantly lower compared to the other two monometallic catalysts. This is due to the ability of copper in preserving the carbon-carbon bond, therefore reducing the chance of ethanol decomposition.

Although low selectivity for ethyl acetate is obtained in the Ni-Cu and Ni-Co bimetallic catalysts, this chemical is the main product of the monometallic copper and cobalt catalysts. Reported

likewise by other research groups [59, 85-88], this observation is attributed to the metal specific causes. For the copper catalyst, coordinatively unsaturated Cu^+ ions are the active centers for ethyl acetate formation. While octahedrally coordinated metal cations are known as ideal structures for the Guerbet reaction, the tetrahedrally coordinated Co^{2+} sites are responsible for the ethyl acetate formation. In addition, the larger crystalline size of copper and cobalt particles compared to nickel on alumina surface suggests that these metals have different types of interactions with the support, leading to the formation of different products [59, 85, 86].

Finally, among the three monometallic catalysts studied, cobalt has the highest activity. This observation is justified by the cobalt's higher d-band center compared to the other two catalysts, corresponding to a lower energy required to activate the metal-hydrogen interaction, and its subsequent higher activity [59].

2.3.4 Mechanistic and Kinetic Studies

Multiple experiments were conducted to investigate the active mechanism and the rate-limiting step of this mechanism for the condensed-phase Guerbet reaction over metallic and bimetallic catalysts. These experiments are discussed in this section.

Throughout the experiments on the Guerbet reaction, there was evidence confirming the occurrence of the aldol condensation mechanism. First, the low ethanol conversion in control experiments with 9.0 wt% La₂O₃/ γ -Al₂O₃ catalyst supports the significant role of nickel as the promoting agent for activating the catalyst. As discussed in Chapter 1, metallic sites are prerequisite for only the aldol condensation mechanism and not the direct dehydration mechanism. Thus, the fact that non-metallic support shows ethanol conversion of less than 3% even at 250 °C supports aldol condensation as the main mechanism for this reaction. Second, experiments show that the addition of acetaldehyde to ethanol feed improves the performance of the Guerbet reaction

accordingly, which confirms the role of acetaldehyde as an active component in the Guerbet mechanism. Finally, to investigate the mechanism of the reaction further, acetaldehyde was fed to the reactor as the sole reactant. The main product formed in acetaldehyde experiments was the condensation product (crotonaldehyde), additional evidence supporting that the Guerbet reaction is proceeding through aldol condensation.

Acetaldehyde experimental results, summarized in Table 2.7, provides further information regarding the kinetics and thermodynamics of the system. The temperature required to activate acetaldehyde is significantly lower than that to activate ethanol; experiments showed that at the temperature range of 210 °C-250 °C, acetaldehyde completely reacts to dimers and polymers that can quickly block the catalysis zone. Therefore, acetaldehyde experiments were conducted in the temperature range of 110 °C-130 °C. This is an indicator that acetaldehyde is significantly more active compared to ethanol and its condensation could not be the rate-limiting step of the Guerbet mechanism.

T (9C)	Conversion	Selectivity (%)					
I (C)	(%)	Crotonaldehyde	Ethanol	Sum All			
110	32.1	45.1	4.7	72.8			
120	54.9	49.9	2.6	77.4			
130	86.6	37.1	2.2	68.1			

Table 2.7. Acetaldehyde experiments over Ni (III) catalyst. All experiments are done at WHSV= 1.42 h⁻¹.

The sum of all chemical selectivities in acetaldehyde experiments is in the range of 65%-80%. This is due to the number and quantity of unidentified liquid compounds in this system. For measuring the unknown product selectivity, a hypothetical average stoichiometry coefficient of three was considered, which might be too low since the chemicals in the system were highly active and capable of forming dimers and longer molecules with a higher stoichiometry ratio. Adjusting

this coefficient to 6.1 for the unknown products will improve the sum of the selectivities to the range of 98%-103%, which further supports this hypothesis. It is worthwhile to note that the mass closure (mass out/mass in) in all of the acetaldehyde experiments are in the range of 96%-102%.

Aside from acetaldehyde experiments, H_2 uptake analysis provides additional evidence for considering the first step of the reaction as rate limiting. It was discussed in Section 2.3.2 that there is a correlation between the amount of H_2 uptake in the 8% nickel catalysts and their activity for the Guerbet reaction. This correlation is shown in Figure 2.6 based on the data from Table 2.2. The linear correlation suggests that the number of available nickel sites for dehydrogenating ethanol molecules is the limiting factor in shifting the reaction toward higher C_4 + alcohols yield. This is a clear evidence that the dehydrogenation step is the rate-limiting step of the Guerbet reaction.



 H_2 Chemisorbed (µmol/g)

*Figure 2.6. Correlation between H*² *adsorption on the surface of different 8 wt% nickel catalysts and the Guerbet products' yield.*

Butanol was also fed to the reactor, and product analysis was done to help with understanding the behavior of the reaction. Feeding butanol to the reactor at 210 °C and 1.42 h⁻¹ flow rate resulted in 16% butanol conversion, 2% ethanol selectivity, and 31% C₆+ selectivity. Considering that feeding ethanol under the similar conditions led to 22% ethanol conversion, 58% butanol selectivity and

13% C_{6+} selectivity, it can be concluded that the ethanol Guerbet reaction at the mentioned conditions is not at thermodynamic equilibrium.

2.4 Conclusions

The continuous condensed-phase reaction of ethanol to *n*-butanol and C_{6+} alcohols has been demonstrated in a laboratory fixed bed reactor. Experimental studies on different Ni/La₂O₃/ γ -Al₂O₃ catalysts show that the WHSV of >0.8 h⁻¹ and the temperature range of 210-250 °C are the optimum conditions for the system. La₂O₃ content of the catalyst is the main contributor to the number of basic sites on the surface of the catalyst. Moreover, the number of Ni sites on the catalyst surface correlate directly with the performance of the Guerbet reaction, a strong evidence that the dehydrogenation step is the rate-limiting step for the Guerbet reaction.

Among several bimetallic nickel catalysts studied for improving the performance of the reaction, Ni-Cu bimetallic was able to shift the reaction selectivity toward *n*-butanol rather than C_{6+} alcohols, and Ni-Co bimetallic catalyst improved the activity of ethanol with no evidence of improving the desired products' selectivity. Both Cu and Co monometallic catalysts were tested in separate experiments and favored the production of ethyl acetate rather than higher alcohols. The base/acid molar ratio of 0.5-0.7 seems to be the necessary, but not sufficient, condition to obtain optimum C_{4+} selectivity. Presence of the right amount of metal sites that are capable of forming metal-hydrogen bonds with the ideal strength is another important benchmark.

Mechanistic studies confirm the aldol condensation mechanism as the governing one for condensed phase Guerbet reaction using the La₂O₃/ γ -Al₂O₃ supported nickel catalysts and introduce the dehydrogenation step as the rate-limiting step of the reaction. Among different catalysts studied, 1.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃ with 41% ethanol conversion and 74% C₄+

selectivity (T= 250 °C, WHSV= 0.79 h⁻¹), and co-impregnated 8.4 wt% (Ni/Cu 20/1)/9.0 wt% La_2O_3/γ -Al₂O₃ with 15% ethanol conversion and 78% C₄+ selectivity (T=230 °C, WHSV= 2.06 h⁻¹) are those with the best performance.

APPENDICES

APPENDIX A: Catalyst Preparation Steps

	А	В	С	D	Е	F
1		Component	Mass (g)	Mass (g)	MW(g/mol)	Conc.(wt%)
2		La ₂ O ₃	=F2*D11	3.9	325.81	0.09
3	Desired	Ni	=F3*D11	3.47	58.69	0.08
4	WL /0	Cu	=F4*D11	1.73	63.55	0.04
5	Raw	$La(NO_3)_3 \cdot 6H_2O$	=D2/E2*E5*2	10.37	433.01	-
6	materials	Ni(NO ₃) ₂ ·6H ₂ O	=D3/E3*E6	17.18	290.79	-
7	used	$Cu(NO_3)_2 \cdot 2.5H_2O$	=D4/E4*E7	6.33	232.59	-
8		γ-Al ₂ O ₃	=D11*F8	35.97	101.96	0.8
9	Final amounts	La_2O_3/γ - Al_2O_3	=D8/F8*(F9)	39.87	123.86	0.89
10		Ni/La ₂ O ₃ /γ-Al ₂ O ₃	=D11*(F8+F2+F3)	43.33	118.65	0.96
11		Catalyst	45	45	116.53	1

Table A.1. The spreadsheet used for obtaining the mass required for different chemicals in preparing catalysts.

- I. La₂O₃ impregnation on γ -Al₂O₃:
 - a. Have 35.97 g of γ -Al₂O₃.
 - b. Have 10.37 g of $La(NO_3)_3 \cdot 6H_2O$.
 - c. The pore volume of γ -Al₂O₃ is 0.5 ml/g. So, multiply the number from (a) by 0.5. The result is 17.99 ml of water and La(NO₃)₃·6H₂O mixture.
 - d. Add the number from part (b) to a small amount of water, and then add water again; until it reaches the ml obtained in (c).
 - e. Add that solution to the amount of γ -Al₂O₃ in part (a) drop by drop, and stir it gradually to get it absorbed by the support.
 - f. Let the mixture stay overnight.
 - g. Dry the mixture in an oven at 130 °C for 18h.

- h. Calcine it at 600 °C for 20 h in 35 ml/min of N₂ flow. The final mass of this step will be 39.87 g.
- II. Ni impregnation on $La_2O_3/\gamma Al_2O_3$:
 - a. Take the whole amount obtained from (1.h).
 - b. Have $17.18 \text{ g of Ni}(NO_3)_2 \cdot 6H_2O$.
 - c. The pore volume of La₂O₃/ γ -Al₂O₃ is still close to 0.5 ml/g. So, multiply the number from (a) to that. The result is 19.94 ml of water and the bimetal mixture.
 - d. Add the number from part (b) to a small amount of water, and then add water again; until it reaches the volume obtained in part (c).
 - e. Add that solution to the amount of La_2O_3/γ -Al₂O₃ in part (a) drop by drop, and stir it gradually to get it absorbed by the support.
 - f. Let the mixture stay overnight.
 - g. Dry the mixture in an oven at 130 °C for 18h.
 - h. Calcine it at 600 °C for 20 h in 35 ml/min of N_2 flow.
 - Reduce it at 520 °C in a tubular flow reactor for 20 h under 35 ml/min H₂. The final mass of this step will be 43.33 g.
- III. Cu impregnation on Ni/La₂O₃/ γ -Al₂O₃:
 - a. Take the whole amount obtained from (2.h).
 - b. Have $17.18 \text{ g of } Cu(NO_3)_2 \cdot 2.5H_2O$.
 - c. The pore volume of Ni-La₂O₃-Al₂O₃ is still close to 0.5 ml/g. So, multiply the number from (a) to that. The result is 21.66 ml of water and the fbimetal mixture.
 - d. Add the number from part (b) to a small amount of water, and then add water again; until it reaches the volume obtained in part (c).

- e. Add that solution to the amount of Ni/La₂O₃/γ-Al₂O₃ in part (a) drop by drop, and stir it gradually to get it absorbed by the support.
- f. Let the mixture stay overnight.
- g. Dry the mixture in an oven at 130 °C for 18h.
- h. Calcine it at 600 $^{\rm o}\!C$ for 20 h in 35 ml/min of N_2 flow.
- i. Reduce it at 520 $^{\circ}$ C in a tubular flow reactor for 20 h under 35 ml/min H₂. The final mass of this step will be 45 g.

APPENDIX B: Feed Flow Rate Calculation

Based on the work reported by Jordison et al. [9] on the batch Guerbet experiments with 8.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃ at 230 °C and autogenous pressure, by using 0.093 grams of catalyst per grams of ethanol fed, after ten hours of the catalyst screening experiments maximum conversion of 55% was achieved. So,

 $\frac{1 \text{ g EtOH Fed}}{0.093 \text{ g Catal}} \times \frac{1 \text{ mol EtOH Fed}}{46 \text{ g EtOH Fed}} \times \frac{0.55 \text{ mol EtOH Reacted}}{\text{mol EtOH Fed}} \times \frac{1}{10 \text{ hr}} = 0.013 \frac{\text{mol EtOH Reacted}}{\text{g Catal. hr}}$ This number correlates the batch and continuous experiments. For the continuous experiments at 230 °C, for achieving 35% conversion of ethanol with 29.9 g of catalyst we have:

 $\begin{array}{l} 0.013 \ \displaystyle \frac{mol \ EtOH \ Reacted}{g \ Catal. \ hr} \times 29.9 \ g \ Catal \times \frac{1 \ mol \ EtOH \ Fed}{0.35 \ mol \ EtOH \ Reacted} \times \frac{46 \ g \ EtOH}{1 \ mol \ EtOH} \\ \displaystyle \times \frac{1 \ g \ EtOH}{0.789 \ ml \ EtOH} \times \frac{1 \ hr}{60 \ min} = 1.08 \ \frac{ml \ EtOH \ Fed}{min} \end{array}$

APPENDIX C: Activation Energy Calculation

Assuming a second order reaction for the consumption of ethanol, we have:

$$-\frac{1}{\rho_{cat}}\frac{dC_E}{d\tau}\left(\frac{mol E}{mass \ catalyst. time}\right) = r_1 = k_1 C_E^{-2} \qquad Equation \ C.1$$

$$\frac{-dC_E}{C_E^2} = k_1 \rho_{cat} d\tau \qquad Equation \ C.2$$

By integrating from both sides of the equation:

$$\frac{1}{C} - \frac{1}{C_0} = k_1 \tau$$
Equation C.3

$$\frac{1}{C_0(1-x)} - \frac{1}{C_0} = k_1 \rho_{cat} \tau$$
Equation C.4

$$\frac{x}{C_0(1-x)} = k_1 \rho_{cat} \tau$$
 Equation C.5

Where C_0 is the feed concentration in mol/m³, x is the feed conversion, k_1 is the reaction rate constant in m⁶ of solution/kg of catalyst/mol ethanol/min assuming a single-step mechanism, ρ_{cat} is the bulk density of the catalyst in kg/m₃, and τ is the superficial residence time in min.

Using the above equation at different reaction temperatures, we will be able to get multiple k_{1s} . Then we need to involve the activation energy equation for each data point.

$$k_1 = Ae^{-\frac{E_a}{RT}}$$
 Equation C.6

$$\ln(k_1) = -\frac{E_a}{R}(\frac{1}{T}) + \ln(A)$$
 Equation C.7

Next, we can draw a diagram for $Rln(k_1)$ from Equation vs. 1/T for different reaction temperatures and find the slope of the diagram to derive an activation energy for the reaction. For instance, for
the 8.0 wt% Ni/4.5 wt% La₂O₃/ γ -Al₂O₃ catalyst the diagram presented in the next page will be obtained:



Figure C.1. Activation energy calculation for the 8.0 wt% Ni/4.5 wt% La₂O₃/γ-Al₂O₃ catalyst.

Using the slope obtained in Figure, the activation energy of the Guerbet reaction for this catalyst will be 121.4 kJ/mol.

APPENDIX D: Nickel Monometallic Experimental Data

D.1. Experimental Details

F == #	E. J	Т	WHSV	Conversion	Se	electivity (9	%)
Exp #	Feed	(°C)	(h ⁻¹)	(%)	BuOH	C ₆ +OH	Gasses
	Control Experi	ment:	9.0 wt% L	a_2O_3/γ -Al ₂ O ₃			
IN116-2	Ethanol	210	1.42	0.8	19.8	0.3	0.0
IN116-1	Ethanol	230	1.42	1.3	17.4	0.0	0.0
IN116-3	Ethanol	250	1.42	2.4	13.0	0.3	17.3
	Ni (I): 8.0 wt	% Ni/4	.5 wt% La	$_{2}O_{3}/\gamma$ -Al ₂ O ₃			_
IN28-4	Ethanol	170	1.42	4.2	27.2	0.4	20.1
IN28-1	Ethanol	190	1.42	10.0	55.1	6.8	10.8
IN48-2	Ethanol	210	0.47	40.6	47.4	12.7	27.0
IN29-3	Ethanol	210	0.79	29.0	59.2	14.0	22.4
IN29-2	Ethanol	210	1.11	25.8	57.3	13.2	17.9
IN28-2	Ethanol	210	1.42	21.9	57.9	12.9	16.0
IN54-1	Ethanol+ 0.7wt% Acetaldehyde	210	1.42	23.8	56.6	17.1	15.0
IN56-1	Ethanol+ 0.4wt% Ethyl Acetate	210	1.42	21.9	54.1	13.6	16.9
IN58-1	Butanol	210	1.46	16.2	-	31.1	19.4
IN65-1	Ethanol+ 4wt% Water	210	1.46	17.3	54.4	8.4	25.3
IN48-3	Ethanol	210	1.74	21.7	56.2	12.8	15.5
IN28-3	Ethanol	230	1.42	42.3	45.5	13.2	28.4
	Ni (II): 8.0 wt	% Ni/9	9.0 wt% La	a_2O_3/γ -Al ₂ O ₃			
IN66-1	Ethanol	210	1.42	27.8	52.1	15.4	18.8
	Ni (III): 8.0 wi	t% Ni/	9.0 wt% L	a_2O_3/γ -Al ₂ O ₃			
IN83-1	Ethanol	210	0.79	11.2	58.8	16.1	10.0
IN83-2	Ethanol	210	1.42	8.2	60.1	13.1	8.6
IN83-3	Ethanol	210	2.06	7.2	59.4	10.6	8.0
IN84-1	Ethanol	230	0.79	23.7	57.1	19.8	15.2
IN84-2	Ethanol	230	1.42	16.3	61.4	17.7	10.8
IN84-3	Ethanol	230	2.06	12.8	63.9	16.2	8.4
IN85-1	Ethanol	250	0.79	40.2	50.6	19.6	18.3

Table D.1. Experimental details for the monometallic nickel experiments.

IN85-2	Ethanol	250	1.42	29.6	54.2	17.9	15.7
IN85-3	Ethanol	250	2.06	25.6	54.9	19.2	12.2
IN124-2	t-butanol+ 5wt% Acetaldehyde	110	1.42	32.1	0.0	0.0	0.0
IN124-3	t-butanol+ 5wt% Acetaldehyde	120	1.42	54.9	0.0	0.0	0.0
IN124-1	t-butanol+ 5wt% Acetaldehyde	130	1.42	86.6	0.0	0.0	0.0
	Ni (IV): 8.0 w	t% Ni/	9.0 wt% L	a_2O_3/γ - Al_2O_3			
IN99-1	Ethanol	210	1.42	18.1	54.4	14.8	12.8
IN99-2	Ethanol	230	1.42	36.1	45.5	16.4	23.7
IN99-3	Ethanol	250	1.42	60.7	29.7	12.9	46.3
	Ni (V): 1.0 wt	% Ni/9	9.0 wt% La	a_2O_3/γ -Al ₂ O ₃		-	
IN111-1	Ethanol	210	1.42	7.0	68.0	10.4	5.5
IN109-1	Ethanol	230	0.79	22.4	58.2	20.5	9.4
IN109-2	Ethanol	230	1.42	14.9	61.6	17.1	8.1
IN109-3	Ethanol	230	2.06	12.0	62.9	14.4	7.7
IN110-1	Ethanol	250	0.79	41.1	50.9	23.4	14.7
IN110-2	Ethanol	250	1.42	28.9	54.4	20.9	12.4
IN110-3	Ethanol	250	2.06	23.2	58.1	10.4	11.2

Table D.1 (cont'd)

D.2. Liquid Products' Selectivity

Table D.2. Liquid products' selectivity for monometallic nickel experiments. ¹ Ethanol selectivity for these
experiments are: IN58-1= 2.2%, IN124-2= 4.7%, IN124-3= 2.6%, IN124-1= 2.2%.

		Selectivity (%)											
Exp #	Ethyl Acetate	Diethyl Ether	Acetal	Acetaldehyde	Butyraldehyde	Crotonaldehyde	Other Liquids						
IN116-2	0.0	7.8	1.2	0.0	0.0	0.0	62.0						
IN116-1	0.0	19.6	2.2	0.0	0.0	0.0	47.2						
IN116-3	0.0	15.0	2.3	0.0	0.0	0.0	60.1						
IN28-4	59.2	3.8	0.0	8.5	0.0	1.0	3.1						
IN28-1	13.6	1.6	0.0	8.2	1.4	0.9	1.3						
IN48-2	1.5	1.3	0.7	2.3	0.4	0.3	1.2						
IN29-3	2.2	1.8	0.9	2.9	0.6	0.4	1.3						
IN29-2	2.0	1.7	1.2	3.0	0.7	0.3	1.2						
IN28-2	2.8	1.4	0.0	6.2	1.8	0.2	0.6						

IN54-1	2.1	1.3	2.0	-0.6	1.1	0.2	1.2
IN56-1	2.9	2.1	2.7	2.9	1.3	0.3	1.3
IN58-1 ¹	1.0	0.2	0.0	0.6	11.0	0.0	19.7
IN65-1	1.5	1.2	1.8	3.4	0.9	0.0	0.6
IN48-3	1.8	1.5	1.8	3.6	1.0	0.2	1.1
IN28-3	0.5	0.5	0.0	5.3	2.5	0.3	0.3
IN66-1	2.2	1.3	1.4	2.5	1.0	0.3	1.3
IN83-1	1.4	1.9	3.3	2.1	0.7	0.3	1.7
IN83-2	0.7	2.3	5.5	2.4	0.8	0.4	2.1
IN83-3	1.0	2.6	6.6	2.5	0.8	0.4	2.4
IN84-1	1.9	1.7	0.6	1.5	0.6	0.1	1.2
IN84-2	1.9	1.9	1.6	1.9	0.8	0.2	1.5
IN84-3	1.7	2.2	2.5	2.3	0.9	0.2	1.5
IN85-1	3.0	2.1	0.1	1.4	0.6	0.0	1.5
IN85-2	2.3	2.2	0.4	1.6	0.7	0.1	1.5
IN85-3	2.4	1.8	0.6	2.0	1.0	0.1	1.4
IN124-2 ¹	0.0	0.0	0.0	-	0.0	45.1	22.9
IN124-3 ¹	0.0	0.0	0.0	-	0.0	49.9	24.9
IN124-1 ¹	0.0	0.0	0.0	-	0.0	37.1	28.8
IN99-1	1.7	2.2	2.5	2.2	1.2	0.0	2.3
IN99-2	2.0	1.7	0.7	1.6	0.9	0.0	3.8
IN99-3	2.2	1.2	0.0	1.1	0.8	0.2	5.5
IN111-1	0.0	1.0	6.0	2.2	0.3	0.4	5.8
IN109-1	0.9	0.8	1.1	1.6	0.7	0.1	4.6
IN109-2	1.0	0.9	1.9	2.0	0.7	0.1	4.4
IN109-3	1.0	1.0	2.7	2.3	0.7	0.0	4.6
IN110-1	1.1	0.8	0.5	1.2	0.9	0.1	4.7
IN110-2	1.2	0.8	0.8	1.6	1.0	0.1	5.2
IN110-3	1.3	0.9	1.2	1.9	1.1	0.1	5.1

Table D.2 (cont'd)

D.3. Gaseous Products' Selectivity

F "		Se	electivity (%)		
Exp #	Carbon Monoxide	Carbon Dioxide	Methane	Ethane	Propane	Sum All ¹
IN28-4	0.1	1.3	17.9	0.5	0.2	123.2
IN28-1	0.1	0.6	9.2	0.5	0.4	99.7
IN48-2	0.2	5.0	15.9	2.1	3.7	94.7
IN29-3	0.6	3.6	14.5	0.9	2.4	105.1
IN29-2	0.4	2.6	12.1	0.8	1.7	98.1
IN28-2	0.3	2.0	11.6	0.7	1.3	99.5
IN54-1	0.1	2.0	9.0	1.2	2.6	96.1
IN56-1	0.1	1.8	10.8	1.6	2.4	98.0
IN58-1	0.1	1.2	2.4	0.7	15.0	85.2
IN65-1	0.3	3.7	16.5	1.5	3.0	97.2
IN48-3	0.1	1.7	10.8	1.1	1.7	95.3
IN28-3	0.4	5.3	17.8	1.2	3.6	96.2
IN66-1	0.2	2.3	11.5	1.4	3.3	96.2
IN83-1	0.0	0.7	6.0	1.9	1.3	96.2
IN83-2	0.1	0.5	6.4	1.5	0.2	96.1
IN83-3	0.0	0.4	6.2	1.3	0.0	94.3
IN84-1	0.1	1.9	6.2	2.3	2.0	97.1
IN84-2	0.1	1.1	6.2	2.1	1.7	100.0
IN84-3	0.1	0.6	6.5	1.6	0.0	100.0
IN85-1	0.2	1.9	10.1	3.0	3.1	97.2
IN85-2	0.7	2.0	7.8	2.1	3.1	96.5
IN85-3	0.3	0.9	8.2	1.8	1.0	95.5
IN124-2	0.0	0.0	0.0	0.0	0.0	72.8
IN124-3	0.0	0.0	0.0	0.0	0.0	77.4
IN124-1	0.0	0.0	0.0	0.0	0.0	68.1
IN99-1	0.4	1.1	7.9	1.4	2.1	94.2
IN99-2	0.6	2.9	11.0	3.4	5.9	96.2
IN99-3	1.5	6.6	19.8	3.8	14.6	99.9
IN111-1	0.1	0.2	4.6	0.2	0.2	99.5

Table D.3. Gaseous products' selectivity for monometallic nickel experiments. ¹*Sum of both liquid and gaseous products' selectivity.*

IN109-1	0.2	1.3	6.0	0.7	1.3	98.0
IN109-2	0.2	0.8	5.8	0.5	0.8	97.7
IN109-3	0.2	0.7	5.7	0.4	0.7	97.3
IN110-1	0.2	2.6	8.0	0.8	3.1	98.1
IN110-2	0.2	1.9	7.3	0.7	2.3	98.4
IN110-3	0.1	5.2	4.2	0.7	1.0	91.3

Table D.3 (cont'd)

APPENDIX E: Nickel Bimetallic Experimental Data

E.1. Experimental Details

Eve #	Т	WHSV	Conv.		Selecti	vity (%)	
Exp #	(°C)	(h ⁻¹)	(%)	BuOH	$C_6 + OH$	$C_4 + OH$	Gasses
	1	1.5 wt% (Ni/Cu 2/1)/8.7 wt%	6 La ₂ O ₃ /γ-A	Al_2O_3	
IN86-1	230	0.79	22.2	63.6	7.7	71.3	14.7
IN86-2	230	1.42	16.8	66.1	7.0	73.0	12.6
IN86-3	230	2.06	14.3	66.7	6.8	73.5	11.6
IN87-1	250	0.79	39.1	54.2	10.5	64.7	22.8
IN87-2	250	1.42	29.5	61.9	10.3	72.2	15.7
IN87-3	250	2.06	25.4	62.2	10.2	72.4	14.2
11.5 wt% (Ni/Cu 2/1)/8.7 wt% La ₂ O ₃ /γ-Al ₂ O ₃ (Co-Impregnated)							
IN74-1	210	1.42	7.3	67.4	3.1	70.5	10.1
IN76-3	230	1.42	16.9	70.8	6.4	77.2	11.3
IN76-2	250	1.42	30.0	61.5	8.6	70.0	15.0
IN76-3	250	3.32	22.3	65.7	8.0	73.7	10.2
8.4	wt% (1	Ni/Cu 20/1)/9.0 wt%	6 La ₂ O ₃ /γ	-Al ₂ O ₃ (Co	-Impregnate	ed)
IN79-3	210	0.79	10.9	67.7	9.1	76.8	8.7
IN78-2	210	1.42	8.8	67.8	7.6	75.5	8.2
IN80-1	210	2.06	7.6	65.3	7.0	72.3	8.1
IN79-2	230	0.79	25.6	60.3	12.1	72.5	16.6
IN78-1	230	1.42	17.9	65.2	11.3	76.5	12.1
IN80-2	230	2.06	15.1	66.1	11.5	77.7	9.2
IN79-1	250	0.79	43.9	52.3	15.2	67.5	20.8
IN80-4	250	1.42	34.6	58.8	15.2	74.0	17.1
IN80-3	250	2.06	29.5	58.2	14.3	72.6	15.5
		8.0 wt	% Cu/9.0	wt% La ₂	O_3/γ -Al ₂ O ₃		
IN97-1	210	1.42	6.6	5.2	0.0	5.2	4.1
IN95-1	230	0.79	13.0	5.2	0.0	5.2	5.1
IN95-2	230	1.42	10.2	5.6	0.0	5.6	5.3
IN95-3	230	2.06	9.3	5.7	0.0	5.7	5.8

 Table E.1. Experimental details for the bimetallic nickel experiments. All bimetallic catalysts are prepared using the separate impregnation method unless otherwise noted.

IN96-1	250	0.79	26.1	6.7	0.0	6.7	9.9
IN96-2	250	1.42	20.3	7.3	0.0	7.3	5.8
IN96-3	250	2.06	19.1	6.7	0.0	6.7	15.7
	1	1.5 wt% (Ni/Co 2/1)/8.7 wt%	6 La2O3/γ-A	Al_2O_3	
IN105-1	210	1.42	11.8	56.8	15.3	72.0	9.3
IN103-1	230	0.79	45.9	40.7	24.6	65.3	18.7
IN103-2	230	1.42	33.4	43.3	22.9	66.2	15.6
IN103-3	230	2.06	26.9	46.0	21.9	67.9	13.9
IN104-1	250	0.79	59.5	22.4	11.9	34.3	45.9
IN104-2	250	1.42	51.4	34.0	17.8	51.8	29.0
IN104-3	250	2.06	43.3	41.6	20.1	61.7	16.1
		8.0 wt	% Co/9.0	wt% La ₂	O_3/γ -Al ₂ O ₃		
IN115-2	210	1.42	12.5	7.5	0.0	7.5	20.7
IN114-1	230	0.79	38.0	0.7	0.0	0.7	24.9
IN115-3	230	1.42	24.0	6.5	0.1	6.6	21.8
IN115-1	250	1.42	49.2	4.3	0.1	4.4	23.6
	9	9.7 wt% (1	Ni/Pd 4/1))/8.8 wt%	La ₂ O ₃ /γ-A	l_2O_3	
IN107-1	210	1.42	9.9	54.3	8.9	63.1	5.9
IN106-1	230	0.79	28.3	51.1	15.7	66.8	14.0
IN106-2	230	1.42	20.3	53.4	13.8	67.1	12.0
IN106-3	230	2.06	16.8	53.1	12.1	65.2	11.7
IN108-1	250	0.79	46.8	41.1	14.9	56.0	24.1
IN108-2	250	1.42	34.4	47.2	14.2	61.4	13.4
IN108-3	250	2.06	27.9	49.4	13.3	62.7	12.1
		9.7 wt% (1	Ni/Pt 4/1)	/8.8 wt%	La ₂ O ₃ /γ-A	l_2O_3	
IN91-1	210	1.42	9.2	55.8	4.9	60.7	19.8
IN89-1	230	0.79	28.2	43.9	7.3	51.3	36.4
IN89-2	230	1.42	20.9	48.9	7.6	56.5	31.3
IN89-3	230	2.06	16.9	51.2	7.3	58.5	28.6
IN90-1	250	0.79	59.2	19.6	4.4	24.0	66.1
IN90-2	250	1.42	40.8	32.9	6.8	39.7	47.9
IN90-3	250	2.06	35.4	35.5	7.9	43.5	46.4

Table E.1 (cont'd)

	1	1.5 wt% (Ni/Fe 2/1)/8.7 wt%	6 La ₂ O ₃ /γ-A	l_2O_3	
IN94-1	210	1.42	8.9	45.9	1.8	47.7	15.0
IN92-1	230	0.79	29.7	42.6	5.6	48.2	27.4
IN92-2	230	1.42	21.9	44.2	5.0	49.2	23.8
IN92-3	230	2.06	17.5	44.3	4.3	48.6	21.9
IN93-1	250	0.79	43.9	37.2	8.7	45.9	31.5
IN93-2	250	1.42	31.8	44.5	9.6	54.1	23.0
IN93-3	250	2.06	25.8	47.0	9.3	56.3	20.1
	1	1.5 wt% (1	Ni/Mo 2/1	l)/8.7 wt%	% La ₂ O ₃ /γ-1	Al_2O_3	
IN102-1	210	1.42	5.2	51.3	2.1	53.4	5.9
IN100-1	230	0.79	9.7	56.3	2.4	58.7	11.2
IN100-2	230	1.42	9.3	51.3	2.4	53.7	10.5
IN100-3	230	2.06	8.1	51.9	2.6	54.5	11.1
IN101-1	250	0.79	16.9	55.3	5.0	60.2	1.8
IN101-2	250	1.42	15.3	52.7	4.8	57.5	9.9
IN101-3	250	2.06	13.3	55.5	4.9	60.5	7.1

Table E.1 (cont'd)

E.2. Liquid Products' Selectivity

Table E.2. Liquid products' selectivity for bimetallic nickel experiments.

				Selecti	vity (%)		
Exp #	Ethyl Acetate	Diethyl Ether	Acetal	Acetaldehyde	Butyraldehyde	Crotonaldehyde	Other Liquids
IN86-1	1.4	6.4	1.5	1.3	0.0	0.0	1.0
IN86-2	1.4	5.4	2.0	1.7	0.0	0.0	1.1
IN86-3	1.4	5.1	2.5	2.0	0.0	0.0	1.1
IN87-1	2.1	4.5	0.0	1.2	0.4	0.0	1.3
IN87-2	2.4	4.6	0.0	1.4	0.0	0.0	1.1
IN87-3	2.7	4.5	0.0	1.7	0.2	0.0	1.0
IN74-1	1.1	7.5	5.3	1.2	0.0	0.0	1.9
IN76-3	2.3	5.0	1.4	1.2	0.0	0.0	1.1
IN76-2	2.3	4.5	0.7	1.0	0.3	0.0	1.7
IN76-3	2.6	3.9	0.9	1.6	0.4	0.0	1.5

Table E.2 (cont'd)

IN79-3	1.1	2.8	3.2	1.3	0.2	0.3	1.7
IN78-2	1.7	2.7	4.2	1.6	0.2	0.4	1.7
IN80-1	1.6	2.6	5.3	1.7	0.2	0.4	1.9
IN79-2	2.4	2.3	0.8	0.9	0.4	0.1	1.3
IN78-1	2.7	2.2	1.4	1.4	0.4	0.2	1.4
IN80-2	1.8	2.3	1.9	1.6	0.5	0.3	1.4
IN79-1	3.4	1.9	0.1	0.9	0.5	0.0	1.4
IN80-4	2.8	2.0	0.4	1.2	0.6	0.1	1.2
IN80-3	2.9	2.0	0.5	1.4	0.7	0.1	1.2
IN97-1	66.6	0.6	0.0	0.0	0.0	0.0	15.4
IN95-1	61.9	1.8	0.0	0.0	0.0	0.0	17.7
IN95-2	61.8	1.3	0.0	0.0	0.0	0.0	19.8
IN95-3	61.9	1.1	0.0	0.0	0.0	0.0	19.2
IN96-1	51.9	2.1	0.0	0.6	0.0	0.0	21.1
IN96-2	56.5	1.6	0.0	0.7	0.0	0.0	21.3
IN96-3	51.9	1.1	0.0	0.5	0.0	0.0	19.2
IN105-1	0.0	0.3	4.4	0.0	0.0	0.0	6.2
IN103-1	1.4	0.4	0.4	0.9	1.1	0.0	7.3
IN103-2	1.4	0.4	0.8	0.8	1.6	0.0	6.6
IN103-3	1.3	0.5	1.1	0.7	1.8	0.0	6.3
IN104-1	1.3	0.4	0.3	2.4	0.9	0.0	7.3
IN104-2	1.5	0.4	0.3	1.4	1.3	0.0	7.3
IN104-3	1.7	0.5	0.4	1.0	1.7	0.0	6.9
IN115-2	52.2	1.8	0.0	0.6	0.0	0.0	12.7
IN114-1	63.4	1.7	0.0	0.3	0.0	0.0	2.7
IN115-3	53.3	2.4	0.0	0.4	0.0	0.0	10.9
IN115-1	55.4	1.2	0.0	0.5	0.0	0.0	8.4
IN107-1	0.9	12.2	3.7	1.9	0.6	0.1	6.3
IN106-1	1.3	5.8	0.7	1.7	0.7	0.1	4.9
IN106-2	1.1	6.6	1.3	2.0	0.8	0.1	4.4
IN106-3	1.1	8.2	1.8	2.3	0.9	0.1	4.3
IN108-1	1.8	4.9	0.0	1.0	0.7	0.1	7.3
IN108-2	1.7	6.5	0.3	1.4	0.7	0.1	7.3

IN108-3	1.4	7.4	0.7	1.6	0.8	0.1	7.2
IN91-1	0.0	4.2	4.6	1.8	0.0	0.0	0.9
IN89-1	1.4	4.7	0.7	1.1	0.0	0.0	0.9
IN89-2	1.5	4.5	1.0	1.3	0.0	0.0	0.9
IN89-3	1.4	4.5	1.4	1.6	0.0	0.0	1.0
IN90-1	0.8	2.3	0.2	0.4	0.0	0.0	1.0
IN90-2	1.4	3.0	0.4	0.8	0.0	0.0	0.9
IN90-3	1.4	2.5	0.5	1.1	0.0	0.0	0.9
IN94-1	7.6	7.9	9.3	2.8	0.0	0.0	2.3
IN92-1	7.3	7.1	0.7	2.0	0.6	0.6	2.9
IN92-2	7.6	8.0	1.0	2.7	0.9	0.6	2.5
IN92-3	6.4	9.3	3.1	3.3	1.0	0.0	2.2
IN93-1	6.5	4.8	0.0	1.6	0.8	0.7	4.7
IN93-2	5.1	5.2	0.5	2.1	1.1	0.7	3.8
IN93-3	5.3	5.7	0.5	2.5	1.2	0.7	3.1
IN102-1	7.3	0.7	9.6	1.8	0.0	0.0	9.4
IN100-1	11.5	2.2	1.3	1.4	0.0	0.0	8.1
IN100-2	14.1	1.3	4.3	1.5	0.0	0.0	6.2
IN100-3	11.2	0.9	6.1	1.8	0.0	0.0	6.4
IN101-1	13.1	2.2	0.0	1.2	0.0	0.0	16.7
IN101-2	7.5	1.6	0.6	1.5	0.0	0.0	15.9
IN101-3	10.4	1.5	0.2	1.9	0.0	0.0	13.8

Table E.2 (cont'd)

E.3. Gaseous Products' Selectivity

Table E.3. Gaseous products' selectivity for bimetallic nickel experiments. ¹*Sum of both liquid and gaseous products' selectivity.*

Exp #	Selectivity (%)								
	Carbon Monoxide	Carbon Dioxide	Methane	Ethane	Propane	Sum All ¹			
IN86-1	0.1	2.5	8.2	2.4	1.4	97.7			
IN86-2	0.2	2.0	7.1	2.4	1.0	97.2			
IN86-3	0.2	1.8	7.0	1.6	0.9	97.1			
IN87-1	0.2	5.1	11.3	2.6	3.5	96.9			

Table E.3 (cont'd)

IN87-2	0.2	3.2	7.6	2.8	2.0	97.5
IN87-3	0.2	2.9	7.2	2.0	1.8	96.7
IN74-1	0.2	1.3	7.8	0.6	0.1	97.3
IN76-3	0.1	2.9	7.2	0.8	0.6	99.9
IN76-2	0.2	4.2	7.8	0.9	1.8	95.5
IN76-3	0.2	2.6	5.1	1.2	1.1	94.7
IN79-3	0.2	0.9	6.3	1.1	0.2	95.9
IN78-2	0.2	0.7	6.5	0.5	0.2	96.1
IN80-1	0.4	0.8	5.9	0.6	0.2	93.9
IN79-2	0.2	2.4	10.3	1.4	2.1	97.1
IN78-1	0.2	1.2	8.3	0.9	1.3	98.1
IN80-2	0.2	1.1	6.9	0.8	0.1	96.5
IN79-1	0.4	4.4	12.0	1.5	1.1	95.1
IN80-4	0.4	2.9	9.9	1.5	2.8	99.7
IN80-3	0.3	2.5	9.3	1.3	1.9	96.6
IN97-1	0.9	0.5	1.6	1.0	0.0	91.9
IN95-1	1.2	0.3	1.8	1.7	0.0	91.6
IN95-2	1.0	0.2	2.6	1.5	0.0	93.8
IN95-3	0.9	0.6	2.8	1.5	0.0	93.7
IN96-1	1.5	2.2	3.2	2.9	0.0	92.2
IN96-2	1.4	1.3	1.2	1.8	0.0	93.2
IN96-3	1.2	2.1	8.5	2.7	1.3	95.3
IN105-1	0.2	0.6	6.1	1.1	1.3	92.2
IN103-1	0.4	2.6	8.0	1.1	6.5	95.5
IN103-2	0.4	1.8	7.4	1.1	5.0	93.4
IN103-3	0.4	1.2	7.0	1.3	4.0	93.5
IN104-1	0.9	7.7	18.6	2.9	15.9	92.7
IN104-2	0.6	4.2	12.1	2.6	9.6	93.1
IN104-3	0.2	2.6	6.3	0.9	6.1	90.1
IN115-2	1.6	0.0	17.0	0.0	2.0	95.5
IN114-1	2.2	0.0	20.8	0.0	1.9	93.7
IN115-3	1.8	0.0	17.8	0.0	2.2	95.4
IN115-1	2.1	0.2	18.3	0.0	3.0	93.5

Table E.3 (cont'd)

IN107-1	0.1	0.3	3.5	1.5	0.5	94.7
IN106-1	0.3	1.7	6.1	3.0	2.9	96.0
IN106-2	0.2	1.2	5.4	3.1	2.2	95.6
IN106-3	0.2	1.0	5.6	3.2	1.7	95.5
IN108-1	0.4	3.4	8.6	5.5	6.2	96.0
IN108-2	0.2	1.6	4.7	3.9	2.9	92.9
IN108-3	0.2	1.3	4.6	3.5	2.5	94.0
IN91-1	0.2	3.7	12.3	2.4	1.3	91.9
IN89-1	0.5	9.0	18.7	3.8	4.3	96.4
IN89-2	0.4	7.3	16.0	4.0	3.7	97.1
IN89-3	0.4	6.2	14.6	4.2	3.2	97.1
IN90-1	0.3	18.4	29.6	7.0	10.7	94.9
IN90-2	0.5	14.6	24.1	5.3	3.5	94.0
IN90-3	0.5	12.4	20.2	6.4	6.8	96.3
IN94-1	0.1	0.4	10.5	2.9	1.0	92.7
IN92-1	0.2	3.7	15.0	4.4	4.1	97.0
IN92-2	0.2	2.7	14.7	2.9	3.4	96.3
IN92-3	0.2	2.0	14.3	2.7	2.7	95.9
IN93-1	0.1	4.8	14.9	5.4	6.3	96.5
IN93-2	0.2	3.0	12.6	3.0	4.2	95.8
IN93-3	0.2	2.3	11.2	3.0	3.5	95.5
IN102-1	0.0	0.1	1.4	4.3	0.1	88.1
IN100-1	0.6	0.2	1.4	9.0	0.0	94.3
IN100-2	0.6	0.4	2.8	6.4	0.2	91.7
IN100-3	0.6	0.6	4.4	4.7	0.7	92.0
IN101-1	0.2	0.1	0.3	1.2	0.0	95.3
IN101-2	0.6	1.0	2.8	4.6	1.0	94.5
IN101-3	0.5	0.3	1.0	5.3	0.0	95.3



F.1. NH₃ TPD (Acidic Sites)



Figure F.1. Acidic sites measurement for bimetallic catalysts. (a) Temperature profile, (b) NH₃ Temperature Programmed Desorption (TPD) diagram.

F.2. CO₂ TPD (Basic Sites)



Figure F.2. Basic sites measurement for bimetallic catalysts. (a) Temperature profile, (b) CO₂ Temperature Programmed Desorption (TPD) diagram.





Figure F.3. H₂ uptake measurement for bimetallic catalysts. (a) Temperature profile, (b) H₂ Temperature Programmed Desorption (TPD) diagram.

3 Guerbet Economical Analysis

3.1 Introduction

In addition to the studies of catalyst performance for the Guerbet reaction, a series of papers have been published [89-92] that compare economics and environmental impacts of *n*-butanol formation from ethanol via the Guerbet reaction with *n*-butanol formation via the traditional petroleum-based "oxo" route [92] and with *n*-butanol production via ABE fermentation. Feed stocks examined for ABE fermentation include Brazilian sugar cane [91, 93], corn grain [93-95], corn stover [95], wheat straw [94], Canadian pulp pre-hydrolysate [96], and others [97].

In the above studies, *n*-butanol production from ethanol is integrated into the biorefinery, and the overall economics and environmental impacts of the integrated refinery are reported. Two scenarios for Guerbet reactions are examined: vapor phase reaction at high temperature and low pressure as proposed by Tsuchida et al. [39, 54], and condensed phase reaction at lower temperature and elevated pressure [22]. These studies make several assumptions regarding reaction rates, catalyst stability, and byproduct purification that have significant effects on the overall economic and environmental impacts from the different processes. Because *n*-butanol production is integrated into the overall ethanol biorefinery, it is difficult to gain a realistic assessment of the environmental impact or economic potential related specifically to *n*-butanol production. The economics of producing 2- ethylhexanol from ethanol via Guerbet reactions has also been examined [98], but yields used in the analysis do not reflect available experimental values so the validity of the analysis is uncertain.

In this chapter, we describe the economic analysis of a continuous condensed phase stand-alone process for the production of *n*-butanol and higher alcohols using ethanol as feed stock. The

process includes an improved distillation concept to purify *n*-butanol, and produces a mixed C_{6+} alcohols stream as a byproduct instead of separating out individual minor products formed. Several alternate process configurations are evaluated as well in order to better ascertain the required selling price of *n*-butanol from ethanol. The economic analysis for each process configuration investigation is based upon a rigorous Aspen Plus V8.4 simulation using the S-R Polar equation of state from our prior work; all parameters were fitted by Jordison et al [25].

3.2 Process Concept and Design Parameters

3.2.1 Process Concept

The initial results in the continuous fixed bed reactor from Chapter 2 form the basis for a process to convert ethanol to *n*-butanol and higher alcohols. The process concept consists of the reactor for ethanol conversion and a separation train to produce pure *n*-butanol and a mixture of C_6 + alcohols as saleable products. In contrast to some other reports of Guerbet reaction processes [89-92, 99], in this work minor gas and liquid byproducts are burned as fuel for steam generation to provide energy for the process; capital and operating expenditures to recover them as pure products are not justified because of their low concentration in the product mix.

The ethanol-to-higher alcohols Guerbet reaction process is intended to be located adjacent to an ethanol plant, and thus there are two strategies for configuring the combined facility. The first approach, used in several economic analyses of Guerbet reactions with sugar cane-based ethanol production [89-92], is to pass the entire product stream from ethanol fermentation through the Guerbet process, wherein partial conversion to higher alcohols takes place and the unreacted ethanol becomes the primary plant output. The second approach, adopted in this work, is to divert

only a portion of the product ethanol to the Guerbet process, and then recycle unreacted ethanol within the Guerbet process to give an overall conversion approaching 100%.

The key reaction parameter for most renewables-based chemical processes is selectivity to desired products. In this ethanol condensation process, both selectivity and ethanol conversion are important, because reactions are sequential and thus selectivity depends on conversion. Further, because the overall process conversion of ethanol is essentially 100%, the extent of ethanol recycle and thus distillation column size depends on per-pass reactor conversion. To illustrate the dependence of process economics on these parameters, a set of four base cases with different combinations of ethanol conversion and alcohol selectivities is examined. These are designated by the two-digit ethanol conversion percentage and either "L" for low (60% *n*-butanol, 16% C₆+ alcohols) selectivity or "H" for high (72% *n*-butanol, 22% C₆+ alcohols) selectivity. The case designated 35L (35% ethanol conversion, low selectivity) represents results obtained in the experimental fixed-bed reactor studies reported in Chapter 1. The other cases (40L, 35H, 70H) reflect higher ethanol conversion or selectivity, in order to ascertain future potential for *n*-butanol production via ethanol condensation.

The flow diagram used as the basis for the Aspen Plus V8.4 simulation of the four base cases for the proposed ethanol condensation process is given in Figure 3.1. Fresh ethanol (Stream F) is combined with recycled ethanol (S6), pressurized to 100 bar, and preheated to the reaction temperature of 230 °C in heat exchangers H1 and H2. The reactor (FBR) is a fixed-bed shell and tube reactor in which the heat of reaction generated on the tube side, where catalyst is loaded, is removed by generating steam on the shell side at approximately 230 °C. This steam is used to partially preheat the reactor feed in H1.



Figure 3.1. Process concept for the four base cases of ethanol conversion to n-butanol and higher alcohols. The values of reboiler, condenser and heat exchanger duties are for Case 35L.

The effluent stream (S2) from the fixed-bed reactor is partially flashed from 100 bar to a lower pressure (Valve V1) and fed to Column TC1, where ethanol, water, and light byproducts are taken as the distillate (S3) and *n*-butanol, mixed C_{6+} alcohols, and in some cases water exit as the bottoms stream (S8) of TC1. Further details regarding the ethanol/*n*-butanol separation carried out in Column TC1 are given below, along with an explanation of the two process alternatives highlighted in Figure 3.1 for recovering pure *n*-butanol and mixed C_{6+} alcohols. The light byproducts formed in reaction (chosen for simulation as ethyl acetate, diethyl ether, CH₄, CO₂, and H₂, see Appendix D for the complete byproduct slate) are recovered as a mixed distillate stream (S4) in Column TC2 and used as fuel for steam generation. The bottoms stream from

Column TC2, consisting of ethanol and water, is separated in Column TC3 into an azeotropic ethanol/water mixture (S6) for recycling and pure water (S7) as a bottoms product.

Several pressures were examined in preliminary simulations of the separation train; an absolute pressure of 5.0 bar was chosen for columns TC1 and TC2, and an absolute pressure of 1.0 bar was chosen for Column TC3 and the *n*-butanol/C₆+ alcohol separation (Column TC4 or Columns TC4-TC6). These pressures are high enough to allow column condensers to operate with air cooling instead of refrigeration, yet are low enough to avoid excessively high temperatures in column reboilers. Other combinations of pressures could conceivably further improve process efficiency and economics, but no other pressure combinations were evaluated in this work.

The two process alternatives highlighted in the lower right side of Figure 3.1 represent two process scenarios depending on whether or not Stream S8 from Column TC1 contains water. If Stream S8 is dry, then *n*-butanol and C₆+ alcohols are separated in Column TC4 into pure (99.87 \pm 0.04 mol%) *n*-butanol (S9) and C₆+ alcohols (chosen for simulation as equimolar quantities of 1-hexanol and 2-ethyl-1-butanol, together >99.75 mol% in S10) as shown in the upper block in Figure 3.1. If Stream S8 contains water, then C₆+ alcohols are recovered as the bottoms stream (>99.75 mol%, S12) of Column TC4, and the distillate (S11) of Column TC4 containing *n*-butanol and water, which form a heterogeneous azeotrope, is separated using the classic approach of two distillation columns (TC5 and TC6) with a decanter as shown in the lower block in Figure 3.1. Capital and operating costs associated with this latter approach are significant, as the *n*-butanol-water separation columns (TC5 and TC6) require high reflux ratios and recycling of intermediate streams to obtain dry (99.87 ± 0.04 mol%) *n*-butanol.

The composition of the reactor effluent (Stream S2) entering Column TC1 determines whether or not Stream S8 from Column TC1 contains water, and thus which of the two process scenarios above is used. The ethanol/water/*n*-butanol residue curve map shown in Figure 3.2 (generated using the S-R Polar equation of state in Aspen Plus V8.4) illustrates the two cases. In this residue curve map, a distillation boundary arises because ethanol and *n*-butanol both form minimum boiling azeotropes with water. If C_{6+} alcohol products (recovered in Column TC4) and light byproducts (recovered in Column TC2) are momentarily neglected, so that Columns TC2 and TC4 can be neglected and Stream S5 can be considered equivalent to Stream S3 in Figure 3.1, then the residue curve map in Figure 3.2 applies directly to Columns TC1 and TC3.

If sufficient ethanol is present in the reactor effluent (S2), generally corresponding to a maximum per-pass ethanol conversion in the FBR of 40% (Cases 35L, 35H, 40L), then all water in Stream S2 (both produced in reaction and present in the reactor feed) can be removed with ethanol into the distillate (S3) of Column TC1. Negligible *n*-butanol is carried to the distillate (S3), leaving dry *n*-butanol as the bottoms product of TC1. This separation is represented as the straight line S8-S2-S3 for Case 35L in Figure 3.2; the distillate (S3) composition lies close to the distillation boundary and contains less than 0.001 mole fraction *n*-butanol, while the bottoms (S8) composition approaches pure *n*-butanol. Separation of the distillate mixture (S3 equivalent to S5 without light byproducts present) in the subsequent Column TC3, represented by the line S7-S3-S6 for Case 35L in Figure 3.2, produces the ethanol-water azeotrope as distillate (S6) and water containing trace *n*-butanol as the bottoms product (S7). This separation in Column TC3 crosses the distillation boundary on the residue curve map. While crossing the distillation boundary is not usually possible, such crossings are possible in cases where the boundary has significant curvature [100]. To ensure that crossing the distillation boundary in the Aspen Plus V8.4 simulation of this system was not an artifact of the S-R Polar properties package, the ethanol/*n*-butanol/water residue curve map was also generated and the separations in Columns TC1 and TC3 were also simulated using the Non-Random Two Liquid (NRTL) properties package. The same results were obtained using the NRTL properties package as with the S-R Polar equation of state; the use of very different thermodynamic properties packages to obtain the same result provides validation of the crossing of the distillation boundary and the separations in Columns TC1 and TC3.



Figure 3.2. Residue curve map for ethanol/n-butanol/water system at 5.0 bar absolute (Aspen Plus V8.4 SR-Polar equation of state). Dashed lines represent material balances for distillation columns TC1 (S8-S2-S3) and TC3 (S6-S3-S7) for Cases 35L and 70H with feed and product streams excluding light byproducts such that S3=S5. ■ – n-butanol/water binary azeotrope; ◆ – ethanol/water binary azeotrope. Distillation boundary is the curved solid line between azeotropes.

As per-pass ethanol conversion in the FBR increase above 40% (Case 70H), the reactor effluent (S2) contains less ethanol and more water and *n*-butanol, thus shifting point S2 in Figure 3.2 away from the ethanol vertex of the residue curve map (to 41 mol% H2O, 32 mol% ethanol, and 27 mol% *n*-butanol for Case 70H). Attempting to recover pure *n*-butanol from Column TC1 as this shift in S2 occurs would result in ~8 mol% *n*-butanol in the distillate stream (S3) from Column TC1, as Stream S3 is limited in composition by the distillation boundary. This *n*-butanol in the distillate Stream S3 from Column TC1 would be lost from the process, or would have to be recovered via additional separation. Thus, for high ethanol conversion in the FBR, a different separation in Column TC1 must be carried out. This separation is shown as the line S3-S2-S8 for Case 70H in Figure 3.2, where an ethanol/water mixture is taken as the distillate stream (S3). The binary *n*-butanol/water mixture is then separated into pure *n*-butanol and pure water with the two column and decanter system shown in the lower box in Figure 3.1.

In the actual process simulation of Column TC1 with the complete reactor effluent (Stream S2), the light byproducts formed in reaction rapidly move upward in the vapor phase of Column TC1 and have little influence on the ethanol/*n*-butanol separation. The C_6 + alcohols in Stream S2, which have low miscibility with water, move rapidly downward in the liquid phase of Column TC1 and actually aid in facilitating the separation of water from *n*-butanol in Column TC1 as described above.

It is noted here that there are other scenarios possible for recovery of *n*-butanol from mixed alcohol streams. Patrascu propose a double wall distillation column integrated with other columns to recovery of dry *n*-butanol from ABE fermentation broth [101]. Pervaporation has also been examined as another route to recovery of *n*-butanol from fermentation [102]. Michaels et al.

described the use of benzene to break the *n*-butanol-water azeotrope in an ethanol condensation reaction process [99].

Energy for distillation reboilers and heating process streams is provided by high pressure steam at 257 °C and 45 bar produced in a steam generator fueled by natural gas and by the light byproducts from the Guerbet reaction. Because the plant is proposed to be located adjacent to an ethanol facility and not necessarily close to an external cooling water source, for the base case analysis all energy removed from the process (reactor, coolers, and column condensers), if not used elsewhere for heating, is ultimately rejected to air via air-cooled heat exchangers. The use of external water cooling is examined as an alternate process configuration.

3.2.2 Definition of Design Parameters

Capital and operating costs for ethanol conversion to higher alcohols have been evaluated from Aspen Plus V8.4 simulations with the SR-Polar equation of state as the properties package [9]. The four base case scenarios and several variations of the base process concept shown in Figure 3.1 have been examined. The outcome of the analysis determines the required selling price of *n*butanol for these different cases as a function of return on investment (ROI). As in any economic analysis, assumptions must be made, and values of parameters defined, in order to properly carry out the calculations. General design parameters used in the techno-economic analysis are summarized in Table 3.1; additional parameters defining unit operations for specific cases are given in Table 3.2 and Table 3.3.

Parameter	Value						
Location	Midwest U.S.						
Plant Capacity (10^6 kg <i>n</i> -butanol/yr)	75 (25 million gallons)						
Plant Lifetime	10 years						
Ethanol feed cost	\$0.53/kg (\$1.65/gallon)						
C ₆ + alcohol selling price (\$/kg)	$0.75 \times n$ -butanol selling price						
UTILITIES							
Natural gas cost	\$3.21/10 ⁶ kJ (\$3.39/10 ⁶ Btu)						
Electricity cost	\$18.6/10 ⁶ kJ (\$0.067/kWh)						
Cooling water cost	\$14.80/10 ³ m ³						
GENERAL DESIGN PARA	METERS						
REACTOR							
Tube size	2.5 cm 20 BWG, 316 SS						
Tube spacing	3.2 cm triangular centers						
Catalyst particle diameter	2.0 mm						
Catalyst cost (8% Ni/8% La ₂ O ₃ /γ-Al ₂ O ₃)	\$100/kg						
DISTILLATION COLU	JMNS						
Tray type	Sieve						
Tray efficiency	60%						
Tray spacing	0.61 m						
Approach to flooding	80%						
AIR-COOLED HEAT EXCHANGERS	AND CONDENSERS						
Configuration	Forced-air finned tube						
Heat transfer coefficient (bare tube area basis)	770 W/m ² /K						
Fin area / bare tube area ratio	17						
REBOILERS							
Configuration	Shell and tube, single pass						
Energy source	Steam (45 bar, 257 °C)						
Heat transfer coefficient	850 W/m ² /K						
WATER- or GLYCOL-COOLED HE	AT EXCHANGERS						
Configuration	Shell and tube, single pass						
Heat transfer coefficient	680 W/m²/K						

Table 3.1. Parameters for techno-economic analysis

Table 3.2. Specifications of reactor and distillation columns for four base case scenarios. ¹Case designations: The number refers to per-pass ethanol conversion in the fixed-bed reactor; "L" refers to low selectivities of 60% to n-butanol, 16% to C_6 + alcohols; "H" refers to high selectivities of 72% to n-butanol and 22% to C_6 + alcohols.

CASE ¹	35L	40L	35H	70H
Reactor (100 bar, 230 °C)				
Number of tubes (1" 20 BWG)	5144	5144	5144	8117
Tube length (m)	16.5	17.8	16.5	18.8
Catalyst mass (10 ⁴ kg)	3.60	3.93	3.60	6.56
WHSV (kg EtOH/kg catalyst/h)	1.45	1.15	1.45	0.33
Cost (10 ³ \$)	2,350	2,580	2,350	4,500
Column 1 (TC1) (5 bar absolute pressure)				
Number of actual stages	44	45	49	67
Feed stage	33	28	33	21
Diameter (m)	3.0	2.8	2.7	1.5
Reflux ratio (L _o /D)	1.2	1.2	1.5	3.0
Boilup ratio (V _N /B)	12.7	11.2	10.8	3.2
Cost (10 ³ \$)	670	670	630	380
Column 2 (TC2) (5 bar absolute pressure)				
Number of actual stages	57	47	57	49
Feed stage	35	33	23	40
Diameter (m)	1.7	1.6	1.2	0.6
Reflux ratio	4.5	4.5	6.8	3.5
Boilup ratio	0.9	1.0	0.5	0.6
Cost (10 ³ \$)	370	330	270	140
Column 3 (TC3) (1 bar absolute pressure)				
Number of actual stages	40	44	50	55
Feed stage	25	28	35	16
Diameter (m)	4.2	3.5	3.5	1.9
Reflux ratio	3.0	2.5	2.5	3.5
Boilup ratio	16.8	11.7	12.5	22.7
Cost (10 ³ \$)	1,110	850	920	420
Column 4 (TC4) (1 bar absolute pressure)				
Number of actual stages	25	25	25	25
Feed stage	13	11	13	13

Diameter (m)	1.9	1.9	1.9	2.7
Reflux ratio	2.5	2.5	2.5	2.0
Boilup ratio	16.6	16.6	14.4	29.1
Cost (10 ³ \$)	290	390	280	460
Column 5 (TC5) (1 bar absolute pressure)				
Number of actual stages	-	-	-	12
Feed stage	-	-	-	11
Diameter (m)	-	-	-	2.4
Reflux ratio	-	-	-	2.5
Boilup ratio	-	-	-	6.2
$Cost (10^3 \$)$	-	-	-	280
Column 6 (TC6) (1 bar absolute pressure)				
Number of actual stages	-	-	-	20
Feed stage	-	-	-	6
Diameter (m)	-	-	-	2.0
Reflux ratio	-	-	-	1.5
Boilup ratio	-	-	-	7.4
$Cost (10^3 \$)$	-	-	-	270
Steam Generator (45 bar, 257 °C)				
Capacity (10 ³ kg/h)	97.4	80.3	67.9	61.0
$Cost (10^3 \$)$	1,520	1,240	1,050	970

Table 3.2 (cont'd)

Location and scale for an initial *n*-butanol-from-ethanol facility fit with existing U.S. ethanol production facilities. The price of ethanol (\$1.65/gallon, or \$0.53/kg) is taken as the average wholesale price over a one year period of 2016-2017 [103]; across-the-fence prices would be expected to be lower. Utility prices are taken as conservative values for the Midwestern U.S. [104, 105]; a sensitivity analysis of process economics vs. ethanol price and utility prices is presented later in this chapter. Reactor and distillation column specifications are taken from standard references [106, 107] and are typical for initial process equipment design. Catalyst cost is conservatively estimated, as nickel and lanthanum oxide are both inexpensive materials. Air-

cooled heat exchanger properties are taken from a handbook on air-cooled exchanger design [108]; heat transfer coefficients for shell and tube heat exchangers were taken as conservative (low) values within the range of typical coefficients for each type of heat exchanger [109].

Table 3.3. Parameters for heat exchangers for Case 35L. ¹*All process heat provided by steam (257 °C, 45 bar) from steam generator except for Heater 1.* ²*All process cooling provided by direct air cooling in forced convection air-cooled heat exchangers. The area reported for air-cooled heat exchangers is bare tube area; fin:tube area ratio = 17:1.*

Unit	Target T (°C)	Approach ΔT (°C)	Heat Duty ^{1,2} (MW)	Area (m ²)	Cost (10 ³ \$)	Function
H1	177	53	5.8	68	60	Feed preheat using steam from reactor
H2	230	27	5.5	133	80	Feed preheat using generated steam
H3	95	55	-10.2	1330	160	Cooler between TC1 and TC2
C1	122	82	-13.7	218	180	Partial condenser on column TC1
R1	176	81	18.1	263	310	Partial reboiler on column TC1
C2	57	17	-8.1	619	520	Partial condenser on column TC2
R2	126	130	8.7	78	120	Partial reboiler on column TC2
C3	78	38	-34.8	1180	980	Total condenser on column TC3
R3	99	158	33.1	246	290	Partial reboiler on column TC3
C4	118	78	-3.6	59	50	Total condenser on column TC4
R4	152	105	4.4	50	80	Partial reboiler on column TC4

In the Aspen Plus simulations, the fixed bed reactor is simulated using the RStoic module with the required catalyst volume calculated from simple second-order kinetics of ethanol conversion with a fixed value of the rate constant ($k = 5.7 \times 10^{-5}$ m⁶/kmol EtOH/kg cat/h). Fixing the catalyst activity for all four cases allows comparison of the effect of selectivity on economics (cases 35L vs. 35H) and the comparison of designated per-pass conversion on economics (35L vs. 40L; 35H vs. 70H). In addition, in our prior work [25] we reported that small quantities of water present in the ethanol feed have little effect on conversion rate – for that reason, we neglect that up to 2.7 wt% water, which comes from ethanol recycle (Stream S6) as the azeotropic composition with water, may be present in the ethanol feed stream (S1) to the reactor.

Distillation columns are simulated using the rigorous column module RadFrac. Number of stages and reflux ratios are adjusted to achieve desired product purities from each column. Cases 35L, 35H, and 40L use the single-column block in the lower part of Figure 3.1 to separate *n*-butanol from C_{6+} alcohols; Case 70H uses the three column plus decanter block in Figure 3.1 to produce the C_{6+} alcohol product and dry *n*-butanol. The specifications of each piece of equipment from the Aspen Plus V8.4 simulation are entered into an in-house Excel spreadsheet that includes standard formulas for calculating the purchase cost of individual pieces of equipment [106-112]; these cost formulas are given in Appendix G. The reactor and distillation column specifications for each case are given in Table 3.2. Specifications for the heat exchangers in Case 35L, including column reboilers and condensers, are given in Table 3.3.

To determine total capital costs of the process, individual equipment purchase costs are summed and multiplied by standard multipliers for installation, facilities, engineering, working capital, etc. to arrive at the total capital costs for the process, which is then normalized with the CPI index to 2016 \$US [113]. Operating costs are similarly determined by entering raw material and utility requirements for each unit operation and using standard multipliers as required for labor, site maintenance, marketing, taxes, etc. [114]. The multipliers used in calculation of various contributions to the overall process economic analysis are given in Table 3.5, where total capital costs and operating costs for each of the four cases are presented.

Depreciation of plant capital costs (10 years, straight line) is combined with operating costs and feed stock costs to determine a total cost of production of *n*-butanol. This value is subtracted from product sale income to give annual net revenue, which is readily converted to an estimated annual return on investment.

3.3 Techno-Economic Analysis Results

3.3.1 Base Case

The compositions and flow rates of each of the streams in Figure 3.1 for Case 35L are given in Table 3.4. The energy demands for each column reboiler and condenser, and for each heat exchanger for Case 35L are shown in Figure 3.1. A summary of total plant capital costs and operating costs for the four base cases is given in Table 3.5. A graph of required *n*-butanol selling price versus desired ROI for the cases is presented in Figure 3.3.

Stream	F	S1	S2	S3	S4	S 5	S6	S7	S8	S9	S10
Temperature (°C)	25.0	230.0	210.0	121.9	57.2	126.5	78.5	98.9	122.1	117.9	151.8
Pressure (bar)	1.0	100.0	100.0	5.0	5.0	5.0	1.0	1.0	5.0	1.0	1.0
		Mole Flows (kmol/h)									
Ethanol	402.8	1124.3	730.7	730.6	9.0	721.6	721.5	0.1	0.1	0.1	0.0
<i>n</i> -Butanol	0.0	0.0	118.0	0.1	0.0	0.1	0.0	0.1	117.9	117.8	0.1
1-Hexanol	0.0	0.0	10.5	0.0	0.0	0.0	0.0	0.0	10.5	0.0	10.5
2-Ethyl-1-Butanol	0.0	0.0	10.5	0.0	0.0	0.0	0.0	0.0	10.5	0.1	10.4
Water	0.0	70.4	242.5	242.5	1.0	241.5	70.4	171.1	0.0	0.0	0.0
Carbon Dioxide	0.0	0.0	29.5	29.5	29.5	0.0	0.0	0.0	0.0	0.0	0.0
Methane	0.0	0.0	99.6	99.6	99.6	0.0	0.0	0.0	0.0	0.0	0.0
Diethyl Ether	0.0	0.0	6.5	6.5	6.5	0.0	0.0	0.0	0.0	0.0	0.0
Ethyl Acetate	0.0	1.1	9.5	9.5	8.4	1.1	1.1	0.0	0.0	0.0	0.0
Hydrogen	0.0	0.0	6.0	6.0	6.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	402.8	1195.8	1263.3	1124.3	160.0	964.3	792.9	171.3	139.0	118.0	21.0

Table 3.4. Composition of Process Streams for 35L Case.

Figure 3.3 shows that producing *n*-butanol via catalytic ethanol Guerbet condensation has significant potential for chemical applications of *n*-butanol, especially if higher selectivity to the desired alcohol products can be achieved. At present, *n*-butanol market prices range from \$1.30/kg to 2.00/kg [115, 116] depending on geographic location, so the required selling price reflected in

Figure 3.3 falls in the range of those values under most conditions. It should be noted that *n*-butanol potential as a fuel component or oxygenate in gasoline in the U.S. is not economical in the present scenario, as *n*-butanol does not compete with current ethanol (0.50-0.60/kg) or gasoline (0.80-1.00/kg) prices.

 Table 3.5. Economic analysis of base cases (Basis: 25 million gallons (75 million kg) n-butanol/yr).

 ¹Fixed costs include capital depreciation, taxes, and insurance. ²General Expenses include administration, distribution and selling costs, R&D, and financing costs

Case (Ethanol conversion, Selectivity)			40L	35H	70H
Ethanol conversion (%)	Ethanol conversion (%)			35	70
<i>n</i> -Butanol selectivity (%)			60	72	72
C ₆ + alcohol selectivity (9	6)	16	16	22	22
Parameter	Parameter Reference				
CAP					
Equipment Purchase Cost (PC)	9.14	8.33	7.64	9.61	
Instrumentation, controls	1.21 PC	11.02	10.05	9.21	11.59
Facility	0.75 PC	6.77	6.18	5.66	7.12
Contractor, engineering	0.82 PC	7.47	6.81	6.24	7.86
Contingency	5% CAPEX	1.88	1.72	1.57	1.98
Working Capital	5% CAPEX	1.81	1.65	1.52	1.91
TOTAL CAPITAL COSTS (CAPEX)	38.09	34.75	31.84	40.07	
OPERA	TING COSTS (10 ⁶ \$/	/yr)			
Raw Materials	Calculated	88.05	89.26	73.83	75.75
Utilities	Calculated	5.10	3.81	6.13	2.58
Labor and maintenance	6% OPEX	8.18	7.89	6.93	7.46
Laboratory / Analytical	1% OPEX	1.30	1.26	1.10	1.16
Royalties / Licensing Fees	2% OPEX	2.68	2.64	2.28	2.30
Fixed Costs ¹	16% CAPEX	6.21	5.66	5.19	6.53
Overhead	6% OPEX	8.04	7.92	6.84	6.90
General Expenses ²	11% OPEX	14.35	13.96	12.17	12.75
TOTAL OPERATING COSTS (OPEX	K) (10^6/yr)	133.90	132.42	114.47	115.43



Figure 3.3. Required n-butanol selling price vs. ROI for four base cases in Table 3.5.

The economic analysis shows that increasing the per-pass ethanol conversion from 35% to 40% at low selectivity values reduces required selling price of *n*-butanol, because the ethanol recycle stream and thus the quantity of ethanol fed to the reactor are smaller at higher conversion. Increasing ethanol conversion also reduces utility costs, as the contribution of the light byproducts formed to overall energy requirements for the process increases from 50% for Case 35L to 60% for case 40L, reducing utility costs by \$1.3 million annually.

Required *n*-butanol selling price increases when per-pass conversion is increased from 35% to 70% at high selectivity, because 1) a much larger reactor is required to achieve 70% conversion, and 2) the smaller quantity of ethanol in the reactor effluent (S2) at 70% conversion requires that the *n*-butanol/water azeotrope be broken with the traditional two column/decanter approach shown in the lower block of Figure 3.1. Thus, for this process, the preferred design is to run the reactor at a per-pass conversion of 35-40% to lower capital costs and avoid having to separate the *n*-

butanol/water azeotrope using multiple columns. Of course, if a more active catalyst can be developed, then the higher per pass conversion through the reactor may become preferred.

3.3.2 Sensitivity Analysis of Key Cost Drivers

An analysis of *n*-butanol required selling price dependence on ethanol feed cost, equipment purchase cost, and utility costs has been carried out for the Case 35L. For each of these parameters, the effect of increasing the base case value by 10%, 20%, and 30% on *n*-butanol required selling price has been evaluated. All other cost calculations in each case are scaled according to guidelines given in Table 3.5. Results for the complete range of ROI are given in Figure 3.4-Figure 3.6.



Figure 3.4. Sensitivity analysis of required n-butanol selling price dependence on purchase equipment costs for Case 35L. Percentage in legend refers to increment in equipment purchase costs over Case 35L equipment purchase costs of \$9.14 million.



Figure 3.5. Sensitivity analysis of required n-butanol selling price dependence on ethanol feed cost for Case 35L. Percentage in legend refers to increment in ethanol feed cost relative to Case 35L cost of \$1.65/gallon (\$0.53/kg).



Figure 3.6. Sensitivity analysis of n-butanol required selling price dependence on utility costs for Case 35L. Percentage in legend refers to increment in total annual utility costs relative to Case 35L utility costs of \$5.1 million.

For 25% ROI, increasing equipment purchase cost by 30% (from \$9.14 million to \$11.88 million) increases the required *n*-butanol selling price by 0.09/kg (Figure 3.4). For the same ROI, increasing ethanol feed cost by 30% (from \$1.65/gallon to \$2.15/gallon) increases the required *n*-butanol selling price by 0.36/kg (Figure 3.5). Finally, at the same ROI, increasing total utility (natural gas + electricity) costs by 30% (from \$5.10 million to \$6.33 million) increases the required *n*-butanol selling price by 0.02/kg (Figure 3.6). Clearly, the process economics for *n*-butanol production from ethanol are most heavily affected by ethanol feed cost.

3.3.3 Alternate Process Configurations

In addition to the four base cases examined, several alternate design scenarios have been simulated in Aspen Plus V8.4, and the techno-economic analysis has been carried out for each scenario. The results of these analyses are described in the following paragraphs.

3.3.3.1 <u>Two-fold Process Scale-up</u>

Case 35L was simulated and analyzed for *n*-butanol production of 150 million kg (50 million gallons) per year, twice the size of the base case capacity. Capital cost increased from \$38.1 million to \$71.1 million; operating costs related to raw materials and utilities essentially double for the larger scale. The overall reduction in required *n*-butanol selling price in scaling up to 150 million kg/yr from 75 million kg *n*-butanol annually is 0.03/kg n-butanol at 25% ROI.

3.3.3.2 <u>Heat Integration</u>

The process configuration in Figure 3.1 with the specified process pressures offers the opportunity for heat integrating the condensers of columns TC1 (121-122 °C) and TC4 (118 °C) with the reboiler of TC3 (99 °C). The heat-integrated process does not require a dedicated heat exchanger or utilities for the condensers of TC1 and TC4, but instead, direct heat exchange can take place between the distillate vapor streams of TC1 and TC4 and the reboiler liquid of TC3. Heat
integration reduces the overall utility costs for the process from \$5.1 million to \$3.2 million annually. A smaller steam generator is also required for the heat integrated case. Unfortunately, modestly larger heat exchangers are required for the heat integrated process, because thermal driving forces are smaller. Because of this, total capital costs for the heat integrated process are \$38.5 million vs. \$38.1 million for base case 35L. But overall, the required selling price of *n*-butanol for an ROI of 25% is approximately \$0.03/kg lower for the heat integrated case than for the base case 35L.

3.3.3.3 Drying of Ethanol/Water Recycle Stream

In the base-case process, unreacted ethanol is recycled as its azeotropic composition with water (Stream S6 in Figure 3.1); it is assumed, based on our prior studies [25], that the recycled water has a negligible effect on ethanol conversion and selectivity to higher alcohols. Nevertheless, the cost of removing water from the ethanol recycle stream (S6) via a conventional two-unit pressure swing molecular sieve unit was estimated for Case 35L. The molecular sieve unit is assumed to adsorb at 1.7 bar absolute and regenerate at 0.14 bar absolute, with 10% of the dry product ethanol stream directed to the regeneration of the saturated bed with an 8 h cycle time. The purchase cost of the molecular sieve unit is \$2.48 million [117, 118], which increases the total process CAPEX from \$38.1 million to \$47.7 million. Utility costs are essentially unchanged with addition of the molecular sieve unit, as the absence of water in S6 reduces the reboiler loads in separation to offset the increased reboiler duty in TC3 from the regenerating ethanol stream. The increased capital and operating costs associated with the molecular sieve unit together increase the required *n*-butanol selling price at 25% ROI by \$0.07/kg *n*-butanol.

It is worth noting that removing water from the recycle stream (S6) makes the process equivalent to a process with once-through ethanol flow of a rate equal to Stream S1 and the same conversion

and selectivity. The increase in cost noted above results from drying unreacted ethanol via molecular sieve before sending it to market. Similarly, the base cases are also equivalent to a process with once-through ethanol feed at a rate equal to S1 where only part of the feed ethanol and the exiting wet ethanol are dried by molecular sieves.

3.3.3.4 Method of Heat Removal

The four cases reported in Table 3.5 use direct air cooling in forced air convection heat exchangers to remove process heat from distillation column condensers and the intercooler between TC1 and TC2. These exchangers are sized according to heat load and approach ΔT , and the electrical power requirements for the fans are included in utility costs for the processes [108]. The process design for Case 40L has also been carried out with two alternative heat exchange systems: 1) the use of cooling water from an external source or cooling ponds on-site in direct exchange with process streams; and 2) a closed-loop glycol cooling system in which process energy is removed via glycol cooling and the glycol is cooled in a secondary air-cooled heat exchanger. For cooling with an external water source, the incoming water is assumed to be at 25 °C and a maximum cooling water ΔT of 10 °C. With these design parameters, cooling water demand for the process is 5.3 × 10³ m³/h. For the closed-loop coolant, two heat exchangers are required for each location, leading to an increase in capital and operating cost. This increase in capital cost results from the large heat exchanger areas required, as the overall temperature driving force for heat removal to air must be divided between two heat exchangers. This renders the cost of a facility with closed loop cooling substantially more expensive, as seen in Table 3.6. The higher costs render the closed loop cooling unattractive; the only likely advantage of such a system would be improved control of condenser heat duty and temperature. In contrast, external water cooling, if such a source is available, is slightly less expensive than air cooling, and has advantages of reduced noise and possible

mechanical failures related to air-cooled heat exchange. Returning external water to a river or lake has possible environmental consequences regarding thermal pollution, so cooling ponds are preferable alternatives if makeup water and sufficient space are available.

Parameter	Air cooling	Glycol closed loop / Air	External water
TOTAL Capital Costs (CAPEX) (\$106)	34.7	66.5	32.5
Utilities (\$10 ⁶ /yr)	3.81	4.17	4.30
TOTAL Production Costs (\$10 ⁶ /yr)	132.4	144.8	132.3
Required <i>n</i> -butanol selling price at 25% ROI (\$/kg)	1.56	1.78	1.55

Table 3.6. Capital and operating costs for different heat removal options for Case 40L.

3.3.3.5 <u>Alternate Location of Ethanol Feed</u>

As stated earlier, for Case 70H (70% ethanol conversion) there is insufficient ethanol present in the reactor effluent to remove all water produced in reaction to the distillate of Column TC1 without taking substantial *n*-butanol into the distillate as well. To further examine the possibility of improving the economics of Case 70H, an alternate scenario was examined in which fresh ethanol to the process is fed into Column TC1 instead of into the FBR. Simulation of this configuration shows that dry *n*-butanol can be produced as a bottoms of Column TC1 with little *n*-butanol in the distillate (similar to Column TC1 represented as the line S8-S2-S3 for Case 35L in Figure 3.2), thus eliminating the need for the two column/decanter system to separate the *n*-butanol/water azeotrope. However, the economic analysis shows that feeding fresh ethanol to Column TC1 leads to substantial increases in capital and utility costs of Columns TC1, TC2, and TC3 that more than offset the capital and operating cost savings from eliminating the butanol/water separation columns. At 25% ROI, the required *n*-butanol selling price with ethanol fed to Column TC1 is \$1.45/kg, as opposed to \$1.35/kg for the base case 70H where fresh ethanol is fed to the

FBR. Thus, the alternate ethanol feed location is impractical, despite the fact that it eliminates separating the *n*-butanol/water azeotrope using two columns and the decanter.

3.4 Conclusions

Based on experimental results and analysis of phase equilibria for the continuous condensed-phase reaction of ethanol to *n*-butanol and C_{6+} alcohols, a process concept has been developed that converts all ethanol and produces pure *n*-butanol and a mixed higher (C_{6+}) alcohols stream as products, while minor byproducts formed are burned to provide process energy. The process has been simulated in Aspen Plus V8.4 for several combinations of per-pass ethanol conversion and selectivity to product alcohols, and an economic analysis of each combination has been carried out. For *n*-butanol selectivities achieved in laboratory studies, the required selling price is \$1.55-\$1.60/kg, close to current *n*-butanol selling prices for chemical applications. If selectivity to higher alcohols can be improved, then the production of *n*-butanol and C_{6+} alcohols from ethanol for use as industrial chemicals becomes attractive.

APPENDICES

APPENDIX G. Formulas for Cost Estimation

The following section contains the formulas used in the estimation of equipment purchase costs for the proposed process. Where identical, the definition of various symbols is not repeated after each equation.

G.1. Reactor (Shell and tube configuration) [107]

$$C_R(\$) = b[(1+C_T)A_{ht}]E_i$$

where

$$b (base cost, \$/ft^2) = \left[\frac{6.6}{1-e^{\left[\frac{7-D_i}{27}\right]}}\right] pfr$$

 $D_i(in) =$ shell I.D.

 p_{cm} = cost multiplier for 0.D., pitch and layout angle = 0.98

 f_{cm} = cost multiplier for TEMA-type front head = 0.95

 r_{cm} = cost multiplier for TEMA-type rear head = 0.9

 C_T = sum of base cost corrections for shell type, expansion joint, tube length, number of tube passes, shell side and tube side design pressures, materials of construction, and tube gage = 2.3

 A_{ht} (ft^2) = surface area for heat transfer

 E_i = escalation index (Chemical Engineering Plant Cost Index) [113]

G.2. Tray column [106]

$$C_{TC}(\$) = (f_1 C_{bs} + N f_2 f_3 f_4 C_{bt} + C_{pl}) E_i$$

where

$$C_{bs} = \text{base shell cost}(\$) = \exp[7.12 + 0.148(lnW) + 0.0249(lnW)^2 + 0.0158\left(\frac{L}{D}\right)\ln(\frac{T_b}{T_p})$$

 C_{bt} = base tray cost (\$) = 375.5exp(0.1379D)

 $C_{pl} = \text{ base platforms and ladders cost ($)} = 204.9D^{0.6332}L^{0.8016}$

 $f_1 = \text{cost}$ multiplier for column material= 2.1

 $f_2 = \text{cost}$ multiplier for column material= 1.7

 $f_3 = \text{cost}$ multiplier for tray type= 0.95

 $f_4 = \text{cost multiplier for tray numbers} = 0.1-1.5$

N=number of trays

W(lb) = vessel weight

L(ft) =column height

D(ft) =column diameter

 T_b (in)=head thickness

 T_p (in) = shell thickness

G.3. Steam generator [114]

$$C_{SG}(\$) = C_{bg}E_i$$

where

 C_{bg} (\$)= base steam generator cost

G.4. Air cooled heat exchanger [108]

$$C_C(\$) = C_{ac}SE_i$$

where

 $S = reduced heat load (kW/°C) = Q/(T_i - T_a)$

 C_{ac} (°C \$/kW) = cost function = 5-11 (process inlet and outlet temperature dependent)

 $T_i (^{o}C) =$ process inlet temperature

 $T_a (^{o}C) =$ ambient temperature= 40 °C (*Except for one heat exchanger in the ethylene glycol case where Ta = 30 °C)

Q(kW) = heat load

G.5. Other heat exchangers [119]

$$C_{HE}(\$) = C_B F_D F_P F_M E_i$$

where

 $C_B = base \ cost \ (\$) = \exp[8.551 - 0.30863(lnA_{HE}) + 0.06811(lnA_{HE})^2]$

 A_{HE} (ft^2) = exchanger surface area

 F_D = cost multiplier for the exchanger type = 0.7 for fixed head and 1.4 for kettle reboiler

 $F_P = \text{cost}$ multiplier for the design-pressure (surface area dependent)

 F_M = cost multiplier for the material of construction (surface area dependent)

4 Fusel Alcohols Production Studies

4.1 Introduction

The predominant pathway for the conversion of hexose sugars (sucrose, glucose, maltose, etc.) in yeast of the Saccharomyces family is the Embden Meyerhof Pathway [120]. In this pathway, the main product (~99%) is ethanol, with the byproducts typically known as "fusel" oils or alcohols [121, 122]. Fusel alcohols, the equivalent German word for "bad liquor", consist of higher carbon number alcohols such as 3-methyl-1-butanol (also known as isoamyl alcohol, which is the major component), *n*-propanol, isobutanol, and optically active amyl alcohol [123]. Produced primarily from fermentation-derived amino acids through a pathway proposed by Ehrlich [124], low concentrations of these compounds have essential applications as aroma and flavoring agents in the food and beverage industry [122, 125-128]. Furthermore, their mixture has the potential for uses in industry such as solvents or cleaners, and can also react with various organic acids to make mixed esters that may have desirable properties for the same general applications or as fuels [129]. Fusel alcohols contain at least one hydrogen on the β -position of the carbon adjacent to their OH group. Thus, they can contribute to Guerbet reactions if exposed to desirable reaction conditions. The Guerbet reaction can be a direct aldol condensation between two fusel alcohol with the same molecular structure, or it can be a cross-condensation reaction between ethanol and a fusel alcohol, or two different fusel alcohols. As mentioned earlier, ethanol and fusel alcohols are the products of the same fermentation process. Large-scale production of bioethanol through the fermentation process leaves large quantities of fusel alcohols available for further processing. Therefore, trying to produce a value-added product from ethanol-fusel alcohols mixture enhances the profitability

of the fermentation process. If successful, the cost of producing ethanol may be reduced significantly through the sale of higher-value fusel alcohol products.

There have been few studies on the Guerbet reaction of fusel alcohols. Matsu-ura et al. studied the conversion of fusel alcohols over a homogeneous Ir-based catalyst at 120 °C and atmospheric pressure and obtained yields of as high as 98% for the self-coupling of C_5 and C_6 alcohols, and 86% for the self-coupling of C_{12} alcohol [130]. They also studied isoamyl alcohol as the feed and were able to get 50% yield of C_{10} alcohol at the same reaction conditions. Later, Busch et al. confirmed the feasibility of the synthesis of branched C_{10} alcohols through the Guerbet reaction of isoamyl alcohols at 180 °C and elevated pressure ranges (1.4-4.6 bar) using a Pd/C based homogeneous catalyst [131]. Unfortunately, the authors did not provide any analytical data for this reaction.

No studies have been conducted on the Guerbet reaction of an ethanol and isoamyl alcohol mixture thus far. Therefore, the prospects of the batch production of value-added products from different combinations of this mixture have been addressed in this study. Later, the feed mixture with the highest isoamyl products selectivity is employed in a continuous reactor to confirm the batch studies and find an ideal reactor configuration for the system. Finally, kinetic modeling has been developed to compare the rate of formation of the main products in the system.

4.2 Materials and Methods

4.2.1 Materials and Catalyst Preparation

The materials used and the catalyst preparation method in this chapter are the same as those described in Section 2.2.1. Isoamyl alcohol (>98%, Sigma-Aldrich) was mixed with anhydrous ethanol (Koptec, 200 proof) in the desired ratios as the feed of the experiments. Moreover, the

catalyst known as Ni (IV) in Chapter 2, with the composition of 8.0 wt% Ni/9.0 wt% La_2O_3/γ -Al₂O₃ was used for both batch and continuous experiments.

4.2.2 Reactor System

4.2.2.1 Batch Experiments

Batch reactions were performed in a 300 ml Parr reactor (Model 4842, Parr Instruments, Chicago, Illinois) with reaction times between 22 and 51 hours. Typically, 120 g of the feed mixture along with the desired amount of catalyst were placed into the reactor. The reactor was purged with nitrogen and sealed with 1 atm of nitrogen overpressure. The reactions were carried out at autogenous pressure.

The Parr reactor contained an Omega 1/8" stainless steel Type J thermocouple which was not calibrated for this study; nevertheless, previous works had shown its accuracy in the range of ± 1 °C [9, 25]. Pressure measurements for all experiments were done using an electronic pressure transducer (200 atm) that was calibrated against a 100 atm mechanical gauge with increments of 0.7 atm. The mechanical stirrer was set at 1000 rpm during the reaction.

An initial liquid sample was taken after purging nitrogen to the reactor and before heating the reactor to the reaction temperature. Usually, a second sample of the liquid phase was taken after 1-2 h via a dip tube into an evacuated 1/8" × 8" stainless steel sample tube with a valve at each end to isolate the liquid sample from the reactor. The sample tube was vented after isolating, and the liquid sample was analyzed by gas chromatography. The reactor pressure was monitored during the reaction and after cooling the reactor at the end of reaction to help with determining product compositions and quantities of gas formed. The quantity of gaseous products in the reaction was determined at the end of each experiment by weighing the entire cooled reactor with

chemicals both before and after depressurization. The gas exhausted during depressurization was collected in a gas bag and analyzed by gas chromatography.

4.2.2.2 Continuous Experiments

Reactor setup and experimental steps in the continuous experiments are the same as ethanol Guerbet experiments discussed in Section 2.2.2. Experiments were done using 29.9 g of catalyst, and for the integrity of the results, the feed had the composition of 80 mol% ethanol and 20 mol% isoamyl alcohol. Experimental temperature was changed from 170 °C to 250 °C, and the liquid feed flow rate was varied from 0.3 ml/min to 1.3 ml/min, corresponding to the WHSV of 0.5 h^{-1} to 2.1 h^{-1} . Products were collected in two different traps; an ice/water trap for condensing liquid components at room temperature, and a gas bag for gaseous products. These samples were analyzed using different gas chromatography instruments discussed in the next section.

4.2.3 Analytical Methods

The analytical methods and instruments used in this chapter are the same as those described in Section 2.2.3.

4.3 Experimental Results

4.3.1 Batch Experiments

Guerbet reactions with two alcohols lead to a significantly wider variety of product species than for a single alcohol. The key products of the mixed isoamyl alcohol (IA) and ethanol experiments are shown on the right side of Figure 4.1; the alcohols responsible for forming the products are shown on the left side of this figure.

Results obtained from batch reaction studies are summarized in Table 4.1. There are two sets of results presented: Reactions B2-B6 were run for approximately 24 h, and reaction B7 was run for

51 h. Both sets were studied at 230 °C on the scale of 120 g of feed. Each reaction had a different composition of alcohols, ranging from 100% ethanol to 100% isoamyl alcohol.



2-isopropyl-5-methyl-1-hexanol

Figure 4.1. Primary products observed from reaction of ethanol and isoamyl alcohol mixtures.

The results in Table 4.1 show that ethanol selectivity to *n*-butanol and C_6 alcohols decline as IA concentration increases until a majority of ethanol is reacting with isoamyl alcohol (B4) instead of with itself.

	Initial		Conv. (%)		Selectivity (%)							
Exp. Molar EtOH/ IAOH	Molar Reaction			E+(E4OU Dro d		EtOH + IA Cross Prod.			IAOH		
	Ratio	time (h)	EtOH	IAOH	EIOH PIOU.			w.r.t. EtOH		w.r.t. IA OH		Prod.
		2.011		C_4	C_6	C_8	C ₇	C ₉	C ₇	C ₉	C ₁₀	
B2	1/0	22	21.1	-	67.5	22.0	5.0	0.0	0.0	-	-	-
B3	3.8/1	23	30.1	13.7	50.8	15.5	3.3	6.0	0.0	50.1	6.8	0.0
B5	1/1	22	35.2	11.4	39.0	9.6	3.0	16.8	0.3	52.1	5.6	0.9
B4	1/4	24	43.3	9.7	25.5	3.2	8.6	39.5	2.9	43.8	2.9	3.2
B6	0/1	24	-	11.1	-	-	-	-	-	0.0	0.0	4.8
B7	3.8/1	51	40.5	14.6	47.9	15.9	3.6	5.9	0.1	62.9	8.7	0.6

Table 4.1. Results of batch reactor experiments with 120 g of (ethanol-isoamyl alcohol) mixture at 230 °C,4.85 g of 8.0 wt% Ni/9.0 wt% La₂O₃/γ-Al₂O₃ is used as the catalyst.

From the two reactions with pure alcohols (B2 and B6), the rate of ethanol conversion is approximately twice that of isoamyl alcohol. A detailed kinetic model for the combined ethanol/isoamyl alcohol reaction system is developed in Section 4.3.3.

4.3.2 Continuous Experiments

Reactions were also carried out in the continuous condensed-phase reactor over the standard 8 wt% Ni/9 wt% La₂O₃/Al₂O₃ catalyst with a reactor feed mixture of 80 mol% ethanol and 20 mol% isoamyl alcohol. Results of these experiments are given in Table 4.2. The results show that isoamyl alcohol reacts with ethanol and with itself to form a variety of straight-chain and branched-chain alcohols. Recoveries for both batch and continuous reactions are reasonable (70-90%) for these preliminary experiments, especially given that gases contribute another 5-10% of total alcohols converted. Nonetheless, unlike alcohol products, the source of gaseous products (ethanol or IA) is indistinguishable.

Conditions				Selectivity (%)							
		Conversion (%)		EtOH Products		EtOH + IAOH Cross Products			IAOH		
						w.r.t. EtOH		w.r.t. IAOH		Products	
T (°C)	WHSV (h ⁻¹)	EtOH	IAOH	C4	C ₆	C ₈	C ₇	C 9	C ₇	C9	C ₁₀
	0.8	10.1	3.5	67.0	11.8	1.5	5.2	0.9	62.2	5.6	0.0
210	1.4	7.8	2.1	66.6	8.9	0.8	4.5	0.7	69.0	5.1	0.0
	2.1	5.8	0.81	62.4	6.4	0.3	3.8	0.5	144.8	9.2	0.0
	0.8	23.4	9.4	58.1	14.4	2.6	6.3	1.4	62.2	7.0	0.3
230	1.4	17.1	5.3	59.8	12.3	1.9	5.9	1.1	76.4	7.4	0.2
	2.1	12.7	6.8	67.6	12.5	1.7	5.7	1.1	42.3	4.1	0.0
	0.8	42.4	11.9	47.9	13.7	2.8	5.5	1.4	78.1	9.8	0.5
250	1.4	38.1	13.7	45.7	14.3	3.2	5.6	1.5	61.5	8.4	0.4
	2.1	31.2	11.0	47.4	13.0	2.6	5.2	1.3	59.4	7.6	0.3

Table 4.2. Results of continuous condensed-phase experiments with 4/1 molar ratio of ethanol/isoamyl alcohol and 29.9 g of 8.0 wt% Ni/9.0 wt% La₂O₃/γ-Al₂O₃ catalyst. ¹Conversion is too low; thus, this set of data are unreliable.

4.3.3 Kinetic Model Development

A kinetic model has been developed for the ethanol/isoamyl reaction mixture. The following key reactions are considered for this modeling:

$$C_{2}H_{5}OH + C_{2}H_{5}OH \xrightarrow{k_{1}} C_{4}H_{9}OH + H_{2}O$$

$$Reaction 4.1$$

$$C_{2}H_{5}OH + C_{5}H_{11}OH \xrightarrow{k_{2}} C_{7}H_{15}OH + H_{2}O$$

$$Reaction 4.2$$

$$C_5H_{11}OH + C_5H_{11}OH \xrightarrow{k_3} C_{10}H_{21}OH + H_2O$$
 Reaction 4.3

For simplicity, C_2H_5OH , $C_5H_{11}OH$, and $C_{10}H_{21}OH$ are shown as E, I, and C10 in the equations, respectively. Initially, the continuous system was modeled for the kinetic studies since it provided experimental results at three different superficial residence times (τ). The following rate equations were developed for the continuous system:

$$r_E = -2k_1 C_E^2 - k_2 C_E C_I = \frac{1}{\rho_{cat}} \frac{dF_E}{dV_{cat}} \times \frac{\dot{V}_{soln}}{\dot{V}_{soln}} = \frac{1}{\rho_{cat}} \frac{dC_E}{d\tau}$$
 Equation 4.1

$$r_I = -k_2 C_E C_I - 2k_3 C_I^2 = \frac{1}{\rho_{cat}} \frac{dF_I}{dV_{cat}} \times \frac{\dot{V}_{soln}}{\dot{V}_{soln}} = \frac{1}{\rho_{cat}} \frac{dC_I}{d\tau}$$
 Equation 4.2

$$r_{C10} = k_3 C_I^2 = \frac{1}{\rho_{cat}} \frac{dF_{C10}}{dV_{cat}} \times \frac{\dot{V}_{soln}}{\dot{V}_{soln}} = \frac{1}{\rho_{cat}} \frac{dC_{C10}}{d\tau}$$
 Equation 4.3

where r_E , r_I , and r_{C10} are in the unit of mol/kg of catalyst/h, and k_1 , k_2 , and k_3 are in the unit of m⁶ of solution/kg of catalyst/mol/h. Euler method of integration with the step size of one minute was used for numerically integrating the above equations:

$$C_{E_{\tau+\Delta\tau}} = -\rho_{cat} \left[2k_1 C_{E_{\tau}}^2 + k_2 C_{E_{\tau}} C_{I_{\tau}} \right] \Delta \tau + C_{E_{\tau}}$$
Equation 4.4

$$c_{I_{\tau+\Delta\tau}} = -\rho_{cat} [\kappa_2 c_{E_{\tau}} c_{I_{\tau}} + 2\kappa_3 c_{I_{\tau}}] \Delta \tau + c_{I_{\tau}}$$
 Equation 4.5

$$C_{C10_{\tau+\Delta\tau}} = -\rho_{cat} \left[k_3 C_{I_{\tau}}^2 \right] \Delta \tau + C_{C10_{\tau}}$$
 Equation 4.6

Modeling was performed for three temperatures (210 °C, 230 °C, and 250 °C) and the contact times of as high as 70 minutes, based on the experimental data available for the continuous system. The experimental data were calculated based on the selectivities reported in Table 4.2. For each one of the components modeled, the following equations were used for calculating the experimental concentrations at different contact times:

$$C_{E} = C_{E_{0}}[1 - X_{E}(S_{B} + S_{C7E})]$$
Equation 4.7
$$C_{I} = C_{I_{0}}[1 - X_{I}(S_{C7I} + S_{C10})]$$
Equation 4.8
$$C_{C10} = C_{C10_{0}}[X_{I} {S_{C10}/2}]$$
Equation 4.9

where C_{E_0} , C_{I_0} , and C_{C10_0} are the initial concentrations of each of the components in mol/L of solution. Moreover, S_B, S_{C7E}, S_{C7I}, and S_{C10} are the selectivities toward butanol, C₇ alcohol products (with respect to ethanol), C₇ alcohol products (with respect to isoamyl alcohol), and C₁₀ alcohol product (i.e. 2-isopropyl-5-methyl-hexanol). In the selectivity calculations, the share of secondary products (such as butanol products) has also been considered and added to the selectivity toward primary products; these calculations are shown in detail in Appendix H.

Figure 4.2-Figure 4.4 show the comparison of the modeling results with experimental data at each temperature for the (4/1) molar ratio of ethanol/isoamyl alcohol mixture. The modeling has not been performed for 2-isopropyl-5-methyl-hexanol (C10) at 210 °C since this chemical was not detected at that temperature. The results indicate a good fit between modeling and experimental data at different temperatures for each of the three species modeled. Based on the modeling results, rate constants were developed for the three reactions at each temperature. For the three temperatures, the ratio of the rate constants for Reaction 4.1 and Reaction 4.2 (k_1/k_2) was between 1.4 and 1.6; this ratio for Reaction 4.3 and Reaction 4.2 (k_3/k_2) was between 0.007 and 0.010. This shows that ethanol-ethanol Guerbet reaction is the fastest reaction among the three, and isoamyl-isoamyl condensation is the slowest, which is explained by the inductive effect; the electron-donating alkyl groups surrounding the OH group of the isoamyl alcohol destabilize the negatively charged oxygen and prevent the dehydrogenation reaction from happening.

Based on the rate constants obtained, an activation energy was calculated for each one of the reactions. The activation energies for ethanol-ethanol (Reaction 4.1), ethanol-isoamyl alcohol (Reaction 4.2), and isoamyl alcohol-isoamyl alcohol (Reaction 4.3) reactions were found to be 80 kJ/mol, 89 kJ/mol, and 110 kJ/mol, respectively. The E_a obtained for Reaction 4.1 is comparable to the global activation energy of 121 kJ/mol calculated based on ethanol conversion in Chapter 2

using Ni(I) (8 wt% Ni/4.5 wt% La₂O₃) catalyst, considering that these two catalysts have different lanthanum compositions.



Figure 4.2. Comparison of simulated and experimental reactor outlet concentrations for the ethanol/isoamyl alcohol continuous Guerbet experiments at T=210 °C using 8.0 wt% Ni/9.0 wt% La_2O_3/γ -Al₂O₃ as the catalyst. (a)Ethanol, (b)Isoamyl alcohol.





Figure 4.3. Comparison of simulated and experimental reactor outlet concentrations for the ethanol/isoamyl alcohol continuous Guerbet experiments at T = 230 °C using 8.0 wt% Ni/9.0 wt% La_2O_3/γ -Al₂O₃ as the catalyst. (a)Ethanol, (b)Isoamyl alcohol, (c)2-Isopropyl-5-methyl-hexanol.





Similar calculations were made for the batch system results, except that the following equations were used in the modeling process:

$$r_E = -2k_1 C_E^2 - k_2 C_E C_I = \frac{1}{m_{cat}} \frac{dN_E}{dt} \times \frac{V_{soln}}{V_{soln}} = \frac{V_{soln}}{m_{cat}} \frac{dC_E}{dt}$$
Reaction 4.4

$$r_{I} = -k_{2}C_{E}C_{I} - 2k_{3}C_{I}^{2} = \frac{1}{m_{cat}}\frac{dN_{I}}{dt} \times \frac{V_{soln}}{V_{soln}} = \frac{V_{soln}}{m_{cat}}\frac{dC_{I}}{dt}$$
Reaction 4.5

$$r_{C10} = k_3 C_I^2 = \frac{1}{m_{cat}} \frac{dN_{C10}}{dt} \times \frac{V_{soln}}{V_{soln}} = \frac{V_{soln}}{m_{cat}} \frac{dC_{C10}}{dt}$$
Reaction 4.6

For the batch system, there is only one data point for each one of the feed compositions. Therefore, the rate constants determined could be less accurate because there are fewer experimental data to confirm the modeling results. Table 4.3 shows the rate constants obtained for each one of the batch experiments and their comparison with the continuous system results obtained at the same reaction temperature. It can be observed that the values of k_1 , k_2 , and k_3 are in the same order of magnitude for each batch experiment and the continuous experiment. Furthermore, the ratios of rate constants are in the same range as those mentioned earlier (1.3-1.9 for k_1/k_2 , and 0.005-0.013 for k_3/k_2). This indicates that even if reaction conditions (such as temperature integrity, catalytic activity, etc.) affect the rate constants, each reaction proceeds at the same proportional rate compared to the others.

Table 4.3. Rate Constants developed for different batch experiments and their comparison with the one
obtained for the continuous system at 230 °C.

Europimont	k_1	k_2	k_3	k_1/k_2	<i>k</i> ₃ / <i>k</i> ₂
Experiment	(m ⁶ sc	olution/kg catalys			
B2	9.3E-06	-	-	-	-
B3	1.3E-05	9.7E-06	4.7E-08	1.3E+00	4.8E-03
B5	2.5E-05	1.9E-05	1.3E-07	1.4E+00	6.8E-03

B4	6.8E-05	3.6E-05	2.6E-07	1.9E+00	7.2E-03
B6	-	-	3.8E-07	-	-
B7	8.9E-06	6.8E-06	9.0E-08	1.3E+00	1.3E-02
Continuous System	9.2E-06	6.6E-06	4.7E-08	1.4E+00	7.1E-03

4.4 Conclusions

Guerbet reactions of ethanol-isoamyl alcohol mixtures were conducted using the 8.0 wt% Ni/9.0 wt% La₂O₃/ γ -Al₂O₃ catalyst in both batch and continuous systems. While ethanol selectivity toward C₄+ alcohols stayed as high as 72% at 42% conversion, isoamyl alcohols selectivity of 88% toward higher alcohols (mainly cross-condensation products with ethanol) at 12% conversion was achieved. Kinetic modeling for three primary Guerbet reactions (C₂-C₂, C₂-C₅, and C₅-C₅) for both continuous and batch systems provided consistent results with respect to the experimental data and different feed compositions. A fixed ratio of the rate constants at different conditions were also obtained. Finally, activation energies determined from the rate constants at different temperatures indicated that the ethanol-ethanol and isoamyl alcohol-isoamyl alcohol reactions possess the smallest and largest barriers for activating the molecules, respectively.

APPENDICES

APPENDIX H. Detailed Selectivity Calculations

The formulas used for the calculation of the total selectivity of different chemicals in Equation 4.7 and Equation 4.9 are as follows:

$$S_{B} = CS_{B} + \frac{2}{3}CS_{C6} + \frac{1}{2}CS_{C2C6} + \frac{4}{5}CS_{C4C4}$$
Equation 4.10
$$S_{C7E} = CS_{C7E} + \frac{1}{2}CS_{C9E}$$
Equation 4.11
$$S_{C7I} = CS_{C7I} + CS_{C9I}$$
Equation 4.12
$$S_{C10} = CS_{C10}$$
Equation 4.13

where:

 CS_B = Calculated selectivity for butanol,

 CS_{C6} = Calculated selectivity for C₆ alcohols,

 CS_{C2C6} = Calculated selectivity of C₈ alcohols that are the result of the reaction of an ethanol and a C₆ alcohol,

 CS_{C4C4} = Calculated selectivity of C₈ alcohols that are the result of the reaction of two C₄ alcohols.

 CS_{C7E} = Calculated selectivity of C₇ alcohols with respect to ethanol,

- CS_{C9E} = Calculated selectivity of C₉ alcohols with respect to ethanol,
- CS_{C7I} = Calculated selectivity of C₇ alcohols with respect to isoamyl alcohol,
- CS_{C9I} = Calculated selectivity of C₉ alcohols with respect to isoamyl alcohol,
- CS_{C10} = Calculated selectivity of C₁₀ alcohols.

All the calculated selectivities are based on the analytical results obtained from GC.

5 Acrylate Production from 2-Acetoxypropanoic Acid Esters

5.1 Introduction

Acrylic acid (2-propenoic acid, C₃H₄O₂) is the simplest alkenoic acid. It can react with itself or other monomers to form polymers that have extensive application as adhesives, polishes, binders, coatings, paints, detergents, fibers, polyelectrolytes, flocculants, diapers, and dispersants. Based on a 2015 report, the acrylic acid market size was 5.8 million metric tons with demand growing at 6.3% per year and prices ranging from \$1600-\$2200 per ton depending on its grade [132, 133]. Acrylic acid is traditionally produced by a petroleum-based two-step gas-phase process (Figure 5.1) which involves the catalytic oxidation of propylene to acrolein, followed by the reaction of acrolein with oxygen in the presence of a catalyst [134]. Acrolein yields of 83-90% and acrylic acid yield of 5-10% are obtained in the first step, and a maximum 97.5% yield of acrylic acid is reported for the second step.



Figure 5.1. Petroleum-based route to acrylic acid from propylene

Recently, renewable biobased routes to acrylic acid have received attention, both to address resource and climate issues and to ensure a stable, inexpensive supply in light of volatile petroleum markets. A few of those routes have garnered the most attention to replace the existing propylene-based process; these include dehydration of glycerol to acrolein, direct dehydration of lactic acid

(2-hydroxypropanoic acid) or 3-hydroxypropanoic acid, and pyrolysis of acetoxy isopropionic acids esters or salts.

5.1.1 *Glycerol Dehydration*

In 1933, Schwenk introduced a method for hydrolyzing glycerol to acrolein in the vapor phase with 80% acrolein yield [135]. Later, several catalysts were proposed for increasing the acrolein yield for this reaction in the gas phase, liquid phase, or in subcritical or supercritical water [136-140]. Among those, Fe₃PO₄ had the best results with 92% acrolein yield [139]. Despite the high yields obtained, catalyst deactivation and by-product formation are challenges for acrolein production via this route.

According to a recent review article [132], there have been attempts to directly produce acrylic acid from glycerol in the presence of different catalysts, with the highest yield of 75% obtained so far. However, in both routes, catalyst deactivation and sustaining selectivity are the primary challenges to commercialization.

5.1.2 Hydroxypropanoic acid Direct Dehydration

Acrylic acid is also produced by the direct dehydration of lactic acid (2-hydroxypropanoic acid) or 3-hydroxypropanoic acid. Holmen first introduced direct lactic acid dehydration by examining several lactate substrates (free lactic acid, ammonium lactate, alkyl lactates) and achieving 68% acrylic acid yield with free lactic acid at 400 °C with Na₂SO₄ and CaSO₄ as the catalyst [141]. Subsequent studies were primarily focused on phosphate [142-149] and sulfate [150-152] catalysts, but none of those gave acrylic acid yields higher than those obtained by Holmen.

Naito and Abe from the same research group used molecular sieve 13X ion-exchanged with cesium and ruthenium and untreated molecular sieve 13X for the direct dehydration of methyl lactate [147, 153]. An unprecedented methyl acrylate yield of 92-93%, which was claimed to be stable over

minimum operation time of 40 h, was reported in these studies. Later, additional attempts were made to modify the structure of molecular sieves with sodium, potassium, alkali phosphates, and lanthanum; but none achieved yields of above 66% [148, 149, 154-160]. Several of these studies showed that diluting the reactant with some material such as methanol [148, 153] or water [156, 158-161] increases the reactant conversion and acrylate ester/acrylic acid selectivity. A recent review [162] gives an excellent summary of lactic acid and lactate ester dehydration pathways.

Besides lactic acid, 3-hydroxypropionic acid is another substrate which can be directly dehydrated to acrylic acid. Studies on this reaction have shown an acrylic acid yield of 88% using solid acid catalysts [163-165]. In 2015, Cargill Corporation started an investment on the commercial development of acrylic acid production through acquiring OPX Biotechnologies, which has proprietary technology for producing acrylic acid from 3-hydroxypropionic acid [166].

5.1.3 2-Acetoxypropanoic Acid Indirect Dehydration

Lactic acid, lactate esters, or lactate salts can react with acetic anhydride or acetic acid to produce 2-acetoxypropanoic acid (APA), its esters, or its salts in high yields. The produced APA or its derivatives can lose an acetic acid molecule to produce the corresponding acrylate via a high-temperature pyrolysis reaction. In 1935, Burns et al. studied the reaction of methyl and butyl lactate esters with acetic anhydride (Figure 5.2) to produce alkyl APA esters, which were then pyrolyzed at 450 °C with quartz chips as the contact material to give methyl acrylate and butyl acrylate yields of 76% and 15-25%, respectively [167]. The same group optimized the operational conditions for this catalyst and obtained 89% acrylate yields at 550 °C and WHSV of 0.6 h⁻¹ using pyrex and quartz as the contact material [168-170]. Godlewski et al. [171] used grounded fused quartz as the packing material for the methyl lactate elimination reaction at 560 °C and were able to obtain 90%

yield for methyl acrylate. Unfortunately, in all of these studies, the yield invariably declines with time on stream, posing a barrier for the practical application of this pathway.



Figure 5.2. Methyl APA production using methyl lactate and acetic anhydride

Several studies show that low-cost acetic acid or acetate esters can be used instead of acetic anhydride in the formation of the APA species. Rehberg et al. [172] was the first one that obtained 28% methyl APA yield through the reaction of lactic acid and methyl acetate (Figure 5.3). Studies in recent years were focusing on the production of APA from lactic acid and acetic acid. Among them, APA yields of more than 90% were reported using homogeneous acid catalysts and solid acid catalysts such as ion exchange resin, zeolites, Amberlyst 70, Nafion, and sulfonated graphene [173, 174]. Besides lactic acid, dilactide is another substrate that can react with acetic acid to produce APA [175].



Figure 5.3. Methyl APA production using lactic acid and methyl acetate

Recently, a new reactive distillation method has been developed to produce APA from lactic acid and acetic acid [176]. During this process, water is removed from the column as it is produced in order to drive the APA production reaction toward completion. Maximum APA yield of 95% is reported using this method. Besides the high yield obtained, other advantages of this method are the absence of acidic homogeneous catalysts that facilitate the separation process, and the use of a continuous reactor that could use the recovered acetic acid that is liberated in the subsequent acrylate formation step. Therefore, developing a stable process for the production of acrylates from APA in high yields is an essential challenge in considering this pathway as a commercially viable one compared to the current methods used for acrylate production. In this work, we present conditions that provide sustained high yields of acrylate from lactic acid-derived APA esters.

5.2 Materials and Methods

5.2.1 Materials and Catalyst Preparation

Methyl (S)-(-)-lactate (98%), ethyl (S)- (-)-lactate (98%), butyl (S)-(-)-lactate (97%), benzyl (S)-(-)-lactate (90%), isobutyl (R)-(+)-lactate (97%), and acetic acid (99.7%) were purchased from Sigma-Aldrich and used as received. Methyl-2-acetoxypropanoate (MAPA) (99%), ethyl-2acetoxypropanoate (EAPA) (96%), butyl-2-acetoxypropanoate (BAPA) (98%), benzyl-2acetoxypropanoate (BeAPA) (96%), and isobutyl-2-acetoxypropanoate (IBAPA) (99%) were produced by reaction of the corresponding lactate ester with excess acetic anhydride under acidic conditions at 25 °C. The acetoxy ester was recovered by mixing the reaction solution with diethyl ether and an aqueous solution of sodium bicarbonate in a separatory funnel. The ether phase, which contain the APA ester, was separated and then washed again with an aqueous solution of sodium chloride. Finally, the APA ester was isolated and purified by centrifuging and distilling off the ether under vacuum.

Several materials were evaluated as contact materials for the process. Nonporous granular quartz (SiO₂, Sigma-Aldrich) as the primary material was ground and sieved to 30-50 mesh size.

Additional contact materials included the porous silica Spherosil (XOA 400) and silicon carbide (SiC).

Modified 13X molecular sieve was prepared as a pyrolysis catalyst by soaking the 13X molecular sieves overnight in 38 wt% cesium acetate (Sigma-Aldrich) in water solution, drying for 24 hours at 100 °C, and calcining at 400 °C for 5 hours. The sieves were then soaked overnight in 0.5 wt% ruthenium chloride (Sigma-Aldrich) in ethanol solution, dried for 24 hours at 100 °C, and finally calcined at reaction temperature for 5 hours before use in reaction. Additional catalyst materials evaluated in this work include porous SiO₂ treated with CsOH or KOH, CeZrO_x, γ -Al₂O₃, MSU-F structured pore zeolite, Zeolite- β -H, and Zeolite-Y-H. All materials were used as obtained from vendors or other laboratories.

5.2.2 Reactor Configuration

Reactions were performed in a 0.5 in. ID \times 40 cm long quartz tube reactor packed with contact material and equipped with a 1/8" OD internal thermowell to measure and control the reaction temperature. A schematic of the reactor system is given in Figure 5.4. Quartz (SiO₂) was chosen for the reactor material because it has been shown [167, 169] to minimize undesired reactant and product decomposition relative to other reactor materials in APA conversion to acrylates. The reactor was sealed on each end with 316 SS O-ring fittings to facilitate reactant input and product collection and placed in a tube furnace. Liquid reactants were fed to the top of the reactor through a 1/16" OD tube that extended downward to approximately 10 cm above the contact material. Initially, diluent gas was fed through the annulus surrounding the liquid feed tube; however, it was found that better vaporization of the liquid feed took place and higher acrylate yields were obtained when the liquid feed and diluent gas were both fed through the 1/16" tube. This arrangement was therefore used in all experiments reported in this work.



Figure 5.4. Schematic of the reactor system

Products were collected in two traps in series: one trap immersed in ice and a second immersed in dry ice/acetone. Gas that passed through both traps was sampled periodically during reaction using gas bags.

Experiments were initiated by loading 1.0 g of contact material supported on quartz wool into the reactor. The reactor was assembled in the tube furnace, and diluent gas was passed through the reactor (10–30 mL STP/min) while it was heated to reaction temperature. During the reaction, liquid feed was metered into the reactor using a PHD 2000 syringe pump at rates of 1.0–5.0 mL/h. All experiments were conducted at atmospheric pressure.

Product samples were collected from the ice trap (0 $^{\circ}$ C) after the first 60 min of reaction and then at 90 min intervals. Product collected in the dry ice trap was analyzed only at the conclusion of the experiment. Liquid and gas samples were analyzed by gas chromatography; details of the analytical methods and yield calculations are given in the Supporting Information.

5.2.3 Analytical Methods

Liquid samples from all experiments except those with ethyl APA as the feed material were diluted 10-fold in acetonitrile and analyzed using a Varian 450 gas chromatograph with flame ionization detector. A 30 m Sol Gel Wax column (0.25 mm ID, 0.25 µm film thickness) was used with the following temperature program: initial temperature 37 °C for 4 min; ramp at 10 °C/min to 90 °C, and hold at 90 °C for 3 min; ramp at 10 °C/min to 150 °C; ramp at 30 °C/min to 230 °C, and hold for 2 min. Liquid samples from ethyl APA experiments were diluted 20-fold in acetonitrile and analyzed using a Perkin Elmer Autosys GC with a thermal conductivity detector. A 2 m long Chromosorb packed column (2 mm ID) was used with the following temperature program: initial temperature 130 °C for 1 min; ramp at 10 °C/min to 250 °C, and hold at 250 °C for 5 min. Gas samples were analyzed using the same instrument (Perkin Elmer Autosys GC) and column, but with the following temperature program: initial temperature of 130 °C for 1 min; ramp at 30 °C/min to 250 °C, and hold at 250 °C for 5 min. Gas samples were also analyzed using a Varian 3300 GC with a thermal conductivity detector. A 15'×1/8" SS 60/80 Carboxen-1000 column (2.1 mm ID) was used with the following temperature program: initial temperature 35 °C for 5 min, then ramp at 20 °C/min to 225 °C.

Species concentration from liquid and gas samples were determined using response factors obtained from the slope of multi-point calibration curves made with reactant and product species solutions of known concentrations. Calculated concentrations were entered into a Microsoft Excel

spreadsheet where reactant fractional conversion, product yields and selectivities, overall carbon recovery, and recovery of molecular fragments were calculated. Yield is defined as the number of moles of the desired products per mole of limiting reactant fed, and selectivity is defined as the number of moles of desired products formed per mole of limiting reactant converted. Unless otherwise noted, yield and selectivity refer to total acrylate produced (acrylate ester + free acrylic acid).

5.2.4 Contact Material Characterization

Nitrogen adsorption at 78 K (-195 °C) in a Micromeritics ASAP 2010 instrument was used to measure the BET surface area of contact materials. Materials were outgassed at 260 °C for 24 hours before adsorption measurements. Surface acidity and basicity were measured by temperature-programmed desorption (TPD) of NH₃ and CO₂, respectively, in a Micromeritics Autochem 2910 instrument. For surface acidity, approximately 0.6 g of contact material was thermally pretreated at 800 °C in 50 cm³/min of He (99.999%) for 60 min, cooled to 25 °C in He, saturated at 25 °C with NH₃ by flowing a mixture of 14.8 vol% NH₃ in helium at 50 cm³/min for 1 hour, and then purged with He (50 cm³/min) for 2 hours to remove all physisorbed NH₃. Desorption was carried out by heating in He from ambient temperature to 600 °C at 10 °C/min and holding for 30 min. The resulting NH₃ peak area was quantified using an NH₃ gas standard of known composition. An identical procedure was used for measuring surface basic site density, except that pure CO₂ (99.8%) was used instead of the NH₃/He blend.

5.3 Experimental Results

Figure 5.5 describes the reaction pathways observed in experiments. Path (a) is acetic acid elimination to form acrylates or, in another sense, elimination of APA as an alkene (acrylate) from acetic acid. Path (b) is elimination of the alkyl ester group as an alkene that can occur when there

is hydrogen on the β -carbon of the ester functionality. Both eliminations are facilitated via the formation of a cyclic six-member transition state involving hydrogen on the β -carbon [177]. Complete product distributions and functional group balances (acetate (C₂), lactate (C₃), and ester (C1 or C4)) were carried out for all reactions; results for key experiments, denoted R1–R5 in the text and figures, are given in Table 5.1.



Acetaldehyde

Figure 5.5. Reaction pathways for APA ester elimination reactions. Path (a): elimination of acetic acid to form alkyl acrylate or acrylic acid; Path (b): elimination of alkene for ester R groups containing hydrogen on β -carbon; Path (c): decarbonylation of APA to acetaldehyde, acetic acid, and CO.

5.3.1 Control Experiments

Two control experiments were conducted by feeding butyl acrylate and acetic acid at 550 °C with a liquid hourly space velocity (LHSV) of 1.9 kg solution/kg contact material/h to determine the stability of these chemicals under typical reaction conditions. The recovery of acetic acid from the reactor after 4 hours of steady state operation was 94%, which is close to complete recovery within the uncertainty of the experiment. Under the same conditions, butyl acrylate was 92% converted to acrylic acid with accompanying quantitative formation of 1-butene.

Experiment	R1	R2	R3	R4	R5				
Reaction Conditions and APA Ester Conversion									
Feed Composition (wt%) APA Ester Acetic Acid	80 20	80 20	80 20	100 0	80 20				
Ester Group	Butyl	Butyl	Methyl	Butyl	Butyl				
Diluent Gas	N ₂	CO ₂	CO ₂	CO ₂	CO ₂				
Temperature (°C)	550	550	550	550	490				
APA Ester Conversion (%)	100	100	88	97	46				
Product Selectivities (mol product/mol APA ester converted)									
Alkyl Acrylate (%)	7.9	3.5	77.8	10.1	21.5				
Acrylic Acid (%)	18.6	31.4	0	22.2	4.8				
Acetic Acid (%)	41.6	60.7	71.0	75.5	26.1				
Alkene (%)	79.3	94.8	0	97.6	51.6				
Acetaldehyde (%)	12.1	14.9	0	13.6	13.9				
Carbon monoxide (%)	8.8	59.2	1.7	56.5	46.7				
Alkyl alcohol (%)	0.8	0.5	0	0.6	1.6				
Unknown (%)	1.3	2.0	0	1.4	1.7				
Functional Group and Carbon Recoveries (mol group/mol APA ester fed)									
Methyl (C1) (%)	-	-	86	-	-				
Acetate (C2) (%)	94	94	93	95	89				
Lactate (C3) (%)	52	76	91	90	87				
Butyl (C4) (%)	80	99	-	109	93				
Total Carbon Recovery ^a (%)	76	90	91	98	90				

Table 5.1. Summary of conditions, functional group balances, and product distributions for selected experiments R1-R5. ^{*a*} *Total carbon recovery does not include the carbon deposited on the contact material.*

5.3.2 Feed Composition

5.3.2.1 Diluent Liquid

Adding acetic acid to butyl APA feed (Figure 5.6) modestly improves acrylate selectivity to a maximum of 35% at 25–45 mol% acetic acid in the feed. Moderate quantities of acetic acid may provide acidity to aid elimination or may interact with the contact material surface to limit side

reactions, but acetic acid most likely aids in dispersing and volatilizing the APA esters. Acetic acid concentrations above 50 mol% lead to reduced acrylate yields because the large excess of acetic acid may enhance unwanted decomposition reactions or thermodynamically limit the extent of acetic acid elimination from APA. Subsequent experiments were carried out with 55 mol% butyl APA + 45 mol% acetic acid (80 wt% APA ester + 20 wt% acetic acid) as the liquid feed.



Figure 5.6. Effect of acetic acid feed concentration on steady state acrylate selectivity from butyl APA (R2, 45 mol% acetic acid; R4, 0% acetic acid). Reaction conditions: T = 550 °C; quartz (SiO₂) contact material; CO₂ diluent gas at 20 ml/min; LHSV = 1.7–2.4 kg feed/kg contact material/h.

5.3.2.2 Diluent Gas

Carbon dioxide and nitrogen were examined as diluent gases with butyl APA and benzyl APA as feed materials over quartz contact material. Conversion of both APA esters is essentially complete under reaction conditions for both gases, but CO₂ increases acrylate selectivity relative to N₂ (Figure 5.7). With butyl APA, the combined acrylate selectivity (butyl acrylate + acrylic acid) with CO₂ is approximately twice that with N₂ as steady state is approached (300 min on-stream). Acrylate selectivity with N₂ declines with time on stream, whereas it remains essentially constant with CO_2 as diluent. The effect is much less dramatic with benzyl APA as the feed, but it is significant during the ramp-up to steady state.



Figure 5.7. Total acrylate selectivity versus time on stream with N_2 or CO_2 as diluent gas (20 ml/min) for benzyl and n-butyl APA ester feed. Reaction conditions: T = 550 °C; 80 wt% APA ester/20 wt% acetic acid feed; LHSV = 1.9 kg feed/kg contact material/h.

Carbon monoxide (CO) is present in the effluent gas stream with both N₂ and CO₂ as diluent gases. If CO was formed only via decarbonylation of the lactate backbone, then on a molar basis, CO formation should be at most equal to that of acetaldehyde (because decarboxylation of lactate can also occur). This is indeed the case for butyl APA conversion with N₂ (R1 in Table 5.1). In contrast, CO formation with CO₂ as diluent is 8-fold greater than that of acetaldehyde. Given that carbon is deposited on the contact material during the reaction by partial decomposition of APA and other species, the large quantity of carbon monoxide produced can be explained by the Boudouard reaction of CO₂ with this deposited carbon (CO₂ + C \implies 2 CO).
The deposited carbon is likely amorphous and porous in nature and is thus an effective "trap" for reactants and products in the system, causing them to remain in the high-temperature environment and further decompose. The presence of CO_2 as diluent gas continually removes these carbon deposits from the contact material, thus ensuring a short residence time for reactants and products that minimizes decomposition and results in higher acrylate selectivity.

To further support the presence of the Boudouard reaction, the contact material was removed from the reactor following experiments with N_2 and CO_2 as diluent gases, weighed, and heated in air to 500 °C. The weight loss upon heating was 3 to 4 times higher for the experiment with N_2 as the diluent gas than with CO_2 as the diluent, indicating greater carbon deposition with N_2 than with CO_2 . This result, along with increased pressure drop through the reactor and reduction in acrylate selectivity after 300 min on stream with the N_2 diluent, supports the hypothesis that CO_2 maintains the integrity of the contact material surface by removing deposited carbon during the reaction.

Finally, the composition of the effluent gas suggests that the reaction of CO₂ with deposited carbon is rapid and even approaches equilibrium. With butyl APA feed and CO₂ as the diluent gas, the reactor effluent contains 10 mol% CO and 50 mol% CO₂. These quantities of CO and CO₂ are close to the composition at P = 1 atm dictated by the equilibrium constant for the Boudouard reaction at 550 °C ($K_P \sim 0.02$ atm = P_{CO}^2/P_{CO_2}) [178].

5.3.3 Acrylate Yields from Different APA Esters

Methyl APA, benzyl APA, isobutyl APA, butyl APA, and ethyl APA were fed over the quartz fixed bed at 550 °C with LHSV = 1.9 kg feed/kg contact material/h. Conversion of APA ester ranged from 90% to nearly 100% for the different esters; total acrylate selectivity is given in Figure 5.8 for each ester.



Figure 5.8. Total acrylate selectivity vs time on stream for different APA ester feeds. Reaction conditions: T = 550 °C; 80 wt% APA ester/20 wt% acetic acid feed; CO₂ diluent gas at 20 ml/min; LHSV = 1.9 kg feed/kg contact material/h.

Figure 5.8 shows that those esters with hydrogen on the β -carbon of the ester functionality (ethyl, isobutyl, butyl) exhibit significantly lower selectivity to acrylates than those without hydrogen on the β -carbon (methyl, benzyl). Furthermore, selectivity to acrylates declines as the number of β -carbon hydrogen atoms increases, and the acrylate product distribution shifts from exclusively acrylate ester for methyl and benzyl APA feeds to a majority of free acrylic acid for ester groups containing β -carbon hydrogens. As shown in Figure 5.5 (Path (b)), the ability of ester groups containing β -carbon hydrogens to eliminate as alkenes from alkyl acrylate, leads to free APA or free acrylic acid formation. These components are significantly more reactive toward undesired decomposition or polymerization than their ester counterparts. Free APA is not observed in the reactor effluent under any conditions in this study, even though nearly stoichiometric quantities of alkene relative to feed are formed in some experiments. Thus, free APA formed must quickly

decompose under the reaction conditions, partially to acrylic acid via the desired acetic acid elimination but also to undesired products via decarbonylation ((Path (c), Figure 5.5) and other decomposition reactions to form acetaldehyde, gases, free acetic acid, and carbon on the contact material surface. Acrylic acid likewise must undergo polymerization or decomposition, leading to reduced yields. The decomposition of free APA and free acrylic acid in the reactor is further supported by low lactate (C3) group recovery for butyl APA reactions (R1 and R2 in Table 5.1) relative to methyl APA reactions (R3 in Table 5.1), partially because acetaldehyde (bp 20 °C) formed via decarbonylation escapes from collection traps and is lost in the gas effluent stream.

5.3.4 Reaction Temperature

Figure 5.9 illustrates the dependence of butyl APA conversion, acrylic acid selectivity, and butyl acrylate selectivity on reaction temperature from 420 °C to 690 °C over quartz contact material. Conversion of butyl APA increases from 10% at 420 °C to nearly 100% at 550 °C, indicating that Paths (a) and (b) in Figure 5.5 go to completion. Selectivity to acrylic acid increases and selectivity to butyl acrylate decreases above 500 °C, as butene elimination from butyl acrylate (Path (b) in Figure 5.5) becomes rapid. Total acrylate yield remains nearly constant at its maximum value between 550 °C and 620 °C, suggesting that acrylic acid occurs. Acrylic acid decomposition predominates above 620 °C such that no acrylic acid exits the reactor at the highest temperature examined (690 °C). An estimate of the activation energy assuming butyl APA conversion as a simple first-order reaction gives a value of 132 kJ/mol ($R^2 = 0.99$). The Arrhenius plot is provided as Figure I.1 in the Appendix I.



Figure 5.9. Steady state butyl APA conversion, butyl acrylate selectivity, and acrylic acid selectivity at steady state versus temperature (R5, 490 °C; R2, 550 °C). Reaction conditions: 80 wt% butyl APA/20 wt% acetic acid feed; CO₂ diluent gas at 20 ml/min; LHSV = 1.9 kg feed/kg contact material/h.

5.3.5 Different Contact Materials

Experiments were performed at 550 °C with 1.0 g of Spherosil (XOA 400) porous silica and silicon carbide (SiC) as contact materials in the quartz tube reactor. Table 5.2 compares acrylate selectivity from butyl APA with total surface area, surface acid site density, and surface basic site density of each of the contact materials. At 550 °C, nearly complete butyl APA conversion was observed for all three materials, and the highest acrylate selectivity was obtained for quartz and SiC. The porous silica contact material does not perform well, most likely because any feed material entering the pores is trapped and decomposes to carbon and gases. In contrast, SiC and quartz are nonporous and do not trap reactants or products; instead, they provide a short contact time heat transfer surface area for volatilization and reaction of APA esters. Silicon carbide and quartz have such low surface areas that their surface acidity and basicity were not measurable.

	Surface	Surface	Surface	Butyl APA	Acrylate
Catalyst	Area	Acidity	Basicity	Conversion	Selectivity
	(m ² /g)	(µmol/g)	(µmol/g)	%	%
SiO ₂ (35-50mesh)	0.08	<10	<10	97.4	36.5
SiC (50 mesh)	0.03	<10	<10	99.5	29.4
γ -Al ₂ O ₃	161	495	75	96.7	24.8
13X Molecular Sieve	175	152	176	99.0	9.0
Spherosil (XOA400)	375	137	45	100	5.1

Table 5.2. Properties and Experimental Results for Contact Materials. Reaction conditions: $T = 550^{\circ}C$;80 wt% butyl APA/20 wt% acetic acid feed at 2.4 mL/h; CO2 diluent gas at 20 ml/min; LHSV = 1.9 kgfeed/kg contact material/h.

One additional set of experiments was carried out with the modified 13X molecular sieve, reported by Mitsubishi Gas Chemical Company research group [147, 153]. Although high acrylate yields from substrates with a similar structure to APA esters such as methyl α -hydroxy isobutyrate, methyl α -methoxy isobutyrate, and methyl lactate at temperatures of 300-350 °C was reported in those studies, no significant acrylate formation was observed from butyl APA using this catalyst over the range of reaction conditions. To further evaluate this catalyst, the reaction was repeated with methyl lactate at the exact reaction conditions as those studies [153] for methyl acrylate production. While a small quantity of methyl acrylate was observed (<5%), the yield obtained was significantly lower compared to the reported values.

As results confirm, lower surface acidity and basicity lead to higher selectivity toward acrylates. Wang et al. discussed that the ideal surface acidity/basicity ratio for this reaction is contact material dependent [179]; nevertheless, it seems that increasing acidic and basic sites improves the selectivity of side reactions such as acid-catalyzed decarbonylation and decarboxylation and basecatalyzed condensation reactions rather than the APA elimination reaction. Thus, contact materials with low concentrations of acid and base sites are the best choices for this reaction.

5.3.6 Space Velocity

Butyl APA conversion and acrylate selectivity were measured at 550 °C with different quantities of quartz (0.3 g, 1 g, and 3g) in the reactor that correspond to LHSV of 6.3, 1.9, and 0.65 kg feed/kg contact material/h. Nearly complete conversion of butyl APA was observed over this range of LHSV along with similar acrylate selectivity, an indication that even higher space velocities should be suitable for APA ester conversion to acrylates at 550 °C.

5.3.7 Extended Reaction

To demonstrate the improved stability of acrylate formation with CO_2 as diluent gas and inclusion of acetic acid as a co-feed, an extended time experiment was carried out for 30 h. The results (Figure 5.10) show that butyl APA conversion (98%) and overall acrylate selectivity (32–35%) were stable over the 30 h period of operation. The run was terminated at 30 h because of depletion of the feed material. Following the reaction, the quartz contact material was removed from the reactor and was found to have a quantity of carbon deposited that was essentially the same as that for a typical 3–5 h run. Overall material balance closure and backbone fragment balances were excellent for this extended experiment.



Figure 5.10. Extended time experiment. Reaction conditions: T = 550 °C; 80 wt% butyl APA/20 wt% acetic acid feed; CO₂ diluent gas at 20 ml/min; LHSV = 1.9/kg feed/kg contact material/h.

5.4 Conclusions

Feed composition and reaction conditions for enhanced acrylate production from APA esters have been identified. Acrylate selectivity of 35% was achieved from butyl APA at 550 °C and atmospheric pressure with 1.0 g of 35–50 mesh low surface area silica (quartz) as the preferred contact material, 20 wt% acetic acid in the liquid feed, and CO₂ as the diluent gas. Experiments with methyl or benzyl APA ester feeds resulted in acrylate selectivity of 70+% under the same conditions and are thus clearly preferred feed materials. Higher alkyl APA esters have hydrogen atoms on the β -carbon of their ester functionality that allows elimination of the ester group as an alkene, liberating free acrylic acid and APA that decompose or polymerize to reduce acrylate yield. Using CO₂ as diluent gas increases acrylate formation from butyl APA and reduces the quantity of deposited carbon on the contact material, thus maintaining reaction rate over extended operation. APPENDICES

APPENDIX I. Rate constant and activation energy of APA conversion

The rate constant activation energy for APA conversion is estimated by assuming that APA reacts via a simple first-order reaction as shown below. A first-order rate constant was determined at each temperature shown in Figure 5.9; the rate constant is plotted in Figure I.1 to obtain the activation energy and pre-exponential factor. The value of the activation energy obtained from the Arrhenius plot is 131.5 kJ/mol; the pre-exponential is 3.9×10^4 (s⁻¹).



$$-\frac{dC_A}{dt} = \mathbf{k}C_A \rightarrow \frac{C_A}{C_{A_0}} = e^{-kt} \rightarrow \ln\left(\frac{C_A}{C_{A_0}}\right) = -kt \rightarrow k(s^{-1}) = \frac{-\ln\left(\frac{C_A}{C_{A_0}}\right)}{t}$$

Figure I.1. Arrhenius plot of first order rate constant for APA decomposition.



I.1. NH₃ TPD (Acidic Sites)

Figure J.1. Acidic sites measurement for different materials studied. (a) Temperature profile, (b) NH₃ Temperature Programmed Desorption (TPD) diagram.

J.2. CO₂ TPD (Basic Sites)



*Figure J.2. Basic sites measurement for different materials studied. (a) Temperature profile, (b) CO*₂ *Temperature Programmed Desorption (TPD) diagram.*

6 Summary and Recommendations for Future Work

6.1 Summary

The main objective of this work is to make higher alcohols, specifically butanol, from efficiently produced fermentation-based ethanol through a process that is known as the Guerbet chemistry. The work done in this study achieved 74% C₄+ alcohols selectivity at 41% ethanol conversion for the Ni/La₂O₃/ γ -Al₂O₃ catalyst. Attempts have been made to improve this result by optimizing reaction conditions such as temperature and feed velocity, characterizing the catalyst via changing nickel density and particle size and studying bi-metallic catalysts, and preliminary screenings on the cross-condensation of fermentation-derived ethanol-fusel alcohols mixtures. Results obtained have been evaluated via the economic analysis of an industrial-scale butanol production plant and proposed a butanol selling price of \$1.55-\$1.60/kg for 25% ROI. To gain consideration for commercial development, the butanol price needs to be in the range of \$1.30-\$1.40/kg, which requires the butanol selectivity to be >90% at 30-35% ethanol conversion. Here are some recommendations for future work that could lead to this objective.

6.2 Ethanol Guerbet Reaction

6.2.1 Catalyst Studies

Guerbet reaction requires a multi-functional metallic acid-base supported catalyst. Metal sites are essential due to their hydrogen bond formation, while acid-base supports provide ideal sites for the aldol condensation step. The presence of these sites in molecular distance from each other can be the key to improve the Guerbet products selectivity rather than the side-reactions. Two strategies could be employed to enhance the number of metal and acid-base sites with molecular proximity to each other. The first one is to reduce the metal particle size and the number of segregated particles so that the dehydrogenated molecules can quickly condense on the neighbor acid-base sites. Catalytic preparation methods that have been developed recently, such as strong electrostatic adsorption (SEA) method [180], or different impregnation, calcination, and reduction techniques [181, 182] need to be employed to this end. Most of these new methods and techniques are still under development and can lead to the formation of coatings on the surface of the metal particles or the leaching and sintering of metal. Therefore, the main challenge facing this strategy is to activate metal particles for the hydrogen exchange. Nickel has been used as the primary metal in this study. Several studies have shown the effect of calcination and reduction temperatures on nickel particle sizes and its reducibility [183-185]. Therefore, optimizing the calcination and reduction step but also affects the overall Guerbet reaction performance through the formation of smaller particles.

The second strategy for enhancing the number of metal and acid-base sites close to each other is using atomic layer deposition (ALD) technique to create an overcoat layer of support over the metal sites on the surface of the catalyst. This technique has been developed in several studies for the Al₂O₃ supported metals [186-189]. A reduction in available surface area [186] has been reported in these studies as a result of covering the surface of the support, that can be addressed by calcining the overcoat at 700 °C [182] and creating multiple fractures on the surface of the deposited layer. Besides increasing the available surface area, this calcination helps with the re-exposure of metal sites to the surface of the catalyst. Therefore, the chances of the exposure of dehydrogenated molecules to the Al₂O₃ sites for the following condensation step can improve significantly.

6.2.2 Separate Performance Improvement for Each Step of the Guerbet Reaction

The Guerbet mechanism consists of three main steps: ethanol dehydrogenation to acetaldehyde, aldol condensation of acetaldehyde to crotonaldehyde, and crotonaldehyde hydrogenation to *n*-butanol. So far, most of the studies have focused on improving the selectivity of butanol using a multi-functional catalyst that facilitates all three steps simultaneously. Nevertheless, this multi-functionality could lead to the production of undesired chemicals during each step of the reaction. Therefore, separately studying the process design, catalyst characterization, chemistry, and kinetic modeling of each step of the Guerbet reaction could be an appropriate strategy for further optimization of the Guerbet reaction.

Literature review on the first step of the Guerbet reaction shows several reports with >97% acetaldehyde selectivity and ethanol conversion of >37% [190-192]. However, little work has been performed on distinctly improving the last two steps of the Guerbet mechanism. Our initial screenings on the aldol condensation reaction show that while acetaldehyde is significantly more active compared to ethanol, the selectivity to crotonaldehyde is within the same range as the *n*-butanol selectivity from ethanol in the successive Guerbet reaction using a multi-functional catalyst. This suggests that the aldol condensation step could be the key reaction in the Guerbet mechanism for improving the butanol selectivity from ethanol. Nevertheless, aldol condensation reaction conditions have not been optimized in this study. Thus, designing reaction setups for exclusively studying the last two steps of the Guerbet reaction can provide an economically and environmentally sustainable process to produce *n*-butanol at high selectivities.

6.2.3 Kinetic Modeling of the Reaction Tree

While "wet-lab" experiments are known as essential methods for investigating the performance of catalytic systems, kinetic modeling of the system can provide valuable insight into the behavior of

different reacting components. The more comprehensive the modeling is in terms of reaction steps and side-reactions considered, the more accurate and predictable results are obtained.

Initial work has been done to model the Guerbet reaction with the batch reaction data using the multi-functional Ni/La₂O₃/ γ -Al₂O₃ catalyst [9]. Reactions considered for the current modeling are the four main steps of the ethanol Guerbet reaction (including two hydrogenation steps), secondary Guerbet reactions involving ethanol and butanol, and ethyl acetate production from acetaldehyde and ethanol. These reactions are considered as equilibrium reactions, and thermodynamic equilibrium constants (K) for each one of them are optimized based on the fit between experimental data and modeling results. Methane production reactions can also be added to this modeling for further accuracy.

Continuous experiments at 230 °C and a wide range of contact times have been developed to verify the modeling results that are obtained based on the batch experimental data. For instance, experimental batch results show that ethyl acetate production reaction moves toward thermodynamic equilibrium at reaction conditions. However, this observation is not verified by the initial continuous reactor experimental results. Thus, continuous data in a wide range of contact times can be employed to fit the modeling results to a more accurate data. Another advantage that continuous data provide compared to the batch results is the precise analytical quantification of gaseous products at different contact times.

Experimental results obtained from each step of the Guerbet reaction that was discussed in Section 6.2.3 will also have a significant role in finding kinetic rate constants. These experiments should be conducted at multiple temperatures to provide an activation energy and a pre-exponential factor for each reaction. Although the rate constants derived from each single reaction might be affected by the presence of other components, the data obtained from these studies provide an ideal starting

point for finding the rate constants or a reliable verification of the previously developed rate constants.

6.3 Guerbet Economic Analysis

One of the challenges in the economic analysis of the Guerbet process was the separation of the azeotropic ethanol/water mixture. As discussed earlier, studies have shown the destructive effect of the presence of water on ethanol conversion [9]. Nevertheless, this effect was assumed to be negligible in the process simulation of the ethanol Guerbet reaction, and the azeotropic ethanol/water mixture was recycled back to the system. Studies were also done to assess the economic feasibility of separating this mixture via a conventional two-unit pressure swing molecular sieve unit. Results indicated that utilizing this unit would increase the final selling price of the *n*-butanol. Among other alternative options for separating these two chemicals such as pervaporation membranes [102] and heterogeneous azeotropic distillation [193], extractive distillation process seems to be the one with the most promising results for commercial development [194]. This process involves the addition of a solvent that interacts differently with the components that are forming an azeotropic mixture. This solvent typically alters the relative volatility of one of the components against the other one, which makes the separation of the two components feasible [194]. This process has been simulated and optimized in several studies for the ethanol/water mixture [195, 196] and can be considered as a potential approach that might improve the costs and quality of the butanol production simultaneously.

The four cases studied in the Guerbet reaction simulation involve two selectivity scenarios. The one indicated as "low" has 60% and 16% selectivity toward butanol and C_6 + alcohols, respectively; the high selectivity scenario corresponds to 72% selectivity toward butanol and 22% selectivity toward C_6 + alcohols. However, experimental results in Chapter 2 have shown that the contribution

of the selectivity toward these two components is different from the mentioned cases and involves higher ratios of C_{6+} alcohols. Running simulation process and economic calculations at the selectivity distributions closer to the experimental results will significantly improve the precision of the economic analysis.

6.4 Fusel Alcohols Guerbet Reaction

Fusel alcohols Guerbet reaction can be optimized in certain ways for both batch and continuous processes. Among those are finding batch products distribution at different reaction times, doing extended batch reactions to address the stability of the catalyst, and studying a wider range of feed compositions and reaction temperatures for the continuous system. Furthermore, the accuracy of the kinetic modeling results can improve if side-reactions and secondary and tertiary Guerbet reactions are also considered in the modeling studies.

6.5 Acrylate Production from 2-Acetoxypropanoic Acid Esters

Several approaches can be suggested for further improving the efficiency of the acrylate production process. First, the carrier gas flow rate can be optimized to lower the contact time of the chemicals with the catalyst and suppress the rate of the decomposition of reactive components. Second, while materials with low ($<1 \text{ m}^2/\text{g}$) and high ($>100 \text{ m}^2/\text{g}$) surface areas have already been tested for the APA elimination reaction, the performance of moderate surface area contact materials (1-10 m²/g) has yet to be determined. Silica-based materials with low acidity and basicity are appropriate options for the initial experiments. The acidity and basicity of the contact material can be adjusted after optimizing the surface area.

Furthermore, 2-acetoxypropanoic acid has not been detected in any of the analytical studies. Therefore, it is assumed that this chemical is being decomposed to smaller molecules or eliminated to acrylic acid upon its formation. Running control experiments with pure 2-acetoxypropanoic acid, and studying the behavior of the 2-acetoxypropanoic acid and APA ester mixtures as the feed at different temperatures would significantly help in better understanding the mechanism and kinetics of the reaction. Finally, although the best results are obtained when methyl APA and benzyl APA were used as the feed, reaction conditions for these chemicals were never optimized. Studying multiple temperatures, liquid feed flow rates, and gas feed flow rates can help in finding higher acrylate ester yields from these chemicals.

REFERENCES

REFERENCES

- 1. Ritchie, H., How Long Before We Run Out of Fossil Fuels?, in Our World in Data2017.
- 2. Daly, H.E., *Toward some operational principles of sustainable development*. Ecological economics, 1990. **2**(1): p. 1-6.
- 3. Kulshreshtha, S., *Agricultural practices as barriers to sustainability*. Public Policy in Food and Agriculture, 2009: p. 220.
- 4. Sánchez, Ó.J. and C.A. Cardona, *Trends in biotechnological production of fuel ethanol from different feedstocks*. Bioresource Technology, 2008. **99**(13): p. 5270-5295.
- 5. Nagy, Z.K., *Model based control of a yeast fermentation bioreactor using optimally designed artificial neural networks*. Chemical Engineering Journal, 2007. **127**(1): p. 95-109.
- 6. Ndaba, B., I. Chiyanzu, and S. Marx, *n-Butanol derived from biochemical and chemical routes: A review*. Biotechnology Reports, 2015. **8**: p. 1-9.
- 7. Wass, D.F.D., George Richard Michael *Conversion of alcohols*, 2013, BP Biofuels UK Limited (Middlesex, GB): United States.
- 8. Ghaziaskar, H.S. and C. Xu, One-step continuous process for the production of 1-butanol and 1-hexanol by catalytic conversion of bio-ethanol at its sub-/supercritical state. RSC Advances, 2013. **3**(13): p. 4271-4280.
- 9. Jordison, T.L., C.T. Lira, and D.J. Miller, *Condensed-Phase Ethanol Conversion to Higher Alcohols*. Industrial & Engineering Chemistry Research, 2015. **54**(44): p. 10991-11000.
- 10. Uyttebroek, M., W. Van Hecke, and K. Vanbroekhoven, *Sustainability metrics of 1-butanol*. Catalysis Today, 2015. **239**: p. 7-10.
- 11. Algayyim, S.J.M., et al., *Production and application of ABE as a biofuel*. Renewable and Sustainable Energy Reviews, 2018. **82**: p. 1195-1214.
- 12. Patakova, P., et al., *Novel and neglected issues of acetone–butanol–ethanol (ABE) fermentation by clostridia: Clostridium metabolic diversity, tools for process mapping and continuous fermentation systems.* Biotechnology Advances, 2013. **31**(1): p. 58-67.
- 13. Pfromm, P.H., et al., *Bio-butanol vs. bio-ethanol: A technical and economic assessment for corn and switchgrass fermented by yeast or Clostridium acetobutylicum.* Biomass and Bioenergy, 2010. **34**(4): p. 515-524.

- 14. Khamaiseh, E.I., et al., *Enhanced butanol production by Clostridium acetobutylicum NCIMB 13357 grown on date fruit as carbon source in P2 medium.* The Scientific World Journal, 2014. **2014**.
- 15. Gabriëls, D., et al., *Review of catalytic systems and thermodynamics for the Guerbet condensation reaction and challenges for biomass valorization*. Catalysis Science & Technology, 2015. **5**(8): p. 3876-3902.
- 16. Guerbet, M., *Condensation de l'alcool isopropylique avec son dérivé sodé; formation du méthylisobutylcarbinol et du diméthyl-2.4-heptanol-6.* Comptes rendus, 1909. **149**: p. 129-132.
- 17. Ndou, A.S., N. Plint, and N.J. Coville, *Dimerisation of ethanol to butanol over solid-base catalysts*. Applied Catalysis A: General, 2003. **251**(2): p. 337-345.
- 18. Ogo, S., et al., *1-Butanol synthesis from ethanol over strontium phosphate hydroxyapatite catalysts with various Sr/P ratios.* Journal of Catalysis, 2012. **296**: p. 24-30.
- 19. Gines, M.J. and E. Iglesia, *Bifunctional condensation reactions of alcohols on basic oxides modified by copper and potassium.* Journal of Catalysis, 1998. **176**(1): p. 155-172.
- 20. Marcu, I.-C., et al., *Catalytic valorization of bioethanol over Cu-Mg-Al mixed oxide catalysts*. Catalysis Today, 2009. **147**(3): p. 231-238.
- 21. Marcu, I.-C., et al., *Catalytic Conversion of Ethanol into Butanol over M–Mg–Al Mixed Oxide Catalysts (M = Pd, Ag, Mn, Fe, Cu, Sm, Yb) Obtained from LDH Precursors.* Catalysis Letters, 2013. **143**(1): p. 23-30.
- Riittonen, T., et al., One-Pot Liquid-Phase Catalytic Conversion of Ethanol to 1-Butanol over Aluminium Oxide—The Effect of the Active Metal on the Selectivity. Catalysts, 2012. 2(1): p. 68.
- 23. Di Cosimo, J.I., et al., *Structural Requirements and Reaction Pathways in Condensation Reactions of Alcohols on MgyAlO_x Catalysts.* Journal of Catalysis, 2000. **190**(2): p. 261-275.
- Ogo, S., A. Onda, and K. Yanagisawa, Selective synthesis of 1-butanol from ethanol over strontium phosphate hydroxyapatite catalysts. Applied Catalysis A: General, 2011.
 402(1): p. 188-195.
- Jordison, T.L., L. Peereboom, and D.J. Miller, *Impact of Water on Condensed Phase Ethanol Guerbet Reactions*. Industrial & Engineering Chemistry Research, 2016. 55(23): p. 6579-6585.
- 26. Wu, X., et al., *Catalytic Upgrading of Ethanol to n-Butanol: Progress in Catalyst Development.* ChemSusChem, 2018. **11**(1): p. 71-85.

- 27. Weizmann, C., E. BERGMANN, and M. Sulzbacher, *Further observations on the Guerbet reaction*. The Journal of Organic Chemistry, 1950. **15**(1): p. 54-57.
- 28. Yang, C. and Z.Y. Meng, *Bimolecular Condensation of Ethanol to 1-Butanol Catalyzed by Alkali Cation Zeolites.* Journal of Catalysis, 1993. **142**(1): p. 37-44.
- 29. Scalbert, J., et al., *Ethanol condensation to butanol at high temperatures over a basic heterogeneous catalyst: How relevant is acetaldehyde self-aldolization?* Journal of Catalysis, 2014. **311**: p. 28-32.
- 30. Dowson, G.R.M., et al., *Catalytic Conversion of Ethanol into an Advanced Biofuel: Unprecedented Selectivity for n-Butanol.* Angewandte Chemie International Edition, 2013. **52**(34): p. 9005-9008.
- 31. Wingad, R.L., et al., *Catalytic Conversion of Ethanol to n-Butanol Using Ruthenium P–N Ligand Complexes*. ACS Catalysis, 2015. **5**(10): p. 5822-5826.
- 32. Tseng, K.-N.T., et al., *Upgrading ethanol to 1-butanol with a homogeneous air-stable ruthenium catalyst.* Chemical Communications, 2016. **52**(14): p. 2901-2904.
- Xie, Y., et al., *Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium Pincer Complexes*. Journal of the American Chemical Society, 2016. 138(29): p. 9077-9080.
- 34. Jones, W.D.C., Sumit *Methods for producing butanol*, 2017, University of Rochester (Rochester, NY, US): United States.
- 35. Ueda, W., et al., *A low-pressure guerbet reaction over magnesium oxide catalyst.* Journal of the Chemical Society, Chemical Communications, 1990(22): p. 1558-1559.
- 36. Ueda, W., et al., *Condensation of alcohol over solid-base catalyst to form higher alcohols*. Catalysis Letters, 1992. **12**(1-3): p. 97-104.
- 37. Kozlowski, J.T. and R.J. Davis, *Heterogeneous Catalysts for the Guerbet Coupling of Alcohols*. ACS Catalysis, 2013. **3**(7): p. 1588-1600.
- 38. Olson, E.S., R.K. Sharma, and T.R. Aulich, *Higher-alcohols biorefinery*. Applied Biochemistry and Biotechnology, 2004. **115**(1): p. 913-932.
- 39. Tsuchida, T., et al., *Reaction of ethanol over hydroxyapatite affected by Ca/P ratio of catalyst*. Journal of Catalysis, 2008. **259**(2): p. 183-189.
- 40. Carvalho, D.L., et al., *Mg and Al mixed oxides and the synthesis of n-butanol from ethanol*. Applied Catalysis A: General, 2012. **415-416**: p. 96-100.
- 41. Otto, F., Wilhelm, Querfurth, *Process for the production of higher alcohols, particularly butyl alcohol, from ethyl alcohol,* 1935, Degussa: United States.

- 42. Di Cosimo, J., et al., *Structure and surface and catalytic properties of Mg-Al basic oxides*. Journal of Catalysis, 1998. **178**(2): p. 499-510.
- 43. León, M., E. Díaz, and S. Ordóñez, *Ethanol catalytic condensation over Mg–Al mixed oxides derived from hydrotalcites*. Catalysis Today, 2011. **164**(1): p. 436-442.
- 44. León, M., et al., *Consequences of the iron–aluminium exchange on the performance of hydrotalcite-derived mixed oxides for ethanol condensation*. Applied Catalysis B: Environmental, 2011. **102**(3): p. 590-599.
- 45. Ordóñez, S., et al., *Hydrotalcite-derived mixed oxides as catalysts for different C–C bond formation reactions from bioorganic materials*. Catalysis Today, 2011. **167**(1): p. 71-76.
- 46. Carlini, C., et al., *Guerbet condensation of methanol with n-propanol to isobutyl alcohol over heterogeneous copper chromite/Mg–Al mixed oxides catalysts*. Journal of Molecular Catalysis A: Chemical, 2004. **220**(2): p. 215-220.
- 47. Benito, P., et al., *Tunable copper-hydrotalcite derived mixed oxides for sustainable ethanol condensation to n-butanol in liquid phase*. Journal of Cleaner Production, 2019.
 209: p. 1614-1623.
- 48. Carlini, C., et al., *Guerbet condensation of methanol with n-propanol to isobutyl alcohol over heterogeneous bifunctional catalysts based on Mg–Al mixed oxides partially substituted by different metal components.* Journal of Molecular Catalysis A: Chemical, 2005. **232**(1): p. 13-20.
- 49. Bravo-Suárez, J.J., B. Subramaniam, and R.V. Chaudhari, *Vapor-phase methanol and ethanol coupling reactions on CuMgAl mixed metal oxides*. Applied Catalysis A: General, 2013. **455**: p. 234-246.
- 50. Hosoglu, F., et al., *High resolution NMR unraveling Cu substitution of Mg in hydrotalcites–ethanol reactivity.* Applied Catalysis A: General, 2015. **504**: p. 533-541.
- 51. Zhang, C.B., Mason ; Weiner, Heiko, *Coated Hydrotalcite Catalysts and Processes for Producing Butanol*, 2014, Celanese International Corporation (Irving, TX, US): United States.
- Hanspal, S., et al., Multiproduct Steady-State Isotopic Transient Kinetic Analysis of the Ethanol Coupling Reaction over Hydroxyapatite and Magnesia. ACS Catalysis, 2015.
 5(3): p. 1737-1746.
- 53. Birky, T.W., J.T. Kozlowski, and R.J. Davis, *Isotopic transient analysis of the ethanol coupling reaction over magnesia*. Journal of Catalysis, 2013. **298**: p. 130-137.
- 54. Tsuchida, T., et al., *Direct Synthesis of n-Butanol from Ethanol over Nonstoichiometric Hydroxyapatite*. Industrial & Engineering Chemistry Research, 2006. **45**(25): p. 8634-8642.

- 55. Hanspal, S., et al., *Influence of surface acid and base sites on the Guerbet coupling of ethanol to butanol over metal phosphate catalysts.* Journal of Catalysis, 2017. **352**: p. 182-190.
- 56. Silvester, L., et al., *Reactivity of ethanol over hydroxyapatite-based Ca-enriched catalysts with various carbonate contents*. Catalysis Science & Technology, 2015. 5(5): p. 2994-3006.
- 57. Kourtakis, K.O., Ronnie ; D'amore, Michael B., *Process for producing guerbet alcohols using water tolerant basic catalysts*, 2010, e.i. du pont de nemours and company (Wilmington, DE, US): United States.
- 58. Yang, K.-W., X.-Z. Jiang, and W.-C. Zhang, *One-step synthesis of n-butanol from ethanol condensation over alumina-supported metal catalysts*. Chinese Chemical Letters, 2004. **15**(12): p. 1497-1500.
- 59. Riittonen, T., et al., *Continuous liquid-phase valorization of bio-ethanol towards biobutanol over metal modified alumina*. Renewable Energy, 2015. **74**: p. 369-378.
- 60. Panchenko, V.N., et al., *Solid Base Assisted n-Pentanol Coupling over VIII Group Metals: Elucidation of the Guerbet Reaction Mechanism by DRIFTS.* Industrial & Engineering Chemistry Research, 2017. **56**(45): p. 13310-13321.
- 61. Hernández, W.Y., et al., One-pot preparation of Ni-Cu nanoparticles supported on γ -Al₂O₃ as selective and stable catalyst for the Guerbet reaction of 1-octanol. Catalysis Communications, 2017. **98**: p. 94-97.
- 62. Earley, J.H., et al., *Continuous catalytic upgrading of ethanol to n-butanol and >C4 products over Cu/CeO₂ catalysts in supercritical CO₂*. Green Chemistry, 2015. **17**(5): p. 3018-3025.
- 63. Jiang, D., et al., *Continuous catalytic upgrading of ethanol to n-butanol over Cu– CeO*₂/AC *catalysts.* Chemical Communications, 2016. **52**(95): p. 13749-13752.
- 64. Onyestyák, G., et al., *Guerbet self-coupling for ethanol valorization over activated carbon supported catalysts*. Reaction Kinetics, Mechanisms and Catalysis, 2017. **121**(1): p. 31-41.
- 65. Onyestyák, G., *Carbon Supported Alkaline Catalysts for Guerbet Coupling of Bioethanol.* Periodica Polytechnica Chemical Engineering, 2018. **62**(1): p. 91-96.
- 66. Yoshioka, T.T., Takashi ; Kubo, Jun ; Sakuma, Shuji *Method for producing alcohol by guerbet reaction*, 2015, Kabushiki Kaisha Sangi (Tokyo, JP): United States.
- 67. Wiles, C. and P. Watts, *Continuous flow reactors: a perspective*. Green Chemistry, 2012. **14**(1): p. 38-54.

- 68. Olcese, R. and M. Bettahar. *Thermodynamics conditions for Guerbet ethanol reaction*. in *MATEC Web of Conferences*. 2013. EDP Sciences.
- 69. Pang, J., et al., *Upgrading ethanol to n-butanol over highly dispersed Ni–MgAlO catalysts*. Journal of Catalysis, 2016. **344**: p. 184-193.
- 70. Seshu Babu, N., N. Lingaiah, and P.S. Sai Prasad, *Characterization and reactivity of Al*₂*O*₃ *supported Pd-Ni bimetallic catalysts for hydrodechlorination of chlorobenzene*. Applied Catalysis B: Environmental, 2012. **111-112**: p. 309-316.
- Sanchez-Sanchez, M.C., et al., *Mechanistic Aspects of the Ethanol Steam Reforming Reaction for Hydrogen Production on Pt, Ni, and PtNi Catalysts Supported on γ-Al₂O₃.* The Journal of Physical Chemistry A, 2010. **114**(11): p. 3873-3882.
- 72. Huang, W., Selective hydrogenation of acetylene on zeolite-supported bimetallic catalysts, 2007, University of Delaware.
- 73. Weatherbee, G.D. and G.A. Jarvi, *Effects of carbon deposits on the specific activity of nickel and nickel bimetallic catalysts au Bartholomew, C.H.* Chemical Engineering Communications, 1980. **5**(1-4): p. 125-134.
- 74. Muhammad, S., et al., *Borohydride reduction of Al₂O₃ supported NiCu bimetallic catalysts for the hydrogenation of styrene: study of surface properties.* Reaction Kinetics, Mechanisms and Catalysis, 2016. **118**(2): p. 537-556.
- 75. Dong, X., et al., The synergy effect of Ni-M (M = Mo, Fe, Co, Mn or Cr) bicomponent catalysts on partial methanation coupling with water gas shift under low H_2/CO conditions. Catalysts, 2017. **7**(2): p. 51.
- 76. Davda, R., et al., A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts. Applied Catalysis B: Environmental, 2005. **56**(1-2): p. 171-186.
- 77. Chen, L.-C. and S.D. Lin, *Effects of the pretreatment of CuNi/SiO₂ on ethanol steam reforming: Influence of bimetal morphology*. Applied Catalysis B: Environmental, 2014. 148-149: p. 509-519.
- 78. Djinović, P., et al., *Influence of active metal loading and oxygen mobility on coke-free dry reforming of Ni–Co bimetallic catalysts*. Applied Catalysis B: Environmental, 2012. 125: p. 259-270.
- 79. Nezam, I., L. Peereboom, and D.J. Miller, *Continuous condensed-phase ethanol conversion to higher alcohols: Experimental results and techno-economic analysis.* Journal of Cleaner Production, 2019. **209**: p. 1365-1375.

- Nezam, I., L. Peereboom, and D.J. Miller, *Enhanced Acrylate Production from 2-Acetoxypropanoic Acid Esters*. Organic Process Research & Development, 2017. 21(5): p. 715-719.
- Chieregato, A., et al., On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet reactions. ChemSusChem, 2015. 8(2): p. 377-388.
- Hernández, W.Y., et al., Ni-Cu Hydrotalcite-Derived Mixed Oxides as Highly Selective and Stable Catalysts for the Synthesis of β-Branched Bioalcohols by the Guerbet Reaction. ChemSusChem, 2016. 9(22): p. 3196-3205.
- 83. Silvester, L., et al., *Guerbet Reaction over Strontium-Substituted Hydroxyapatite Catalysts Prepared at Various (Ca+Sr)/P Ratios.* ChemCatChem, 2017. **9**(12): p. 2250-2261.
- 84. Ho, C.R., S. Shylesh, and A.T. Bell, *Mechanism and Kinetics of Ethanol Coupling to Butanol over Hydroxyapatite*. ACS Catalysis, 2016. **6**(2): p. 939-948.
- 85. Wang, L., et al., *Direct transformation of ethanol to ethyl acetate on Cu/ZrO₂ catalyst*. Reaction Kinetics, Mechanisms and Catalysis, 2010. **101**(2): p. 365-375.
- 86. Voß, M., D. Borgmann, and G. Wedler, *Characterization of Alumina, Silica, and Titania Supported Cobalt Catalysts*. Journal of Catalysis, 2002. **212**(1): p. 10-21.
- 87. Sato, A.G., et al., *Effect of the ZrO*₂ *phase on the structure and behavior of supported Cu catalysts for ethanol conversion*. Journal of Catalysis, 2013. **307**: p. 1-17.
- Sirijaruphan, A., et al., Cobalt Aluminate Formation in Alumina-Supported Cobalt Catalysts: Effects of Cobalt Reduction State and Water Vapor. Catalysis Letters, 2003. 91(1): p. 89-94.
- 89. Dias, M.O.S., et al., *Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part I: Integration to a first generation sugarcane distillery.* Chemical Engineering Research and Design, 2014. **92**(8): p. 1441-1451.
- 90. Pereira, L.G., et al., *Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part II: Integration to a second generation sugarcane distillery.* Chemical Engineering Research and Design, 2014. **92**(8): p. 1452-1462.
- 91. Pereira, L.G., et al., *Life cycle assessment of butanol production in sugarcane biorefineries in Brazil.* Journal of Cleaner Production, 2015. **96**: p. 557-568.
- 92. Pereira, L.G., et al., *Economic and environmental assessment of n-butanol production in an integrated first and second generation sugarcane biorefinery: Fermentative versus catalytic routes.* Applied Energy, 2015. **160**: p. 120-131.

- 93. Väisänen, S., et al., *Carbon footprint of biobutanol by ABE fermentation from corn and sugarcane*. Renewable Energy, 2016. **89**: p. 401-410.
- 94. Brito, M. and F. Martins, *Life cycle assessment of butanol production*. Fuel, 2017. **208**: p. 476-482.
- 95. Tao, L., et al., *Comparative techno-economic analysis and reviews of n-butanol production from corn grain and corn stover*. Biofuels, Bioproducts & amp; Biorefining, 2014. **8**(3): p. 342-361.
- 96. Levasseur, A., et al., *Assessing butanol from integrated forest biorefinery: A combined techno-economic and life cycle approach.* Applied Energy, 2017. **198**: p. 440-452.
- 97. Quiroz-Ramírez, J.J., et al., *Optimal Planning of Feedstock for Butanol Production Considering Economic and Environmental Aspects*. ACS Sustainable Chemistry & Engineering, 2017. **5**(5): p. 4018-4030.
- 98. Patel, A.D., et al., *Analysis of sustainability metrics and application to the catalytic production of higher alcohols from ethanol.* Catalysis Today, 2015. **239**: p. 56-79.
- 99. Michaels, W., et al., *Design of a separation section in an ethanol-to-butanol process*. Biomass and Bioenergy, 2018. **109**: p. 231-238.
- 100. Fidkowski, Z.T., M.F. Doherty, and M.F. Malone, *Feasibility of separations for distillation of nonideal ternary mixtures*. AIChE Journal, 1993. **39**(8): p. 1303-1321.
- 101. Patraşcu, I., C.S. Bîldea, and A.A. Kiss, *Eco-efficient butanol separation in the ABE fermentation process*. Separation and Purification Technology, 2017. **177**: p. 49-61.
- Kießlich, S., et al., Pervaporative butanol removal from PBE fermentation broths for the bioconversion of glycerol by Clostridium pasteurianum. Journal of Membrane Science, 2017. 535: p. 79-88.
- 103. Anonymous, Ethanol Historical Prices, 2017, Business Insider.
- 104. Anonymous, *Electric Power Monthly*, 2017, Energy Information Administration.
- 105. Anonymous, U.S. Natural Gas Prices, 2017, Energy Information Administration.
- 106. Couper, J.R., et al., 21 Costs of Individual Equipment, in Chemical Process Equipment (*Third Edition*), J.R. Couper, et al., Editors. 2012, Butterworth-Heinemann: Boston. p. 731-741.
- 107. Purohit, G., *Estimating costs of shell-and-tube heat exchangers*. Chemical engineering, 1983. **90**(17): p. 56-67.
- 108. Anonymous, *Process Engineering Guide: Air Cooled Heat Exchanger Design*. Vol. 1. 2010: GBH Enterprises, Ltd. 80.

- 109. Kern, D.Q., *Process heat transfer*1950: Tata McGraw-Hill Education.
- 110. Megyesy, E.F. and P. Buthod, *Pressure vessel handbook*2008, Oklahoma: PV Pub.
- 111. Primo, J., *Shell and tube heat exchangers basic calculations*. nd): n. pag. PDH Online. PDH, 2012.
- 112. McKetta Jr, J.J., *Encyclopedia of Chemical Processing and Design*. Vol. 50. 1987: CRC Press.
- 113. Anonymous, *Economic Indicators*. Chemical Engineering, 2017. **124**(10): p. 1.
- 114. Peters, M.S., et al., *Plant design and economics for chemical engineers*. Vol. 4. 1968: McGraw-Hill New York.
- 115. Anonymous, *n-Butanol: Chemical Market Insight and Foresight*, in *Chem-Net Facts*2013, Tecnon OrbiChem. p. 1.
- 116. Mariano, A.P., et al., *Butanol production in a first-generation Brazilian sugarcane biorefinery: Technical aspects and economics of greenfield projects.* Bioresource Technology, 2013. **135**: p. 316-323.
- 117. Bastidas, P., et al., *Alcohol Distillation Plant Simulation: Thermal and Hydraulic Studies*. Procedia Engineering, 2012. **42**: p. 80-89.
- 118. Dale, R.T. and W.E. Tyner, *Economic and technical analysis of ethanol dry milling: Model description.* Staff Paper (06-04), Dept. of Ag. Econ., Purdue University, 2006.
- 119. Fraas, A.P., Heat exchanger design1989: John Wiley & Sons.
- 120. Al Abdallah, Q., B.T. Nixon, and J.R. Fortwendel, *The enzymatic conversion of major algal and cyanobacterial carbohydrates to bioethanol.* Frontiers in energy research, 2016. **4**: p. 36.
- 121. Tesfaw, A. and F. Assefa, *Current trends in bioethanol production by Saccharomyces cerevisiae: substrate, inhibitor reduction, growth variables, coculture, and immobilization.* International Scholarly Research Notices, 2014. **2014**.
- 122. Hazelwood, L.A., et al., *The Ehrlich Pathway for Fusel Alcohol Production: a Century of Research on Saccharomyces cerevisiae Metabolism.* Applied and Environmental Microbiology, 2008. **74**(8): p. 2259.
- 123. Boumba, V.A., K.S. Ziavrou, and T. Vougiouklakis, *Biochemical pathways generating post-mortem volatile compounds co-detected during forensic ethanol analyses*. Forensic Science International, 2008. **174**(2): p. 133-151.

- 124. Ehrlich, F., Über die Bedingungen der Fuselölbildung und über ihren Zusammenhang mit dem Eiweissaufbau der Hefe. Berichte der deutschen chemischen Gesellschaft, 1907.
 40(1): p. 1027-1047.
- 125. Jackson, R.S., 7 *Fermentation*, in *Wine Science (Third Edition)*, R.S. Jackson, Editor 2008, Academic Press: San Diego. p. 332-417.
- 126. Jackson, R.S., *Chapter 6 Qualitative Wine Assessment*, in *Wine Tasting (Third Edition)*, R.S. Jackson, Editor 2017, Academic Press. p. 253-291.
- 127. Vilanova, M., I.S. Pretorius, and P.A. Henschke, Chapter 58 Influence of Diammonium Phosphate Addition to Fermentation on Wine Biologicals, in Processing and Impact on Active Components in Food, V. Preedy, Editor 2015, Academic Press: San Diego. p. 483-491.
- 128. Marullo, P. and D. Dubourdieu, *Yeast selection for wine flavour modulation*, in *Managing Wine Quality: Oenology and Wine Quality* 2010, Elsevier. p. 293-345.
- 129. Branduardi, P. and D. Porro, *n-butanol: challenges and solutions for shifting natural metabolic pathways into a viable microbial production*. FEMS microbiology letters, 2016. **363**(8).
- 130. Matsu-ura, T., et al., Guerbet Reaction of Primary Alcohols Leading to β-Alkylated Dimer Alcohols Catalyzed by Iridium Complexes. The Journal of Organic Chemistry, 2006. 71(21): p. 8306-8308.
- 131. Busch, S.F.-s., Ingo; Mack, Sandra ; Mahnke, Eike Ulf ; Wick, Anja *Biocide compositions comprising alkoxylation products of isoamyl alcohol derivatives*, 2016, Cognis IP Management GMBH (Dusseldorf, DE): United States.
- Beerthuis, R., G. Rothenberg, and N.R. Shiju, *Catalytic routes towards acrylic acid, adipic acid and ε-caprolactam starting from biorenewables*. Green Chemistry, 2015. 17(3): p. 1341-1361.
- Anonymous, Acrylic Acid Market Analysis, By Product, By End-Use, Bio Acrylic Acid Downstream Potential And Segment Forecasts To 2022, 2015, Grand View Research. p. 120.
- 134. Matar, S., M.J. Mirbach, and H.A. Tayim, *Catalytic Oxidation Reactions*, in *Catalysis in Petrochemical Processes*, S. Matar, M.J. Mirbach, and H.A. Tayim, Editors. 1989, Springer Netherlands: Dordrecht. p. 84-108.
- 135. Erwin, S., Max, Gehrke, Franz, Aichner, *Production of acrolein*, 1933, Schering Kahlbaum AG: United States.
- Bühler, W., et al., *Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water*. The Journal of Supercritical Fluids, 2002. 22(1): p. 37-53.

- 137. Corma, A., et al., *Biomass to chemicals: Catalytic conversion of glycerol/water mixtures into acrolein, reaction network.* Journal of Catalysis, 2008. **257**(1): p. 163-171.
- Ott, L., M. Bicker, and H. Vogel, *Catalytic dehydration of glycerol in sub- and supercritical water: a new chemical process for acrolein production*. Green Chemistry, 2006. 8(2): p. 214-220.
- 139. Deleplanque, J., et al., *Production of acrolein and acrylic acid through dehydration and oxydehydration of glycerol with mixed oxide catalysts*. Catalysis Today, 2010. **157**(1): p. 351-358.
- Lourenço, J.P., M.I. Macedo, and A. Fernandes, Sulfonic-functionalized SBA-15 as an active catalyst for the gas-phase dehydration of Glycerol. Catalysis Communications, 2012. 19: p. 105-109.
- 141. Holmen, R.E., *Production of acrylates by catalytic dehydration of lactic acid and alkyl lactates*, 1958, Minnesota Mining & MFG: United States.
- Odell, B., G. Earlam, and D.J. Cole-Hamilton, *Hydrothermal reactions of lactic acid catalysed by group: VIII Metal complexes*. Journal of Organometallic Chemistry, 1985. 290(2): p. 241-248.
- 143. Sawicki, R.A.S., NY), *Catalyst for dehydration of lactic acid to acrylic acid*, 1988, Texaco Inc. (White Plains, NY): United States.
- 144. Paparizos, C.W., OH), Dolhyj, Serge R. (Parma, OH), Shaw, Wilfrid G. (Lyndhurst, OH), *Catalytic conversion of lactic acid and ammonium lactate to acrylic acid*, 1988, The Standard Oil Company (Cleveland, OH): United States.
- 145. Mok, W.S.L., M.J. Antal, and M. Jones, *Formation of acrylic acid from lactic acid in supercritical water*. The Journal of Organic Chemistry, 1989. **54**(19): p. 4596-4602.
- 146. Lira, C.T. and P.J. McCrackin, *Conversion of lactic acid to acrylic acid in near-critical water*. Industrial & Engineering Chemistry Research, 1993. **32**(11): p. 2608-2613.
- 147. Abe, T.N., JP), Hieda, Shinichi (Niigata, JP), *Process for preparing unsaturated carboxylic acid or ester thereof*, 1993, Mitsubishi Gas Chemical Company, Inc. (Tokyo, JP): United States.
- 148. Wang, H., et al., *Rare earth metal modified NaY: Structure and catalytic performance for lactic acid dehydration to acrylic acid.* Catalysis Communications, 2008. **9**(9): p. 1799-1803.
- 149. Sun, P., et al., *Potassium modified NaY: A selective and durable catalyst for dehydration of lactic acid to acrylic acid.* Catalysis Communications, 2009. **10**(9): p. 1345-1349.
- 150. Walkup, P.C.R., WA), Rohrmann, Charles A. (Kennewick, WA), Hallen, Richard T. (Richland, WA), Eakin, David E. (Kennewick, WA), *Production of esters of lactic acid*,

esters of acrylic acid, lactic acid, and acrylic acid, 1993, Battelle, Memorial Institute (Richland, WA): United States.

- 151. Zhang, J., et al., *Evaluation of Catalysts and Optimization of Reaction Conditions for the Dehydration of Methyl Lactate to Acrylates**. Chinese Journal of Chemical Engineering, 2008. **16**(2): p. 263-269.
- 152. Zhang, J., J. Lin, and P. Cen, *Catalytic dehydration of lactic acid to acrylic acid over sulfate catalysts*. Canadian Journal of Chemical Engineering, 2008. **86**(6): p. 1047.
- 153. Naito, S.K., Takao; Ikeda, Ritoko, *Process for preparing unsaturated carboxylic acid ester*, 1991, Mitsubishi Gas Chemical Company, Inc. (Tokyo, JP): United States.
- 154. Zhang, J., et al., *Efficient Acrylic Acid Production through Bio Lactic Acid Dehydration* over NaY Zeolite Modified by Alkali Phosphates. ACS Catalysis, 2011. **1**(1): p. 32-41.
- 155. Sun, P., et al., *NaY Zeolites Catalyze Dehydration of Lactic Acid to Acrylic Acid: Studies on the Effects of Anions in Potassium Salts.* Industrial & Engineering Chemistry Research, 2010. **49**(19): p. 9082-9087.
- 156. Näfe, G., et al., *True Catalytic Behavior of Lactic Acid Dehydration on Zeolite Na-Y in the Gas Phase Measured by Means of a Novel Apparatus Design*. Catalysis Letters, 2014. 144(7): p. 1144-1150.
- 157. Tang, C., et al., *Catalytic dehydration of lactic acid to acrylic acid over dibarium pyrophosphate*. Catalysis Communications, 2014. **43**: p. 231-234.
- Li, C., et al., *Efficient catalytic dehydration of methyl lactate to acrylic acid using sulphate and phosphate modified MCM-41 catalysts*. Applied Catalysis A: General, 2014.
 487: p. 219-225.
- 159. Ghantani, V.C., et al., *Catalytic dehydration of lactic acid to acrylic acid using calcium hydroxyapatite catalysts*. Green Chemistry, 2013. **15**(5): p. 1211-1217.
- 160. Zhang, J., et al., *Sodium nitrate modified SBA-15 and fumed silica for efficient production of acrylic acid and 2,3-pentanedione from lactic acid.* Journal of Industrial and Engineering Chemistry, 2014. **20**(4): p. 1353-1358.
- 161. Ghantani, V.C., M.K. Dongare, and S.B. Umbarkar, *Nonstoichiometric calcium pyrophosphate: a highly efficient and selective catalyst for dehydration of lactic acid to acrylic acid.* RSC Advances, 2014. **4**(63): p. 33319-33326.
- 162. Mäki-Arvela, P., et al., *Production of Lactic Acid/Lactates from Biomass and Their Catalytic Transformations to Commodities*. Chemical Reviews, 2014. **114**(3): p. 1909-1971.

- 163. Kuppinger, Franz-felix; Hengstermann, Axel ; Stochniol, Guido ; Bub, Günther; Mosler, Jürgen; Sabbagh, Andreas *Process for preparing acrylic acid purified by crystallization from hydroxypropionic acid and apparatus therefore*, 2011: United States.
- 164. Decoster, D., S. Hoyt, and S. Roach, *Dehydration of 3-hydroxypropionic acid to acrylic acid.* Patent WO2013192451, USA, 2013.
- 165. Craciun, L.B., Gerald P. ; Dewing, John;Schriver, George W.; Peer, William J. ; Siebenhaar, Bernd ; Siegrist, Urs *Preparation of acrylic acid derivatives from alpha-or beta-hydroxy carboxylic acids*, 2005: United States.
- 166. Lane, J. Cargill acquires OPX Biotechnologies. 2015.
- 167. Burns, R., D.T. Jones, and P.D. Ritchie, 88. Studies in pyrolysis. Part I. The pyrolysis of derivatives of α-acetoxypropionic acid, and related substances. Journal of the Chemical Society (Resumed), 1935: p. 400-406.
- 168. Smith, L.T., et al., *Pyrolysis of lactic acid derivatives*. Industrial & Engineering Chemistry, 1942. **34**(4): p. 473-479.
- 169. Fisher, C., W. Ratchford, and L.T. Smith, *Methyl acrylate production by pyrolysis of methyl acetoxypropionate*. Industrial & Engineering Chemistry, 1944. **36**(3): p. 229-234.
- 170. Ratchford, W. and C. Fisher, *Methyl acrylate by pyrolysis of methyl acetoxypropionate*. Industrial & Engineering Chemistry, 1945. **37**(4): p. 382-387.
- 171. Godlewski, J.E.V., Juan Esteban ; Collias, Dimitris Ioannis *Conversion of Methyl-2-Acetoxy Propionate to Methyl Acrylate and Acrylic Acid*, 2013, Godlewski Jane Ellen, Velasquez Juan Esteban, Collias Dimitris Ionnis: United States.
- Rehberg, C., W. Faucette, and C. Fisher, *Preparation of methyl acetoxypropionate: reaction of lactic acid with methyl acetate.* Industrial & Engineering Chemistry, 1944.
 36(5): p. 469-472.
- 173. Lilga, M.A.W., Todd A. ; Holladay, Johnathan E., *Methods of forming alpha, beta-unsaturated acids and esters*, 2006, Battelle Memorial Institute (Richland, WA, US): United States.
- 174. Beerthuis, R., et al., *Catalytic acetoxylation of lactic acid to 2-acetoxypropionic acid, en route to acrylic acid.* RSC Advances, 2015. **5**(6): p. 4103-4108.
- 175. Fruchey, O.S.H., WV, US), Malisezewski, Thomas A. (Charleston, WV, US), Sawyer, John E. (Charleston, WV, US), *Acrylic acid from lactide and process*, 2015, Fruchey Olan S., Malisezewski Thomas A., Sawyer John E.: United States.
- 176. Miller, D.L., Carl T.; Peereboom, Lars; Kolah, Aspi K., Method for producing acyloxy carboxylic acids and derivatives thereof, 2013, board of trustees of michigan state university (East Lansing, MI, US): United States.

- 177. Chuchani, G., et al., *Kinetics and mechanism of the gas-phase elimination of primary, secondary and tertiary 2-acetoxycarboxylic acids.* Journal of Physical Organic Chemistry, 2000. **13**(11): p. 757-764.
- 178. Elliott, J.R. and C.T. Lira, *Introductory chemical engineering thermodynamics*. Vol. 184. 1999: Prentice Hall PTR Upper Saddle River, NJ.
- 179. Wang, B., et al., *The effect of K*₂*HPO*₄ *and Al*₂(*SO*₄)₃ *modified MCM-41 on the dehydration of methyl lactate to acrylic acid.* RSC Advances, 2014. **4**(86): p. 45679-45686.
- 180. Hakim, S.H., et al., Synthesis of supported bimetallic nanoparticles with controlled size and composition distributions for active site elucidation. Journal of Catalysis, 2015. 328: p. 75-90.
- 181. Chen, D.H. and S.H. Wu, *Synthesis of Nickel Nanoparticles in Water-in-Oil Microemulsions*. Chemistry of Materials, 2000. **12**(5): p. 1354-1360.
- 182. Cargnello, M., et al., Efficient Removal of Organic Ligands from Supported Nanocrystals by Fast Thermal Annealing Enables Catalytic Studies on Well-Defined Active Phases. Journal of the American Chemical Society, 2015. 137(21): p. 6906-6911.
- 183. Al-Fatesh, A.S.A. and A.H. Fakeeha, *Effects of calcination and activation temperature on dry reforming catalysts.* Journal of Saudi Chemical Society, 2012. **16**(1): p. 55-61.
- 184. Manukyan, K.V., et al., *Nickel Oxide Reduction by Hydrogen: Kinetics and Structural Transformations*. The Journal of Physical Chemistry C, 2015. **119**(28): p. 16131-16138.
- 185. Smoláková, L., et al., *Effect of Calcination Temperature on the Structure and Catalytic Performance of the Ni/Al₂O₃ and Ni–Ce/Al₂O₃ Catalysts in Oxidative Dehydrogenation of <i>Ethane*. Industrial & Engineering Chemistry Research, 2015. **54**(51): p. 12730-12740.
- 186. O'Neill, B.J., et al., Stabilization of Copper Catalysts for Liquid-Phase Reactions by Atomic Layer Deposition. Angewandte Chemie International Edition, 2013. 52(51): p. 13808-13812.
- 187. O'Neill, B.J., et al., Control of Thickness and Chemical Properties of Atomic Layer Deposition Overcoats for Stabilizing Cu/γ-Al₂O₃ Catalysts. ChemSusChem, 2014. 7(12): p. 3247-3251.
- O'Neill, B.J., et al., Operando X-ray Absorption Spectroscopy Studies of Sintering for Supported Copper Catalysts during Liquid-phase Reaction. ChemCatChem, 2014. 6(9): p. 2493-2496.
- O'Neill, B.J., et al., *Catalyst Design with Atomic Layer Deposition*. ACS Catalysis, 2015.
 5(3): p. 1804-1825.

- Morales, M.V., et al., *Bioethanol dehydrogenation over copper supported on functionalized graphene materials and a high surface area graphite*. Carbon, 2016. 102: p. 426-436.
- Zhang, P., et al., A Highly Porous Carbon Support Rich in Graphitic-N Stabilizes Copper Nanocatalysts for Efficient Ethanol Dehydrogenation. ChemCatChem, 2017. 9(3): p. 505-510.
- 192. Lu, W.-D., et al., *Copper Supported on Hybrid C@SiO*₌ *Hollow Submicron Spheres as Active Ethanol Dehydrogenation Catalyst.* ChemNanoMat, 2018. **4**(5): p. 505-509.
- 193. Gomis, V., et al., *Dehydration of Ethanol Using Azeotropic Distillation with Isooctane*. Industrial & Engineering Chemistry Research, 2007. **46**(13): p. 4572-4576.
- Gil, I., L. García, and G. Rodríguez, *Simulation of ethanol extractive distillation with mixed glycols as separating agent*. Brazilian Journal of Chemical Engineering, 2014. 31(1): p. 259-270.
- 195. Gil, I., et al., Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: process simulation. Brazilian Journal of Chemical Engineering, 2008. **25**(1): p. 207-215.
- 196. Kiss, A.A., R.M. Ignat, and C.S. Bildea, *Optimal Extractive Distillation Process for Bioethanol Dehydration*, in *Computer Aided Chemical Engineering*, J.J. Klemeš, P.S. Varbanov, and P.Y. Liew, Editors. 2014, Elsevier. p. 1333-1338.