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Biomass Catalytic Upconversion with a Metallic Catalyst Bed under Radio Frequency Induction Heating

Mohammad Abu-Laban
Louisiana State University and Agricultural and Mechanical College, molaban90@gmail.com

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BIOMASS CATALYTIC UPCONVERSION WITH A METALLIC CATALYST BED UNDER RADIO FREQUENCY INDUCTION HEATING

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science

in

The Department of Biological and Agricultural Engineering

by

Mohammad Marwan Abu-Laban
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Abstract

This study investigated the thermal performances of platinum particles when coupled on a steel support, under the application of a radio frequency (RF) field. Platinum nanoparticles were reduced on the surfaces of type-316 stainless steel balls, based on published methods of Pt reduction from chloroplatinic acid. Alternatively, 1wt. % Pt/Al₂O₃ commercial catalyst pellets were mixed with stainless steel balls and investigated for hydro-deoxygenation of pyrolysis oil from pine sawdust biomass. The catalysts were placed inside an electric insulator tube suspended within a looping copper coil connected to the induction heater, and heated at different power levels. An infrared camera was utilized to record the surface temperature profile during heating of Pt-coated balls and non-coated balls. Pt particles deposited onto silica beads showed no surface heating when placed inside an RF field. The Pt-coated steel systems, however, showed rapid heating of the surfaces following a first order response. The catalysts were characterized via SEM/EDX, XPS and XRD. Preliminary upgrading tests using these Pt-steel balls did not indicate any effect. The lack of catalytic activity was attributed to the limited surface area per unit volume of the Pt coating due to the large sizes and non-porous structure of the steel balls. For the catalytic upgrading experiment with the use of the Pt/Al₂O₃ commercial catalyst pellets mixed with steel balls, heating of the catalyst bed with the induction heater was compared with a conventional method of heating using electric tape around the catalyst bed reactor. Partial deoxygenation was successfully achieved in the catalytic upgrading of pyrolysis oil using Pt/Al₂O₃ pellets mixed with steel balls at 234°C, with the use of the induction heater. The molar O/C ratio of the oil decreased from 1.36 to 0.51. No deoxygenation was observed using the conventional heating method with the electric tape
under identical conditions as both carbon and oxygen appeared to be removed at approximately equal rates, with the carbon being deposited in the form of coke onto the catalyst instead of being recovered in the liquid.
Chapter 1
Literature Review

1.1 Biofuels

Research into alternative energy sources has grown as conventional fuel sources dwindle in supply, and demand for energy increases. In 2006, non-renewable energy resources accounted for 97% of all transportation needs in the United States\(^1\). The growing demand for energy in Asia as economies and populations grow highlights the urgent need for a more reliable and flexible energy supply. In addition, pollution concerns over the release of sulfur- and nitrogen-based chemicals, as well as greenhouse gas emissions associated with fossil fuel combustion have led researchers towards investigating more environmentally friendly energy sources.

One promising alternative being studied is the pyrolysis and gasification of woody biomass. Biomass is considered a cleaner fuel due to fewer SO\(_2\) and NO\(_x\) emissions and its net zero emission of CO\(_2\) gas. The growth of plants needed to yield biomass sources negates most of the CO\(_2\) released as a result of burning biomass fuel. Currently in the US, 33% of the land area is classified as forest land\(^1\), and the burning of timber for heating is widespread due to its compatibility with already existing infrastructures.

Plant matter is composed of low molecular weight substances including organic and inorganic matter (ash), and macromolecular substances including lignin and polysaccharides (cellulose, hemicellulose)\(^1\). The thermal degradation of lignocellulosic material produces aliphatic and polyaromatic compounds which can be used as a source of fuel. These thermal-based processes include gasification, liquefaction and pyrolysis.
The bio-oil product obtained contains hundreds, or even thousands, of organic compounds, making the process of separating and collecting the desired compounds arduous and costly. It also increases the reactivity within the oil makeup as these mostly oxygenated compounds interact with each other and alter the chemical composition of the oil. This ‘aging’ of the oil not only deteriorates the quality of the oil, but also complicates the chemical extraction process. The storage stability of bio-oil is an important factor and numerous studies have investigated techniques to monitor and upgrade the oil’s storage ability. These include antioxidant addition, catalytic cracking, and emulsification. Such improvements also lead to a higher energy density of the oil. In the next section, a brief review of the pyrolytic parameters and achievements with biomass is discussed.

1.2 Biomass Pyrolysis

Biomass pyrolysis is utilized to produce a liquid pyrolytic bio-oil that can be used as a fuel. One type of pyrolysis is fast pyrolysis which operates at temperatures around 500°C under anaerobic conditions. Bio-oil yields from fast pyrolysis have been reported between 40-70 wt.%, with variations stemming from altering operating parameters that include temperature, feedstock type, particle size and vapor residence times.

Typically with fast pyrolysis, ground wood particles are heated rapidly to high temperatures in the absence of oxygen, cracking and vaporizing them into volatile smaller organic and oxygenated molecules. This vapor is then liquefied rapidly via condensation at room temperature or below, including below water freezing. The liquid product, referred to as bio-oil, contains both the aqueous and organic phases.
In the reported study by Onay et al.\textsuperscript{7}, the fast pyrolysis of rapeseed biomass in a fixed bed reactor was carried out with maximum liquid yield of 68 wt.% obtained at 550°C, under nitrogen gas flow. The particle size of the feedstock was studied, and it was observed that the maximum yield was obtained within the particle size range 0.6 and 1.8mm. Sizes below and above this range gave yields around 55-65 wt.%.

In addition, reactor temperatures less than 500°C showed higher char yields and lower liquid conversions, with oil yields increasing as the temperature was increased to 500-550°C, but again decreasing at 700°C, as the gaseous phase yield increased. There is of course a sequential increase in biomass conversion with increasing temperature, up to a maximum. In the mentioned rapeseed study that maximum was reported at 500-550°C. At low temperatures (<300°C) hemicellulosic decomposition and moisture evolution predominate the reaction pathway, while at relatively higher temperatures (300-400°C) cellulosic molecules begin to depolymerize, and finally at temperatures greater than 400°C lignin molecules begin to decompose\textsuperscript{8}. At excessive high temperatures, however, the
depolymerized products begin to undergo a secondary decomposition reaction, resulting in gas yield increases at the expense of char and oil yields.

With respect to size, generally a sufficiently small particle size yields more uniform delivery of heat to the biomass. In the cited study, 0.6-1.8mm is prescribed as the optimal size for maximum yield. In Beiss et al.\textsuperscript{9}, 0.425mm-sized safflower gave the highest yield in a fixed bed reactor under fast pyrolysis, while Nurul Islam et al.\textsuperscript{10} recommends >1mm for the fast pyrolysis of municipal solid waste. These conflicting reports suggest that size alone is insufficient to give a general trend about maximum liquid yield, as the optimal size range appears to be dependent on other factors such as the type of feedstock, type of reactor and method of heating.

The pyrolysis of sawdust has been studied and reported extensively in literature\textsuperscript{1,6-9}. According to a report from the USDA at the Southern Research Station, more than 4.5 million cubic foot of logging residue was produced nationwide in the US in 2006 as a result of timber harvesting operations\textsuperscript{11}. The woody material’s high content in cellulose and lignin make it an attractive supplement, or alternative, to fossil fuels and as a chemical feedstock.

Park et al.\textsuperscript{12} reports the fast pyrolysis of radiata pine sawdust, in a bubbling fluidized bed reactor, equipped with a char removal system. The reaction conditions studied include reactor temperature and size distribution. The optimal liquid yield of 50 wt.% was obtained within the temperature range 400-500°C. Particle sizes less than 3mm showed a decrease in liquid yield as the biomass was overheated, causing an increase in the gas yield.

In the work reported by Ningbo et al.\textsuperscript{13}, pine sawdust was pyrolyzed in a screw reactor for continuous operation. The maximum gas yield of 54.5 wt.% was obtained at 900°C. Analysis
of the oil and gas products show phenolic compounds as the main component in the liquid, and carbon monoxide in the gas. Meanwhile, optimal oil yields were observed below 600°C reactor temperature. The composition of phenols in the oil increased as temperatures increased, while ketones, alcohols, esters and aldehyde compositions decreased. This is explained through the favorability for unsaturated bond condensation and secondary cracking of the carbonyl bonds at higher temperatures.

In the above cited studies, multiple factors affecting the pyrolysis and oil yields were studied, but it is the oil energy content and other properties that have been looked at more extensively by the research community. The next section discusses the work achieved in catalytic bio-oil up-conversion for the purpose of upgrading and improving bio-oil quality relative to crude oil.

**1.3 Catalytic Bio-oil Upconversion**

The bio-oil produced from the thermochemical decomposition of biomass is inherently low in heating value as a result of its large percentage of oxygenated molecules, primarily phenolic compounds. The relatively high moisture content of bio-oil, derived from the original moisture of the biomass source as well as dehydration reactions, also reduces its heating value relative to the HHV of crude oil. Heavy fuel oil has an average reported HHV of 40MJ/kg, with 0.1% and 1% water and oxygen compositions, respectively\(^1\). In comparison, average values of bio-oil HHVs range between 16-19MJ/kg, with oxygen compositions ranging at approximately 35-40%\(^2\) by weight. Water content varies based on the biomass source, but typically ranges from 15-30 wt.% of the bio-oil collected, and in some cases 50 wt.%\(^3\). As a result of these
properties, biomass conversion products are typically upgraded via a hydro deoxygenation (HDO) pathway or by zeolite cracking, to reduce oxygen content in the oil.

The mechanism through which HDO or zeolite catalysts perform has been studied on model compounds present in specific bio-oil samples\textsuperscript{14,15}. Understanding these reaction pathways allow for a generalization to be applied towards basic structures inside the complex makeup of bio-oil. For instance in Barin\textsuperscript{16}, the hydro deoxygenation of phenol yields benzene and water as the products. A series of experiments conducted by Fisk et al.\textsuperscript{17} concluded that small oxygenated compounds in bio-oil undergo reforming with Pt/Al\textsubscript{2}O\textsubscript{3} catalysts, in which the C-O bonds are broken to produce CO\textsubscript{2} and H\textsubscript{2}. In the case of aromatic compounds, the same bonds are broken but this time yielding benzene and cyclohexane.

HDO is the process in which oxygen is eliminated from the sample of interest, with the consumption of hydrogen necessary for this reaction to occur. The hydrogen plays a key role in removing oxygen and saturating double bonds. This results in a decrease in the oxygen-to-carbon ratio, and an increase in the hydrogen-to-carbon ratio, both of which contribute to higher heating values of the oil. At the elemental scale, a metal catalyst in its reduced form is needed for the binding of hydrogen atoms to occur. The reduced metal must also be combined with an oxide support holding acidic sites, in order to exchange electrons with the oxygenated compounds and bind the oxygen groups. The hydrogen atoms bond with the oxygen groups to form water molecules, and a deoxygenated molecule\textsuperscript{18,19}. Most if not all HDO metal catalysts are noble metals such as Pt and Pd, due to their naturally reduced state.
In Olazar et al.\textsuperscript{20}, pyrolysis experiments of sawdust were performed through HZMS-5 catalyst in a cone spouted-bed reactor, for the partial deoxygenation of the oil. The reaction was tested at temperatures of 400°C, 450°C and 500°C. The organic fraction yield of the oil was observed to have reduced from 42.5 wt.% to 20.2wt.% at 400°C. At 450°C, the molar O/C ratio is reported to have gone from 0.48 without catalyst, to 0.26 with the catalyst. That represents a 45.8% reduction in the molar composition of oxygen in the oil achieved in the cited study.

A more significant O/C molar reduction is achieved with the use of Pt/Al\textsubscript{2}O\textsubscript{3} as the deoxygenation catalyst, in the presence of hydrogen gas as reported in Payormhorm et al.\textsuperscript{21}. The catalysis was run in a high pressure reactor, in which collected bio-oil was mixed with the catalysts. Different biomasses were tested, but the O/C ratio of the sawdust biomass was reported to have been reduced from 0.40 to 0.16, an achievement of 60% reduction in the molar composition of oxygen in the oil fraction.

To mimic the organic compositions of actual pyrolysis oil, synthetic oil was used in Fisk et al.’s\textsuperscript{17} study as a basis to test hydro-deoxygenation using Pt on different support catalysts.
The metal loading was 1 wt.% for all catalysts, and the upconversion was run in a stainless steel autoclave reactor under stirring conditions. The lowest O/C ratio achieved was with Pt/Al₂O₃ which is reported at 0.05. Without catalyst, the O/C ratio was 0.33, yielding an approximately 85% reduction in molar oxygen content.

Table 1.1 Summary of molar O/C ratios reported in cited studies

<table>
<thead>
<tr>
<th>Study</th>
<th>Catalyst</th>
<th>Bio-oil O/C (Without upgrading)</th>
<th>Bio-oil O/C (With upgrading)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olazar et al.¹⁶</td>
<td>HZMS-5</td>
<td>0.48</td>
<td>0.26</td>
</tr>
<tr>
<td>Payormhorm et al.¹⁷</td>
<td>Pt/Al₂O₃</td>
<td>0.40</td>
<td>0.16</td>
</tr>
<tr>
<td>Fisk et al.¹³</td>
<td>Pt/Al₂O₃</td>
<td>0.33</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The studies cited above all show a significant deoxygenation effect in their upconversion studies using HDO catalysts and are summarized in Table 1.1. Pt on alumina catalysts revealed strong reactivity towards reducing the oxygenated molecules from the bio-oil composition, compared to the other HDO catalysts reported.

One of the crucial factors of catalysis is the lifetime of the catalyst and its deactivation rate. The struggle with pyrolysis oil up-conversion is the highly viscous property of the liquid product in addition to the high coke and tar formation yielded from the biomass thermochemical decomposition. In the next section, the potential of induction heating is discussed relative to this matter, in which the heating of the catalyst can be manipulated to deter condensation and accumulation of impurities on the catalyst surface sites.
1.4 Induction Heating

Induction heating technology has been spearheading technological advances in industrial, medical and domestic applications. What makes induction heating so desirable is its contactless method of heating and, more importantly, its efficiency in terms of heating rate and loss. The internal heat generation of the load means very high temperatures can be readily reached.

Induction heating operates via an A.C. source, where an alternating voltage is passed through a copper, or any electrically-conductive metal, coil. This induces an alternating magnetic field within the volume enveloped by the coil, which in turn induces eddy currents within any electrically conductive load placed inside this volume, building up resistance and rapid heating of the load. Any ferromagnetic material, in addition to this Joule heating effect, will also heat up via magnetic hysteresis loss in which the magnetic dipole shifts result in heat losses. The electromagnetic phenomena of induction heating can be determined using Maxwell’s equations, which are solved and simplified specifically for a given system.

As a result of its high power densities, inductive sources rapidly heat their targets with minimal loss to surroundings, yielding higher temperatures than conventional methods. The spatial limitations on the load means the heating is localized within the target and defined by the geometry of the coil, granting localized temperature profiles while allowing for a cleaner and safer environment. In addition, its consistent and coherent design improves the productivity process.

The high heating rate attributed with induction heating makes it a lucrative option for the fast pyrolysis of biomass. In Lee et al., the pyrolysis of napier grass using an induction
heating reactor was reported. And in Tsai et al.’s work\textsuperscript{28}, the pyrolysis of rice straws, sugarcane bagasse and coconut shells were examined and a maximum yield of 50 wt.% was obtained using induction heating technology. Therefore, pyrolysis via inductive heating can be successfully run and in some cases outperform other heating methods.

The proposed study for this thesis is, in addition to heating the biomass via an inductive source, the heating of the catalyst bed required for up-conversion will also be tested by the same method. Up-conversion by hydro-deoxygenation can be accomplished with the use of a noble metal (e.g. Pt, Pd) supported on acidic sites. The hypothesis is that by directly heating the catalyst from the interior of the bed, the rate of condensation of the oil vapors and coke formation on the catalytic sites can be significantly reduced, relative to a conventional heating method.

The pyrolysis of the biomass is based on the studies reported in Muley et al.\textsuperscript{29} and Henkel et al.\textsuperscript{30} using pine sawdust. According to the reported study, pre-treated pine sawdust collected from a wood shop was closely packed inside a steel tubular reactor. The optimal residence time for the pyrolysis reaction to proceed was determined by weighing the biochar product at the end of each run, i.e. the percentage of original mass retained. A constant mass with increasing time suggested the complete pyrolysis of the biomass at each respective temperature. The optimal biomass temperature for maximum liquid yield was observed within the range 500-600°C, similar to what was observed in Tsai et al. and Lee et al.

The temperature and residence time, as well as other relevant parameters from the reported studies by Muley et al. and Henkel et al., were used as a basis for this proposed study in the upgrading of pyrolysis bio-oil. In chapter 3 of this document, the use of a hydro-
deoxygenating (HDO) catalyst coupled with steel balls is tested by heating directly via a high-frequency induction source. The performance of the catalyst based on common adsorption and desorption tests (TPR, TPD), and the oil’s qualitative properties (O/C ratio), are compared to a conventional heating method using the same catalyst bed.

In the 2nd chapter, the thermal heating profiles of a bed of steel balls are examined under varying inductive heating power levels, as well as other parameters. Pure Pt nanoparticles deposited on the steel balls were synthesized and tested for any effect of the substrate surface heating performance. This catalyst was also assessed for any up-conversion activity of pyrolysis oil.

1.5 References


Chapter 2
Thermal Performance and Surface Analysis of Steel-Supported Platinum Nanoparticles

2.1 Introduction

Catalyst deactivation and regeneration is a significant concern for most industrial processes in the multi-billion dollar catalyst market. All catalysts eventually decay, and the mortality rate depends on the catalyst and the process in which it is used. For catalytic cracking processes this rate is a matter of hours, while for iron catalyst in the production of ammonia the catalyst can be recycled for 5-10 years\(^1\).

Coke formation on catalysts like zeolites in the catalytic cracking of bio-oil makes up-conversion expensive for this process. The rapid coke formation mechanism was reported to occur via two pathways: (i) heavy coke fraction from the condensation and linking of aromatic compounds, and (ii) a lighter fraction due to the formation of oxygen-containing coke\(^2,3\).

Coke formation over acidic sites at temperatures lower than 200°C usually occurs via condensation of reactants due to their affinity for adsorption\(^4\), followed by reactions between the adsorbed species to form a large network of carbon chains. The retention of the coke molecules, especially in microporous catalysts, is due to the steric hindrance within the pores of the catalyst.

Efforts to mitigate the formation of coke molecules include the use of catalytic coating to convert coke to carbon oxides by reaction with steam\(^5\). In addition, neutralization of external acidic sites on zeolite catalysts to prevent coke adsorption has been reported with the use of alkali molecules such as MgO and 2,4-dimethylquinoline\(^6\). These agents help prevent the growth of filamentous carbons on the surface, but are ineffective in preventing the diffusion of
the carbon polymers into the catalyst. Chemical agents like SiO₂ can be used to mitigate the condensation of coke molecules on the surface as well as their diffusion into the particle⁷.

While several studies have looked at the mitigation of coke formation, there is little understanding of the effect of the surface catalyst temperature and the role it plays in the adsorption of coke molecules. Generally, adsorption is exothermic and an increase in temperature leads to a decrease in adsorption. However, the condensation of molecules on the surfaces can also be due to the temperature gradient across the surface of the catalyst. A negative temperature gradient can lead to a faster rate of the coke adsorption. Hence, the heating method of the catalyst reactor can play a significant role in the formation of fouling compounds on the surface sites that reduce the catalysts longevity.

Induction heating is an efficient method of heating that involves the passing of an alternating current through a metal coil which induces an alternating magnetic field as discovered by Lorentz, Ampere and Maxwell⁸. This alternating magnetic field induces eddy currents on any electrically conductive load placed within the volume of the coil, and/or hysteresis loss in magnetic loads⁹,¹⁰,¹¹. Direct resistance from these effects result in heating of the load. Since the heat originates from the load itself, this method yields rapid heating rates with minimal losses to the surroundings during induction. The electromagnetic phenomena involved in induction heaters can be described using Maxwell’s equations¹².

To apply this heating method to the issue of coke formation, the design of a metallic-supported catalyst is needed in which the heat directly emanates from the surface to deter condensation of unsaturated hydrocarbons and aromatics that form coke. While some catalysts contain material with high magnetic permeability and electric permittivity, these quantities are
typically too small to induce a large heating effect in the catalyst bed. Most catalytic upgrading processes require a temperature of at least 200°C, especially if the reaction is occurring in the gaseous phase, to prevent oil condensations in the catalyst bed. Therefore, a macro-sized support is needed to anchor the active catalysts and maintain high temperatures for the bed.

In this study, we propose a steel-supported Pt-nanoparticle system. Platinum’s hydrodeoxygenating catalytic properties have led to its use in various applications, such as the removal of trans fatty acids by hydrogenation in cottonseed oil\(^{13}\), the electro reduction of oxygen in fuel cells\(^{14}\), and the hydro-dechlorination of tetrachloromethane\(^{15}\). The popularity of nanocatalysts for catalytic reactions is a result of their high surface area retention.

Platinum reduction reported in Tang et al.\(^{16}\) is used to synthesize Pt nanoparticles and deposit them onto the surfaces of steel balls. Steel is an electric conductor that heats up directly under RF fields via the Joule heating effect from the induced eddy currents. The purpose of this method would be to establish a positive temperature gradient across the surface of the catalyst and deter coke and oil condensation (Figure 2.1).

The objectives of the current study were to monitor the heating profiles of steel balls in an induction heater and analyze the surfaces after Pt-modification. Furthermore, the effectiveness of the catalysts was tested for the upgrading of pyrolysis bio-oil from sawdust biomass.

Generally, the process of making bio-oils involves breaking down organic complex molecules in biomass material into smaller molecules, via a thermo- or bio-chemical reaction\(^{17}\). Multiple factors have put the production of biofuels to the forefront as an energy source. Government regulations, the high cost of petroleum and its environmental costs, as well as its production in unstable parts of the globe, have all led to in-depth studies into this field and
increasing its efficiency\textsuperscript{18}. However, pyrolysis produces a significant amount of water and oxygen in the final product, which renders it unusable as transportation fuel. By hydrodeoxygenation of the organic compounds, the low energy value of the oil can be mitigated with Pt nanocatalysts.

![Diagram](image)

**Figure 2.1** (Not to scale) Heat transfer flow from a) tube walls towards the interior, and b) from the steel ball surfaces to the tube walls. Only one steel functionalized-ball is shown for illustration purposes. Arrows indicate direction of heat flux.

### 2.2 Materials

Type 316 stainless steel spheres (0.1875” and 0.25” diameter), and type 316 steel foil (0.004in thick), were purchased from McMaster-Carr\textsuperscript{®}. H\textsubscript{2}PtCl\textsubscript{6}·6H\textsubscript{2}O and CH\textsubscript{2}O were purchased from Sigma-Aldrich Co. LLC,. NaOH was obtained from Thermo Fisher Scientific Inc., and C\textsubscript{6}H\textsubscript{16}O\textsubscript{2}SSi from Gelest, Inc. Custom-made quartz tubes were ordered from Technical Glass Products, Inc. The chemicals and reagents purchased were analytical grade and used without any additional treatment.
2.3 Methods

2.3.1 Synthesis of Pt nanoparticles on supported steel

Silane functionalization of the steel balls was carried out as outlined in Gelest’s *Applying a Silane Coupling Agent* protocol, available on their website[^19]. Stainless steel balls were first rinsed with water and ethanol and left to dry for 1-2 hours at 100°C. The surfaces of the balls were subsequently modified with an oxide layer via plasma oxidation in vacuum for 30 seconds. An alternative approach for comparison used was heating the balls up to 1000°C to oxidize and blacken the surface to increase the surface area available for nucleation and growth. Silane monolayer assembly (C$_6$H$_{16}$O$_2$SSi) was conducted following the oxidation treatment. The plasma oxidized steel were immersed in 2% silane linker in 95% ethanol solution and agitated for 2-3 minutes at room temperature. The silane solution was decanted and the stainless steel rinsed with ethanol and left to dry overnight. This was followed by rinsing with DI water, and drying in the oven.

The deposition protocol outlined in Tang et al[^16] was followed to reduce Pt onto the stainless steel surfaces. A 20mM aqueous solution of H$_2$PtCl$_6$ was prepared and mixed with the stainless steel balls. The solution was gradually basified with 0.1M sodium hydroxide solution until the pH reached 12. The solution was then heated to approximately 90 °C, under vigorous stirring conditions. At this point, excess formaldehyde (36.5%) was added, at a 10:1 molar ratio with respect to PtCl$_6$ $^2\text{-}$2. Indication of reaction was observed by solution color change (Figure 2.2).
The steel balls were rinsed with hot DI water until the filtrate tested negative for formation of a white precipitate using 0.1M silver nitrate solution. This was followed by overnight heating in an oven at 150 °C. The stainless steel balls were then allowed to cool to room temperature before their testing in the induction heater. As a control, this technique was also applied to silica balls.

2.3.2 Surface Analysis

Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy-Electron Dispersive Spectroscopy (SEM-EDS), X-ray Diffraction (XRD), and Photoelectron Spectroscopy (XPS) were run on the Pt deposited onto the steel. Due to the geometrical nature of the steel balls, most of the x-ray analyses and the FTIR were incompatible. To perform these analyses, the same deposition technique was applied onto stainless steel foil.

XRD analysis of the Pt nanoparticles reduced in solution was carried out with a Panalytical Empyrean multipurpose diffractometer equipped with PreFIX (pre-aligned, fast interchangeable X-ray) modules using CuKα radiation. The sample was measured between 20°<2θ<100° at Kα=1.54nm, and the Scherrer formula was used on the first peak to determine the crystal size of the Pt.
XPS analysis was performed with a Kratos AXIS 165 XPS/SAM system equipped with a Scanning Auger Electrostatic gun (LaB6 filament, 15kV, 100µA). The binding energies of Pt species were identified, using the C peaks as a reference to rectify any shifts.

To quantify the surface Pt, as well as Au, relative to other species and image the Pt nano-clusters, a JSM -6610 LV SEM equipped with EDS was utilized. This was operated under high vacuum at beam voltage of 20kV. For this analysis, the steel balls were compatible with the system’s settings for testing.

Finally, the adherence of the silane linker to the steel was verified using the Bruker Tensor 27 FTIR machine, and collecting the absorption spectra. The background signal of the steel was subtracted from the final spectra.

2.3.3 Heating by Induction

The platinum functionalized stainless steel balls were heated with an induction heater (HFI model, RDO) initially at the following power levels: 150W (3%), 250W (5%) and 350W (7%). The heating was performed in a small ceramic tube placed within a small vertical coil, to directly measure the surface temperature of the balls (Figure 2.3a). The temperature was monitored and recorded in real time using an IR camera (FLIR A4009sc, FLIR Systems, Inc.) connected to a thermal data acquisition software (ThermaCAM Professional 2.9), as shown in Figure 2.3c. Two different sized balls were used: 0.1875” and 0.25” diameters. These were tested individually and placed in a ceramic crucible for heating inside the coil for 3 minutes during each run. The emissivity values were averaged from three attempts via trial and error with the thermocouple reading. In addition, steel balls pre-oxidized at 1000°C to create a uniform oxide film were also measured with and without Pt to compare surface heating effects. Finally, the steel balls that
yielded the most ideal temperature profiles were loaded into a quartz tube (1.25”OD X 0.70”ID, 12” long), within a larger coil at different power levels of the induction heater (250W, 500W, 750W), as shown in Figure 2.3b. The transmissivity value of the quartz tube was set at 0.7 and verified similarly to the emissivity of the steel.

![Image](a) Small coil set-up. (b) Large coil set-up. (c) Overall setup of RF induction heating of steel balls with temperature measurements using IR camera and data acquisition.

**Figure 2.3.** (a) Small coil set-up. (b) Large coil set-up. (c) Overall setup of RF induction heating of steel balls with temperature measurements using IR camera and data acquisition.

### 2.3.4 Pyrolysis, GCMS & CHN Analysis

Pyrolysis of sawdust biomass was based on the work reported by Muley et al.²⁰ and Henkel et al.²¹ 10g of dried sawdust was packed inside a 310-stainless steel tubular reactor. This biomass reactor was suspended within an RF induction coil (10-loop, rubber-insulated copper coil, 285mm in length and 59mm ID), connected to an RDO LFI-model power supply (35-100kHz). The biomass reactor was connected to a 5%H₂/bal. N₂ gas line, and to the catalyst bed
in the quartz tube in series. 100g of the smaller (0.1875”) steel balls functionalized with Pt were packed inside the quartz tube which was maintained at 470K for the duration of the pyrolysis.

The liquid product collected after pyrolysis was analyzed with Gas Chromatography Mass Spectroscopy (Varian Saturn 2200). The oil phase of the liquid product was extracted using DCM (5:1). The column oven was initially heated to 40°C and held for 6min, ramped to 240°C at 4°C/min and held for 10min, and then again ramped to 280°C at 20°C/min and held for 5 min, for a total time of 73min (Muley et al\textsuperscript{20}). The peaks were identified using the built in MS library software. Carbon, Hydrogen and Nitrogen compositions for the oil samples were determined using a 2400 Series 2 CHN (Perkin Elmer, Inc.) elemental analyzer as also described in Muley et al. The oxygen content was determined by taking the difference between 100% and the sum of C, H, and N content.

2.4 Results & Discussion

2.4.1 Surface Analysis

FTIR analysis post-application of the silane linker confirmed the presence of silane bondage to the steel surface. Peaks for Si-O-metal (1000-900cm\textsuperscript{-1}), Si-O-Si (1130-1000cm\textsuperscript{-1}), Si-CH\textsubscript{3} (1275-1245cm\textsuperscript{-1}), C-H (3000-2700cm\textsuperscript{-1}), and O-H (3000-3500cm\textsuperscript{-1}) were observed. The S-H peak, a relatively weak peak, was not visible.

The platinum nanoparticles on the surface of the stainless steel observed with Scanning Electron Microscopy (SEM) reveal crystalline nanoparticle formation, along with aggregations (Figure 2.4). The smallest crystals observable ranged in sizes from 20-50nm, while some clusters reached micro sizes. The average crystal size determined from the XRD peak associated with miller index (111) was 21nm (Figure 2.5). The remaining peaks and their respective miller
indices associated with the face-centered cubic structure of the Pt particles are also labeled at their respective angles.

Figure 2.4. (a) to (c) SEM imaging, from high to low magnification, of nanoparticles forming on steel surface and aggregating to form nano-scale islands.

Figure 2.5. X-ray diffraction spectra collected for Pt NPs in solution
To verify the purity of the reduced Pt species, XPS analysis is presented in Figure 2.6 and Table 2.1. Deconvolution of the spectra yielded two Pt species only, Pt$^0$ and Pt$^{2+}$(Table 2.1). The high Pt/Cl ratio indicated low presence of unreduced Pt salt, suggesting the Pt$^{2+}$ to be primarily in the form of PtO.

![Figure 2.6. XPS spectrum for Pt-4f with deconvolution to yields two Pt species, Pt$^0$ and Pt$^{2+}$.](image)

Table 2.1. XPS data measured for reduced Pt on steel

<table>
<thead>
<tr>
<th>Species</th>
<th>BE of Pt 4f (eV)</th>
<th>Relative Percentage (%)</th>
<th>Atomic Ratio (Pt/Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$^0$</td>
<td>72.1</td>
<td>57%</td>
<td>13.3</td>
</tr>
<tr>
<td>Pt$^{2+}$</td>
<td>73.5</td>
<td>43%</td>
<td></td>
</tr>
</tbody>
</table>

The verification of Pt with EDX, as well as the gold seeding nanoparticles, on the surface of the balls are presented in Figure 2.7. This technique was primarily used to quantify the Pt relative to the surface compounds of the steel. This was also performed for the steel balls.
before and after heating to observe any change in the amount of Pt on the surfaces (Figure 2.7). The balls tested included the two different sized stainless steel balls, and the pre-oxidized steel balls. Between the stainless and pre-oxidized steel balls, it can be deduced that the latter retains a much larger Pt quantity on its surface than the former. This is due to the roughness induced as a result of the oxidization, increasing the surface area for nucleation and growth of Pt nanoparticles.

![Figure 2.7. EDX spectra for a Pt-reduced steel surface](image)

Another trend worth noting is the decrease in the relative Pt quantity after heating in all systems. In the case of the smaller steel balls, shown in Figure 2.8 to be heated twice consecutively at 3% power, we observe a downward trend in Pt quantity after each heat application. One theory behind this phenomena is that of differential diffusion. With heating of the surfaces the stainless steel begin to oxidize, resulting in an uneven layer with porous pathways across the surface. The concentration gradient now established results in the migration of the Pt deeper into the surface.
2.3.2 Temperature Profiles

The emissivity values for each steel ball are listed in Table 2.2. The complete temperature plots of the particles with platinum and those without (control), at the 3 different power levels inside the small coil, are shown in Figure 2.9. It can be observed, temperatures of the steel balls increased to approximately 300°C in less than 20s. No observable difference in profiles was noted with having the Pt on the surface of the steel balls. The temperature profiles for both the smaller (0.1875in) and larger (0.25in) steel balls also showed similar trends. Note that the final temperatures at the higher powers reached much higher values than necessary for catalytic activity which typically ranges between 600K and 800K.²³

Table 2.2. Emissivity values for each system

<table>
<thead>
<tr>
<th></th>
<th>Small Control</th>
<th>Small w/Pt</th>
<th>Large Control</th>
<th>Large with/Pt</th>
<th>Pre-oxidized control</th>
<th>Pre-oxidized w/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissivity</td>
<td>0.545 ±0.019</td>
<td>0.585 ±0.049</td>
<td>0.620 ±0.024</td>
<td>0.677 ±0.036</td>
<td>1 ±0.05</td>
<td>1 ±0.05</td>
</tr>
</tbody>
</table>
Temperature profiles at different power levels

a)

b)
Figure 2.9. a) Temperature plots comparing smaller steel balls with Pt and without, at 3 power levels: 3%, 5%, and 7% (output= 5kW). b) Temperature plots comparing the heating profiles of the larger sized steel balls. c) Temperature plots for pre-oxidized small steel balls with and without Pt, compared also to their stainless counterpart.

All the temperature profiles above were normalized to room temperature (298K) and fitted into a simple exponential rise to maximum correlation with 2 parameters ($a$ and $b$):

$$T(K) = a \ast (1 - e^{-bt(s)})$$

The parameter values for each plot are recorded in Table 2.4.

Table 2.4. Parameter values for curves fit to temperature plots.

<table>
<thead>
<tr>
<th>Control steel balls</th>
<th>0.1875in SS balls</th>
<th>0.25in SS balls</th>
<th>Pre-oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power (W)</strong></td>
<td><strong>a</strong></td>
<td><strong>b</strong></td>
<td><strong>R^2</strong></td>
</tr>
<tr>
<td>150</td>
<td>554.05</td>
<td>0.0170</td>
<td>0.983</td>
</tr>
<tr>
<td>250</td>
<td>675.12</td>
<td>0.0173</td>
<td>0.999</td>
</tr>
<tr>
<td>350</td>
<td>817.74</td>
<td>0.0209</td>
<td>0.999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Steel balls with Pt</th>
<th>0.1875in SS balls</th>
<th>0.25in SS balls</th>
<th>Pre-oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power (W)</strong></td>
<td><strong>a</strong></td>
<td><strong>b</strong></td>
<td><strong>R^2</strong></td>
</tr>
<tr>
<td>150</td>
<td>553.81</td>
<td>0.0156</td>
<td>0.988</td>
</tr>
<tr>
<td>250</td>
<td>677.43</td>
<td>0.0184</td>
<td>0.997</td>
</tr>
<tr>
<td>350</td>
<td>930.72</td>
<td>0.0175</td>
<td>0.999</td>
</tr>
</tbody>
</table>
Even at low powers, these steel balls reached significantly high temperatures as a result of the applied RF field. From the above heating profiles, the heating rate of the oxidized steel balls appeared faster than that of the stainless steel balls of the same size. The $b$ parameter, or the decay constant, fitted for each of the profiles does in fact have a larger value for the oxidized steel balls (0.028-0.0296) than that of their stainless counterparts (0.0105-0.0209). Since the heat generated originates from the direct resistance of the eddy currents circulating on the surfaces, the heat generated from the oxidized steel balls is much greater due to its lower electrical conductivity relative to its non-oxidized form. An increase in the electrical resistance is also expected as a result of the increased roughness with oxidization.

To further investigate the heating effect of the Pt nanoparticles alone, the same deposition technique was applied to silica beads and the surface temperature was monitored. Both the temperature of the bare silica and the Pt-modified silica beads remained at the same temperature under an RF field: room temperature. The lack of any heating from the nanoparticles is somewhat expected as the load is too small to possess significant impedance. In addition, most ferromagnetic and paramagnetic nanoparticles require a fluid medium to release heat, as a result of the magnetic dipole shifts paired with the Brownian motions causing friction between the rotations of the particles with the solvent molecules.

SEM imaging of the steel surfaces after heating at the 3 power levels (3%, 5%, and 7%) with the small coil revealed melting and degradation of the nanoparticles at such high temperatures (Figure 2.10). At 3%, the maximum temperature reached was approximately 800K. While the melting point of Pt is 2041K, the melting points of materials generally decrease
as their size decreases\textsuperscript{26}. Fortunately, for the up-conversion of pyrolysis oil, temperatures of 800K are extreme and unnecessary.

Figure 2.10(a)-(c). SEM imaging of steel surfaces after heating. At the higher levels, melting of nanoparticles can be observed.

To investigate the ability of the balls to heat a potential catalyst bed to reasonable temperatures, the oxidized-film steel balls, which showed the fastest heating rate, were loaded into a quartz tube and suspended within the larger coil. The temperature profiles at the different power levels are presented in Figure 2.11 with the fitting parameters listed in Table 2.5. With the larger loading, the same applied power at 5% resulted in a more moderate temperature increase compared to the small coil experiment. Overall, higher powers were necessary to gain higher bed temperatures. Despite this, even at the lowest power (5\% or 250W), the maximum temperature reached was sufficient enough to run catalytic upgrading through. The maximum steady state temperature for each experiment in the large coil was correlated to the power and plotted in figure 2.12. Up-conversion using Pt-modified steel balls is discussed in the next section.

\[ T(K) = y_0 + a \times (1 - e^{-bt(s)}) \]
Table 2.5. Parameter values for curves fit to temperature plots.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>y₀</th>
<th>a</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 (5%)</td>
<td>292.48</td>
<td>179.24</td>
<td>0.0063</td>
<td>0.995</td>
</tr>
<tr>
<td>500 (10%)</td>
<td>288.82</td>
<td>287.93</td>
<td>0.0086</td>
<td>0.991</td>
</tr>
<tr>
<td>750 (15%)</td>
<td>288.49</td>
<td>365.20</td>
<td>0.0109</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Figure 2.11. (a) Heating profiles for the smaller oxidized steel balls at 5% (250W), 10%, (500W), and 15% (750W).

Figure 2.12. Maximum steady state temperature (K) as a function of induction heating power (W).
2.3.3 GC-MS

The GC-MS spectra of the oil without up-conversion and that passed through the steel-Pt bed are shown in Figure 2.13. The peak locations and intensities look roughly similar, and after identifying and classifying the compounds, any differences in the chemical make-up of both samples (Figure 2.14) were largely insignificant based on their proportional weights in solution. A statistical one-tail t-test ($\alpha=0.05$) between the two groups for each organic compound class suggested no significant variations. The only exception to this was the ketones group which increased from 12 wt.% to 18 wt.%, but was disregarded as inconsequential due to the results of the elemental analysis. The molar O/C ratios of the organic phase in the oil were determined to be 1.58 for the bio-oil without upgrading, and 1.64 for the oil treated with Pt-steel. Based on these results no deoxygenation was deduced to have occurred.

One major drawback with this particle design is the limited surface area per volume available with the use of the steel balls. The mass of the Pt on the surface of the balls for the up-conversion totaled less than half a gram, while the biomass loading was 10g. This large feed-to-catalyst ratio inhibits any possible upgrading. Increasing the catalyst load may be one solution, but not a practical one due to the weight of the steel balls needed. In addition, the calculated residence time for the catalyst bed was determined to be 4.25s which, coupled with the small catalyst area available, further disadvantages any catalytic adsorption and activity. A longer bed in this case would mitigate the short catalyst contact time.

A more practical alternative would be a repeat of the design on a more porous steel structure, such as wool or a mesh structure, to seed and grow the catalyst particles and
maximize the surface area available. Temperature studies to ensure these structures maintain a high enough catalyst bed temperature would also be required.

Figure 2.13. GC Spectra of a non-upgraded pyrolysis oil sample compared to sample passed through bed of Pt-steel.

Figure 2.14 Chemical composition of pyrolysis oil without up-conversion (a), and oil upgraded with Pt/Steel.
2.5 Conclusion

To investigate the efficiency of heating catalyst supports directly with an RF induction heater, we utilized steel balls modified with Pt on the surfaces. The high electric conductivity of the steel balls resulted in their rapid heating, which created a positive temperature across the surface. This form of heating has the potential to mitigate the effects of coke formation, such as in the up-conversion pyrolysis oil. With the use of the steel bed, the tube reached high enough temperatures for upgrading processes. While no upgrading was observed with catalysts designed in this study, for wood-derived bio-oil, it does offer a precursor to further studies in which the main inhibitor, the limited surface area, can be alleviated with the use of mesh supports for the catalyst.

2.6 References


Chapter 3
Up-conversion of Pyrolysis Bio-oil using Pt/Al₂O₃ Catalyst Pellets Mixed with Steel Balls under a Radio-Frequency Induction Heater

3.1 Introduction

Research into biofuels as an alternative energy source to crude oil has drawn much attention and success for the up-conversion of bio-oil with the use of catalytic hydro deoxygenation¹-⁴. One of the most widely used methods for the thermochemical decomposition of pine sawdust to produce bio-oil is fast pyrolysis. This process involves rapid heating of biomass in the absence of oxygen. Raw bio-oil possesses a relatively small heating value, due mainly to its highly oxygenated organic, mostly phenolic, compounds that make up a significant amount of its chemical composition. Water composition of the liquid product from pine pyrolysis is reported at an average 17% by weight, while average oxygen content is reported at 47 wt. % of the organic phase⁵. The higher heating value (HHV) of wood pyrolysis oil averages around 16-19MJ/kg compared to heavy fuel which is reported at 40MJ/kg⁶. In addition, the high oxygen content makes the bio-oil non-ideal for storage due to its reactivity. This volatility in the chemical makeup of the oil would make the chemical extraction difficult as the properties alter.

As mentioned, up-conversion of the bio-oil to reduce oxygen content and respectively increase the energy density and quality of the bio-oil can be achieved via catalytic deoxygenation. In this process, through a series of hydrogenation, deoxygenation and dehydration reactions, the carbonyl groups are hydrolyzed and removed to produce water and lower the oxygen content in the organic oil phase. In the reported study by Zanuttini et al³, m-cresol was used as a bio-oil model compound to study its deoxygenation over Pt/γ-Al₂O₃ catalysts under low pressure hydrogen gas. The main products of the hydro deoxygenation
reaction were reported to be toluene, benzene and methylcyclohexane. Selection of Pt as the most selective reducing metal toward benzene formation was thus based on existing literature data\textsuperscript{7-12}.

In Payormhorm et al.\textsuperscript{4}, the catalytic deoxygenation of \textit{Leucaena leucocephala} pyrolysis oil and other wood species, including pine sawdust, was also studied using Pt/Al\textsubscript{2}O\textsubscript{3} catalysts. The study reports a decrease in the molar O/C ratio from 0.4 to 0.16 after deoxygenation. In this case, the liquid oil was first generated and then mixed with the catalyst in a heated CSTR.

In the proposed study we look at a unique method of heating the catalyst using radiofrequency inductive heating. This method is also applied to pyrolyzing the packed biomass discussed in previous reports by Henkel et al\textsuperscript{13} and Muley et al\textsuperscript{14}. These reports set the foundation needed for the upconversion study proposed here. With the insight gained from these reports into optimal reactor residence times, biomass pyrolysis temperature and yields, the current study builds on that information to upgrade the quality of the oil by passing the vapors through a steel-Pt/Al\textsubscript{2}O\textsubscript{3}-mix catalyst bed for hydrodeoxygenation, where inductive heating of the steel balls was used to maintain the temperature of the bed.

The principle of an induction heater is well established, and involves an alternating current passing through a coil which induces an alternating magnetic field within the volume enveloped by the coil. The alternating magnetic field in turn induces eddy currents on any electrically-conductive load placed in the same volume\textsuperscript{15}. Benefits of the induction heating include the efficient and rapid heating of the load, since the only heat generated originates from the load itself with very little to no heat loss to the surrounding. More importantly, the
positive temperature gradient established across the catalyst surface would ideally deter the polycondensation and polymerization of the vapor molecules to form coke and tar.

In the proposed study, we look at the heating profiles under different powers for the catalyst bed using stainless steel balls mixed with HDO pellets within a non-conductive tube. Components in pyrolysis oil can begin to condense at temperatures $<300^\circ$C, depending on the biomass and its organic compounds. Therefore, it is necessary to maintain the bed temperature to avoid cooling of the pyrolysis vapors coming from the biomass reactor, and also for optimal reducing activity of our catalyst based on their temperature-programmed reduction and desorption profiles. The feed-to-catalyst ratio was set after using a high ratio which was subsequently reduced until significant production of benzene and reduction of phenolic compounds was observed from the GC-MS spectra of the oil phase. The molar O/C ratio of the oil was monitored for the different bed temperatures and also compared to a conventional heating method of the bed using heating tape.

### 3.2 Materials

3.2mm Pt (1wt. %) /Al$_2$O$_3$ pellets and 99% dichloromethanol (DCM) were purchased from Sigma-Aldrich®, one 5% H$_2$/balance N$_2$ gas cylinder (200ft$^3$) was purchased from AirLiquide and Type 316 stainless steel precision balls, 7/32" diameter, were purchased from McMaster-Carr. A custom-made alumina ceramic tube was ordered from SentroTech. Pine shavings from scrap wood (untreated) were collected from an in-house wood shop.
3.3 Methods

3.3.1 Catalyst Characterization

The Pt/Al₂O₃ pellets were tested as received for Temperature-Programmed Reduction, Desorption (TPR, TPD) and BET analysis. All analyses were performed using an Altamira 200R-HP unit with the pellet placed inside a 1/4” ID u-shaped quartz tube. Products were analyzed with a thermal conductivity detector (TCD).

3.3.1.1 TPR³

For pre-treatment, Helium gas was flushed through at 30cc/min. The temperature was ramped to 150°C at 10°C/min and held for 30 minutes, and then cooled to 40°C at 10°C/min. The TPR treatment followed with the use of 10% H₂/Ar gas at 30cc/min, and ramped to 900°C at 10°C/min.

3.3.1.2 TPD⁴

The pellets were first pre-treated with Helium gas flushed at 30cc/min, heated to 250°C at 10°C/min and held for 60 minutes. The bed was then cooled to 100°C at the same rate. To adsorb NH₃, 10% NH₃/He was injected at 30cc/min for 10 minutes. This was followed by flushing again with He gas to desorb the ammonia, at 30cc/min and temperature ramping to 900°C at 10°C/min.

3.3.1.3 BET

A 3-point Brunauer-Emmett-Teller analysis was performed¹⁷, and again the catalyst was first pre-treated with He gas, with temperature increased to 150°C at 10°C/min and held for 30min. The bed was then cooled to 40°C at the same rate. The catalyst was then outgassed with
pure nitrogen at 50cc/min. Data was collected over three pulse periods during which the bed was submerged in liquid nitrogen three times for 300s long each.

3.3.2 Biomass Pyrolysis

The experimental parameters for the pyrolysis of sawdust were previously developed in Henkel et al\textsuperscript{13}. and Muley et al\textsuperscript{14}. Pine sawdust shavings were ground and filtered to <0.5mm in diameter and dried overnight. 10g of the treated sawdust was packed into the center of an insulated 310-stainless steel tubular reactor. This biomass reactor was suspended within an RF induction coil (10-loop, rubber-insulated copper coil, 285mm in length and 59mm ID), connected to an RDO LFI-model power supply (35-100kHz). The biomass reactor was connected to a 5%H\textsubscript{2}/bal. N\textsubscript{2} gas line, and to the catalyst bed in series. The catalyst bed consisted of 25g of 1wt. % Pt on Al\textsubscript{2}O\textsubscript{3} pellets inside a 1.25“OD X 0.70“ID, 10” long 99.8% alumina tube with low magnetic permittivity. The pellets were mixed with 7/32“ diameter stainless steel balls to full capacity of the tube in order to increase the load for inductive heating. The catalyst bed was under its own induction heater (6-loop coil, rubber insulated, 203mm in length and 49mm ID), with an RDO HFI-model supply unit (150-400kHz). The system was purged with 5% hydrogen gas flowing at 3 CFH for 1h prior to the burning of the biomass. During this time, the catalyst bed was heated to the desired temperature and maintained for one hour to reduce any oxidized Pt prior to initiating pyrolysis. This temperature was maintained during the pyrolysis process. Vapors from the biomass reactor passed through the catalyst bed and entered a condensation flask submerged in ice which was connected to an electrostatic precipitator. The exit stream from the condenser lead to ethanol and water traps, connected serially to collect
any soluble compounds, and then to the outlet stream. Gas samples were collected at the junction prior to the water and ethanol traps and analyzed with gas chromatography.

An infrared sensor coupled to an Omega iR2C PID controller was used to control the temperature of the biomass reactor at 550°C by adjusting the power output of the LFI induction heater. The temperature of the catalyst bed tube was manipulated manually by setting the power level to one value and allowing the surface temperature of the tube to reach a maximum steady state value. This was performed for 3 different power levels (250W, 350W, and 500W) to achieve 3 different bed temperatures (234°C, 286°C, and 375°C). The surface temperature of the alumina tube was monitored and recorded in real time using an IR camera (FLIR A325sc, FLIR Systems, Inc.) connected to thermal data acquisition software (ThermaCAM Professional 9.1). The temperature readings at four different points along the length of the tube were recorded and averaged to obtain the tube surface temperature (Figure 3.1). The emissivity value of the alumina tube was set to 0.9 and confirmed via trial and error using a thermocouple.

To compare the inductive heating method to a conventional heating source, an electrical heating tape was used as our control experiment. The electrical tape operated with an on-off feedback controller. The temperature set point was set equal to the induction-heated run at the lowest temperature. In addition, a baseline experiment was set up and tested in which the pyrolysis of sawdust was carried out under identical conditions, but without any catalytic up-conversion. All experiments were performed in duplicates.

Based on the parameters reported in Henkel et al. and Muley et al., pyrolysis of the sawdust proceeded for 20-25min followed by natural cooling. The catalyst bed was post-
treated by maintaining its temperature for another 30 min after the biomass pyrolysis reactor was turned off, under hydrogen/nitrogen flow. The residence times of the vapors were determined by adjusting the volumetric flow rate exiting the biomass pyrolysis reactor to expansions as a result of the temperature changes based on the ideal gas law, over the constant void volume of the catalyst bed. Bio char left inside the biomass reactor, and liquid product inside the condenser were collected, quantified and analyzed by GC-MS, KF-titration, and CHN analysis.

![Image](image-url)

Figure 3.1. User interface of the ThermaCAM Professional 9.1 data acquisition software (left), used to measure infrared radiation of heated surfaces, compared to image of actual catalyst bed enveloped in coil (right).

3.3.3 GC

The oil phase of the liquid product was extracted using DCM (5:1), of which a 5 µL sample was injected into a GC column (Varian Saturn 2200). The column oven was heated to 40°C and held for 6 min, ramped to 240°C at 4°C/min and held for 10 min, and then again ramped to 280°C at 20°C/min and held for 5 min, for a total time of 73 min (Muley et al.). The GC mass spectra peaks were identified using the built in MS library software and the peak areas were integrated to determine the proportional wt. % of each compound in the organic phase. Non-condensable gas samples were collected for composition analysis using GC (SRI 8610C, SRI...
Instruments) to measure the concentrations of CO, CO₂ and CH₄. A valuable product, H₂ released was not measured due to the lack of the required detector in our GC equipment set up.

3.3.4 KF Titration

The aqueous content of the liquid product was determined using a KF coulometric titrator (Karl Fischer Titrator Metrohm Model 831 KF Coulometer) (ASTM E203-08). 50µL of the oil sample was mixed with 50mL of ethanol. A 0.5mL sample of the mixture was injected into the coulometer to yield the water content reading in ppm. An ethanol sample was also read to account for any water contributed by the hygroscopic ethanol.

3.3.6 Elemental Analysis

Carbon, Hydrogen and Nitrogen compositions for the biomass, char and oil samples were determined using a 2400 Series 2 CHN (Perkin Elmer, Inc.) elemental analyzer as described in Muley et al. The oxygen content was determined by taking the difference between 100% and the sum of C, H, and N content.

3.3.7 Higher Heating Value

The HHVs for the oil phases were determined using Dulong’s formula\(^1\)\(^8\), where the %CHO values from our elemental analysis were used.

\[
HHV \left( \frac{MJ}{kg} \right) = \left[ 338.2 \times C\% + 1442.8 \times \left( H\% - \frac{Q}{8} \right) \right] \times 0.001
\]

For the char solids, the HHV was determined using Demirbas’ formula\(^1\)\(^9\),

\[
HHV \left( \frac{MJ}{kg} \right) = 0.3856(C\% + H\%) - 1.6938
\]
3.3.8 Statistical Analysis

A one tail t-test was run wherever mentioned assuming unequal variations, at \( \alpha = 0.05 \). An ANOVA analysis was also run where mentioned, again assuming unequal variations with \( \alpha = 0.05 \). P values less than \( \alpha \) were ruled statistically significant between two or more groups of data.

3.4 Results & Discussion

3.4.1 Catalyst Analyses

The temperature-programmed reduction and desorption profiles for the Pt/Al\(_2\)O\(_3\) catalyst pellets are shown in Figure 3.2. The profiles show two principle peaks suggesting two different sites with different adsorption strengths. The first reduction peak appeared at around 167°C, as the platinum oxide is reduced to its metallic form\(^20\). However, the peak at around 356°C indicates a class of platinum oxide exhibiting stronger interactions with the support and, hence, requiring higher temperature to reduce\(^21\).

![Figure 3.2. Temperature-programmed reduction with H\(_2\) (blue) and temperature-programmed desorption with NH\(_3\) (green) profiles for the Pt (1 wt.%)/Al\(_2\)O\(_3\) pellets.](image-url)
BET analysis on the Pt/Al₂O₃ pellets yielded a specific surface area of 5162m²/g, with an average pore radius of 96Å. The acidity of the catalyst, determined from the peak area of the NH₃-TPD profile (Figure 3.2), was determined to be 1.69 NH₃ mmol/g, catalyst.

3.4.2 Heating Profiles

The temperature profiles for both the 3 pyrolysis sets heated at different powers using the induction heater, and the one set for the electrical heating tape are shown in Figure 3.3. In all cases, the temperature rose exponentially to a maximum value as the radiative and convective heat losses began to equal the heat induced. The curves were fitted to a 2-parameter exponential formula after normalizing to 25°C (Table 3.1). The maximum steady state temperatures are plotted in Figure 3.4, showing also the maximum temperature of the ceramic tube loaded with the catalyst pellets only, without steel balls and enveloped within the inductive coil. High temperatures were therefore unachievable without the presence of the steel balls acting as a heating medium. From the induction profiles it can be deduced that with higher power the maximum temperature increased linearly as more current was induced on the surfaces of the balls. The heating rate also appears faster for the conventional heating method compared to the inductive heating method. This is predictable for an automated on-off temperature controller as opposed to the manually-set operation of the induction heater.

\[ T(K) = a * (1 - e^{-bt(s)}) \]

Table 3.1. Fitting parameters for temperature profiles in each experiment, fitted to an exponential rise to a maximum (2 parameter) formula.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>a</th>
<th>b</th>
<th>Adj. ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IH 250 W</td>
<td>244</td>
<td>0.0008</td>
<td>0.983</td>
</tr>
<tr>
<td>IH 350 W</td>
<td>232</td>
<td>0.0017</td>
<td>0.980</td>
</tr>
<tr>
<td>IH 500 W</td>
<td>382</td>
<td>0.0011</td>
<td>0.989</td>
</tr>
<tr>
<td>HT 300 W</td>
<td>311</td>
<td>0.0008</td>
<td>0.991</td>
</tr>
</tbody>
</table>
Figure 3.3. Temperature plots recorded using IR camera and ThermaCam data acquisition for catalyst bed heated under RF inductive field at 3 different powers: 250W, 350W, and 500W, and with electrical heating tape.

Figure 3.4. Maximum steady state temperature are plotted for the catalyst bed with no steel balls, the bed mixed with steel balls and heated at 3 different power levels, and the bed heated with electrical heating tape.
3.4.3 Yields

The masses of the liquid product and the char left behind were collected and quantified. The difference from the original biomass was taken to determine the mass of gas released for each experiment. With HDO, higher gas yields are expected as organic compounds from the decomposition of lignin and cellulose undergo secondary cracking to produce more CO, CO₂ and CH₄. Water compositions also increased as dehydration reactions took place (Figure 3.5). Both of these resulted in a lower oil yield for the catalyzed runs, which is commonly reported in literature for these types of processes and reactions³, ⁴, ¹³, ²². The complete yield values are listed in Table 3.2.

![Figure 3.5. Water and oil composition of pyrolysis liquid product, determined using KF titration.](image)
### Table 3.2 Yield values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water (wt. %)</th>
<th>Oil (wt. %)</th>
<th>Char (wt. %)</th>
<th>Gas (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>18.48 ± 0.31</td>
<td>22.52 ± 1.31</td>
<td>20.00 ± 0.00</td>
<td>39.00 ± 1.00</td>
</tr>
<tr>
<td>HT 237°C</td>
<td>16.59 ± 4.57</td>
<td>13.41 ± 3.57</td>
<td>21.00 ± 0.00</td>
<td>49.00 ± 1.00</td>
</tr>
<tr>
<td>IH 234°C</td>
<td>19.23 ± 1.85</td>
<td>6.77 ± 0.85</td>
<td>20.00 ± 2.00</td>
<td>54.00 ± 1.00</td>
</tr>
<tr>
<td>IH 286°C</td>
<td>17.74 ± 1.45</td>
<td>6.76 ± 2.05</td>
<td>21.00 ± 1.00</td>
<td>54.50 ± 4.50</td>
</tr>
<tr>
<td>IH 375°C</td>
<td>16.09 ± 0.62</td>
<td>5.41 ± 2.12</td>
<td>23.50 ± 1.50</td>
<td>55.00 ± 0.00</td>
</tr>
</tbody>
</table>

3.4.4 Gas Chromatography

The GC-MS spectra collected from the oil phase of the liquid products are shown in Figure 3.6. The peaks were largely identified as phenolic compounds, with traces of alcohols, aldehydes and ketones. Without up-conversion (baseline), the only hydrocarbon identified was that attributed to ethyl benzene. This peak increased in intensity for all up-conversion experiments, but markedly so for the inductive heating experiments. The phenolic peaks, however, were lowest with the induction heating run at 234°C and gradually increased as the temperature of the bed increased. Phenolic compounds generally undergo the HDO reaction to form benzene or cyclohexane after the hydroxyl group is removed via dehydration reactions\(^3\).

However, alkyl ether groups have been reported to negatively influence the reactivity of the phenols while alkyl groups have a positive influence\(^23\). The peaks shown in figure 3.6 show most of the latter removed after upgrading with the induction heater, while the former persist albeit at relatively lower intensities. A summary of the compounds identified were classified as hydrocarbons, phenols, or others (included alcohols, aldehydes and ketones) and are listed for each experiment in Table 3.3.
Figure 3.6. GC-MS spectra for the inductive and conventional heating experiments.

Table 3.3. Summary of organic compounds present in each pyrolysis oil, based on wt. %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrocarbons (Wt. %)</th>
<th>Phenols (Wt. %)</th>
<th>Other (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>7.95 ±2.93</td>
<td>66.52 ±2.17</td>
<td>25.53 ±1.31</td>
</tr>
<tr>
<td>HT 237°C</td>
<td>13.73 ±1.18</td>
<td>61.37 ±0.64</td>
<td>24.90 ±0.44</td>
</tr>
<tr>
<td>IH 234°C</td>
<td>29.48 ±0.62</td>
<td>39.9 ±0.69</td>
<td>30.61 ±0.98</td>
</tr>
<tr>
<td>IH 286°C</td>
<td>25.83 ±1.34</td>
<td>47.65 ±2.67</td>
<td>26.52 ±3.83</td>
</tr>
<tr>
<td>IH 375°C</td>
<td>33.15 ±0.96</td>
<td>48.22 ±7.35</td>
<td>18.63 ±3.14</td>
</tr>
</tbody>
</table>

Phenolic compounds made up two-thirds of the oil composition before upgrading. For the first catalyzed experiment using the induction heater at the lowest catalyst bed temperature, the composition of phenols decreased to 40 wt.%, while the amount of hydrocarbons increased from 8 to 30 wt.%. With the presence of the HDO catalyst, partial deoxygenation of the phenols to benzene can be inferred. The other induction heating
experiments run at higher bed temperatures gave similar trends for the hydrocarbons, but also showed a gradual increase in phenols with increasing bed temperature.

For the heating tape experiment, a smaller rise in hydrocarbon composition is observed (to 14 wt.%) but the profile is largely identical with respect to the baseline experiment. This suggests that the catalyst surface sites in this experiment were fouled or inhibited, preventing the initiation of adsorption of the organic compound. This would imply a high temperature gradient as a result of the slow transfer of heat from the exterior of the tube to the interior. This phenomena is discussed in the next section, where the catalyst surfaces are analyzed post-experiment.

In addition to the GC-MS of the oil phase, GC analysis of the gas product for CO, CO₂ and CH₄ was performed and is presented in Figure 3.7. Besides HDO, catalytic cracking, which results in the removal of the organic elements from the oil into the gaseous phase, can also take place. The results for the induction heating runs show a slight increasing trend for all the gaseous products as the bed temperature increased, with the exception of the CO under 375°C, which dropped sharply. As the bed temperature increases, the vaporized organic molecules are more likely to undergo additional cracking producing more gaseous products in the form of carbon monoxide, dioxide and smaller-chain hydrocarbons²⁴. The large standard error produced for the IH 375°C GC test, suggests the data point as a possible outlier. Besides this increasing trend with temperature, there is no discernible pattern of significance for the GC gas analysis. The absence of a decrease in CO and increase of CO₂ as a result of the common oxidation activity for Pt catalyst²⁵, suggests unfavorable conditions for this particular reaction.
3.4.5 Elemental Analysis

The dry basis C, H and O compositions are listed in table 3.4 for the different experiments as well as the biomass and char samples. Using this data we can determine the O/C and H/C molar ratio of the oil samples for the induction-heated and conventionally-heated upgrading experiments and compare them to the oil without deoxygenation. The ratios are presented in Figure 3.8. For the experiment run at 234°C with the induction heater, the O/C molar ratio decreased to 0.51 from 1.36, a 62.5% reduction in the molar oxygen, the highest reduction from all the experiments. The 284°C experiment had the second highest reduction, down to 0.81, a 40% reduction. The highest bed temperature at 375°C and the heating tape experiment have almost identical O/C ratios compared to the baseline.
Table 3.4 Summary of the elemental composition for each pyrolysis run

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon (Wt. %)</th>
<th>Hydrogen (Wt. %)</th>
<th>Oxygen (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSD Biomass</td>
<td>49.46 ±1.00</td>
<td>6.14 ±0.85</td>
<td>44.66 ±0.52</td>
</tr>
<tr>
<td>Char</td>
<td>84.40 ±0.69</td>
<td>1.81 ±0.08</td>
<td>13.49 ±0.72</td>
</tr>
<tr>
<td>Baseline Bio-oil</td>
<td>32.30 ±1.61</td>
<td>9.49 ±0.66</td>
<td>58.20 ±2.28</td>
</tr>
<tr>
<td>Bio-oil HT 237°C</td>
<td>29.20 ±0.08</td>
<td>11.025 ±0.00</td>
<td>59.77 ±0.08</td>
</tr>
<tr>
<td>Bio-oil IH 234°C</td>
<td>52.83 ±5.32</td>
<td>12.67 ±2.35</td>
<td>34.49 ±3.02</td>
</tr>
<tr>
<td>Bio-oil IH 286°C</td>
<td>42.85 ±0.82</td>
<td>11.025 ±0.00</td>
<td>46.13 ±0.82</td>
</tr>
<tr>
<td>Bio-oil IH 375°C</td>
<td>28.50 ±0.67</td>
<td>9.44 ±1.59</td>
<td>62.06 ±0.92</td>
</tr>
</tbody>
</table>

Figure 3.8. Oxygen-to-carbon, and hydrogen-to-carbon molar ratios for the control and upgrading experiments.

A t-test analysis for each experiment compared to the baseline O/C showed statistical significance for the IH 234 °C run only, and no significance for the remaining. In addition, no
statistical significance between any groups was determined using an ANOVA test for the H/C ratios.

The coke formed in the catalyst was also accounted for by running elemental analysis on the pellets, after single pyrolysis runs with the different heating methods. This data is presented in Figure 3.9. Clearly, in addition to removing O from the feed, a significant portion of the C is also being removed, leading to an increase in the O/C ratio in the oil. For the case of the heating tape, 26.75% of the total biomass weight was found lost in the catalyst bed in the form of coke. If the C from coke is accounted for as shown in Figure 3.8, the calculated O/C molar ratio would be 0.06. The difference between this value and the reported value of the oil-only value of 1.53 (96%) for the heating suggests the deoxygenation effect with this method is hampered due to the loss of the C from the oil. In other words, the results from the heating tape and baseline experiment are insignificant from one another, due to the fact that the measured loss of O is offset by the loss of C in the formation of coke. To a lesser extent, this is also seen with the IH 234°C experiment, where an 8.75% loss of C mass was noticed due to the coke formation on the catalyst bed. The O/C ratio calculated included the C from the coke would be 0.047. Data for coke deposition was not collected at the other temperatures.

Figure 3.9. CHN analysis on the Pt/Al2O3 pellets after single pyrolysis upgrading runs.
In addition to losing C over the catalyst bed in the form of coking, elemental mass balances reveal that C and O are also escaping into the gas phase proportionately different compared to the baseline compositions (Figure 3.10). The higher O/C ratios in the gas phase appear lower at the higher temperatures, which would lead to our observed results, a respective decrease in the O/C ratio of the oil phase at these temperatures.
3.4.6 Catalyst fouling and activity analyses

To understand the discrepancy between the conventional heating and induction heating method for pyrolysis upgrading, the surfaces of the catalysts were examined using NH$_3$-TPD and BET, and CHN analysis for coke formation. The acidity for the catalysts after a single run using the induction heating method at 234°C decreased from 1.69 to 1.62 NH$_3$ mmol/g, catalyst. Meanwhile, for the heating tape method, the acidic sites decreased from 1.69 to 0.924 NH$_3$ mmol/g, catalyst after a single run (Figure 3.11). The specific BET surface areas for both catalysts revealed a surface area reduction from 5162 to 4928 m$^2$/g for the induction heating method, and to 3122 m$^2$/g for the heating tape method. Based on these results it can be deduced that the catalytic active sites are being fouled under the heating tape at a higher rate than the induction heating method. It was earlier shown in Figure 3.9, elemental analysis run on the catalyst pellets revealed higher C wt. % content for the heating tape experiment after a single run. The rapid poisoning suggests inability of the catalyst to adsorb the organic molecules to further deoxygenate and release water, as well as a loss of the carbon content in the catalyst.
bed. This phenomena was also deduced from the GC, KF, and CHN analysis performed for the heating tape experiment, where the results resembled closely to the pyrolysis oil run without catalytic upgrading.

![NH₃-TPD profiles](image)

Figure 3.11. NH₃-TPD profiles for fresh catalysts (control) compared to inductively-heated and conventionally-heated catalysts after single run pyrolysis up-conversion.

Looking only at the induction heating experiments, a trend appears to show that with increasing temperatures starting from 234°C, the molar O/C decreases, and hence so would the HHV of the oil. A higher percentage of C was observed to have been lost at the higher temperatures in the gaseous phase. However, one must also look at the interior temperature
obtained in the catalyst bed and overlay that information with the TPR and TPD profiles of the catalyst for hydrogen consumption and reactant adsorption. From Figure 3.11, the two active peaks for reduction and acid site adsorption appear at around 167°C and 356°C.

The bed temperature was calculated for each of the three experiments from the surface tube temperature measured using the IR camera. Using Fourier’s Heat by Conduction law for a multi-layered cylindrical shell, the temperature within the tube was estimated, taking into account heat lost due to radiative and convective heat transfer to the surroundings. The results for the interior temperatures for each experiment are listed in Table 3.5. For simplification, $T_1$ is taken at half the radial distance from the center to the interior wall, and the bed of steel balls is assumed to be one solid shell. These temperatures are marked over the TP profiles in Figure 3.11 above. The bed temperature at 383°C for IH 375 falls just outside of the second reduction peak, suggesting very little to no hydrogen consumption on the catalyst sites are possible at this temperature.

Meanwhile, the experiments run at 292°C and 239°C fall close to the peak of the first reduction and desorption peak. The former showed the second-highest reduction in the O/C ratio, with the loss of more C into the gas phase possibly exacerbating the quality of the oil. At the same time, the lower temperature, which lies closer to the first peak, reflecting the weaker acid sites and reactive metal sites on the catalyst surface, showed the highest deoxygenation effect. The difference between experiments IH 234 and HT 237 (relatively same temperature) underscores the advantage of using induction heating as a heating source for the catalyst bed. Attempting to reach the first peak with the conventional heating method was shown to be problematic as a result of the polycondensation of the bio oil vapors at the low temperature.
This is likely due to the cold spots developed as the heat transfers from the walls to the interior of the bed, and the pellets developing negative temperature gradients across their surfaces. Meanwhile, at the same temperature with the induction heating, partial deoxygenation indicates that moving closer to the first peak is much more possible to avoid significant condensation, as the heat transfers from the interior of the bed to the walls, and minimizing the temperature gradients across the surface.

Another factor to consider is the contact time of the reactants with the catalyst sites. The residence times for each experiment are also listed in Table 3.5, with the expansion of the gas with temperature increases taken into account using the ideal gas law. With higher temperatures, the catalyst contact time decreased significantly which suggests little time for HDO to take place. A recommendation for future work would be to increase the length of the tube, as well as the coil, for higher residence times.

Table 3.5. Interior temperatures for the catalyst bed determined using Fourier’s Heat by Conduction Law for a 3-layered shell cylinder, and the calculated residence times for each experiment.

\[ Q = \frac{T_3 - T_1}{R_{\text{STEEL}} + R_{\text{TUBE}}} \]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HT 237°C</td>
<td>169</td>
<td>237</td>
<td>232</td>
<td>7.16</td>
</tr>
<tr>
<td>IH 234°C</td>
<td>122</td>
<td>234</td>
<td>239</td>
<td>7.25</td>
</tr>
<tr>
<td>IH 286°C</td>
<td>168</td>
<td>286</td>
<td>292</td>
<td>5.93</td>
</tr>
<tr>
<td>IH 375°C</td>
<td>193</td>
<td>375</td>
<td>383</td>
<td>4.52</td>
</tr>
</tbody>
</table>
3.4.5 Energy Balances

The HHVs of the oil phases for each experiment are listed in table 3.6. As shown, the HHV value of the bio-oil upgraded at the lowest induction heated catalyst bed, 28.82MJ/kg, is almost twice the value obtained for the heating tape experiment (14.12MJ/kg), which is almost identical to the HHV of the oil without up-conversion.

The energy inputs and outputs for each pyrolysis experiment over the duration of the run (20min) are also listed in Table 3.6, with the net loss listed in the third column. The input energy included the operational equipment running during the pyrolysis such as the induction heater, ESP, as well as the calorific values of the biomass and hydrogen gas flowing in. The values in the energy output were the derived calorific values of the char, oil and gas products. Being unable to measure the hydrogen exiting the system as well as other low molecular weight hydrocarbons (C₂-C₅)\textsuperscript{14}, our net losses may appear larger than what they might actually be.

The determined net loss appeared higher for the heating tape experiment compared to its similar induction heating counterpart. This is a result of the minimal-to-none amount of deoxygenation achieved in the heating tape experiment, compared to the induction heated run. The induction heating experiments at higher bed temperatures (286°C and 375°C) predictably showed much higher net losses as a result of the necessary additional power to maintain the higher temperatures, with little additional upgrading of the oil to contribute toward a higher HHV.

The energy recovered in our products from the original biomass are listed for each experiment. All tests revealed roughly equal recovery amounts, except for the heating tape experiment which had the highest loss of C in the catalyst bed. While the energy recovered is
identical for both the upgraded and non-upgraded experiments, mainly due to the loss of the oil yield in the former, it is important to note that the energy is distributed among fewer molecules as shown in our GC-MS spectra earlier compared to the baseline. This indicates the upgraded product is more homogenous, stable and extractable comparatively.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Higher Heating Value of the oil (MJ/kg)</th>
<th>Input Energy (kJ)-process equipment, biomass</th>
<th>Output Energy (kJ)-char, oil, gas</th>
<th>Net Loss (kJ)</th>
<th>Biomass Energy Recovered (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONTROL</td>
<td>14.12 ± 1.91</td>
<td>1466 ± 7.14</td>
<td>105 ± 4.50</td>
<td>1361 ± 5.97</td>
<td>53.2 ± 0.36</td>
</tr>
<tr>
<td>HT 237°C</td>
<td>15.00 ± 0.04</td>
<td>1826 ± 7.14</td>
<td>88 ± 0.14</td>
<td>1738 ± 5.05</td>
<td>44.6 ± 1.69</td>
</tr>
<tr>
<td>IH 234°C</td>
<td>28.82 ± 0.55</td>
<td>1766 ± 7.14</td>
<td>105 ± 3.55</td>
<td>1661 ± 5.64</td>
<td>53.3 ± 0.13</td>
</tr>
<tr>
<td>IH 286°C</td>
<td>22.81 ± 0.16</td>
<td>1886 ± 7.14</td>
<td>108 ± 4.21</td>
<td>1779 ± 5.86</td>
<td>54.7 ± 0.15</td>
</tr>
<tr>
<td>IH 375°C</td>
<td>12.06 ± 2.23</td>
<td>2066 ± 7.14</td>
<td>110 ± 2.87</td>
<td>1956 ± 5.44</td>
<td>56.0 ± 0.57</td>
</tr>
</tbody>
</table>

To mitigate the energy losses for this process, the use of insulation on both the biomass and catalyst bed tubes will help reduce the amount of power needed to maintain both reactor temperatures, by minimizing radiative and convective heat losses. In addition, a scale up of the biomass and catalyst amounts will help reduce the net loss by increasing our output-to-input energy. To maintain a roughly constant energy input, the reactor sizes must remain identical, as they were not maximized in this experiment, but with larger biomass and catalyst pellet loadings to increase the amount of HDO.
3.5 Conclusion

Using induction heating as a source for a steel-packed catalyst bed, up-conversion of sawdust pyrolysis oil was achieved by partial deoxygenation with Pt/Al₂O₃. The optimal temperature of the bed needed for hydrogen reduction, was determined at around 230-240°C. As a conventional heating method, in which the bed walls are heated by an external source, an electric heating tape was compared with. In this experiment, heating the bed to the same optimal temperature resulted in rapid fouling of the catalyst in the form of coke formation. Hence, deoxygenation based on this method was largely unsuccessful. The study helps support induction heating as a lucrative heating source for a catalyst bed coupled with conductive material to aid in driving the temperature gradient from the interior to the exterior of the tube, and avoiding heat transfer loss. This opens the door to looking at catalytic supports with high electrical conductivity to increase the lifetime of the catalyst by heating the pellets directly and preventing the deposition of coke and other pollutants.

3.6 References


Chapter 4
Summary and Future Work

The aim of the current thesis was to investigate the efficiency of induction heating in directly heating a steel core catalyst bed. In Chapter 2, we looked at seeding Pt nanoparticles on steel ball surfaces to gauge the morphology and feasibility of the process, and also determine the heating profiles of the supports. The main challenge with using a steel support is the limited area in which our catalyst deposited. Most catalysts require powder supports to increase the surface area significantly. The issue with using powder iron or any metal powder is that the heat induced from the radiofrequency induction heater would essentially be minor for use in a catalyst bed due to the small loading, where temperatures need to reach at least 150°C depending on the catalyst’s activity and vapor pressures. That being said, the challenge of surface area can be circumvented with the use of porous metallic pellets or supports, such as steel mesh made from wool, or cobalt foams and meshes. The network of pores in these structures would enhance the available catalyst sites needed for deoxygenation. Another alternative would be the use of microwave heating. Most Pt catalysts are supported on alumina, which has favorable dielectric properties to heat up directly under 2.45GHz microwave heating. Tests would need to be carried out to determine the heating efficiency of these catalysts, and also any physical effects such as sintering that may damage the sites available.

In Chapter 3, we investigated the heating effect on a catalyst bed that consisted of commercial pellets embedded within a bed of stainless steel balls. Upconversion of sawdust pyrolysis oil with the induction heater to heat the catalyst bed was compared to the use of a conventional heating method under identical conditions. The results revealed that the use of a
conventional heating method lead to an equal removal of carbon content due to the polycondensation of the bio oil vapors in the bed, in pace with the removal of oxygen by the catalyst. This not only resulted in the fouling of catalysts but also a constant O/C ratio compared to our baseline experiment. Coking was observed with the use of induction heating as well, but to a lesser extent. We were still able to detect a decrease in the O/C of the oil phase as a result of fewer C removal in the bed phase. Since both these methods were carried out at relatively the same temperatures, we see that we can achieve deoxygenation with induction heating more efficiently at lower temperatures, allowing us to reach the weaker and more reactive catalytic sites that occur at these temperatures. With the conventional heating method, higher temperatures would be needed to observe a decrease in the O/C content of the oil, to mitigate the effect of coke formation. The main problem with higher temperatures in increasing the energy yield of the oil phase, is the favorability of catalytic cracking leading to an increase in the gaseous phase at the expense of the oil yield.

Potential future work would be the design of a metal-supported HDO catalyst, looking at the activities of different noble metals, and possibly different supports in upgrading the oil quality. The temperature effects would also need to be monitored in their efficiency to drive away polycondensations of the oil vapors. In conclusion, this study has opened the door to studying the electromagnetic phenomena on responsive catalyst supports to mitigate the effect of poisoning and coking that is much too common in the processes of bio-oil upconversion.
VITA

Mohammad Marwan Abulaban was born in 1990, is a native of Amman, Jordan, and received his bachelor’s degree of science in Chemical Engineering at Louisiana State University in 2012. Thereafter, he made the decision to continue his graduate studies in the Department of Biological & Agricultural Engineering at Louisiana State University. He will receive his masters degree in May 2016 and plans to begin his doctorate upon graduation.