VAPOUR PHASE PARTIAL OXIDATION OF PYROLYSIS OIL MODEL COMPOUNDS IN PRESENCE OF VANADIA-TITANIA CATALYST

by

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in Chemical and Biological Engineering

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Abstract

Pyrolysis oil obtained from biomass has complex chemistry with more than 300 compounds. The utilization of pyrolysis oil as a transportation fuel is challenged by the high water and oxygen content in the pyrolysis oil. In this study, an alternate approach to improve the economic viability of pyrolysis oil is explored by employing oxidative catalysis to convert bio-oil ketones and alcohols to carboxylic acids.

Due to bio-oil’s complex chemistry, this study examined two representative compounds from alcohol and ketone functional groups: ethanol (ETH) and hydroxyacetone (HAC). The model compounds were subjected to partial oxidation in presence of vanadium pentoxide on titanium dioxide (V/TiO₂) support. The effect of temperature, oxygen ratio in the feed, and weight hourly space velocity (WHSV) on conversion, selectivity, and yield from the oxidation reaction were investigated in a packed bed reactor.

Partial oxidation of HAC in presence of V/TiO₂ produced lactic acid, acetic acid, and formic acid. 92.8% conversion was achieved at 473K, O₂/HAC molar ratio = 1.5 at WHSV of 1100 cm³·min⁻¹·g_cat⁻¹. Temperature, O₂/HAC and WHSV was found to impact the conversion of HAC and yield of LA. The overall reaction followed second-order kinetics and the activation energy was estimated to be 31.35 kJ·mol⁻¹.

Acetic acid (AA), acetaldehyde, CO₂, and CO were identified as the major products from partial oxidation of ethanol in V/TiO₂ catalyst. Complete conversion of ETH was achieved at higher temperatures (>523K) and low WHSV conditions (<250 cm³·min⁻¹·g_cat⁻¹). Only temperature and WHSV were identified as variables with significant influence on the conversion of ETH and yield of AA. A first-order rate law was used to describe overall kinetics and the activation energy was estimated to be 76.03kJ·mol⁻¹.

The influence of acetic acid in the feed mixture was also investigated. The conversion of HAC and ETH in presence of acetic acid decreased slightly. However, the selectivity and yield of desired acids were similar to the reaction of aqueous HAC and ETH alone.

This work successfully demonstrated the selective oxidation of model compounds with alcohol and ketone functional groups to carboxylic acid in presence of V/TiO₂ catalysts.
Lay Summary

When biomass is subjected to high temperature in absence of oxygen, a complex hydrocarbon liquid called pyrolysis oil is produced. However, the high water and oxygen content creates challenges for the utilization of pyrolysis oil as a transportation fuel. Hence, an alternate approach to improve the economic viability of pyrolysis oil is needed. Rather than expend energy to remove oxygen from pyrolysis oil, the potential of catalytic partial oxidation of light molecular weight oxygenated compounds to carboxylic acids is explored in this study. Two model compounds were successfully converted.
Preface

All the experimental reported in this work was performed in the Department of Chemical and Biological Engineering at the University of British Columbia, Vancouver campus under the supervision of Dr. Heather Trajano.

I, Anuradha Ramachandran was the investigator of this research and was responsible for performing literature review, synthesizing the catalyst, conducting the experiments, analyzing and interpreting the results, and constructing this thesis. The gas chromatography (GC) calibration was performed by Dr. Fahimeh Yazdan Panah. Ammonia-temperature programmed desorption (TPD) was performed by a PhD student, Majed Alamoudi. X-ray diffraction (XRD) and inductively coupled plasma optical emission spectrometry (ICP-OES) analyses were conducted at the OES center at UBC. X-ray photon spectroscopy (XPS) analysis was conducted at the University of Alberta.
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<tbody>
<tr>
<td>AA</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>ACH</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CCD</td>
<td>Central composite design</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon di oxide</td>
</tr>
<tr>
<td>CPO</td>
<td>Catalytic Partial Oxidation</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized Water</td>
</tr>
<tr>
<td>Eₐ</td>
<td>Activation energy</td>
</tr>
<tr>
<td>ETH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FA</td>
<td>Formic acid</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HAC</td>
<td>Hydroxyacetone</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>IEA</td>
<td>International energy agency</td>
</tr>
<tr>
<td>kₐ</td>
<td>Rate constant</td>
</tr>
<tr>
<td>LA</td>
<td>Lactic acid</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
</tbody>
</table>
OH – hydroxy group
PA – Pyruvic acid
RID - Refractive Index Detector
STP – Standard Temperature and Pressure
TCD - Thermal Conductivity Detector
TPD - Temperature programmed desorption
V – Vanadium
V/TiO₂ – Vanadium/Titanium dioxide
V₂O₅ – Vanadium pentaoxide
VOR – Valve override
WHSV - weight hourly space velocity
XPS – Xray photon spectroscopy
XRD – Xray diffraction
List of symbols

\( \tau \) – Tortuosity

\( \sigma _{c} \) – Constriction factor

\( \Phi _{p} \) – pellet porosity

\( \rho _{b} \) – bulk density of bed

\( \eta \) – Internal effectiveness factor

\( \Phi \) – Thiele modulus
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Chapter 1: Introduction

1.1 Background

Before the COVID-19 pandemic, IEA had projected the global energy demand to grow by 12% between 2019 and 2030. Since the pandemic, the adjusted energy demand growth over this period has been reduced to 9%\(^1\). 79\% of global energy demand is provided by fossil fuels\(^2\). It has been established that greenhouse gases and carbon emissions associated with fossil fuel resources are remarkably high. In addition to environmental degradation, fossil fuel resources are prone to volatile pricing, depleting supplies, and energy security concerns. Due to the uncertainty surrounding fossil fuel resources as well as their accompanying environmental impact, clean energy technology exploration and development have become an important goal for many countries around the world. As a part of the Paris Climate Agreement in 2015, 194 countries agreed to limit global temperature rise to 2\(^{\circ}\)C by reducing greenhouse gas emissions.

Global chemical production is also largely dependent on fossil fuel resources. The primary demand for oil and gas by the chemical manufacturing sector is 15\% and 9\% respectively (IEA)\(^3\). The chemical sector is also the third-largest direct CO\(_2\) emitter behind the iron, steel, and cement industry\(^3\). Many countries are looking for sustainable alternatives to meet the rising demand for industrial chemicals. Among renewable resources, biomass has the greatest potential to reduce the dependence on oil and gas for industrial chemical production. Biomass is the only renewable resource that can meet society’s need for liquid fuels and can be refined into a wide spectrum of products\(^4\). US Department of Energy - Bioenergy Technologies Office has recognized biomass utilization for fuels, products, and power as a critical component in reducing the US’s dependence on fossil fuels\(^5\). In Canada, new renewable products are being developed from forest biomass through initiatives such as the Transformative Technologies Program organized by FPInnovations and Natural Resources Canada\(^6\).

1.1.1 Pyrolysis of Biomass

Value-added products from biomass can be obtained via various thermochemical and biological processes. Pyrolysis is the thermal decomposition of biomass in absence of oxygen to yield liquid bio-oil, solid char, and pyrolytic gases. Pyrolysis is classified as slow or fast depending on the heating rate (Table 1-1).
The main product of slow pyrolysis is biochar. However, the primary product of interest is bio-oil or pyrolysis oil, as it is rich in organic compounds that can be processed further to yield fuels and chemicals. Typical yields from fast pyrolysis of biomass include 50-70wt% of bio-oil, 13-25wt% of biochar, and 12-15wt% of gaseous products including CO₂, CO, H₂, and traces of volatile hydrocarbons⁸. Fast pyrolysis is performed at moderate temperatures of 450°C-600°C in absence of air with rapid heating rates of biomass particles (>100 °C/min). The residence time is kept low at 0.5-2s to obtain higher yields of good-quality pyrolysis liquids⁸. A wide variety of biomass feedstock can be used in the pyrolysis process to produce bio-oil. Liquid yields up to 80wt% of dry feed can be obtained from most woody biomass at 500-520°C with residence time less than 1s⁹. Many parameters influence the yield and composition of pyrolysis products including biomass feedstock type, pre-treatment conditions, pyrolysis temperature, heating rate, carrier gas type, etc.

### 1.1.2 Chemical properties of Bio-oil

Biomass is primarily composed of lignin, cellulose, hemicellulose, and extractives. The thermal decomposition of these different groups will vary depending on the cracking severity as well as the type of biomass. This heterogeneity contributes to the complex composition and physio-chemical properties of bio-oil¹⁰. Table 1-2 shows the properties of bio-oil from various feedstock¹⁰. The composition of bio-oil changes according to the type of biomass feedstock.

---

**Table 1-1: Classification of Biomass Pyrolysis** ⁷ © 2020 Elsevier B.V.

<table>
<thead>
<tr>
<th>Pyrolysis types</th>
<th>Temperature (°C)</th>
<th>Heating rate (°C/s)</th>
<th>Residence time</th>
<th>Major products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torrefaction</td>
<td>200-300</td>
<td>-</td>
<td>Days</td>
<td>Charcoal</td>
</tr>
<tr>
<td>Slow pyrolysis</td>
<td>400-600</td>
<td>0.1-0.3</td>
<td>30-60 min</td>
<td>Biochar, bio-oil, gas</td>
</tr>
<tr>
<td>Fast pyrolysis</td>
<td>700-1200</td>
<td>10-100</td>
<td>10 s</td>
<td>Bio-oil</td>
</tr>
<tr>
<td>Flash pyrolysis</td>
<td>800-1150</td>
<td>&gt; 1000</td>
<td>1 s</td>
<td>Bio-oil</td>
</tr>
</tbody>
</table>
The typical oxygen and water content of fast pyrolysis oil is presented in Table 1-3\(^9\). From Table 1-3, bio-oil contains ~46-48wt% of oxygen and ~20-30wt% of water.

### Table 1-2: Properties of bio-oil from different biomass feedstock\(^{10}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Birch</th>
<th>Pine</th>
<th>Poplar</th>
<th>Various</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids (wt%)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.045</td>
<td>0.01-1</td>
</tr>
<tr>
<td>PH</td>
<td>2.5</td>
<td>2.4</td>
<td>2.8</td>
<td>2.0-3.7</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>18.9</td>
<td>17.0</td>
<td>16.8</td>
<td>15-30</td>
</tr>
<tr>
<td>Density (kg/m(^3))</td>
<td>1.25</td>
<td>1.24</td>
<td>1.20</td>
<td>1.2-1.3</td>
</tr>
<tr>
<td>Viscosity, cSt @ 50°C</td>
<td>28</td>
<td>28</td>
<td>13.5</td>
<td>13-80</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>16.5</td>
<td>17.2</td>
<td>17.3</td>
<td>13-18</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>0.004</td>
<td>0.03</td>
<td>0.007</td>
<td>0.004-0.3</td>
</tr>
<tr>
<td>CCR (wt%)</td>
<td>20</td>
<td>16</td>
<td>N/M</td>
<td>14-23</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>44.0</td>
<td>45.7</td>
<td>48.1</td>
<td>32-49</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>6.9</td>
<td>7.0</td>
<td>5.3</td>
<td>6.9-8.6</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.14</td>
<td>0.0-0.2</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>0.00</td>
<td>0.02</td>
<td>0.04</td>
<td>0.0-0.05</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>49.0</td>
<td>47.0</td>
<td>46.1</td>
<td>44-60</td>
</tr>
<tr>
<td>Na + K (ppm)</td>
<td>29</td>
<td>22</td>
<td>2</td>
<td>5-500</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>50</td>
<td>23</td>
<td>1</td>
<td>4-600</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>12</td>
<td>5</td>
<td>0.7</td>
<td>N/M</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>62</td>
<td>95</td>
<td>64</td>
<td>50-100</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-24</td>
<td>-19</td>
<td>N/M</td>
<td>-36 -9</td>
</tr>
</tbody>
</table>

### Table 1-3: Typical composition of bio-oil\(^9\) © 1999 Elsevier Science Ltd

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20–30</td>
</tr>
<tr>
<td>Carbon</td>
<td>44–47</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6–7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>46–48</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0–0.2</td>
</tr>
</tbody>
</table>
Hydrophobic and hydrophilic (aqueous) compounds are present in bio-oil. Most of the low molecular weight compounds in bio-oil are hydrophilic in nature. Compounds found in bio-oil fall include acids, alcohols, ketones, aldehydes, esters, phenols, furans, sugars, syringols, guaiacols, aromatics, and miscellaneous oxygenates\(^{11,12}\). Table 1-4 summarizes the most abundant compounds of each functional group and their corresponding amount present in typical bio-oil samples\(^{12}\).

**Table 1-4: Major compounds identified in pyrolysis-oil\(^{12}\)**

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Major compounds</th>
<th>Composition range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Acetic acid</td>
<td>0.5-12wt%</td>
</tr>
<tr>
<td></td>
<td>Formic acid</td>
<td>0.3-9.1wt%</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Methanol</td>
<td>0.4-2.4wt%</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.6-1.4wt%</td>
</tr>
<tr>
<td>Ketone</td>
<td>Acetone</td>
<td>2.8wt%</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>Acetaldehyde</td>
<td>0.1-8.5wt%</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>0.1-3.3wt%</td>
</tr>
<tr>
<td>Ester</td>
<td>Methyl formate</td>
<td>0.1-0.9wt%</td>
</tr>
<tr>
<td>Phenol</td>
<td>Phenol</td>
<td>0.1-3.8wt%</td>
</tr>
<tr>
<td>Furan</td>
<td>Furfural alcohol</td>
<td>0.1-5.2wt%</td>
</tr>
<tr>
<td></td>
<td>5-OH-methyl-2-furfural</td>
<td>0.3-2.2wt%</td>
</tr>
<tr>
<td>Ester</td>
<td>Methyl formate</td>
<td>0.1-0.9wt%</td>
</tr>
<tr>
<td>Misc. Oxygenates</td>
<td>Hydroxyacetaldehyde</td>
<td>0.9-13wt%</td>
</tr>
<tr>
<td></td>
<td>Hydroxyacetone</td>
<td>0.7-7.4wt%</td>
</tr>
<tr>
<td>Syringols</td>
<td>2,6 Dimethoxyphenol</td>
<td>0.7-4.8wt%</td>
</tr>
<tr>
<td>Guaiacols</td>
<td>Isoeugenol</td>
<td>0.1-7.2wt%</td>
</tr>
<tr>
<td></td>
<td>4-methyl guiacol</td>
<td>0.1-1.9wt%</td>
</tr>
<tr>
<td>Sugars</td>
<td>Fructose</td>
<td>0.7-2.9wt%</td>
</tr>
<tr>
<td></td>
<td>Levoglucosan</td>
<td>0.4-1.4wt%</td>
</tr>
</tbody>
</table>
1.1.3 Physical properties of Bio-oil

Since the production of bio-oil from fast pyrolysis is thermodynamically a nonequilibrium process, many oxygenated compounds in bio-oil undergo additional reactions during storage thereby increasing the viscosity of bio-oil. The viscosity increase is also accompanied by a phase separation of bio-oil in which tars, sludges, and waxes separate from the water and hydrophilic compounds. The high oxygen content also leads to higher boiling points and poor chemical stability. Unlike crude oil, bio-oil can not be vaporized from a liquid state. As the temperature of bio-oil is increased, the volatiles in the bio-oil are released, then water is vaporized and the remaining compounds are polymerized.

1.1.4 Potential uses of Bio-oil

Bio-oil can be used in a variety of applications including heat and power generation and upgradation to value-added products. A combustion study of bio-oil demonstrated at MIT and CANMET showed similar combustion behavior as fuel oil. However, soot formation was high during combustion. The low pH of bio-oil caused extensive wear and corrosion in the injector loop and the carbon deposits caused plugging issues when the bio-oil was used in diesel engines. Moreover, the acidity of bio-oil and high oxygen content in bio-oil limit their use as a transportation fuel. Upgrading bio-oil by deoxygenation is required to improve the heating value of bio-oil and reduce the oxygen content to levels comparable to that of hydrocarbon fuels. The primary approaches to upgrading bio-oil involve catalytic cracking and catalytic hydrotreating. However, these processes are conducted at high temperatures and pressure and require a source of hydrogen. High coking rates reduce process yields. An alternate approach to produce value-added products from bio-oil will greatly improve the overall economic prospects of bio-oil.

1.2 Motivation

Catalytic upgrading of bio-oil by deoxygenation to transportation fuel standard is a challenging and energy-intensive process. An alternate approach to improve the economic viability of pyrolysis oil might be to employ oxidative catalytic approaches to convert aldehydes, ketones, and alcohols in bio-oil to carboxylic acids. Potential products include acetic acid, lactic acid, formic acid, maleic acid, gluconic acid, formaldehyde, acetaldehyde, and glyoxal. The market value of these products is higher than the original reactants. Further, the global market for carboxylic acids is projected to grow to $13.6 billion by 2022 at an annual growth rate of 3.9%. Moreover, the oxidation process can also simplify the composition of the product stream by increasing the concentration of carboxylic acids thus facilitating downstream separation processes.
Fig 1-1 illustrates how catalytic partial oxidation could be integrated with pyrolysis. The vapors from the pyrolysis reactor would be sent through a series of partial condensers to separate the oxygen-rich hydrophilic compounds from the high molecular-weight hydrophobic compounds. These hydrophobic compounds are well-suited for use as fuel due to reduced water content and acidity and will be upgraded via deoxygenation. The low molecular-weight hydrophilic compounds will be subjected to gas-phase oxidation to produce carboxylic acids. Since the low molecular weight aqueous fraction of bio-oil contains many functional groups, it is essential to understand the oxidation behavior and product yield from representative model compounds present in this fraction.

**Fig 1-1: Schematic diagram of proposed partial oxidation**

### 1.3 Model compound study

The development of the bio-oil partial oxidation process requires a complete understanding of process chemistry. However, bio-oil is a complex mixture of compounds and functional groups. Hence, subjecting model compounds to partial oxidation will provide a better understanding of the behavior of functional groups in bio-oil. Previously, Zhu conducted studies of partial oxidation of compounds from two main functional groups: acids and aldehydes\(^8\). There are few reported studies on gas-phase oxidation of multi-functional compounds. In this thesis, the behavior of compounds with ketone and alcohol functional groups were investigated: hydroxyacetone and ethanol. Hydroxyacetone (HAC) is a multi-functional compound containing both a hydroxyl and a ketone group. According to the compositional analysis reported by Milne
et al, hydroxyacetone is found in quantities ranging from 0.7-7.4wt% in bio-oil. Hydroxyacetone is also a common multifunctional atmospheric oxygenated volatile organic compound that is formed from isoprene oxidation. Most studies reported in the literature consider atmospheric oxidation of HAC. In a few studies, oxidation of HAC has been shown to produce high yields of lactic acid with various catalysts. Since lactic acid (LA) is a highly valuable carboxylic acid, the viability of LA production from gas-phase oxidation of HAC is explored in this thesis. Further oxidation of LA yields pyruvic acid and acetic acid.

Ethanol is one of the most common monofunctional alcohol compounds identified in the aqueous phase of pyrolysis oil; its content ranges from 0.6-1.4wt%. Catalytic partial oxidation of ethanol leads to the formation of acetic acid and acetaldehyde. Complete oxidation of ethanol leads to the formation of undesirable CO₂ and CO.

Hydroxy acetaldehyde represents another functional group that is present in significant quantity in the aqueous phase of bio-oil. Hydroxy acetaldehyde is commercially available in dimer form as white solid crystals. However, upon dissolution different monomeric and dimeric species (Fig 1-2) may exist at equilibrium. As a pure solution of hydroxy acetaldehyde is difficult to obtain, it was not chosen for further investigation in this thesis.

Fig 1-2: Different monomeric and dimeric species in hydroxyacetaldehyde solution. Reprinted (adapted) with permission from [23]. Copyright 2013 American Chemical Society.
Glyoxal is a di-aldehyde compound present in quantities ranging from 0.9-4.6wt% in the aqueous phase of bio-oil\textsuperscript{10}. Initial attempts to oxidize glyoxal resulted in the preheated feed line becoming plugged with coke. Since glyoxal could not be easily vaporized, it was excluded from this study.

1.4 Literature review

There are a limited number of studies on the catalytic partial oxidation of pyrolysis oil model compounds in the literature. A general description of results from those studies is presented. Reports on the oxidation of hydroxyacetone and ethanol are discussed in detail. Finally, the chemical and structural properties of vanadium catalysts are presented.

1.4.1 Catalytic Partial Oxidation (CPO) of pyrolysis oil model compounds

Catalytic partial oxidation (CPO) of different pyrolysis oil model compounds has been reported in literature\textsuperscript{18-26}. NREL sought to produce hydrogen through partial oxidation and catalytic thermal reforming of bio-oil\textsuperscript{24} and examined the process with four catalysts: 1\% Rh, 1\% Ce on Al\textsubscript{2}O\textsubscript{3}, 1\% Ni, 0.5\% Rh on Al\textsubscript{2}O\textsubscript{3}. Syngas production through CPO of pyrolysis oil has also been reported in the literature. Kruger et al. examined the autothermal partial oxidation of pyrolysis oil on Pt/\(\alpha\)-Al\textsubscript{2}O\textsubscript{3} and Rh/\(\alpha\)-Al\textsubscript{2}O\textsubscript{3} catalysts and they concluded that higher conversion was achieved with Rh catalysts and that the product spectrum depended on catalyst identity\textsuperscript{25}.

The catalytic conversion of other functional groups in pyrolysis oil like esters and carboxylic acids into synthesis gas or chemicals could permit optimal utilization of bio-oils\textsuperscript{26}. To examine the ester moiety, two esters, ethyl lactate, and ethyl propionate, and two acids, lactic acid, and propionic acid were reformed by catalytic partial oxidation. Auto-thermal reforming was examined over platinum and rhodium-based catalysts supported on alumina foam monoliths. Conversions >98\% were observed for all four fuels. The results provide evidence that the homogeneous decomposition of esters to intermediate acids can contribute to the overall reforming process. It was found that the products were highly tunable between synthesis gas and olefins by varying the fuel-to-oxygen ratio and the catalyst.

Two abundant but simple hydrophilic molecules in pyrolysis oil are acetaldehyde and acetic acid. These molecules were previously chosen as model compounds to evaluate the feasibility of gas-phase partial oxidation of pyrolysis oil\textsuperscript{18}. Thermal oxidation of acetaldehyde and acetic acid produced CO\textsubscript{2} with selectivity greater than 99.5\%, indicating both compounds were fully oxidized. All subsequent studies were conducted using vanadia-titania (V/TiO\textsubscript{2}) catalysts\textsuperscript{18}. Conversion of acetic acid was low even with the catalyst and CO\textsubscript{2} was the only detectable product. However, oxidation of acetaldehyde with V/TiO\textsubscript{2} resulted in the production of partial oxidation products such as acetic acid and formic acid in addition to CO\textsubscript{2} and
CO. By adjusting temperature, V loading, and oxygen concentration selectivity to acetic acid was increased to 70%. It was also demonstrated that conversion and selectivity of acetaldehyde were unchanged by the addition of acetic acid to the reactor feed.

1.4.2 Catalytic partial oxidation of hydroxyacetone

The oxidation of isoprene, a biogenic hydrocarbon contributes to ozone production in rural regions\textsuperscript{27}. Initial oxidation products of isoprene include methyl vinyl ketone and methacrolein. These compounds undergo further oxidation to produce multifunctional species such as methylglyoxal, hydroxyl acetone, and glycolaldehyde. Atmospheric oxidation of hydroxyacetone provides some insight into the anticipated products and reaction mechanisms for CPO. The degradation of HAC in the troposphere has been attributed to its reaction with OH radicals and Cl atoms\textsuperscript{28-30}. Aqueous phase oxidation of HAC over commercial Pt/Al\textsubscript{2}O\textsubscript{3} powder catalysts\textsuperscript{20} produced lactic acid. They concluded that catalytic activity and selectivity to lactic acid depended on the pH of the reaction medium. Increasing to pH10 from pH8 increased selectivity to LA while decreasing pyruvic acid formation (Fig 1-3).

![Fig 1-3: Variation in conversion of liquid phase oxidation of HAC and selectivity of lactic acid with varying pH on 5 wt% Pt/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{20}](image)

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Reaction conditions that promoted the initial oxidation of HAC and the intramolecular disproportionation of the resulting pyruvaldehyde were essential for lactic acid formation. In subsequent work, Albuquerque et al. replaced the alkali hydroxide with a dual metal/base catalyst and obtained a remarkable 100% selectivity to lactic acid\textsuperscript{21}. Over this highly selective Pt/MgO-Al\textsubscript{2}O\textsubscript{3} bifunctional catalyst, the cascade oxidation of lactic acid to pyruvic acid was hindered. Lactic acid selectivity was always greater than 50% and pyruvic acid was the only other product formed. It was suggested that HAC tautomerization and subsequent oxidation could be the key for lactic acid formation. Two reaction pathways for conversion of HAC over dual catalytic systems were proposed as shown in Fig 1-4\textsuperscript{21}. Based on their observations, Albuquerque et al. concluded the different reaction pathways could be responsible for the formation of lactic acid from HAC.

![Fig 1-4: Two possible reaction pathways for selective oxidation of HAC on bifunctional catalyst\textsuperscript{21}](image)

© The Royal Society of Chemistry 2015

Albuquerque et al. also examined the relationship between acid-base properties for the Cannizzaro reaction of pyruvaldehyde to lactic acid in presence of ZrO\textsubscript{2} catalysts\textsuperscript{22}. They established that there is a strong correlation between reaction rate and Lewis acid sites of sufficient strength. Yan et al (2017) examined the production of lactic acid from HAC over dealuminated Sn-beta supported gold catalysts and concluded that proximity of Lewis acid Sn and Au sites favors the conversion of HAC to lactic acid\textsuperscript{31}. They proposed two reaction pathways under base-free conditions: a 1,2-hydride shift followed by oxidation or oxidation followed by hydration and a 1,2-hydride shift (Fig 1-5). From experimental results, the most likely path was oxidation of hydroxyacetone catalyzed by Au nanoparticles to pyruvaldehyde followed by hydration and a 1,2-hydride shift on Sn-Beta Lewis sites to yield lactic acid.
However, no vapour phase partial oxidation of HAC has been reported in the literature to the best of our knowledge.

### 1.4.3 CPO of ethanol

Ethanol oxidation has been widely reported in the literature and a wide variety of catalysts have been employed: V/TiO$_2$, ZrO$_2$/V, VMgO, TiO$_2$/SiO$_2$, Au/TiO$_2$, and Mo-V-Nb. Ethanol oxidation yields acetic acid, acetaldehyde, CO$_2$, CO, and traces of ethyl acetate. The temperature of the reaction, amount of oxygen and water in the feed mixture, the concentration of ethanol in the feed, and catalyst type have a significant effect on the conversion of ethanol and selectivity to acetic acid. At temperatures below 150°C, acetaldehyde was formed as the major product. At temperatures greater than 250°C, acetic acid is decarboxylated to CO and CO$_2$.

Jorgensen et al. conducted gas-phase oxidation of aqueous ethanol by nanoparticle V/TiO$_2$ catalysts at space velocities from 2,500-50,000 h$^{-1}$. They reported that as residence time increased, the reaction shifted towards the formation of acetic acid. Acetaldehyde formation from ethanol is known to occur through the Mars-Van Krevelen type mechanism using lattice oxygen on catalyst surface as shown in Fig 1-6.
It has been proposed that acetic acid sequentially forms after acetaldehyde production (Fig 1-11). CO₂ and CO are produced via further oxidation of acetaldehyde and acetic acid. The reaction scheme for acetic acid formation from ethanol is shown in Fig 1-7.

Li et al. observed that although ethanol conversion decreased, acetic acid selectivity increased with water partial pressure.

Fig 1-6: Mars Van Krevelen mechanism proposed for ethanol oxidation
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Fig 1-7: Sequential oxidation of Ethanol © 2007 Wiley-VCH
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1.4.4 Oxidation catalyst

V/TiO₂ is one of the most efficient catalysts and has been widely used for oxidative dehydrogenation of C₂-C₄ hydrocarbons, selective catalytic reduction, and ammoxidation⁴¹. Moreover, this heterogeneous catalyst is very promising for gas-phase oxidation of lower hydrocarbons. Suprun et al⁴⁰ investigated the oxidation of acetaldehyde and propionaldehyde on 6wt% V/TiO₂ (anatase) at temperatures from 120-280°C. They were able to produce acetic acid with selectivity up to 82% and propionic acid with a selectivity of about 20% from oxidation of acetaldehyde and propionaldehyde, respectively. They found that the presence of water and an increase in the concentration of oxygen in the feed enabled better selectivity towards C₁-C₃ carboxylic acids as it inhibited the total oxidation of aldehydes and carboxylic acids. V/TiO₂ catalysts also demonstrated high selectivity to acetic acid during oxidation of acetaldehyde at 150-300°C with a residence time of 0.18-0.9s¹⁸. Ethanol oxidation on V/TiO₂ has been demonstrated to yield acetic acid⁴⁷ at temperatures >200°C with O₂/ETH ratio = 9 at a space velocity of 5500 h⁻¹. However, to the best of our knowledge, selective gas-phase oxidation of hydroxyacetone has not been investigated in presence of V/TiO₂.

As vanadium is a transition metal, the possible oxidation states are +2, +3, +4, and +5. Vanadium oxide can be found as V₂O₅, VO₂, V₂O₃, and VO⁴¹. V₂O₅ is the most common oxide form of vanadium and V ions are present in distorted octahedrons. The formation of specific oxidation states depends on the solution pH as well as vanadium oxide concentration⁴¹. Moreover, V₂O₅ supported on a metal oxide surface can exist as isolated vanadium ions, dimeric or polymeric species, two-dimensional vanadium chains, or crystals. Vanadium catalysts have been prepared by many techniques including sol-gel, wetness impregnation, incipient wetness impregnation, and co-precipitated⁴¹. The preparation technique does not affect the local coordination of vanadium oxides with the support but does influence the dispersion of vanadium oxide on the metal oxide support. Vanadium-oxide bonds in monomeric and polymeric VO₄ species are presented in Fig 1-10.
At low vanadium loading, the vanadium oxide species are present as isolated VO$_4$ units. However, as vanadium loading increases, a corresponding increase in dimeric and polymeric chains of VO$_4$ is noticed. At high levels of vanadium loading, VO$_6$ units agglomerate to form amorphous and crystalline V$_2$O$_5$ units. Crystalline V$_2$O$_5$ has been reported to reduce the exposed vanadium sites and dramatically reduce methane turnover frequency during oxidation.

Water vapour in the reaction system can potentially decrease catalytic activity of vanadia catalysts. Studies conducted to examine the deactivation vanadia catalysts in ammonia-selective catalytic reduction (SCR) systems, report that water molecules could cover the active sites of the catalyst and can potentially distort the catalyst structure due to vaporization and swelling. Chemisorption of water molecules on the catalyst surface can also decrease the catalytic activity due to competitive adsorption of reactant species and water molecules on the active sites. In addition, accelerated phase transition from anatase to rutile phase of TiO$_2$ has been reported in studies of oxidative dehydrogenation reactions on vanadia-titania catalysts.

Kootenaei et al. reported a decrease in BET surface area from 48 to 40 m$^2$g$^{-1}$ accompanied by an increase in crystal size from 24 to 26 nm. They attributed the decrease in the catalytic activity of Vanadia-Titania catalyst to these physical changes.

**1.5 Literature review summary**

Catalytic partial oxidation of many pyrolysis oil model compounds has been presented in the previous sections. Metal oxide supported catalysts and bimetallic support catalysts have been employed for these oxidations. Oxidation of hydroxyacetone has been studied in the context of atmospheric chemistry and aqueous conditions. For both systems, complex product distributions were observed. Lactic acid was the primary product and by-products included acetic acid, pyruvic acid, and formic acid. Many reports have concluded that reaction medium pH and catalyst basicity significantly influence lactic acid yield. Different cascade reaction mechanisms have been proposed depending on catalyst activity. Ethanol oxidation has been investigated with a variety of catalysts. Selective oxidation of ethanol is reported to favour
acetaldehyde production at temperatures <150°C and acetic acid production at temperatures >180°C. The amount of oxygen and water in the feed affects conversion and product selectivity. Ethanol oxidation is known to proceed via a two-step reaction mechanism. The first step involves oxidation of ethanol to acetaldehyde followed by autooxidation to acetic acid.

Vanadium oxide on anatase TiO$_2$ is widely used to catalyze partial oxidation reactions. The incipient wetness impregnation method is one of the most common methods for the preparation of vanadia catalysts. Catalysts with vanadium loading greater than >10wt% consist of V$_2$O$_5$ crystals.

### 1.6 Objectives

This study is aimed at investigating the response of two prominent functional groups to the selective oxidation process. Previously, the response of acetaldehyde (C1 aldehyde) and acetic acid (C1 carboxylic acid) was investigated. In this study, ethanol (C2 alcohol) and hydroxyacetone (C3 multifunctional ketone and alcohol) will be considered. These compounds were selected for their functional groups and increased size. Selective oxidation of these species will be investigated in presence of V/TiO$_2$ at atmospheric pressure.

The specific objectives are as follows:

1. Determine the activity of 3.06wt% V/TiO$_2$ and 8.81wt% V/TiO$_2$ in selective oxidation of HAC and ethanol
2. Identify product distribution from partial oxidation of hydroxyacetone and ethanol in presence of V/TiO$_2$ catalyst
3. Determine the impact of process parameters such as temperature, feed ratio, and space velocity on the yield of desired carboxylic acids. Identify the process parameters of significance to achieve maximum yield of desired carboxylic acids
4. Estimate the activation energy from overall reaction kinetic data.
5. Investigate changes in conversion, yield, and selectivity of hydroxyacetone and ethanol in presence of acetic acid.
Chapter 2: Experimental

2.1 Experiment setup

The gas-phase oxidation of pyrolysis model compounds is carried out in a packed bed reactor system. The process flow diagram is shown in Fig 2-1. The oxygen and helium required for the reaction were supplied via cylinders connected to the reactor. Both gases were purchased from Praxair with 99% purity. These cylinders were fitted with pressure regulators and were considered empty when the pressure was less than 200 psi. The mass flow controllers (MFC, SLA5850 Brooks Instrument) for the inlet gases, oxygen and helium, were calibrated at 273K and 1 atm (STP). These MFCs required an inlet pressure of 15 psi for smooth uninterrupted flow hence, the cylinder regulator pressure was set at 50 psi. For safety considerations, the pressure relief valve was set at 35 psi. Check valves were also installed to shut off flows during an emergency. A flow meter (SAL5860, Brooks Instrument) was installed to measure the flow rate of gases exiting the condenser. Since this flowmeter was used to measure a variety of gases, it was calibrated for nitrogen and an appropriate gas conversion factor was applied to determine the actual flowrate. The MFCs and the flow meter were connected to the computer via the 0254 (model 0254AB1B15A) display unit. O₂ and He flowrates were controlled through a 0254 readout application. A pressure gauge and pressure transducer were installed to monitor the pressure of the system. The pressure transducer connected to the PC recorded pressure via a USBH application (Omega Engineering). A syringe pump (PHD Ultra Infusion Only, Harvard Apparatus) was used to control the flow of liquid feed into the reactor. The reactant feed solution was loaded into a 50 mL gas tight syringe and the desired flow rate was entered on the EZ Pro Software. A ball valve is provided to control flow of the reactant. A check valve prevented gas flow to the syringe. The reactor temperature was monitored using a K-type thermocouple positioned near the catalyst bed and connected to a data acquisition unit (OM-DAQ-USB-2401, Omega Engineering). The reactor was a 3/8” OD 316SS pipe with a length of 48 cm and a wall thickness of 0.065”. The reactor was housed in a furnace (Lindberg Blue M Tube) which has a maximum operating temperature of 1200°C. The liquid reactant and helium feed lines were wrapped with fiberglass heating tapes (OMEGALUX™, Omega Engineering) to preheat reactants before entering the reactor. The temperature of these heating tapes was controlled by a Variac transformer. The outlet of the reactor was connected to a condenser placed in an ice bath to condense and collect liquid products. The non-condensable gases were directed to the vent and a ball valve was installed so gas samples could be collected for analysis. The liquid products were identified and quantified using high-performance liquid chromatography (HPLC) with a refractive index detector (RID). The gas products were identified and quantified using gas chromatography (GC) with thermal conductivity detector (TCD) and flame ionization detector (FID).
2.2 Experimental procedure

Before each run, a leak test was performed by flowing helium at the maximum flow rate and utilizing Swagelok SNOOP® agent at all piping fittings. Significant bubble formation indicated the presence of a leak.

The gas conversion factors for helium and oxygen\(^\text{13}\) used for the condenser flow meter (SAL5860, Brooks Instrument) is

- \(\text{O}_2 = 0.98\)
- \(\text{Helium} = 1.34\)

After the leak test, the reactor was packed with inert glass beads and SiC of varying mesh sizes (mesh number 46 to 16), and the required amount of catalyst. Catalyst mass was determined from the target WHSV. The bed was packed so that the catalyst was located at the middle of the bed with respect to length;
a schematic of the packing is provided in Appendix F. The thermocouple was attached to the reactor and then connected to the system piping. Helium was flown through the system and Swagelok SNOOP® was re-applied to detect leaks at the reactor joints. On completion of the leak test, the furnace was heated to the desired reaction temperature at a ramp rate of 10°C/min. The heating tapes were maintained at 70°C using the Variac transformer. The condenser jacket was filled with ice to condense liquid products coming from the reactor. The desired flow rates of helium and oxygen and the valve over ride (VOR) were set at normal in the 0254 readout application software to begin the flow of these reactants into the reactor. The pressure transducer was closely monitored until the pressure stabilized. The thermocouple signal was also closely monitored until the temperature inside the reactor stabilized. During a run, the temperature remained within ±1°C of target temperature. The liquid feed was prepared by mixing the organic feed with water and loaded into the gas-tight syringe. The desired liquid feed flowrate was set on the EZ Pro Software in the Harvard pump. Once the pressure and temperature stabilized, the ball valve on the liquid feed line was opened to introduce liquid feed into the reactor. The reaction run time was 3 hours. After the reaction, the gas samples were collected in inert multilayer foil gas sampling bags (SUPELCO Supel™). The liquid products were collected in a graduated cylinder and the volume of liquid obtained was recorded. After completion of the experiment, the system, including the reactor, was flushed with helium for 30 min and then oxygen was supplied for 15 minutes to oxidize any unreacted reactant present inside the reactor.
Experimental Setup

Fig 2-3 (a) Waters e2765 HPLC with UV and RID; (b) GC-2014 with FID and TCD
2.3 Compositional Analysis

2.3.1 Liquid phase analysis

The liquid product obtained from the oxidation reactions was analyzed in Waters e2675 Alliance HPLC equipped with refractive index detector (RID) and Biorad Aminex 87-H column. The major compounds expected in the liquid phase after hydroxyacetone oxidation were lactic acid, acetic acid, pyruvic acid, formic acid, and unreacted hydroxyacetone. The major compounds expected in the liquid phase after ethanol oxidation were acetic acid, acetaldehyde, and unreacted ethanol. The temperature of the RID was kept constant at 40°C. The column was operated at 65°C\textsuperscript{21}. The column was operated in an isocratic elution mode with 0.01 N sulphuric acid as a mobile phase at a constant flow rate of 0.6 mL/min. Calibration standards for the expected compounds were prepared at 5 concentrations using the mobile phase as the solvent. Calibration curves for model reactants and expected products in the liquid phase can be found in Appendix B-1. The retention time for the expected compounds is summarized in Table 2-1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (RID), min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>21.29</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>18.38</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>17.16</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>15.19</td>
</tr>
<tr>
<td>Formic acid</td>
<td>13.97</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>12.84</td>
</tr>
<tr>
<td>Pyruvic acid</td>
<td>9.64</td>
</tr>
</tbody>
</table>

For HPLC analysis of the liquid product sample, 0.5 mL of the sample was diluted in 50 mL of the mobile phase. All the solutions were filtered through a 0.45 mm membrane filter before loading the sample vials to the HPLC. Each analysis was carried out for 30 mins, to capture all the peaks in the sample.
2.3.2 Gas phase analysis

The composition of the sampled gas was analyzed by a Shimadzu GC-2014 equipped with TCD (thermal conductivity detector) and FID (flame ionization detector). The GC has three packed columns in series: Porapak-N (80/100 mesh, 3 m), Porapak-Q (80/100 mesh, 3 m), and an MS-5A (60/80, 2.25 m). For CO, CO₂, and CH₄ the FID detector was used; and TCD was used for N₂, O₂, and H₂. Argon was the carrier and reference gas for the TCD. Compressed air and argon were used as the reference and carrier gases for the FID. The GC was regularly calibrated with 3 standard calibration gases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Detector</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>FID</td>
<td>8.99</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>FID</td>
<td>17.86</td>
</tr>
<tr>
<td>Methane</td>
<td>FID</td>
<td>13.20</td>
</tr>
<tr>
<td>Helium</td>
<td>TCD</td>
<td>3.25</td>
</tr>
<tr>
<td>Oxygen</td>
<td>TCD</td>
<td>5.05</td>
</tr>
</tbody>
</table>

Table 2-2: Retention time of expected compounds in GC

2.4 Catalyst preparation

Catalysts with two different loadings 5wt% and 10wt% vanadium loading were prepared using the incipient wetness impregnation method. Anatase TiO₂ was used as the support. The BET surface area and the pore volume of the TiO₂ pellets (VWR) were measured by N₂ adsorption at 77K and were found to 202.41 m²/g and 0.50 cm³/g respectively. Vanadium oxalate (C₂O₅V, City Chemical) was used as the precursor for impregnating the TiO₂ support. The solubility of vanadium oxalate in water at 20 °C is 22 g in 100 mL distilled water. Due to poor solubility, two-step incipient wetness impregnation was adopted. To prepare 10 g of the catalyst with 10 wt% vanadium, 8.215 g of TiO₂ pellets were crushed and sieved to be within 90-125 µm size particles. For the first step impregnation, 1.53 g C₂O₅V was dissolved in 4.14 ml of deionized (DI) water and was placed in a sonicator with a hot water bath for 60-90 minutes until a blue transparent homogenous solution was obtained. The particles were collected and dried at room temperature for 24 hours. This air-dried catalyst was next dried in an oven at 100°C for 24 hours and calcined at 450°C for 5 hours. The calcined and cooled catalyst was impregnated for the second time using 1.53 g C₂O₅V dissolved in 4.14 ml of DI water. The particles were dried again at room temperature for 24 hours and then
in the oven at 100°C for 24 hours. After oven-drying the catalyst was calcined at 450°C for 5 hours and sieved to the desired particle size of 90-125 µm.

This procedure was repeated to prepare 10 g of 5wt% vanadium-loaded catalyst. Impregnation was conducted using 0.765 g of C2O5V dissolved in 4.59 ml of DI water and 9.107 g of TiO2 support of size 90-125 µm. The wet catalyst was dried and calcined in a similar procedure as the 10 wt% V catalysts.

### 2.5 Catalyst Characterization

The properties of the prepared catalysts were characterized using by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photon spectroscopy (XPS), inductively coupled plasma optical emission spectrometry (ICP-OES), and temperature-programmed desorption (TPD).

#### 2.5.1 BET

Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer were used to measure the BET surface area, pore-volume, and pore size of 5 wt% V and 10 wt% V catalysts. 0.1 g of catalyst was loaded in a glass tube and degassed at 473K for 4 hours in a vacuum to remove any excess moisture from the catalyst. After degassing, the adsorption/desorption isotherm was measured at 77K with nitrogen. The full analysis report is found in Appendix A-1.

#### 2.5.2 XRD

The phases of titanium and vanadium metal in the catalysts were analyzed using a Bruker D8 Focus Bragg-Brentano diffractometer equipped with a Fe filter foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Sollerslits, and a LynxEye detector. Continuous-scan X-ray powder-diffraction data were collected over a range of 3-80°2θ CoKa radiation on a long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. XRD sample preparation and analysis was carried out by the UBC Earth and Ocean Sciences Department. The diffraction data were processed by automated ‘search match’ software that utilizes International Centre for Diffraction Data PDF-4+ database. The spectra of both catalysts are found in Appendix A-2.
2.5.3 XPS

The oxidation state of vanadium oxide in the supported catalyst was identified through XPS analysis. XPS analysis was carried out in the nanoFAB laboratory at the University of Alberta using Kratos Axis (Ultra) spectrometer with monochromatized Al kα (hυ = 1486.71 eV). The spectrometer was calibrated by the binding energy of Au 4f7/2. A hemispherical electron-energy analyzer working at the pass energy of 20 eV was used to collect core-level spectra while a survey spectrum within a range of binding energies from 0 to 1100 eV was collected at analyzer pass energy of 160 eV. The model peak parameters were determined using Marquardt Algorithm and the curve fitting to describe XPS core-level lines were obtained using Gaussian and Lorentzian functions. CasaXPS was used for component analysis and peak identification. The XPS spectra are presented in Appendix A-3.

2.5.4 ICP-OES

The true amount of vanadium metal loading on the catalysts was measured by Varian 725 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) instrument in the UBC Earth and Ocean Sciences department. For the standard calibration, vanadium standard for ICP was purchased from Sigma Aldrich Canada Ltd. Sample preparation for analysis involved digesting 10 mg of catalyst in concentrated nitric acid and sulfuric acid multiple times at 513K until all metal was dissolved in the solution.

2.5.5 NH₃-TPD

NH₃ – temperature-programmed desorption was conducted in Micrometrics Autochem II 2920. About 100 mg of sample was dried at 200 °C for 2 hours and then cooled to 70°C in helium. 15% NH₃ in helium at 40mL (STP)/min and 70°C was flown over the samples. For NH₃ desorption, a thermal conductivity detector was used to monitor the increase in sample temperature from 120°C to 550°C at 10°C/min.
2.6 Design of experiments

2.6.1 Catalyst selection experiments

The selection tests for hydroxyacetone partial oxidation with 3.06 wt% V and 8.81 wt% V were performed at the process conditions presented in Tables 2-3 with 80wt% HAC aqueous solution. The reaction time for each experiment was 3 hours.

Table 2-3: Process conditions for catalyst screening test with HAC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>473</td>
</tr>
<tr>
<td>Oxygen/HAC molar ratio</td>
<td>1</td>
</tr>
<tr>
<td>WHSV (STP) cm$^3$/min.g$_{cat}$</td>
<td>730</td>
</tr>
<tr>
<td>Composition of liquid feed</td>
<td></td>
</tr>
<tr>
<td>HAC (wt%)</td>
<td>80</td>
</tr>
<tr>
<td>H$_2$O (wt%)</td>
<td>20</td>
</tr>
</tbody>
</table>

2.6.2 Central Composite Design (CCD)

The catalyst that produced the highest conversion was selected for further experiments. To develop a model for the yield of carboxylic acids, a central composite design (CCD) was utilized. Considering the reaction system limitations, an inscribed CCD was chosen. Three factors: temperature, oxygen to reactant mole ratio, weight hourly space velocity (WHSV), were selected for investigation and yield was the response variable. The CCD was developed using the ‘ccdesign’ package in MATLAB. The chosen CCD with 3 factors and two levels (high (+), low (-)) consists of 8 factorial points, 6 axial points, and one center point. In total, the design consists of 15 experimental conditions. For all HAC oxidation experiments, the liquid feed was 80 wt% HAC and 20 wt% H$_2$O. For all ETH oxidation experiments, the liquid feed was 25 wt% ETH and 75 wt% H$_2$O. Before proceeding with the central composite design experiments, blank runs with only inert SiC and TiO$_2$ support were conducted at 473K, with O$_2$/HAC ratio =1 and at 487 cm$^3$.min$^{-1}$.g$_{cat}^{-1}$. No conversion of HAC was observed in the blank runs.
Table 2-4: High and low levels for HAC oxidation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low level</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>423</td>
<td>523</td>
</tr>
<tr>
<td>Oxygen / HAC molar feed ratio</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>WHSV (STP), cm³min.g⁻¹cat</td>
<td>200</td>
<td>2000</td>
</tr>
</tbody>
</table>

Table 2-5: Central composite design experiments for HAC oxidation

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Temp (K)</th>
<th>O₂/HAC</th>
<th>WHSV (STP) cm³.min⁻¹.g⁻¹cat⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>443</td>
<td>0.7</td>
<td>560</td>
</tr>
<tr>
<td>2</td>
<td>443</td>
<td>0.7</td>
<td>1640</td>
</tr>
<tr>
<td>3</td>
<td>443</td>
<td>1.3</td>
<td>560</td>
</tr>
<tr>
<td>4</td>
<td>443</td>
<td>1.3</td>
<td>1640</td>
</tr>
<tr>
<td>5</td>
<td>503</td>
<td>0.7</td>
<td>560</td>
</tr>
<tr>
<td>6</td>
<td>503</td>
<td>0.7</td>
<td>1640</td>
</tr>
<tr>
<td>7</td>
<td>503</td>
<td>1.3</td>
<td>560</td>
</tr>
<tr>
<td>8</td>
<td>503</td>
<td>1.3</td>
<td>1640</td>
</tr>
<tr>
<td>9</td>
<td>423</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>10</td>
<td>523</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>11</td>
<td>473</td>
<td>0.5</td>
<td>1100</td>
</tr>
<tr>
<td>12</td>
<td>473</td>
<td>1.5</td>
<td>1100</td>
</tr>
<tr>
<td>13</td>
<td>473</td>
<td>1</td>
<td>200</td>
</tr>
<tr>
<td>14</td>
<td>473</td>
<td>1</td>
<td>2000</td>
</tr>
<tr>
<td>15</td>
<td>473</td>
<td>1</td>
<td>1100</td>
</tr>
</tbody>
</table>
### Table 2-6: High and low level for ethanol oxidation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low level</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>423</td>
<td>523</td>
</tr>
<tr>
<td>Oxygen / ETH molar feed ratio</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>WHSV (STP), cm³.min⁻¹.g⁻¹cat⁻¹</td>
<td>200</td>
<td>2000</td>
</tr>
</tbody>
</table>

### Table 2-7: Central composite design experiments for ethanol oxidation

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Temp, K</th>
<th>O₂/ETH</th>
<th>WHSV (STP), cm³.min⁻¹.g⁻¹cat⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>443</td>
<td>1.4</td>
<td>560</td>
</tr>
<tr>
<td>2</td>
<td>443</td>
<td>1.4</td>
<td>1640</td>
</tr>
<tr>
<td>3</td>
<td>443</td>
<td>2.6</td>
<td>560</td>
</tr>
<tr>
<td>4</td>
<td>443</td>
<td>2.6</td>
<td>1640</td>
</tr>
<tr>
<td>5</td>
<td>503</td>
<td>1.4</td>
<td>560</td>
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<tr>
<td>6</td>
<td>503</td>
<td>1.4</td>
<td>1640</td>
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<tr>
<td>7</td>
<td>503</td>
<td>2.6</td>
<td>560</td>
</tr>
<tr>
<td>8</td>
<td>503</td>
<td>2.6</td>
<td>1640</td>
</tr>
<tr>
<td>9</td>
<td>423</td>
<td>2</td>
<td>1100</td>
</tr>
<tr>
<td>10</td>
<td>523</td>
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<td>1100</td>
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<tr>
<td>11</td>
<td>473</td>
<td>1</td>
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<td>12</td>
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</tr>
<tr>
<td>15</td>
<td>473</td>
<td>2</td>
<td>1100</td>
</tr>
</tbody>
</table>

From the literature, the high WHSV and low O₂/ETH molar ratio in Table 2-6 and 2-7 were likely to result in low yields of desired carboxylic acid. Hence, low WHSV, high O₂/ETH molar ratio, and high-temperature conditions were also explored. The conditions for this alternate case are presented in Table 2-8.
As acetic acid (AA) is present in high amounts in aqueous bio-oil fraction, the influence of AA on oxidation of hydroxyacetone and ethanol was investigated. The experimental conditions for these reactions are presented in Table 2-9 and 2-10.

**Table 2-8: Experimental conditions for ethanol oxidation at high temperature, high oxygen and low WHSV conditions**

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Temp, K</th>
<th>O₂/ETH</th>
<th>WHSV (STP), cm³.min⁻¹. g_cat⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>473</td>
<td>5.5</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>523</td>
<td>5.5</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>573</td>
<td>5.5</td>
<td>150</td>
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<tr>
<td>4</td>
<td>523</td>
<td>10</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>523</td>
<td>1</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>523</td>
<td>5.5</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>523</td>
<td>5.5</td>
<td>250</td>
</tr>
</tbody>
</table>

**Table 2-9: Experimental conditions for catalytic partial oxidation of mixed HAC and acetic acid.**

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>HAC/(HAC+AA), wt%</th>
<th>Temp, K</th>
<th>O₂/HAC</th>
<th>WHSV (STP), cm³.min⁻¹. g_cat⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>523</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>523</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>523</td>
<td>1</td>
<td>1100</td>
</tr>
</tbody>
</table>

**Table 2-10: Experimental conditions for catalytic partial oxidation of mixed ETH and acetic acid.**

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>ETH/(ETH+AA), wt%</th>
<th>Temp, K</th>
<th>O₂/ETH</th>
<th>WHSV (STP), cm³.min⁻¹. g_cat⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>523</td>
<td>2</td>
<td>1100</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>523</td>
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<tr>
<td>3</td>
<td>75</td>
<td>523</td>
<td>2</td>
<td>1100</td>
</tr>
</tbody>
</table>
2.7 Carbon balance and standard deviation

In this study, the largest standard deviation of conversion from both systems obtained was approximately ± 7%. The sample calculation of standard error is presented in detail in Appendix E. The carbon mass closure for the HAC oxidation ranged from 1.3% to 6% while the carbon mass balance closure for the ETH oxidation ranged from 2.7% to 7.5%. The carbon mass balance formula can be found in Appendix C4. This discrepancy may have been due to mass loss during sample preparation and sample collection. In particular, gas may have been lost from the gas sample bags between sample collection and GC analysis.

2.8 Conversion, selectivity, and yield expression

In this study, conversion, selectivity, and yield are calculated as presented in equation 2.8.1-2.8.3

\[
Conversion \ of \ A \ (X_A) = 1 - \frac{\text{moles of A in product}}{\text{moles of A in feed}} \quad (2.8.1)
\]

\[
Selectivity \ (S_i) = \frac{\text{moles of desired product } i}{\text{moles of all products}} \quad (2.8.2)
\]

\[
Yield \ (Y_i) = S_i \times X_A \quad (2.8.3)
\]
Chapter 3: Catalytic Partial Oxidation of Hydroxyacetone

3.1 Catalyst Properties

The 5 wt% and 10 wt% V/TiO₂ catalysts were prepared and characterized according to the procedure outlined in Chapter 2. The surface properties of the catalyst obtained from BET analysis are tabulated in Table 3-1. From ICP-OES, the true vanadium content of the catalysts was determined 3.06 wt% and 8.81 wt%, respectively. Only anatase phase TiO₂ was identified by the XRD analysis of 3.06 wt% V/TiO₂ catalyst. However, in addition to anatase TiO₂, a small amount of crystalline V₂O₅ was identified in the 8.81 wt% V/TiO₂ catalyst. The oxidation state of V₂O₅ was confirmed from the binding energy obtained by XPS. For both catalysts, the binding energy of 516.5 eV was identified for V2p3/2, indicating the +5 oxidation state of vanadium. XRD and XPS spectra for both the catalysts can be found in Appendix A-2 & A-3. The acid sites on the catalyst were quantified using NH₃ TPD analysis, and the results are presented in Table 3-1. The internal effectiveness factor of the catalyst was estimated to be approximately 1 (Appendix C3) indicating no mass transfer limitations.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area, m²/g</th>
<th>Pore Volume, cm³/g</th>
<th>Pore diameter, Å</th>
<th>Acid sites Quantity (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.06 wt% V/TiO₂</td>
<td>189.94</td>
<td>0.49</td>
<td>102.74</td>
<td>540.99</td>
</tr>
<tr>
<td>8.81 wt% V/TiO₂</td>
<td>149.09</td>
<td>0.43</td>
<td>116.58</td>
<td>869.625</td>
</tr>
</tbody>
</table>

Table 3-1: BET properties of V/TiO₂ catalyst

3.2 Catalyst selection test

A blank test conducted with SiC and TiO₂ resulted in no conversion of hydroxyacetone (HAC). HAC oxidation was conducted at 473 K with a WHSV of 730 cm³·min⁻¹·g.cat⁻¹. HAC conversion over the 3.06 wt% V/TiO₂ and 8.81 wt% V/TiO₂ catalysts was 52% and 40%, respectively. However, both catalysts resulted in an average selectivity of 78% to lactic acid (LA). Selectivity towards acetic acid and formic acid in both cases was 9.9% and 11%, respectively. The 3.06 wt% V/TiO₂ catalyst produced a yield of 42% LA whereas the 10 wt% V/TiO₂ catalyst produced a yield of 31.2% LA. Hence for all the CCD experimental conditions, 3.06 wt% V/TiO₂ was used. Greater LA selectivity from the low V loading catalyst may be attributed to the number of acid sites in the catalyst. It has been widely reported that the yield of LA from liquid-phase HAC oxidation is favoured under alkaline/basic conditions²⁰,²¹. As seen in Table 3-2, 8.81 wt% V/TiO₂ has a greater concentration of acid sites than 3.06 wt% V/TiO₂ catalyst. In addition, from the XRD spectra presented in Appendix A-2, a small amount of crystalline V₂O₅ was detected in 8.81 wt% V/TiO₂ catalyst.
Moreover, a lower BET surface on 8.81wt% V/TiO$_2$ catalyst could also indicate agglomeration of vanadium oxide leading to formation of small quantity of crystal V$_2$O$_5$. All these factors combined could have attributed to lower performance of 8.81wt% V/TiO$_2$ catalyst. Faraldos et al.\textsuperscript{42} showed that methane turnover frequency is drastically reduced in presence of crystalline V$_2$O$_5$ catalyst. Machold et al.\textsuperscript{44} reported a lower acetic acid selectivity after methyl ethyl ketone oxidation with a >6wt% V/Ti catalyst compared to 4-6wt% V/Ti catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of HAC</th>
<th>Selectivity to LA</th>
<th>Yield of LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.06wt% V-TiO$_2$</td>
<td>52%</td>
<td>79%</td>
<td>42%</td>
</tr>
<tr>
<td>8.81wt% V-TiO$_2$</td>
<td>40%</td>
<td>77%</td>
<td>31.2%</td>
</tr>
</tbody>
</table>

### 3.3 Central Composite Design experiments

Experiments were conducted using a feed of 80wt% HAC and 20 wt% H$_2$O following the protocols described in section 2.2. The experiment was carried out in the presence of 3.06wt% V/TiO$_2$ catalyst with properties mentioned in section 3.1. The liquid products were analyzed by HPLC (section 2.3.1) and the gas products were analyzed by GC (section 2.3.2). Conversion, selectivity, and yield were calculated as described in section 2.8. The CCD experiments summarized in Table 2-9 were carried out in random order and the analysis of the results was carried out in Design Expert Version 13. The axial points provided information about the curvature and interactive effects between the independent factors.

#### 3.3.1 Effect of operating variables

The effect of 3 independent factors, as well as their interactive effects on the yield of lactic acid, are explained in this section. The significance of the three independent factors and the interaction term is presented in Table 3-3. All three independent factors had a p-value of <0.05. Only the interaction between temperature and WHSV was found to be significant. Discussion in sections 3.3.2 – 3.3.4 examines the results from experiments conducted by varying one parameter while others are maintained at the mid-level.

<p>| Table 3-3: Significance of factors in CCD model |</p>
<table>
<thead>
<tr>
<th>Source</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>&lt; 0.0001</td>
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</table>
3.3.2 Effect of temperature

The effect of temperature on yield of LA and conversion of HAC as shown in Fig 3-1 and 3-2 was observed when WHSV and oxygen to feed ratio was fixed at $1100 \text{ cm}^3\cdot\text{min}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ and 1, respectively. As seen from Fig 3-1, the conversion of HAC increased with increasing temperature. At 423 K, just above the boiling point of HAC, the conversion was 25.4% and conversion increased to 74.6% at 523K. This behavior reflects an increasing reaction rate with increasing temperature. Yan et al\textsuperscript{31} also reported a trend of increasing conversion with a rise in temperature when they investigated aqueous phase selective oxidation of HAC in presence of de-aluminated Sn-Beta supported gold catalyst from 373 to 413K. They were able to achieve a 100% conversion at 413K. At 423K, the selectivity towards LA was 62.5%. However, at 473K and 523K, selectivity reached 80% (Fig 3-2). As a result of increasing conversion and selectivity, the LA yield increased from 15.9% at 423K to a maximum value of 60.5% at 523 K (Fig 3-3).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
<tr>
<td>A-Temperature</td>
<td>$&lt; 0.0001$</td>
</tr>
<tr>
<td>B-Feed ratio</td>
<td>$&lt; 0.0001$</td>
</tr>
<tr>
<td>C-WHSV</td>
<td>0.0003</td>
</tr>
<tr>
<td>AC (Temperature * WHSV)</td>
<td>0.0453</td>
</tr>
</tbody>
</table>

![Fig 3-1: Effect of temperature on conversion of HAC](image)

(3.06wt% V/TiO$_2$, 1100 cm$^3\cdot$min$^{-1}\cdot$g$_{\text{cat}}^{-1}$, O$_2$/HAC = 1, 80wt% HAC)
Fig 3-2: Effect of temperature on selectivity of oxidation products from CPO of HAC
(3.06wt% V/TiO₂, 1100 cm³·min⁻¹·g⁻¹cat, O₂/HAC =1, 80wt% HAC)

Fig 3-3: Effect of temperature on yield of oxidation products from CPO of HAC
(3.06wt% V/TiO₂, 1100 cm³·min⁻¹·g⁻¹cat, O₂/HAC =1, 80wt% HAC)
Variation in temperature was the most influential factor among the three independent factors as shown in Table 3-3.

Fig 3-4 and Fig 3-5 present conversion and the LA yield at the factorial points of the CCD, respectively. In cases when excess oxygen was provided and the WHSV was low, the effect of temperature was not significant. At an O$_2$/HAC ratio of 1.3, and WHSV 560 cm$^3$·min$^{-1}$·g$_{cat}$$^{-1}$, HAC conversion was 92.6% at 503K and 91% at 443K. The selectivity towards LA was also constant at 78% and thus the yield to LA was 72.7% at 503K and 70.5% at 443K.

In cases when oxygen was limited (O$_2$/HAC=0.7) and WHSV was 560 cm$^3$·min$^{-1}$·g$_{cat}$$^{-1}$, the temperature had a significant effect on conversion and yield. From Fig 3-4, HAC conversion of 31% was observed at 443K (green bar); this increased to 69.5% when the temperature was increased to 503K (yellow bar). The LA yield increased from 22% at 443K to 56% at 503K as shown in Fig 3-5.

Fig 3-4 and 3-5 depict that in experiments where WHSV was kept constant at 1640 cm$^3$·min$^{-1}$·g$_{cat}$$^{-1}$, the temperature had a profound impact on the conversion of HAC as well as yield of LA.
3.3.3 Effect of Oxygen to HAC feed ratio

Fig 3-6 to 3-8 show the effect of oxygen to HAC ratio when WHSV and temperature were kept constant at 1100 cm$^3$.min$^{-1}$.g$_{cat}^{-1}$ and 473K, respectively. The increase in the ratio of oxygen to HAC was accompanied by a corresponding increase in conversion of HAC and yield of LA. 37% conversion was achieved when the O$_2$/HAC was 0.5 and reached a maximum of 92.8% when the ratio was increased to 1.5. Selectivity of LA remained in the range of 73-79% (Fig 3.7). The yield of LA followed the same trend as conversion, increasing from 27% to 67.9% as the O$_2$/HAC ratio was increased from 0.5 to 1.5. However, an increase in the formation of acetic acid in the excess oxygen environment was observed, as the selectivity of acetic acid increased from 10% (O$_2$/HAC=0.5) to 19% (O$_2$/HAC=1.5) as shown in Fig 3-7. These results suggest that oxygen-rich feed is essential for high conversion of HAC, and yield of LA. Similar findings were reported by Yan et al’s investigation of aqueous phase oxidation of HAC$^{31}$. Without oxygen, they reported only 10.9% conversion with a 1.4% LA yield at 393K. They were able to achieve maximum conversion of 68.4% using a pressure of 0.1MPa O$_2$. 

Fig 3-5: Yield of LA at factorial points in CCD
Fig 3-6: Effect of O\textsubscript{2}/HAC ratio on conversion of HAC
(3.06wt\% V/TiO\textsubscript{2}, 473K, 1100 cm\textsuperscript{3} min\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}, 80wt\% HAC)

Fig 3-7: Effect of O\textsubscript{2}/HAC ratio on selectivity of oxidation products from CPO of HAC
(3.06wt\% V/TiO\textsubscript{2}, 473K, 1100 cm\textsuperscript{3} min\textsuperscript{-1} g\textsubscript{cat} \textsuperscript{-1}, 80wt\% HAC)
In all the factorial points in the experimental design, oxygen/HAC feed ratio was seen to have significant effect on conversion and yield as shown in Fig 3-4 and 3-5.

Fig 3-8: Effect of O$_2$/HAC ratio on yield of oxidation products from CPO of HAC

(3.06wt% V/TiO$_2$, 473K, 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, 80wt% HAC)
3.3.4 Effect of WHSV

The effect of WHSV on conversion of HAC and the yield of LA presented in Fig 3-9 and 3-11 was investigated at 473K with an O₂/HAC ratio of 1. When the WHSV was increased from 200 to 2000 cm³·min⁻¹·g_cat⁻¹, the conversion of HAC decreased from 77% to 44.4% respectively. At high WHSV, the residence time of the reactant in the catalyst bed was limited. This could have resulted in the lower conversion obtained at higher WHSV. Selectivity of LA remained in the range of 76-80% in all three cases as shown in Fig 3-10. Selectivity of acetic acid and formic acid were also unaffected by WHSV. Consequently, as shown in Fig 3-11, the yield of LA also decreased from 62% to 33.9% when the WHSV was increased to 2000 cm³·min⁻¹·g_cat⁻¹. Acetic yield decreased from 9.2% to 5.2% in the studied range of 200-2000 cm³·min⁻¹·g_cat⁻¹.

![Fig 3-9: Effect of WHSV on conversion of HAC](3.06wt% V/TiO₂, 473K, O₂/HAC = 1, 80wt% HAC)
Fig 3-10: Effect of WHSV on selectivity of oxidation products from CPO of HAC
(3.06wt% V/TiO$_2$, 473K, O$_2$/HAC =1, 80wt% HAC)

Fig 3-11: Effect of WHSV on yield of oxidation products from CPO of HAC
(3.06wt% V/TiO$_2$, 473K, O$_2$/HAC =1, 80wt% HAC)
The influence of WHSV was lower compared to $O_2$/HAC and temperature variation as shown in Table 3-3. At higher temperatures of 503K and 1.3 $O_2$/HAC ratio, varying WHSV was found to have no significant effect on the conversion of HAC or yield of LA as indicated by the red bars in Fig 3-4 and 3-5. The conversion of HAC in these conditions was 92% and the yield of LA was 73%.

From Fig 3-4 and 3-5, at all other factorial experimental conditions, space velocity was found to significantly impact the conversion of HAC and yield of LA. Low conversion of 23% was obtained at 443K, 0.7 $O_2$/HAC ratio, and at a space velocity of 1640 cm$^3$·min$^{-1}$·g$^{-1}$. cat.
3.3.5 Statistical Analysis Results

The response surface analysis for selective oxidation of HAC was carried out in Design Expert Version 13 software. Of the 3 factors, temperature and O₂/HAC feed ratio had a more significant effect on the yield of LA than WHSV as shown in Table 3-3. The effect of each variable on the yield of LA is shown in Fig 3-12. Conclusively, the yield of LA increases with an increase in temperature and O₂/HAC feed ratio and decreases with an increase in WHSV.

![Perturbation graph](image)

**Fig 3-12**: Effect of independent factors on yield of LA obtained from Design Expert 13. In the figure: A- temperature, B- O₂/HAC, and C-WHSV

The model equation predicts LA yield ($Y_{LA}$) from temperature (T), O₂/HAC feed ratio (FR), WHSV, and the interaction effect of temperature and WHSV. The $R^2$ of the model is 0.95. The predicted values are presented in Table 3-4.

$$Y_{LA} = -7.14 + 0.058 \times T(K) + 43.29 \times (FR) - 0.1938 \times WHSV \ (cm^3 \cdot min^{-1} \cdot g_{cat}^{-1})$$
Only one interactive effect, between WHSV and temperature was found to be statistically significant. The surface plot shown in Fig 3-13 represents the interactive effect between WHSV and temperature at a constant O₂/HAC feed ratio of 1. Temperature had a greater influence on maximizing the yield than WHSV. At lower temperatures, increase in WHSV resulted in a decrease in yield, reaching a minimum at highest WHSV. As the temperature increased, effect of WHSV diminishes. At high temperatures (>503 K), WHSV was seen to have no significant effect on yield of LA. A steeper increase in yield of LA with increase in temperature was seen at high WHSV. Comparatively, at low WHSV, temperature’s influence on yield of LA was not high. However, the interactive effect had less significance than the individual effects of the two factors on the response.

Table 3-4: Actual and predicted value of yield of LA from CCD experiments and model respectively

<table>
<thead>
<tr>
<th>Run Order</th>
<th>Actual yield of LA</th>
<th>Predicted yield of LA</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>17.56</td>
<td>19.29</td>
</tr>
<tr>
<td>2</td>
<td>63.06</td>
<td>69.05</td>
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<tr>
<td>3</td>
<td>29.60</td>
<td>30.32</td>
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<td>44.17</td>
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<tr>
<td>5</td>
<td>63.58</td>
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<td>6</td>
<td>27.55</td>
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<td>64.02</td>
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<tr>
<td>14</td>
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<td>50.60</td>
</tr>
<tr>
<td>15</td>
<td>39.31</td>
<td>43.25</td>
</tr>
</tbody>
</table>
3.4 Rate constant and activation energy estimation

Various studies in the literature have proposed different reaction mechanisms for partial oxidation of HAC to lactic acid\textsuperscript{21,31}. The intermediates identified in those reports include lactaldehyde and pyruvaldehyde. However, in the current study of gas-phase oxidation of HAC in V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst, these intermediates were not detected in the liquid products analyzed by HPLC. Moreover, in the current study acetic acid was also identified. Acetic acid can be formed from lactic acid through two parallel pathways\textsuperscript{45}: (a) oxidative dehydrogenation of LA to pyruvic acid (PA) followed by decarboxylation of PA to acetic acid and (b) decarbonylation of LA to acetaldehyde and further oxidation of acetaldehyde to acetic acid. Acetic acid has been reported as one of the oxidation products from the reaction of HAC with OH radicals or Cl atoms\textsuperscript{27,30}.

As HAC is a multifunctional compound with a hydroxy and ketone group, a multitude of reactions may have resulted in the production of these carboxylic acids. However, using the current experimental design, it is not viable to determine the true intrinsic kinetics and reaction steps on the catalyst surface.
As seen from section 3.3.3, concentration of oxygen in the feed influenced conversion of HAC greatly. Yan et al\textsuperscript{31}, also reported that oxygen rich atmosphere was essential for efficient conversion of HAC to LA. In this section, the overall rate constant and the activation energy was estimated assuming first order dependence on both HAC and O\textsubscript{2} concentration. The overall reaction rate used to estimate $k_A$ is given by equation (3-1)

$$-r_A = k_A C_A C_B$$

(3-1)

Where $C_A$ is the concentration of HAC (mol.cm\textsuperscript{-3}), and $C_B$ is the concentration of oxygen (mol.cm\textsuperscript{-3}). The activation energy ($E_a$) was estimated using the Arrhenius equation and plotting ln($k_A$) vs (1/T).

$$\ln(K_A) = - \frac{E_a}{RT} + \ln(A)$$

(3-2)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3-14.png}
\caption{Arrhenius plot of ln($k_A$) vs (1/T) to estimate activation energy and pre-exponential factor \newline (3.06wt\% V/TiO\textsubscript{2}, 1100 cm\textsuperscript{3}·min\textsuperscript{-1}·g\textsubscript{cat}\textsuperscript{-1}, O\textsubscript{2}/HAC =1, 80wt\% HAC)}
\end{figure}
Fig 3-14 presents the plot of ln(kₐ) vs (1/T). The regression line shows a good fit with R² = 0.99. The activation energy and the pre-exponential factor (A) were determined from the slope and intercept of the fitted line. The parameters are provided in Table 3-5. The detailed rate constant equation derivation can be found in Appendix D-1. No comparable studies reporting activation energy for oxidation of HAC are available in the literature.

Table 3-5: Estimated Eₐ and ln(A) with R² value for oxidation of HAC on 3.06wt% V/TiO₂ catalyst

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eₐ, kJmol⁻¹</td>
<td>31.35</td>
</tr>
<tr>
<td>ln(A), cm⁶mol⁻¹min⁻¹g_cat⁻¹</td>
<td>27.39</td>
</tr>
<tr>
<td>R²</td>
<td>0.99</td>
</tr>
</tbody>
</table>

3.5 Summary

Vapour phase partial oxidation of hydroxyacetone was conducted in presence of vanadia-titania catalyst in a packed bed reactor. The 3.06wt% vanadium loading catalyst produced a higher yield of lactic acid relative to the 8.81% V catalyst. The lower quantity of acid sites, higher surface area and absence of crystalline V₂O₅ on the 3.06wt% V catalyst may have contributed to its superior performance. From the CCD experimental design results, all three independent factors temperature, O₂/HAC feed ratio, and WHSV influenced the conversion of HAC and yield of LA. Only the interaction between temperature and WHSV was found to be significant but had a lower impact than the individual factors. A maximum selectivity of 82% LA was obtained at 523K, O₂/HAC = 1, 1100 cm³.min⁻¹.g_cat⁻¹. A maximum yield of 73% LA was obtained at 503K, O₂/HAC = 1.3, 560 cm³.min⁻¹. g_cat⁻¹. A second-order overall reaction rate was fit to the experimental data and the activation energy for selective oxidation of HAC on 3.06wt% V/TiO₂ was estimated to be 31 kJ/mol.
Chapter 4: Catalytic Partial Oxidation of Ethanol

Ethanol (ETH) partial oxidation to carboxylic acid was carried out using 25 wt% feed of ETH in 75 wt% deionized water (DI). The experiment was carried out in the presence of 3.06 wt% V/TiO₂ catalyst with properties mentioned in section 3.1. The experiment was conducted according to the procedure presented in section 2.2. The liquid products were analyzed as mentioned in section 2.3.1 and the gas products were analyzed as described in section 2.3.2. The conversion, selectivity and yield of the desired components and unreacted reactants were calculated as described in section 2.8.

4.1 Central composite design experiments

The two-level factors for ETH partial oxidation in presence of V/TiO₂ are presented in Table 2-6. The CCD experiments reported in Table 2-7 were carried out in random order and the analysis of the results were carried out in Design Expert Version 13.

From the CCD experiment results, it was seen that conversion of ETH and yield of acetic acid was low. In order to identify conditions at which a higher yield of acetic acid can be produced, a second array for catalytic partial ethanol oxidation was conducted at low WHSV, high temperature and high oxygen to ethanol ratio; these conditions are presented in Table 2-8. The results from these experiments are presented in section 4.2.

4.1.1 Effect of operating variables

The effect of the independent factors (temperature, WHSV and O₂/ETH molar ratio), as well as their interactive effects on the yield of acetic acid, are explained in this section. Only two out of the three independent factors were found to have a p-value <0.05. The significance of the temperature and WHSV is presented in Table 4-1. Discussion in sections 4.1.2 – 4.1.4 examines results from experiments conducted by varying one parameter while others are maintained at the mid-level.

<table>
<thead>
<tr>
<th>Source</th>
<th>p-value</th>
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</thead>
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<td>Model</td>
<td>&lt; 0.0001</td>
</tr>
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<td>A-Temperature</td>
<td>0.0002</td>
</tr>
<tr>
<td>C-WHSV</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

Table 4-1: Significance of factors in CCD model – Ethanol oxidation
4.1.2 Effect of temperature

The influence of temperature on conversion of ethanol (ETH) and selectivity of acetic acid (AA) are shown in Fig 4-1 and Fig 4-2. Yield of acetic acid is presented in Fig 4-3. These results were observed when the O₂/ETH feed ratio and WHSV were maintained at 2 and 1100 cm³·min⁻¹·g_cat⁻¹, respectively. Under these conditions, conversion of ETH increased with increasing temperature to reach a maximum of 60% at 523K. Conversion was a mere 2% at 423K. This observation is likely due to the increase in reaction rate with increasing temperature. Due to the low conversion at 423K, no liquid products were detected by HPLC. The selectivity of acetic acid decreased with increasing temperature, as it dropped from 88% at 473K to 45% at 523K. This was accompanied by an increase in the selectivity of acetaldehyde. Increased acetaldehyde production may be the result of a series reaction of ETH to acetic acid via acetaldehyde as shown in Fig 1-7. From section 4.1.3, O₂/ETH ratio did not significantly affect the conversion of ETH. This could indicate the reaction proceeding via Mars Van Krevelen mechanism utilizing lattice oxygen on the catalyst surface as presented in Fig 1.6. However, at higher temperature of 523K, there could be differences in the rate of uptake of lattice oxygen from the catalyst and rate of replenishment of those sites by gaseous O₂ from the feed. This could have led to reduction in the oxidation state of vanadium in the catalyst and may have led to lower selectivity to acetic acid. High temperature might have also promoted complete oxidation of ethanol to CO₂. At the factorial points in the experimental design, temperature significantly affected the conversion of ETH and yield of AA. From Table 4-1, variation in temperature had significant impact on yield of acetic acid obtained. At 560 cm³·min⁻¹·g_cat⁻¹ WHSV and 2.6 O₂/ETH ratio, conversion of ETH increased from 17.3% at 443K to 58.9% at 503K. The same trend was observed at 560 cm³·min⁻¹·g_cat⁻¹ and 1.4 O₂/ETH ratio as shown in Fig 4-4. Conversion and yield at other factorial points are presented in Fig 4-4 and 4-5.
Fig 4-1: Effect of Temperature on conversion of ETH
(3.06wt% V/TiO₂, 1100 cm³·min⁻¹·g_cat⁻¹, O₂/ETH =2, 25wt% ETH)

Fig 4-2: Effect of Temperature on selectivity of oxidation products from CPO of ETH
(3.06wt% V/TiO₂, 1100 cm³·min⁻¹·g_cat⁻¹, O₂/ETH =2, 25wt% ETH)
Fig 4-3: Effect of Temperature on Yield of oxidation products from CPO of ETH

(3.06wt% V/TiO₂, 1100 cm³·min⁻¹·gₘₚ⁻¹, O₂/ETH = 2, 25wt% ETH)

Fig 4-4: Conversion of ETH at factorial points in CCD- CPO of ethanol
4.1.3 Effect of Oxygen to Ethanol ratio

Fig 4-6 presents the effect of oxygen to ethanol feed ratio on conversion of ethanol at 473K and 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$. The conversion of ethanol increased with increasing concentration of oxygen in the feed stream. At O$_2$/ETH ratio =1, the conversion of ETH was 10.7%. When the oxygen to ethanol ratio was 3, the conversion increased to 18.6%. As the oxygen ratio is increased, there is slight reduction in the selectivity to acetic acid (Fig 4-7) from 90% to 83% in the range studied. However, acetaldehyde selectivity increased from 2.57% at O$_2$/ETH ratio = 2 to 6.5% at O$_2$/ETH ratio=3. Yield of acetic acid increases from 9.6% to 15.6% in the range studied. In all three cases, CO$_2$ yield was low, around 2%. This could indicate the reaction proceeding via Mars Van Krevelen mechanism. In Mars Van Krevelen mechanism, the lattice oxygen on the catalyst surface is involved in the reaction, with gaseous O$_2$ in the feed replenishing the depleted oxygen on the catalyst surface.

Fig 4-5: Yield of acetic acid at factorial points in CCD – CPO of ethanol
As seen from Fig 4-4, conversion of ETH at 503K was not significantly influenced by amount of O\textsubscript{2} in the feed stream. As a result, in the CCD model, variation in O\textsubscript{2}/ETH ratio was not seen to be significant. The red and yellow bars in Fig 4-5 represent reduction in the yield of acetic acid at 503K as O\textsubscript{2} levels increased. This was accompanied by an increase in the yield of CO\textsubscript{2} and acetaldehyde at 560 and 1640 cm\textsuperscript{3}· min\textsuperscript{-1}· g\textsubscript{cat}\textsuperscript{-1} WHSV, respectively. However, conversion of ETH doubled at 443K and 560 cm\textsuperscript{3}· min\textsuperscript{-1}· g\textsubscript{cat}\textsuperscript{-1} when O\textsubscript{2}/ETH ratio increased from 1.4 to 2.6 (orange and green bars, Fig 4-4).

**Fig 4-6: Effect of O\textsubscript{2}/ETH ratio on conversion of ETH**

(3.06wt% V/TiO\textsubscript{2}, 1100 cm\textsuperscript{3}· min\textsuperscript{-1}· g\textsubscript{cat}\textsuperscript{-1}, 473K, 25wt% ETH)
Fig 4-7: Effect of O$_2$/ETH ratio on selectivity of oxidation products from CPO of ETH

(3.06wt% V/TiO$_2$, 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, 473K, 25wt% ETH)

Fig 4-8: Effect of O$_2$/ETH ratio on yield of oxidation products from CPO of ETH

(3.06wt% V/TiO$_2$, 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, 473K, 25wt% ETH)
4.1.4 Effect of WHSV

The effect of WHSV on ethanol conversion and acetic acid selectivity are presented in Fig 4-9 and 4-10 at 473K and an oxygen/ETH ratio of 2. The effect of WHSV was investigated for the range of 200-2000 cm³·min⁻¹·g_cat⁻¹. Increasing WHSV resulted in low conversion of ethanol. At 200 cm³·min⁻¹·g_cat⁻¹, conversion reached a maximum of 75.7% with acetic acid selectivity of 42%. At 1100 cm³·min⁻¹·g_cat⁻¹, 16% conversion of ethanol corresponded to acetic acid selectivity of 88%. Low acetic acid selectivity at 200 cm³·min⁻¹·g_cat⁻¹ was accompanied by elevated acetaldehyde and CO₂ selectivity. As conversion in 2000 cm³·min⁻¹·g_cat⁻¹ was low, no liquid products were detected by HPLC. Increase in residence time due to reduced WHSV may have resulted in higher conversion of ethanol at 200 cm³·min⁻¹·g_cat⁻¹. At lower space velocity of 200 cm³·min⁻¹·g_cat⁻¹, the decrease in selectivity to acetic acid may have been attributed to the decrease in the availability of lattice oxygen in the catalyst surface as explained in section 4.1.2, where a similar trend was observed at elevated temperatures.

At 503K, reduction in space velocity had a significant impact on conversion at both O₂/ETH ratio as seen from the red and yellow bars in Fig 4-4. The orange and green bars in Fig 4-4 and 4-5 show changing space velocity had a negligible impact on conversion and acetic acid yield at 443K.

![Fig 4-9: Effect of WHSV on conversion of ETH](image)

(3.06wt% V/TiO₂, 473K, O₂/ETH ratio=2, 25wt% ETH)
Fig 4-10: Effect of WHSV on selectivity of oxidation products from CPO of ETH
(3.06wt% V/TiO₂, 473K, O₂/ETH ratio=2, 25wt% ETH)

Fig 4-11: Effect of WHSV on yield of oxidation products from CPO of ETH
(3.06wt% V/TiO₂, 473K, O₂/ETH ratio=2, 25wt% ETH)
4.1.5 Statistical Analysis

The response surface analysis for selective oxidation of ETH was carried out in Design Expert 13. Of the 3 factors, only temperature and WHSV had significant effect on yield of acetic acid as shown in Table 4-1. In section 4.1.2-4.1.4, it was shown that acetic acid yield increases with increase in temperature and decreases with increase in WHSV. The R^2 of the model is 0.81. Actual and predicted values are presented in Table 4-2. Equation 4-1 presents the prediction of acetic acid yield ($Y_{AA}$) as a function of temperature (K) and WHSV (cm$^3$·min$^{-1}$·g$_{cat}^{-1}$):

$$Y_{AA} = -81.976 + 0.231 \times T(K) - 0.011 \times \text{WHSV (cm}^3\text{· min}^{-1}\text{· g}_{cat}^{-1})$$

(4-1)

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Table 4-2: Actual and predicted value of yield of AA from CCD experiments and model respectively
4.2 Oxidation of Ethanol at Low WHSV, High O₂/ETH and High Temperature

The experimental conditions investigated in this section are tabulated in Table 2-8.

4.2.1 Effect of Temperature

The influence of temperature on ethanol oxidation was investigated at a WHSV of 150 cm³·min⁻¹·g₉cat⁻¹ and at an O₂/ETH ratio of 5.5. From Fig 4-12, as the temperature increased from 473K to 573K, conversion was seen to increase from 84% to 100%. Selectivity of acetic acid decreased as temperature increased reaching a minimum of 19% at 573K. Acetaldehyde selectivity of 31% was observed at 473K; at temperatures greater than 473K, acetaldehyde was not detected in the product. However, an increase in selectivity for undesirable oxidation products such as CO₂ and CO were observed at 573K. At higher temperatures, complete oxidation of ethanol likely resulted in an increase in CO₂ and CO yields. Maximum selectivity and yield of acetic acid was observed at 423K and 473K, respectively as shown in Fig 4-13 & 4-14.

Fig 4-12: Effect of temperature on conversion of ETH
(3.06wt% V/TiO₂, 150 cm³·min⁻¹·g₉cat⁻¹, O₂/ETH ratio=5.5, 25wt% ETH)
Fig 4-13: Effect of Temperature on selectivity of oxidation products from CPO of ETH
(3.06wt% V/TiO$_2$, 150 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, O$_2$/ETH ratio=5.5, 25wt% ETH)

Fig 4-14: Effect of Temperature on yield of oxidation products from CPO of ETH
(3.06wt% V/TiO$_2$, 150 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, O$_2$/ETH ratio=5.5, 25wt% ETH)
4.2.2 Effect of Oxygen/Ethanol ratio

O₂/ETH feed ratio is investigated in the range of 1 to 10 at 523 K and a WHSV of 150 cm³·min⁻¹·g_cat⁻¹. A conversion of 100% is obtained in all three cases as presented in Fig 4-15. When O₂/ETH ratio was increased, the selectivity of acetic acid was seen to increase as shown in Fig 4-16. At O₂/ETH ratio = 1, selectivity of acetic acid was 53%. At O₂/ETH = 10, the selectivity of acetic acid was 67%. As O₂/ETH was increased CO selectivity increased from 11% to 17%. However, the selectivity of acetaldehyde decreased as O₂/ETH ratio was increased. This may have resulted from further oxidation of acetaldehyde to acetic acid. Acetic acid yield increased from 53% to 67% in the studied range as shown in Fig 4-16.

![Fig 4-15: Effect of O₂/ETH ratio on conversion of ETH](image)

(3.06wt% V/TiO₂, 150 cm³·min⁻¹·g_cat⁻¹, 523K, 25wt% ETH)
Fig 4-16: Effect of O$_2$/ETH ratio on selectivity of oxidation products from CPO of ETH
(3.06wt% V/TiO$_2$, 150 cm$^3\cdot$min$^{-1}\cdot$g$_{cat}^{-1}$, 523K, 25wt% ETH)

Fig 4-17: Effect of O$_2$/ETH ratio on yield of oxidation products from CPO of ETH
(3.06wt% V/TiO$_2$, 150 cm$^3\cdot$min$^{-1}\cdot$g$_{cat}^{-1}$, 523K, 25wt% ETH)
4.2.3 Effect of WHSV

Fig 4-18 and 4-19 summarize ethanol conversion and product selectivity obtained at WHSV 50-250 cm$^3 \cdot$min$^{-1} \cdot$g$_{cat}^{-1}$, while temperature and O$_2$/ETH ratio were kept constant at 523K and 5.5 respectively. Complete ethanol conversion was achieved in all these cases. The selectivity of acetic acid is 73% at 250 cm$^3 \cdot$min$^{-1} \cdot$g$_{cat}^{-1}$ and drops to 39% at 50 cm$^3 \cdot$min$^{-1} \cdot$g$_{cat}^{-1}$. The yield of acetic acid also followed the same trend, producing a maximum yield of 73% at 250 cm$^3 \cdot$min$^{-1} \cdot$g$_{cat}^{-1}$(Fig 4-20). However, the yield of CO$_2$ and CO decreased as WHSV increased. At 50 cm$^3 \cdot$min$^{-1} \cdot$g$_{cat}^{-1}$, yield of CO$_2$ and CO was 28% and 31% respectively and decreased to 16% and 8.3% at 250 cm$^3 \cdot$min$^{-1} \cdot$g$_{cat}^{-1}$. As higher space velocities result in reduced residence time, complete oxidation of ethanol is likely limited. However, at low WHSV, ethanol may have undergone further oxidation to CO$_2$ and CO.

Fig 4-18: Effect of WHSV on conversion of ETH
(3.06wt% V/TiO$_2$, 523K, O$_2$/ETH ratio=5.5, 25wt% ETH)
Fig 4-19: Effect of WHSV on selectivity of oxidation products from CPO of ETH
(3.06wt% V/TiO₂, 523K, O₂/ETH ratio=5.5, 25wt% ETH)

Fig 4-20: Effect of WHSV on yield of oxidation products from CPO of ETH
(3.06wt% V/TiO₂, 523K, O₂/ETH ratio=5.5, 25wt% ETH)
4.3 Rate Constant and Activation Energy Estimation

At the higher WHSV conditions (200-2000 cm$^3$·min$^{-1}$·g$^{-1}$) presented in section 4.1.3, concentration of oxygen in the feed had little impact on ethanol conversion. In the CCD model, O$_2$/ETH ratio had no significant effect on acetic acid yield. Even at high O$_2$/ETH ratio (1-10, section 4.2.3), concentration of oxygen in the feed influenced only the yield of oxidation products and had no effect on ethanol conversion. Li et al$^{37}$ used the Mars Van Krevelen mechanism involving lattice oxygen to describe oxidation of ethanol on Mo-V-Nb oxide catalyst. The same reaction mechanism was adopted by Gomez et al. to describe ethanol oxidation on VMgO catalyst$^{34}$. However, using the current experimental design, it is not viable to determine the true intrinsic kinetics and reaction steps on the catalyst surface.

In this section, the overall rate constant and the activation energy was estimated assuming a first order dependence on ethanol concentration ($C_A$, mol.cm$^{-3}$). Gas phase oxygen concentration was omitted from this model as reaction rate likely depends on the lattice oxygen of the catalyst. The overall reaction rate used to estimate $k_A$ is given by equation (4-2):

$$-r_A = k_A C_A$$

The activation energy ($E_a$) was estimated using the Arrhenius equation (3-2) by plotting ln($k_A$) vs (1/T). Fig 4-21 presents the plot of ln($k_A$) vs (1/T). The regression line fitted through these points shows a good fit with $R^2 = 0.99$. The activation energy and the pre-exponential factor (A) were determined from the slope and intercept of the fitted line. The estimated activation energy and ln(A) values are provided in Table 4-4. The detailed rate constant equation derivation can be found in Appendix D-2. Similar values for activation energy have been reported by Yun et al$^{46}$ using VO$_x$/TiO$_2$ catalyst with V loading from 1.5wt% to 6.02wt% for partial oxidation of ETH. The estimated Ea at 200°C and 5KPa O$_2$ were 75.5 ± 7.2 kJmol$^{-1}$.

<table>
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<td>$E_a$, kJmol$^{-1}$</td>
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<td>ln(A), cm$^3$·min$^{-1}$·g$^{-1}$</td>
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<tr>
<td>$R^2$</td>
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Table 4-4: Estimated $E_a$ and ln(A) with $R^2$ value for oxidation of ETH on 3.06wt% V/TiO$_2$ catalyst
4.4 Summary

Two scenarios for ethanol oxidation in presence of vanadia-titania catalyst in a packed reactor. From the CCD experimental design results, only temperature and WHSV influenced the yield of acetic acid. Complete conversion of ETH was achieved at higher temperatures (>523K) and low WHSV conditions (<250 cm$^3 \cdot$min$^{-1} \cdot $g$_{cat}^{-1}$). A maximum selectivity of 89% AA was obtained at 473K, O$_2$/ETH = 1, 1100 cm$^3 \cdot$min$^{-1} \cdot $g$_{cat}^{-1}$. A maximum yield of 73% AA was obtained at 523K, O$_2$/ETH = 5.5, 250 cm$^3 \cdot$min$^{-1} \cdot $g$_{cat}^{-1}$. A first order overall reaction was fit to the experimental data and the activation energy for selective oxidation of ETH on 3.06wt% V/TiO$_2$ was estimated to be 76.03 kJ/mol.
Chapter 5: Catalytic partial oxidation of mixed feeds

Since acetic acid is found in large quantities in the aqueous phase of bio-oil, catalytic partial oxidation of HAC and ETH in presence of acetic acid was also investigated to understand effects of AA in feed on reaction pathway as well as catalytic activity. For this study, the weight fraction of HAC with respect to HAC and acetic acid weight (HAC/(HAC+AA)) was varied from 25wt% to 75wt%. Similarly, weight fraction of ETH with respect to ETH and acetic acid weight (ETH/(ETH+AA)) was varied from 25wt% to 75wt%. These reactions were carried out at the conditions tabulated in Table 2-9 and 2-10. From the study conducted by Zhu et al, it was concluded that due to the refractory nature of acetic acid, CPO of acetic acid in presence of 6.9wt% V/TiO$_2$ catalyst was limited. Conversion of acetic acid at 200°C with O$_2$/AA ratio = 6 was reported to be only 4.5%. From these results, it was assumed that acetic acid did not react when evaluating the selectivity and yield of products obtained when acetic acid was added to the feed.

5.1 CPO of HAC and acetic acid mixed feed

Conversion of HAC obtained from the HAC and acetic acid mixed feed is presented in Fig 5-1. The results correspond to reactions carried out at 523K, and O$_2$/HAC molar ratio = 1 and at a WHSV of 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$. The HAC conversion in all three cases was approximately 66% (Fig 5-1). The selectivity and yield of oxidation products are presented in Fig 5-2 and Fig 5-3 respectively. The selectivity to lactic acid (LA) was 77%. The yield of LA obtained was 51%. At the same conditions, 80 wt% aqueous HAC solution resulted in 74.6±3.29% conversion of HAC and the lactic acid selectivity and yield were 81% and 60%, respectively. The selectivity of acetic acid and formic acid was 12.9% and 10%, respectively and were independent of HAC/(HAC+AA) ratio (Fig 5-2). As the selectivity to LA in presence of AA, remains unchanged compared to the 80wt% aqueous HAC case, it can be concluded that the oxidation pathways of HAC are not affected by the presence of AA in the feed.
Fig 5-1: Effect of varying HAC/(HAC+AA) wt% on conversion of HAC
(3.06wt% V/TiO$_2$, 523K, O$_2$/HAC = 1, WHSV = 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, 80wt% HAC)

Fig 5-2: Effect of varying HAC/(HAC+AA) wt% on selectivity of oxidation products
(3.06wt% V/TiO$_2$, 523K, O$_2$/HAC = 1, WHSV = 1100 cm$^3$·min$^{-1}$·g$_{cat}^{-1}$, 80wt% HAC)
Conversion of ETH obtained from the ETH and acetic acid mixed feed is presented in Fig 5-4. The results correspond to reactions carried out at 523K, and O<sub>2</sub>/ETH molar ratio = 2 and at a WHSV of 1100 cm<sup>3</sup>·min<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup>. Ethanol conversion in all three cases was approximately 50%. The selectivity and yield of oxidation products are presented in Fig 5-5 and Fig 5-6 respectively. The selectivity to acetic acid was 43%. The yield of acetic acid obtained was 21.2%. At the same conditions, 25wt% aqueous ETH solution resulted in 60±5.5% conversion of ETH. In the same conditions, selectivity and yield of acetic acid were 45% and 26.8% respectively. The selectivity of acetaldehyde and CO<sub>2</sub> and CO were also similar across all three varying feed concentrations. The selectivity of acetaldehyde was 21.7% as shown in Fig 5-5. However, the selectivity and yield of oxidation products were found to be similar to the 25wt% aqueous ETH solution. Hence, it can be concluded that the oxidation pathways of ETH are not affected by AA.

**5.2 CPO of ETH and acetic acid mixed feed**

Conversion of ETH obtained from the ETH and acetic acid mixed feed is presented in Fig 5-4. The results correspond to reactions carried out at 523K, and O<sub>2</sub>/ETH molar ratio = 2 and at a WHSV of 1100 cm<sup>3</sup>·min<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup>. Ethanol conversion in all three cases was approximately 50%. The selectivity and yield of oxidation products are presented in Fig 5-5 and Fig 5-6 respectively. The selectivity to acetic acid was 43%. The yield of acetic acid obtained was 21.2%. At the same conditions, 25wt% aqueous ETH solution resulted in 60±5.5% conversion of ETH. In the same conditions, selectivity and yield of acetic acid were 45% and 26.8% respectively. The selectivity of acetaldehyde and CO<sub>2</sub> and CO were also similar across all three varying feed concentrations. The selectivity of acetaldehyde was 21.7% as shown in Fig 5-5. However, the selectivity and yield of oxidation products were found to be similar to the 25wt% aqueous ETH solution. Hence, it can be concluded that the oxidation pathways of ETH are not affected by AA.
Fig 5-4: Effect of varying ETH/(ETH+AA) wt% on conversion of ETH
(3.06wt% V/TiO₂, 523K, O₂/ETH = 2, WHSV = 1100 cm³·min⁻¹·g⁻¹, 25wt% ETH)

Fig 5-5: Effect of varying ETH/(ETH+AA) wt% on selectivity of oxidation products
(3.06wt% V/TiO₂, 523K, O₂/ETH = 2, WHSV = 1100 cm³·min⁻¹·g⁻¹, 25wt% ETH)
5.3 Summary of mixed feed scenarios

HAC and ETH were individually mixed with acetic acid to investigate their oxidation performance in presence of acetic acid. HAC/(HAC+AA) was varied from 25wt% to 75wt%. In all three scenarios, there was a slight decrease in the conversion of HAC compared to the 80wt% aqueous HAC solution. The selectivity and yield of LA were found to be 77% and 51%, respectively. Similar to HAC, ETH/(ETH+AA) was varied from 25wt% to 75wt%. In all three scenarios, there was a slight decrease in the conversion of ETH compared to the 25wt% aqueous HAC solution. However, the selectivity and yield of oxidation products from ethanol were found to be similar to CPO of 25wt% aqueous ETH solution. From these investigations, it can be concluded that the presence of acetic acid has a small effect on the conversion of HAC and ETH. Selectivity of oxidation products from HAC and ETH largely remain unchanged in presence of acetic acid.
5.4 Comparison between hydroxyacetone and ethanol oxidation

The activation energy of HAC was estimated to be 31kJ·mol\(^{-1}\), however the activation energy of ethanol was estimated to 76 kJ·mol\(^{-1}\). On comparing the oxidation behavior of these two compounds, HAC was more reactive than ETH in presence of V/TiO\(_2\). This may be attributed to the lower activation energy for HAC oxidation reaction compared to ETH oxidation. The pre-exponential factor of HAC oxidation determined from second order rate assumption is \(7.86 \times 10^{11}\) (cm\(^6\).mol\(^{-1}\).min\(^{-1}\).g\(_{\text{cat}}\)^{-1}). For ethanol oxidation, the pre-exponential factor determined from first order approximation is \(4.88 \times 10^{10}\) (cm\(^3\).min\(^{-1}\).g\(_{\text{cat}}\)^{-1}). Pre-exponential factor signifies the frequency of collision between reactant molecules. A higher pre-exponential factor for HAC may have resulted in increased collision between reactant molecules leading to higher conversion of HAC than ETH. HAC has ketone and hydroxyl groups that could be undergo oxidation reaction, whereas ETH has only hydroxyl group. These differences in the chemical structure of the species could have resulted in the increase in reaction rate for HAC compared to ETH. The possible reaction pathways presented in Fig 1.5 and 1.6 for oxidation of HAC and ETH both include aldehydes as an intermediate. From section 3.3.3, conversion of HAC varied significantly as O\(_2\)/HAC ratio increased. However, variation in O\(_2\)/ETH ratio did not affect the conversion of ETH significantly. These observations may indicate that ETH have follow Mars Van Krevelen mechanism while HAC may follow one of the pathways described in section 1.4.2.
Chapter 6: Conclusion and Recommendations

Feasibility of carboxylic acid production from vapour phase oxidation of pyrolysis oil model compounds was investigated in this study. For this purpose, partial oxidation of ethanol, a monofunctional hydroxy compound, and hydroxyacetone, a multifunctional hydroxy compound, was conducted. The experiments were carried out in a packed bed reactor with V/TiO₂ catalyst.

The V/TiO₂ catalyst was prepared using 2-step incipient wetness impregnation method with vanadium oxalate as a precursor. The prepared catalysts were characterized using BET, XPS, ICP-OES, XPS and NH₃-TPD.

Lactic acid selectivity from hydroxyacetone oxidation was greater over the 3.06 wt% V/TiO₂ catalyst than the 8.81wt% V/TiO₂. This may have been due to the lower number of acid sites, higher surface area and absence of crystalline V₂O₅ on the 3.06 wt% V/TiO₂ catalyst. Temperature, O₂/HAC feed ratio and WHSV had significant impact on hydroxyacetone conversion and lactic acid selectivity and yield. At 503K, O₂/HAC ratio of 1.3, and WHSV of 560 cm³·min⁻¹·g⁻¹ cat⁻¹, a maximum hydroxyacetone conversion of 93% and lactic acid yield of 73% was obtained. A maximum lactic acid selectivity of 81% was obtained at 503K, O₂/HAC ratio of 0.7 and 560 cm³·min⁻¹·g⁻¹ WHSV. A second order overall rate equation was used to estimate the activation energy of the reaction. With a fit of R² = 0.99, the activation energy of oxidation of HAC on 3.06wt% V/TiO₂ was estimated to be 31 kJ/mol.

In the first experimental array for ethanol CPO, low temperature range (423-523K), low O₂/ETH ratio (1-3) and high WHSV range (200-2000 cm³·min⁻¹·g⁻¹ cat⁻¹) were tested. A maximum ethanol conversion of 76% and acetic acid yield of 32% was achieved at 473K, O₂/ETH ratio = 2, and 200 cm³·min⁻¹·g⁻¹ cat⁻¹. Maximum acetic acid selectivity of 90% was achieved at 473K, O₂/ETH ratio = 1, and 1100 cm³·min⁻¹·g⁻¹ cat⁻¹. As temperature increased, the yield of complete oxidation products, such as CO₂ and CO, increased. In order to improve the conversion and yield of AA, a second experimental array with high temperature range (473-573K), high O₂/ETH ratio (1-10) and low WHSV range (50-250 cm³·min⁻¹·g⁻¹ cat⁻¹) was investigated. Ethanol conversion was seen to increase with increase in temperature. Complete conversion was achieved at temperatures greater than 473K. Varying oxygen ratio in the feed stream did not affect the conversion significantly. However, selectivity of oxidation products was influenced by varying O₂/ETH ratios. A maximum yield of 73% of acetic acid was obtained at 523K, O₂/ETH ratio = 5.5 and WHSV 250 cm³·min⁻¹·g⁻¹ cat⁻¹. As oxygen did not affect conversion in either array, a first order rate equation dependent on ethanol concentration was used to determine the activation energy of the reaction. A good fit was achieved with R² = 0.99 and the activation energy was estimated to be 76 kJ/mol.
HAC and ETH were individually mixed with acetic acid and reaction conversion was investigated. The conversion obtained from mixing acetic acid with HAC in the reactant feed was slightly lower than aqueous HAC solution. However, the selectivity to LA was largely unchanged in the mixed feed scenario. Similarly, for ETH and acetic acid mixed feed conditions, the conversion slightly decreased to 50% whereas, 60% conversion was observed with 25wt% aqueous ETH solution. Acetic acid selectivity was 43%, which is similar to selectivity obtained from 25wt% aqueous ETH feed at same conditions. As selectivity of oxidation products from HAC and ETH remain unchanged in presence of AA, it can be concluded that the oxidation pathways of HAC and ETH are not affected by AA.

In this study, carboxylic acids were produced successfully from two model compounds in the aqueous phase pyrolysis oil with high yield and selectivity. The true reaction mechanism was not established in this study. In the future, different experimental designs to evaluate the effect of reactant concentration, influence of water vapour in the feed, and catalyst stability must be used to assess the true mechanism of the reactions in the system. To understand the complete reaction mechanism on the surface of the catalyst, detailed surface analysis regarding the adsorption of reactant species on catalyst surface, along with participation of lattice oxygen and desorption of product species must be conducted. In addition to testing individual model compounds, CPO of mixture of model compounds from prominent functional groups in bio-oil must be investigated to understand the interaction between different compounds and identify competing reactions (if any). This study could also provide valuable information about the interaction of compounds from different functional groups during the reaction and can be used to identify any competitive reactions between compounds from different functional groups.

Examination of the surface of spent catalyst must be investigated to understand the structural changes in the catalyst due to the reaction. Detailed analysis of catalyst performance including deactivation and stability must be conducted. These studies may provide detailed information about the changes in oxidation state of vanadium and structural changes in the catalyst due to the reaction. Detailed analysis of these structural changes as mentioned in section 1.4.4, can identify deactivation conditions. In addition, the performance of commercial vanadium catalysts should be compared to that of the lab-generated V/TiO$_2$ catalyst.

Finally, experiments must be carried out using aqueous phase pyrolysis oil samples. As more model compounds are investigated for partial oxidation, the economic feasibility of a pyrolysis facility producing fuel from the organic phase and carboxylic acids from the aqueous phase must be assessed. A life cycle analysis of the process is also needed.
References


38. Nair, H. et al. Method for quantifying redox site densities in metal oxide catalysts: Application to the comparison of turnover frequencies for ethanol oxidative dehydrogenation over alumina-supported V0x, MoOx and WOx catalysts, 258, 1-4 (2008)


Appendix A: Catalyst Characterization

A.1 BET Surface area calculation

Micrometrics ASAP 2020 was used to evaluate the surface area, pore volume, and pore diameter of the catalysts. The N\textsubscript{2} adsorption isotherm was measured at 77K. Assuming Langmuir adsorption isotherm, BET surface area can be estimated by equation A-1.

\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_mC} + \frac{C - 1}{V_mC} \left( \frac{P}{P_0} \right) \quad (A - 1)
\]

Where,

P - equilibrium pressure

P\textsubscript{0} – saturation pressure of N\textsubscript{2}

V – Volume of adsorbed gas

V\textsubscript{m} – Adsorbed volume at the monolayer coverage

C - Constant

From the isotherm as well as the pore distribution, the catalyst can be classified as mesoporous.
A.1.1 BET Analysis for 3.06wt% V/TiO$_2$

Fig A-1. BET report for 3.06wt% V/TiO$_2$
Fig A-2. BET isotherm report for 3.06wt% V/TiO₂

Fig A-3. BET isotherm linear plot for 3.06wt% V/TiO₂
A.1.2 BET Analysis for 8.81wt% V/TiO$_2$

Fig A-4. BET report for 8.81wt% V/TiO$_2$
Fig A-5. BET isotherm report for 8.81wt% V/TiO$_2$

Fig A-6. BET isotherm linear plot for 8.81wt% V/TiO$_2$
A.2 XRD Spectra

Fig A-7: XRD spectra for 3.06wt% V/TiO$_2$ catalyst

Fig A-8: XRD spectra for 8.81wt% V/TiO$_2$ catalyst
A.3. XPS Spectra

Fig A-9: XPS spectra for 3.06wt% V/TiO₂ catalyst

Fig A-10: XPS spectra for 8.81wt% V/TiO₂ catalyst
Appendix B – Calibration curves

B.1 HPLC calibration curves

Calibration standards for the expected compounds were prepared at 5 concentrations using the mobile phase (0.01N $\text{H}_2\text{SO}_4$) as the solvent. Calibration curves for model reactants and expected products in liquid phase can be found in Fig B.1.1. Retention time for the expected compounds is summarized in Table 2-1.

Fig B-1: HPLC Calibration curve
Appendix C – Sample calculation

C.1 Catalyst preparation calculation

Sample calculation for 10wt% V/TiO\textsubscript{2} catalyst is provided in this section

Pore volume of TiO\textsubscript{2} support (from BET) = 0.505 cm\textsuperscript{3}/g

Molecular weight (MW) of V\textsubscript{2}O\textsubscript{5} = 181.88 g/mol

Molecular weight (MW) of Vanadium = 50.9 g/mol

Molecular weight (MW) of Vanadium oxalate (C\textsubscript{2}O\textsubscript{5}V) = 154.96 g/mol

Total weight of catalyst – 10g

Weight of Vanadium – 10*0.1 = 1g

Weight of V\textsubscript{2}O\textsubscript{5} formed = Weight of Vanadium * MW of V\textsubscript{2}O\textsubscript{5} / (2* MW of Vanadium) = 1.78g

Mass of C\textsubscript{2}O\textsubscript{5}V precursor required = Weight of V\textsubscript{2}O\textsubscript{5} formed * MW of C\textsubscript{2}O\textsubscript{5}V / MW of Vanadium

= 3.06 g

Mass of TiO\textsubscript{2} support = Total weight of catalyst – Mass of V\textsubscript{2}O\textsubscript{5} formed = 8.215g

Volume of Deionized water required = Mass of TiO\textsubscript{2} support * Pore volume of TiO\textsubscript{2} support = 4.15ml

C.2 Conversion, selectivity, and yield calculation

\[
Conversion \text{ } (X_A) = 1 - \frac{\text{moles of } A \text{ in product}}{\text{moles of } A \text{ in feed}}
\]

\[
Selectivity \text{ (} S_i \text{)} = \frac{\text{moles of desired product } i}{\text{moles of all products}}
\]

\[
Yield \text{ (} Y_i \text{)} = S_i \times X_A
\]

Sample calculation for ETH partial oxidation at 473K, O\textsubscript{2}/ETH = 3, WHSV = 1100 cm\textsuperscript{3}min\textsuperscript{-1}. g\textsuperscript{-1}

Moles of ETH in feed = 0.0265

Moles of ETH in product = 0.0215
Sum of all products (AA+ACH+CO_2+CO) = 0.0023
Conversion of ETH = 19%
Selectivity of AA = 83.86%
Selectivity of ACH = 6.45%
Selectivity of CO2 = 9.65%
Yield of AA = 15.65%
Yield of ACH = 1.21%
Yield of CO2 = 1.80%

C.3. Internal mass transfer estimation

Internal mass transfer limitation was estimated by evaluating the internal effectiveness factor for first order reaction given in equation C.3.1

\[ \eta = \frac{3}{\Phi^2} (\Phi \coth \Phi - 1) \quad (C.3.1) \]

Where \( \Phi \) is the Thiele modulus for \( n \)th order reaction is estimated using equation C.3.2 and effective diffusivity was estimated using C.3.3.

\[ \Phi_n = R \frac{k_n C_A^{n-1}}{D_e} \quad (C.3.2) \]
\[ D_e = \frac{D_{AB} \Phi \sigma_c}{\tau} \quad (C.3.3) \]

Here,

n – order of reaction

\( D_e \) – Effective diffusivity (m^2/s)

\( D_A \) – Diffusivity of A (m^2/s)

\( \tau \) – Tortuosity (dimensionless), 3

\( \sigma_c \) – Constriction factor (dimensionless), 0.8
Φρ – pellet porosity (dimensionless), 0.4<sup>48</sup>

R – Radius of catalyst particle (m)

k<sub>n</sub> – rate constant of nth order reaction (s<sup>-1</sup>)

ρ<sub>b</sub> (g/cm<sup>3</sup>) – bulk density of bed

**Calculation of Thiele modulus**

**For ETH oxidation at 250°C**

The rate constant units were converted from cm<sup>3</sup>/min.g<sub>cat</sub> to s<sup>-1</sup>, by multiplying first order rate constant by bulk density of the bed (ρ<sub>b</sub> = 0.22g.cm<sup>-3</sup>)

Rate constant, k<sub>A</sub> (s<sup>-1</sup>) = 4.25

Average catalyst radius, R (m) = 53.75*10<sup>-6</sup>

D<sub>A</sub> (m<sup>2</sup>/s) = 0.821*10<sup>-4</sup> (ref 52)

D<sub>c</sub> (m<sup>2</sup>/s) = 8.75*10<sup>-6</sup>

Φ = 0.04

η = 1

**For HAC oxidation at 250°C**

The rate constant units were converted from cm<sup>6</sup>·mol<sup>-1</sup>·min<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup> to s<sup>-1</sup>, by multiplying second order rate constant by bulk density of the bed (ρ<sub>b</sub> = 0.22g.cm<sup>-3</sup>) and C<sub>A0</sub> (mol.cm<sup>-3</sup>)

Rate constant, k<sub>A</sub> (s<sup>-1</sup>) = 8.63

Average catalyst radius, R (m) = 53.75*10<sup>-6</sup>

D<sub>A</sub> (m<sup>2</sup>/s) = 0.098*10<sup>-4</sup> (ref 53)

D<sub>c</sub> (m<sup>2</sup>/s) = 1.04*10<sup>-6</sup>

Φ = 0.15

From Figure 12-5 in Fogler’s Elements of Chemical Reaction Engineering 48, it can be estimated that at Φ = 0.15, for a second order reaction, η = 1.
C.4 Carbon balance equations

**Ethanol oxidation:**

$$\text{Carbon difference} = \frac{[2 \times 12 \times C_{\text{ETH}_{\text{feed}}} - (2 \times 12 \times C_{\text{ETH}_{\text{unreacted}}} + 2 \times 12 \times C_{\text{AA}} + 2 \times 12 \times C_{\text{ACH}} + 12 \times C_{\text{CO}_2} + 12 \times C_{\text{CO}})]}{(2 \times 12 \times C_{\text{ETH}_{\text{feed}}})}$$

**HAC oxidation:**

$$\text{Carbon difference} = \frac{[3 \times 12 \times C_{\text{HAC}} - (3 \times 12 \times C_{\text{HAC}_{\text{unreacted}}} + 3 \times 12 \times C_{\text{LA}} + 2 \times 12 \times C_{\text{AA}} + 12 \times C_{\text{FA}})]}{(3 \times 12 \times C_{\text{HAC}})}$$

Sample calculation:

- Moles of HAC in feed: 0.186823
- Moles of unreacted HAC: 0.02315
- Moles of LA: 0.140947
- Moles of FA: 0.011958
- Moles of AA: 0.024376
- Carbon difference: 1.33%
Appendix D - Rate constant equation

D.1 HAC oxidation - second order reaction

Overall partial oxidation of HAC to LA can be represented as

\[ C_3H_6O_2 + \frac{1}{2} O_2 \rightarrow C_3H_6O_3 \]

Second order overall rate equation is represented as

\[-r_A = k_A C_A C_B \] (D.1.1)

Where, A – HAC; B – O\textsubscript{2}

\[ C_A = C_{A0} (1 - X_A) \] (D.1.2)

\[ C_B = C_{A0} (1 - 0.5 X_A) \] (D.1.3)

Packed bed reactor design equation is given by:

\[ \int_0^X \frac{dX}{-r_A} = \int_0^W \frac{dW}{F_{A0}} \] (D.1.4)

Rearranging and expressing \(-r_A\) using equation D.1.1-D.1.4, the second order rate constant is expressed as

\[ k_A = 2 \frac{F_{A0}}{WC_{A0}^2} \left( \ln \left( \frac{2 - X_A}{1 - X_A} \right) - \ln(2) \right) \]

Here,

\(F_{A0}\) – Molar flow rate of HAC (mol/min)

\(C_A\) – Concentration of HAC (mol/cm\textsuperscript{3})

\(C_B\) – Concentration of \(O_2\) (mol/cm\textsuperscript{3})

\(C_{A0}\) – Initial concentration of HAC (mol/cm\textsuperscript{3})

\(W\) – weight of catalyst in the packed bed (g)

\(X_A\) – Conversion of HAC (no unit)

\(k_A\) – second order rate constant (cm\textsuperscript{6}mol\textsuperscript{-1}min\textsuperscript{-1}g\textsubscript{cat}\textsuperscript{-1})
D.2 ETH oxidation – first order reaction

Overall partial oxidation of ETH to AA can be represented as

\[ C_2H_5OH + O_2 \rightarrow C_2H_4O_2 + H_2O \]

First order overall rate equation is represented as

\[-r_A = k_A C_A\]  \hspace{1cm} (D.2.1)

Where, \( A \) – ETH

\[ C_A = C_{A0} (1 - X_A) \]  \hspace{1cm} (D.2.2)

Packed bed reactor design equation is given by:

\[ \int_0^X \frac{dX}{-r_A} = \int_0^W \frac{dW}{F_{A0}} \]  \hspace{1cm} (D.2.3)

Rearranging and expressing \(-r_A\) using equation D.2.1-D.2.3, the first order rate constant is expressed as

\[ k_A = \frac{F_{A0}}{WC_{A0}} (-\ln(1 - X_A)) \]

Here,

\( F_{A0} \) – Molar flow rate of ETH (mol/min)

\( C_A \) – Concentration of ETH (mol/cm\(^3\))

\( C_{A0} \) – Initial concentration of ETH (mol/cm\(^3\))

\( W \) – weight of catalyst in the packed bed (g)

\( X_A \) – Conversion of ETH (no unit)

\( k_A \) – first order rate constant (cm\(^3\)min\(^{-1}\)g\(_{cat}\)\(^{-1}\))
Appendix E – Standard Deviation

The experiments were repeated twice, and the standard deviation was calculated using equation E.1 to estimate the experimental error.

\[
\sigma = \sqrt{\frac{\sum(x_i - \mu)^2}{N - 1}} \quad (E. 1)
\]

Here,

\( \sigma \) – Standard deviation

\( \mu \) - Mean of \( x_i \)

\( N \) – Total number of samples

Sample calculation

Standard deviation for conversion of HAC at 503K, \( O_2/HAC = 1.3 \) and WHSV = 560 cm\(^3\).min\(^{-1}\)gcat\(^{-1}\)

\( N = 2 \)

\( x_1 = 91.627 \)

\( x_2 = 93.582 \)

\( \mu = 92.604 \)

\( \sigma = \pm 1.38 \)

In the study of HAC and ETH oxidation, the largest standard deviation of conversion obtained was approximately \( \pm 7\% \). The largest difference in carbon balance error for HAC oxidation was 6\% and ETH oxidation was 7.5\%. This might have resulted from mass loss during sample preparation and sample collection. The difference may have resulted from the loss of gas samples from gas sample bags after collection.
Appendix F – Column packing structure

Sample packing of reactor column is presented in Fig F-1. This packing is for a reaction carried out at a WHSV of 730 cm³.min⁻¹. g_cat⁻¹. Catalyst bed length will depend on the weight of the catalyst loading used for the experimental run. The height of the inert packings was adjusted so that the total length was constant at 48 cm.

Fig F-1: Catalyst bed packing structure
Appendix G – Mixed HAC and ETH feed results

Some runs were conducted with HAC and ETH mixed feed at various ETH/(ETH+HAC) weight fractions. The results are presented in Table G-1. In preparing the mixed feed of different variations as presented in Table G-1, 25wt% of ETH in water was mixed with 80wt% of HAC in water. Results from individual aqueous feed of 80wt% HAC and 25wt% ETH are presented in Table G-2.

<table>
<thead>
<tr>
<th>ETH/(ETH+HAC), wt%</th>
<th>Conversion of HAC, (%)</th>
<th>Conversion of ETH, (%)</th>
<th>Concentration of products (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>LA</td>
</tr>
<tr>
<td>25</td>
<td>95</td>
<td>0</td>
<td>3.9</td>
</tr>
<tr>
<td>50</td>
<td>97</td>
<td>47</td>
<td>2.5</td>
</tr>
<tr>
<td>75</td>
<td>98</td>
<td>75</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table G-2: Results from aqueous solution of HAC and ETH (473K, O2/reactant = 2, WHSV = 200 cm³.min⁻¹. gcat⁻¹)

<table>
<thead>
<tr>
<th>Aqueous solution</th>
<th>Conversion (%)</th>
<th>Concentration of products (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>LA</td>
</tr>
<tr>
<td>80wt% HAC</td>
<td>92</td>
<td>6.0</td>
</tr>
<tr>
<td>25wt% ETH</td>
<td>75</td>
<td>-</td>
</tr>
</tbody>
</table>