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# The effect of process variables on pyrolysis in a freefall reactor

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**The effect of process variables on pyrolysis in a freefall reactor**

by

**Preston Alec Gable**

A thesis submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of  
**MASTER OF SCIENCE**

Co-Majors: Mechanical Engineering; Biorenewable Resources and Technology

Program of Study Committee:

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Ames, Iowa

2014

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## ABSTRACT

The focus of this work is to test variables of fast pyrolysis conditions in a free fall reactor in order to better understand their impact on pyrolysis products, specifically optimization of bio-oil yields. In the first study, a design of experiments was performed and products were analyzed to evaluate the effects of temperature, sweep gas flow rates, and particle heating time, on bio-oil yields. This study proved particle heating time to be a very important variable effecting bio-oil yields, and that a heating time of greater than the traditionally assumed two seconds must be achieved in order to optimize yields. The second study focused on the effects of extended solids heating time on bio-oil yields. Six experiments were conducted to test two collection methods, under both heated and cooled conditions, in order to better understand phenomena occurring after the solid particles have passed through the reactor. The products were analyzed, and results concluded that particles are not completely volatilized after two second in the heating portion of the reactor. Analysis also proved that vapors are still produced over 40 seconds after the particles have left the heating portion of the reactor.

Overall, these experiments have concluded that the some often neglected variables may have a larger impact on bio-oil yields than previously believed.

## CHAPTER I

### INTRODUCTION

Pyrolysis is a process typically carried out in the absence of oxygen, at atmospheric pressure, and in temperatures ranging 300-600°C [1]. Pyrolysis has been used to produce charcoal for thousands of years. In recent history however, there has been an interest in harnessing pyrolysis for the production of liquids known as bio-oil to reduce our dependence on non-renewable energy sources [2].

By manipulating the conditions of pyrolysis one can alter the distribution of products and their compositions. Liquid yields of as high as 78% are possible but are very difficult to obtain at any level other than the micro scale. Bio-oil can be used as a direct replacement for heating oil or bunker fuel, or it can also be upgraded to transportation fuels. Pyrolysis is typically applied to ligno-cellulosic feedstock, with the type and quality of feedstock having a large impact on yield and composition of products [3].

The time required to complete pyrolysis is relatively unknown. The literature frequently mentions that pyrolysis reaction times are on the order of 0.5 seconds to 10 seconds [4-5] although sometimes it is not clear whether these times refer to biomass devolatilization or vapor residence [2]. Studies of biomass devolatilization indicate that particle size and reaction temperature strongly influence devolatilization time, but the resulting correlations suggest that devolatilization is over in 1-2 seconds [6]. Thus, the general impression appears to be that devolatilization is almost instantaneous and the overall reaction time is determined by the time it takes to quench vapors released during devolatilization. Once devolatilization of biomass particles is complete, it is thought that vapors should be rapidly separated from the residual

solids and cooled to prevent reactions that promote production of secondary char and light gases [2]. Secondary reactions of vapors are thought to be influenced by vapor concentration and temperature and the presence of char.

Accordingly, most pyrolyzers are designed to rapidly heat the biomass to optimal pyrolysis temperature, rapidly separate the vapor and char products, and rapidly cool the vapors. Relatively little attention has been given to the time history of the char product. This thesis explores the effect of solids heating time on the production of bio-oil.

### Thesis Organization

Chapter two details the research related to the effects of temperature, sweep gas flow, and particle heating time on fast pyrolysis of red oak in a free fall reactor. Chapter three reviews the work completed in relation to the effect of solids heating time on bio-oil yield. Chapter four summarizes all of the conclusions drawn from the research and highlights areas for further work. References for each chapter's contents are given at the end of each individual chapter.

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## CHAPTER 2

EFFECTS OF TEMPERATURE, SWEEP GAS FLOW AND PARTICLE HEATING TIME ON  
FAST PYROLYSIS OF RED OAK IN A FREE FALL REACTOR

## Abstract

The focus of this work is to study the effects of varying temperatures, sweep gas flow rates, and particle heating times on the products of the fast pyrolysis of red oak in a free fall reactor. Thirty-five tests were completed as part of a design of experiments to acquire a better understanding of the effects of these variables on pyrolysis products. The range of reactor temperatures varied from 400°C – 800°C, sweep gas flow rates varied from 2 L/min to 18 L/min, and particle heating times varied from 0.58 seconds to 2.25 seconds.

The collected bio-oil, char, and non-condensable gas samples were analyzed to understand the chemical composition of these products. Using the results of this analysis, a linear regression model was generated to better understand the relationship between the dependent and independent variables.

From this analysis, the conclusion can be made that particle heating time is an important variable in optimizing bio-oil yields, and maximum yields would be achieved with particle heating time greater than two seconds.

## Introduction

The efficient production of fuels from renewable sources is becoming increasingly important as concerns rise over the security of our current fuel sources. Biomass feedstocks, such as forestry residues, agricultural crops and their residues, and municipal solid waste have great potential to meet this demand because of the diversity of solid, liquid, and gaseous fuel products that can be created from them [1]. There are several pathways for producing biofuels from biomass. Recent techno-economic analysis of these possible pathways indicates that fast pyrolysis is among the least capital intensive and most cost effective pathways. Fast pyrolysis is the rapid heating of biomass in the absence of oxygen to produce predominately liquid product (bio-oil) [2-9].

The goal of this study was to develop a statistical model of the effects of pyrolysis temperature, sweep gas volume, and particle heating time on bio-oil yield. Particle heating time was hypothesized to be an important variable effecting yields and concentration of products. It is believed that the volatilization of biomass was not occurring instantly and that a length of time longer than two seconds is required to completely break down and volatilize the biomass.

A free fall or drop tube reactor was selected for this study because of their simple design and ease of operation in a variety of tested applications. Free fall reactors have been used extensively in the desulfurization of coal to reduce sulfur emissions. [10-14]. Free fall reactors have also been used in the pyrolysis of legume straw, apricot stone, rapeseed, olive waste, wheat straw, bagasse, tobacco stalk, and many different types of wood. In general, biomass is fed at the top of the vertical reactor tube at a specific rate. The biomass flows through the reactor via gravitational force and is heated by radiation and convection from the walls of the reactor tube.

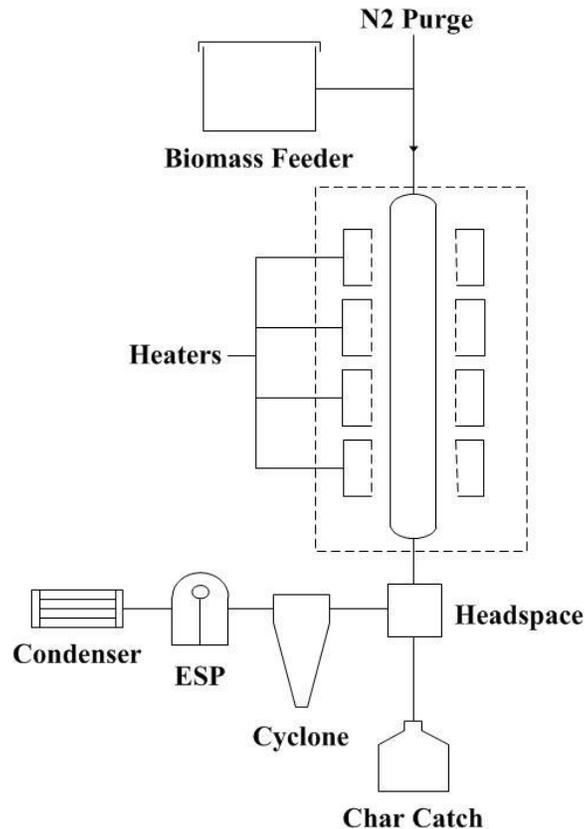
Many preceding studies have focused on this variation of feedstocks under typical pyrolysis conditions. More recently, researchers have focused on the relationship between bio-oil yield and temperature, particle size, and sweep gas flowrate. In these studies researchers found that conditions of around 575°C with particle sizes of 300um to 500um are near optimum, with bio-oil yields of up to 75% of the feedstock mass. Researchers have found sweep gas to have minimal effects on overall results. These pyrolysis studies have not addressed the relationship between pyrolysis products and the solids heating time [15-21].

Biomass studies have utilized reactor diameters ranging from 0.012 m up to 0.036 m with reactor lengths ranging from 0.7 m to 2.9 m. Reactor wall temperatures in these studies have ranged from 350°C to 960°C. Feed rates have also widely varied, from as little as 12 g/h up to 2000 g/h. These systems were all semi-continuous in operation: they did not allow for continuous removal of char, limiting duration of tests to only 30-120 minutes [10-21].

### Experimental Methodology

The reactor system used in this study, shown in Figure 1, was designed to allow for continuous operation. Biomass was fed into the system using an Acrison BDFM volumetric feeder with the ability to meter feedstock at rates ranging from 0.25 kg/hr to 2 kg/hr. The reactor was 3.05 m tall, designed for 2.5 seconds of free-fall time for the biomass particles used in the experiments in the absence of sweep gas. The reactor was built from 1¼" Schedule 40 316L stainless steel pipe providing an inside diameter of 0.035 m. The drop tube portion of the reactor was heated using Watlow high temperature ceramic radiative heaters while the remaining parts of the reactor were heated using high temperature heat tapes. All heaters and exposed surfaces were insulated using high temperature ceramic insulation.

Temperature was controlled via manipulation of the heater set points. Sweep gas volumetric flow rate was manipulated by altering the amount of sweep gas introduced at the top of the reactor. Particle heating time was mainly a function of the heated length of the reactor although the volumetric flow rate of sweep gas also affected particle heating time.



**Figure 1: Free Fall Process Flow Diagram.**

The liquid collection system consisted of the cold quench system 2.2. The cold quench system is capable of cooling reactor vapors from reactor temperature to 120 °C in less than 1 second. After cooling vapors pass through an electrostatic precipitator held at 15 KV by a Glassman high voltage controller. Vapors were then passed through a condenser cyclone maintained at 0 °C then through a tube shell condenser maintained at 0 °C. Vapors then passed through a glass wool filter to remove an remaining aerosols followed by a desiccant filter to

remove any residual water vapor. All of the liquid products were funneled into 1 liter Nalgene bottles where they were stored until ready for analysis.

Red oak was selected as the feedstock for these trials because of its commercial availability as a relatively uniform material. The wood was ground and sieved to a particle size range of 250 to 850  $\mu\text{m}$ . Nitrogen was used as inert sweep gas through the reactor. A feed rate of 1.0 kg/h was assumed to be a reliable feed rate for the system based on previous work. Solid residues from pyrolysis were augered from the bottom of the reactor at 600 rpm, limiting solids heating time in the bottom of the reactor to 10 s.

Experiments were performed for a minimum of 90 minutes. Solids and liquids were collected during the entire duration of the test and for at least 5 minutes after biomass was stopped feeding. Non-condensable gases were measured during steady state conditions usually achieved after 5 minutes of run time. Solids were collected, cooled, and removed from the reactor by means of a char auger. The system was able to achieve mass closures of at least 95%.

The variables investigated in this study and their respective ranges are found in Table 1.

**Table 1: Variables and Ranges Tested.**

Feedrate	0.25 - 2 kg/h
Sweep Gas Flow Rate	0-60 L/min
Heated Reactor Length	0-3 Meters
Reactor Wall Temperature	20- 1050 °C

A design of experiments was performed using a Response Surface Methodology in order to produce a thirty-eight point central composite design. Ten additional tests were added at points of interest and extremes to acquire a better understanding of the relationship of the inputs

and outputs of the system, bringing the total number of tests to thirty-five. After exiting the bottom of the vertical reactor, the majority of the char particles (>99% by mass) disengage from the sweep gas and are collected by the char auger. This continuous removal of solid residue allowed long duration tests and measurable char residence times. The auger tube is water-cooled, helping to rapidly cool particles that are large enough to fall to the bottom of the reactor. The produced vapors, sweep gas, and any entrained solids exit near the bottom of the reactor and pass through a cyclone to remove most of the remaining solids. The sweep gas and produced vapors then enter a novel cold quench system where the vapors and aerosols are quickly cooled from 550°C to 120°C and enter an electrostatic precipitator (ESP) held at a voltage of 15 kV. The walls of this ESP are heated to 150°C to reduce the viscosity of the condensed bio-oil, facilitating its downward flow into a collection bottle. The material collected at this point is designated as stage fraction one (SF 1). Uncondensed vapors next enter a condenser cyclone, consisting of a cyclone with a cooling jacket held at 0°C. Remaining vapors then enter a tube condenser also held by a chiller at 0°C. Products collected in the two condensers have proven to be identical and are mixed into what is referred to as stage fraction 2 (SF 2). The vapor stream is then passed through a glass wool filter removing any remaining aerosols and then onto a desiccant filter to collect any water vapor remaining in the vapor stream. The volumetric flow of non-condensable gases (NCGs) is measured with a Ritter TG25/4 wet test meter (WTM). A slip stream is pulled and analyzed by a micro gas chromatograph (micro GC) while the rest of the gases are vented.

### Solid Products Analysis

Solid products were analyzed using proximate analysis performed via thermo-gravimetric analysis (TGA) on a Metler Toledo TGA/DSC1 STAR System. Samples were weighed to 20 mg +/- 5mg into a ceramic crucible and then loaded into the TGA pan. Samples were heated in a

stream of pure nitrogen to 105°C and held for 48 minutes to drive off moisture in the sample. Sample mass was recorded before heating to 950°C, where it was held for 100 minutes to drive off any volatiles in the sample. The mass was once again recorded; the mass lost in this portion was compared to the original mass of the sample giving the mass of the volatiles that were still in the bio-char sample. At this point, the nitrogen sweep gas was switched to air and the sample held for an additional 30 minutes to burn off any fixed carbon in the sample. The remaining residue at the end of this procedure was assumed to be ash.

Each sample was tested in duplicate and the average of the two samples was recorded. This figure was then multiplied by the percent yield of the bio-char in order to compare these figures to the original weight of the biomass before pyrolysis had occurred.

Ultimate analysis was performed with a Varian MIRCOCube. This instrument analyzed the mass fractions of carbon, nitrogen, hydrogen, and sulfur. Each sample was tested in triplicate and the average of the three tests was recorded. This figure was multiplied by the bio-char yield to present the results on a biomass weight basis.

### Bio-oil Analysis

Water soluble sugars were analyzed using a Dionex UltiMate 3000 High-Performance Liquid Chromatograph (HPLC). Sugars quantified by this test included: cellobiose, cellobiosan, xylose, galactose, mannose and levoglucosan. 500 mg of bio-oil was measured into a centrifuge tube and 5 mL of deionized water added. The centrifuge tube was then heated and mixed by vortexing. After it was sufficiently mixed, a sample was taken from the centrifuge tube and filtered into a sample vial. This vial was then analyzed twice and the average of the two numbers

taken as the actual value. This was done once for each stage fraction and the resulting mass concentrations are multiplied by the stage fraction distribution of the bio-oil. These results were then combined to put them on a bio-oil basis and then multiplied by the bio-oil yield to calculate the water soluble sugar yield on a biomass basis.

Total sugars were analyzed using a Dionex UltiMate 3000 High-performance liquid chromatograph. The sugars that were quantified were cellobiose, cellobiosan, glucose, xylose, sorbitol and levoglucosan. 60 mg of bio-oil was measured into a centrifuge tube and then 6 mL of 400 mM sulfuric acid and a stir bar was added. The centrifuge tube was then heated to 125°C and mixed via the stir bar for 44 minutes. The samples were then allowed to cool and a sample was taken from the centrifuge tube to be filtered into a sample vial. This vial was then analyzed twice and the average of the two numbers taken as the actual value. This was done twice for each stage fraction and the resulting mass concentrations are multiplied by the stage fraction distribution of the bio-oil. These results were then combined to put them on a bio-oil basis and then multiplied by the bio-oil yield to calculate the total sugar yield on a biomass basis.

Acids were analyzed using a Dionex Ion Chromatography (IC) System-3000. The acids that were quantified include: glycolate, formate, acetate, and propionate. 100 mg of bio-oil was measured into a centrifuge tube and 1.5 mg of methanol and 6 mL of deionized water were added. The centrifuge tube was then heated and mixed by vortexing. After it was sufficiently mixed a sample was taken from the centrifuge tube and then filtered into a sample vial. This vial was then analyzed twice and the average of the two readings was recorded. This was done once for each stage fraction and the resulting mass concentrations are then multiplied by the stage fraction distribution. These were then added together to put them on a bio-oil basis and multiplied by the bio-oil yield to calculate the acid yield on a biomass basis.

Moisture analysis was performed with a KEM MKS-500 Karl-Fischer Moisture Titrator. Moisture analysis was performed only on SF2 bio-oil, as SF1 was collected at 120°C and therefore contained an unmeasurably small amount of moisture. The percentage of moisture found in the SF2 samples was then multiplied by the stage fraction distribution. This figure was then multiplied by the bio-oil yield to convert moisture content to a biomass basis.

Ultimate analysis of the bio-oil was performed with a Varian MIRCO Cube. This instrument provided mass fractions of carbon, nitrogen, hydrogen, and sulfur. Samples of each stage fraction were tested in triplicate and the average of the three tests recorded. This average was multiplied by the stage fraction distribution and the bio-oil yield to convert the analysis on a biomass basis.

JMP statistical software was used to model the effects of the changing variables on the pyrolysis products. Independent variables used in the modeling included wall temperature set point, volumetric sweep gas, and particle heating time. Particle heating time was calculated by dividing the heated length of the reactor by the average particle velocity. The average particle velocity was calculated by adding the sweep gas velocity normalized to the reactor temperature and the average particle terminal velocity. These independent variables and their dependent variables were then analyzed in JMP using a standard least square fit.

## Results and Discussion

Different model effects were tested to identify the model that best reflected the bio-oil yield data. First, second, and third order polynomial fits were tested with varying orders of cross terms as shown in Table 2. The best fit was found by using a 3<sup>rd</sup> order polynomial with 1<sup>st</sup> order

cross terms. However, this was only marginally better than a 2<sup>nd</sup> order polynomial with 1<sup>st</sup> order cross terms. Due to the increased complexity required for the 3<sup>rd</sup> order and only a slight increase in accuracy was observed, a 2<sup>nd</sup> order polynomial fit with 1<sup>st</sup> order cross terms was selected to represent the data. This equation is shown in Eq. 1:

$$Y = A + BX_1 + CX_2 + DX_3 + EX_1^2 + FX_2^2 + GX_3^2 + HX_1X_2 + IX_2X_3 + JX_1X_3 \quad \text{Eq 1}$$

where  $X_1$  being reactor wall temperature,  $X_2$  being reactor sweep gas flowrate, and  $X_3$  being reactor heated length. JMP statistical software was used to generate a governing equation for each of the chosen dependent variables. The variables as well as their corresponding correlations are shown in Table 3.

**Table 2: Resulting Fit of Different Models.**

Variable Order	1 <sup>st</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	2 <sup>nd</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	3 <sup>rd</sup>	3 <sup>rd</sup>
Cross Term								
Polynomial Order	None	1 <sup>st</sup>	None	1 <sup>st</sup>	2 <sup>nd</sup>	None	1 <sup>st</sup>	2 <sup>nd</sup>
Root Mean Squared Value	0.54	0.67	0.75	0.86	0.86	0.75	0.86	0.86
Root Mean Square Error	0.077	0.069	0.061	0.048	0.049	0.063	0.050	0.051
F Ratio (Variance)	12.20	9.48	13.67	16.74	14.60	8.53	11.63	10.27
F Ratio (Lack of Fit)	243.6	195.4	150.7	95.2	98.7	164.5	104.8	110.1

Models that were simply dependent on reactor operation and weighing components produced the most accurate models. Those that were comprised of many steps of analysis produced models with less accuracy due to the compounding of error. The accuracy of these models is still dependable, although less conclusive.

**Table 3: Dependent Variable Correlation to Constructed Model**

Dependent Variable	Root Mean Squared Value	Root Mean Squared Error	Lower Range of Values	Upper Range of Values
Liquid Yield	0.86	0.049	9.78%	56.70%
Solid Yield	0.90	0.072	6.81%	86.64%
NCG Yield	0.75	0.068	3.58%	52.37%
Volatiles Remaining	0.91	0.062	1.96%	72.27%
Theoretical Liquid Yield	0.77	0.058	42.9%	83.9%
Carbon Into Liquid	0.85	0.024	0.64%	47.89%
Carbon Left in Solid	0.87	0.039	11.12%	92.42%
Water Production	0.73	0.017	9.17%	24.44%
Acid Production	0.69	0.006	0.23%	4.85%
WSS Production	0.72	0.017	0.10%	8.92%
AH Production	0.78	0.013	0.23%	9.54%

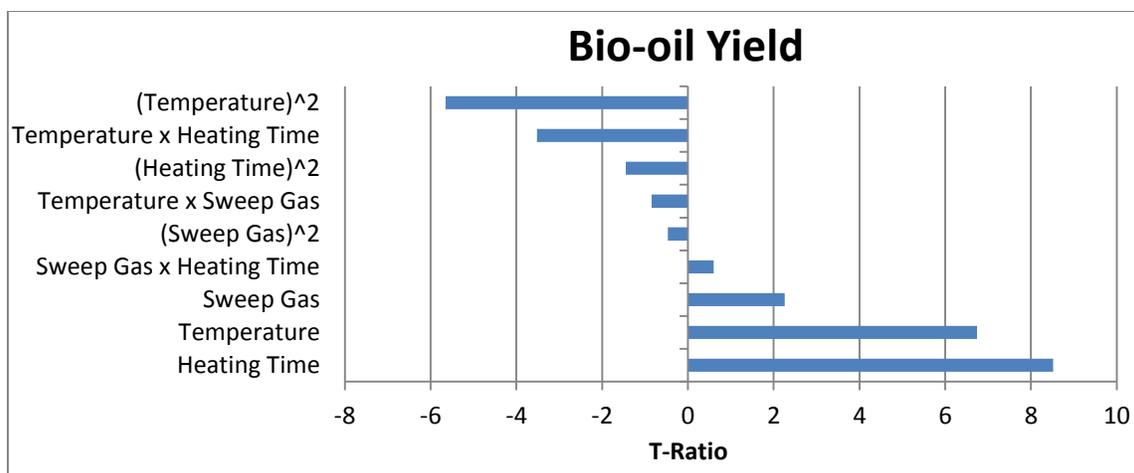
Resulting T-Values were calculated using JMP statistical software and are displayed in Figure 2. Variables with positive T-ratios increased bio-oil yield while those with negative ratios

decrease yield. The magnitude of the T-ratio proves the effect of each variable; those variables with a large T-ratio have proven to have the greatest effect.

Particle heating time, shown in Figure 2 as “Heating Time”, had the greatest effect on increasing bio-oil yields, proving that the longer biomass is heated, the more of its mass is converted into liquid products. Due to the constraints of reactor length, an effective mean particle heating time of 2.25 seconds was the longest heating time obtained. The graph of the bio-oil yield with respect to heat time in Figure 3 suggests that at longer times a maximum oil yield may occur, but it was not reached within the temperature range tested. Heating time squared only proved to have a small negative impact in liquid yields, thus suggesting a very long heating time would have to be reached before the liquid yields would be negatively impacted.

Reactor wall temperature also proved to have a large positive effect on liquid yield. As temperature increases, more mass shifts from solid products to condensable volatile products. However, temperature squared resulted in having the largest negative effect on liquid yield, most likely caused by the conversion of volatile condensable products into non-condensable gases. This data proves that optimization of reactor temperature is most important as it can have one of the largest positive effects on production of liquid, but it can also most negatively impact oil yields as well.

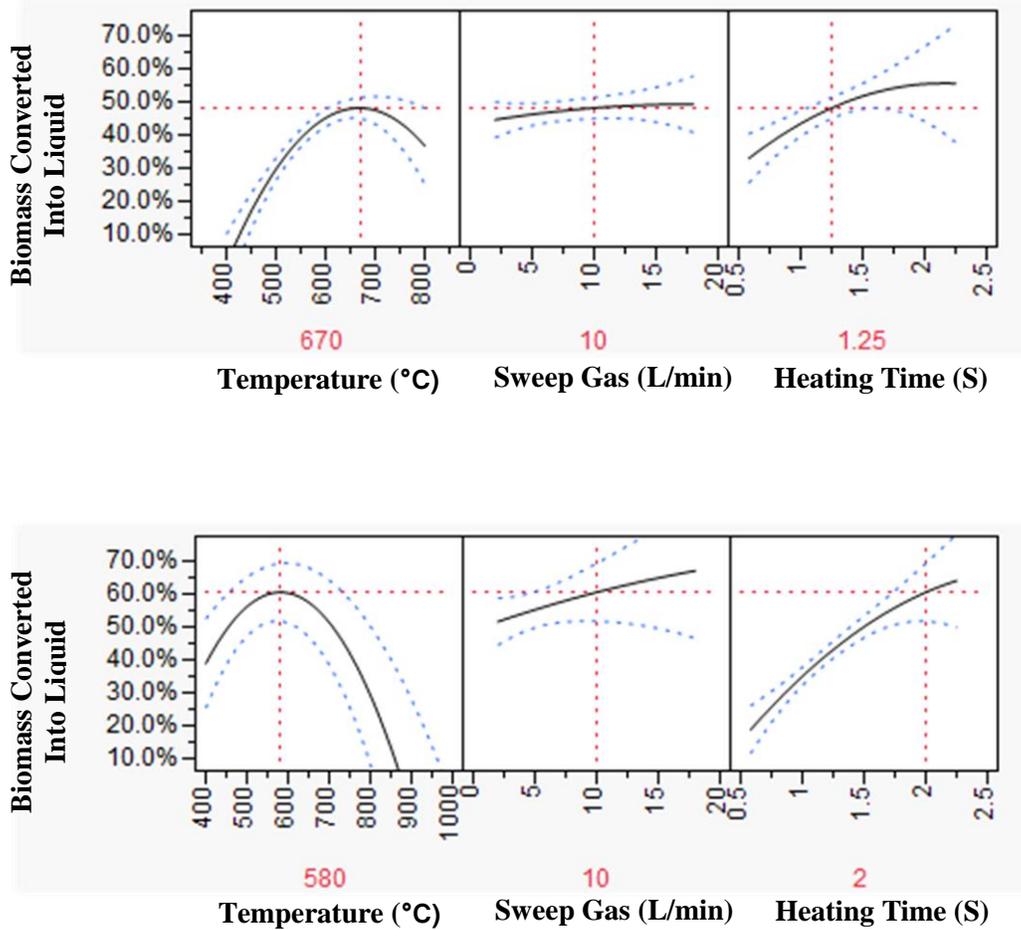
Sweep gas proved to have a slightly positive impact on liquid yields. This can be attributed to increased vapor dilution and prevention of tertiary reactions. The slight negative impact of sweep gas squared can be attributed to the reactors inability to heat extremely large amounts of sweep gas.



**Figure 2: Bio-oil Yield Sorted Parameter Estimates.**

Reactor temperature was also an important variable influencing bio-oil yield. Each wall temperature tested had its own optimal heating length to achieve maximum liquid yields. Two of these situations are illustrated in Figure 3. The top set of graphs in Figure 3 shows a heating time of 1.25 seconds, and a corresponding optimum reactor wall temperature of 670°C. The blue dotted lines are showing the 95% confidence interval based on the data points used to create the model. In comparison the optimum wall temperature was 580°C for heating time of 2 seconds. This reactor wall temperature of 580°C is close to optimum found in other free fall fast pyrolysis research [21].

A particle heating time of 2.25 seconds was the maximum obtained in this study. This was limited to the 3.05 meters of reactor and the free fall time of the particles passing through it. Even at this heating time particles, could not be called completely pyrolyzed. Modeling of the heating time shows us the liquid yield has not been optimized in this study, leading to the understanding that particles require a heating time longer than 2.25 seconds in the free fall reactor.



**Figure 3: Bio-oil Yield of Different Heating Times.**

### Conclusion

These experiments have proven that there exists an optimal particle heating time in the free fall reactor which is longer than 2 seconds; however, the optimal heating time was not found within the realms of the performed experiments. Ultimately, our study has proven reaction temperature and reaction duration as the key variables that must be optimized in order to produce the maximum amount of liquid products without destroying these desirable liquid products in the process.

More testing must be completed in each of these categories to more fully understand the optimal fast pyrolysis conditions. As was noted in the results not all of the maximums for the independent variables were identified in this study, the most important of those being the particle heating time. Given the constraints of the facilities in which the reactor is located, optimization is not currently possible on our system. Further work should explore the relationship between the variables tested and other variables such as particle size and solids heating time on the freefall system. In addition, modifications to the reactor to allow for pre-heating of sweep gas may reduce error associated with increased thermal leading from large amount of sweep gas.

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## CHAPTER 3

EFFECT OF SOLIDS HEATING TIME ON BIO-OIL YIELDS IN A FREE FALL FAST  
PYROLYSIS REACTOR

## Abstract

In this study, two solids collection methods were tested in a free fall reactor in a total of six configurations to better understand the importance of total solids heating time to increased bio oil yields. All other process variables were held constant during these tests. Reactor wall temperature was held at 550°C, sweep gas flowrate was a constant 18 L/min, and the heated reactor length was 2.77m, allowing for a particle residence time of approximately 1.4 seconds. The products of these trials were analyzed to better understand any chemical reactions occurring after the particles leave the heated portion of the reactor. Analysis concluded that particles were continuing to pyrolyze for more than 40 seconds after leaving the heated portion of the reactor. Analysis also concluded that all components of biomass continued to devolatilize for times longer than 40 seconds.

## Introduction

Fast pyrolysis is the rapid heating, followed by rapid cooling, of a finely ground biomass feedstock in the absence of oxygen to produce predominately liquid product that can ideally be a drop in replacement for current liquid fuel applications such as heat, power, transportation fuels,

and specialty chemicals. Techno-economic analyses of a variety of biomass conversion pathways indicate that fast pyrolysis is among the most cost effective of these technologies [1-9.]

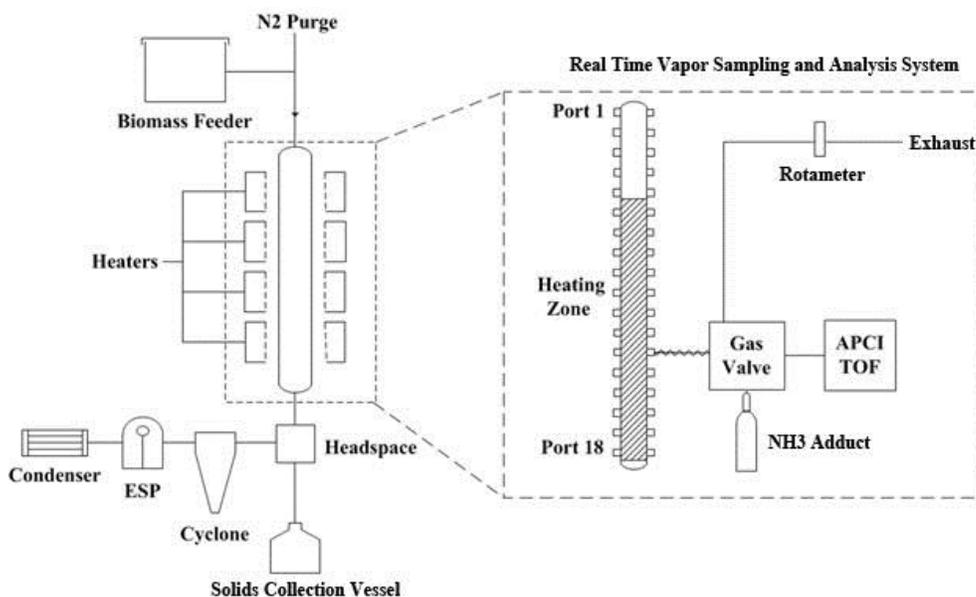
Fast pyrolysis is often thought to be essentially complete after just a few seconds, although this assumption has not been explicitly investigated [10]. Fluidized bed and auger reactors, the two most common configurations for fast pyrolyzer, do not lend themselves to measurements of devolatilization times for pyrolyzing biomass. Typically biomass remains in a fluidized bed until it is converted to char sufficiently fine to be elutriated from the reactor [11]. Auger reactors move biomass through the pyrolysis zone at rates that are much longer than the one to two seconds usually assumed for completion of fast pyrolysis [12]. Micropyrolyzer systems are usually operated in conjunction with a gas chromatograph–mass spectrometer (GC-MS), making dynamic measurements of pyrolysis impractical. Thus, an investigation of biomass devolatilization times during fast pyrolysis requires a reactor that allows some level of control over solids heating time after it has been rapidly heated to pyrolysis temperature.

This study investigates fast pyrolysis in a free-fall reactor, designed to rapidly heat biomass to the desired pyrolysis temperature as it falls through a long, vertical column followed by controlled solids heating time in a heated catch pot at the bottom of the column. We have found that biomass continues to pyrolyze in the heated catch pot, contrary to our original expectation that essentially devolatilized biomass (char) would exit the bottom of the column [13]. The present study is to understand the effect of solids heating time on bio-oil yields from pyrolyzing biomass.

## Experimental Methodology

## Free Fall Reactor

The reactor system used in this study, shown in Figure 1, was designed to allow for continuous operation. Biomass was fed into the system using an Acrison BDFM volumetric feeder with the ability to meter feedstock at rates ranging from 0.25 kg/hr to 2 kg/hr. The reactor was 3.05 m tall, designed for 2.5 seconds of free-fall time for the biomass particles used in the experiments in the absence of sweep gas. The reactor was built from 1¼" Schedule 40 316L stainless steel pipe providing an inside diameter of 0.035 m. The drop tube portion of the reactor was heated using Watlow high temperature ceramic radiative heaters while the remaining parts of the reactor were heated using high temperature heat tapes. All heaters and exposed surfaces were insulated using high temperature ceramic insulation.



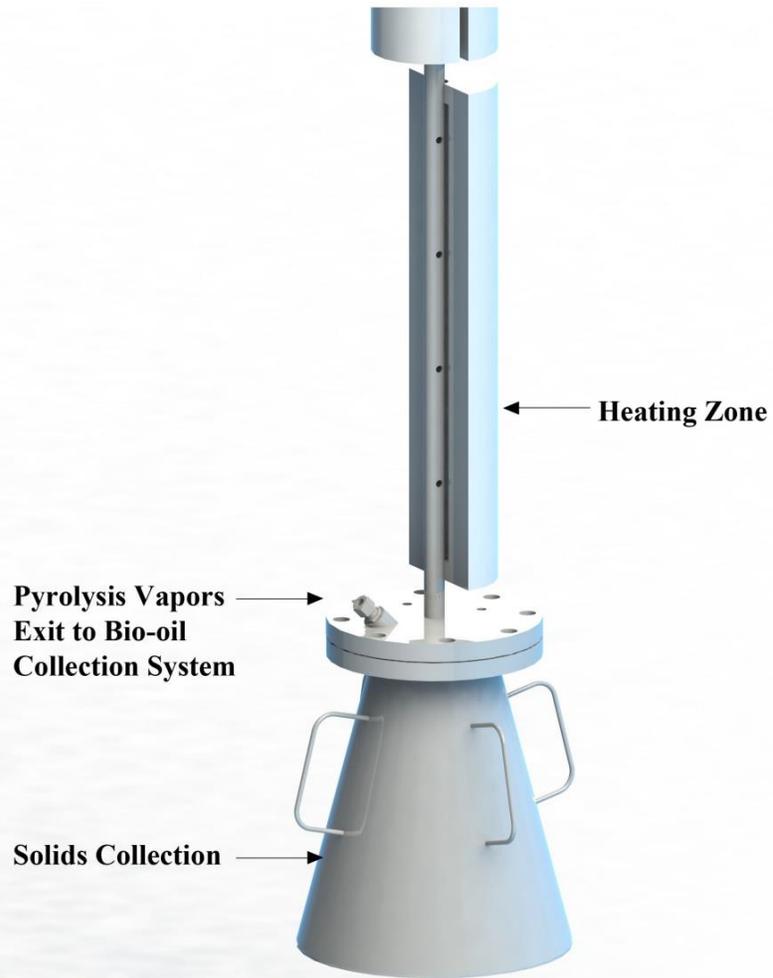
**Figure 1: Schematic of experimental apparatus including pyrolysis reactor, solids collection, and gas analysis.**

Temperature was controlled via manipulation of the heater set points. Sweep gas volumetric flow rate was manipulated by altering the amount of sweep gas introduced at the top of the reactor. Particle heating time was mainly a function of the heated length of the reactor and the time that the solids remained heated in the system.

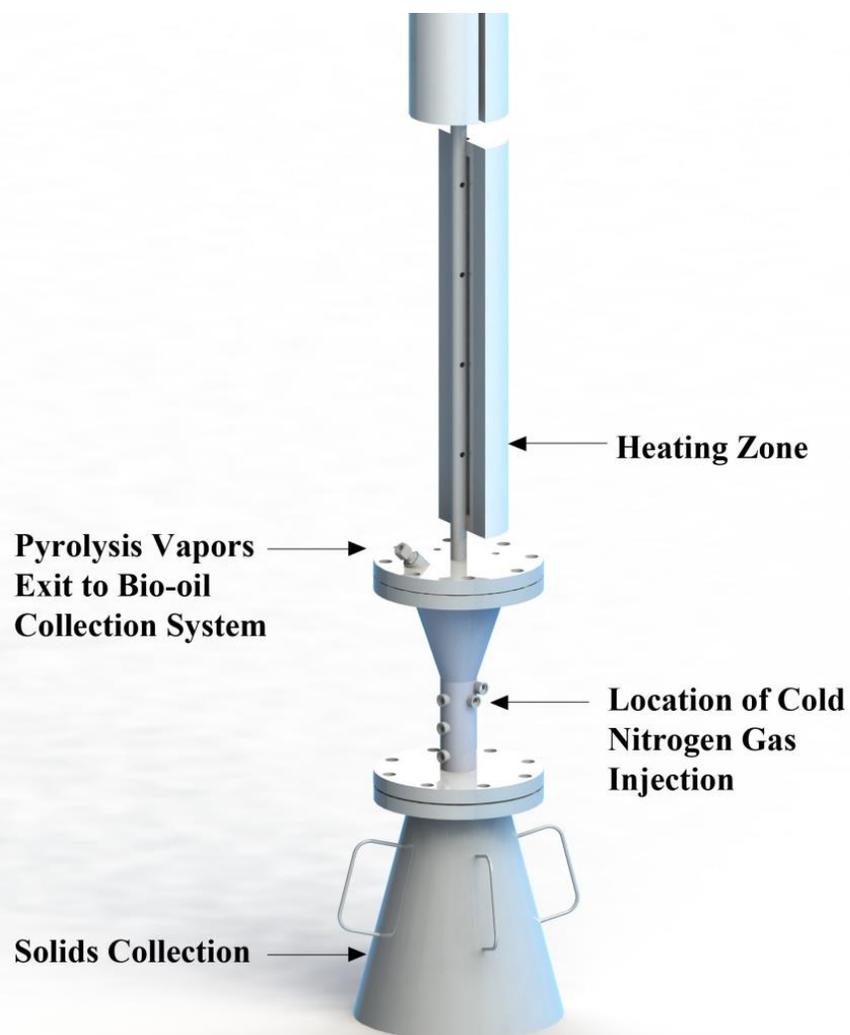
### Solids Collection Methods

Two methods were used to capture solids exiting the bottom of the vertical heating zone of the reactor. The static solids catch method simply allows the solid particles to accumulate in a catch pot for the duration of the test as illustrated in Figure 2, a method previously used by Ellens [13] and Li [14]. In some experiments the catch pot was heat traced to the pyrolysis temperature allowing the collected solids to continue to pyrolyze, giving a solids heating time that was effectively infinite. In other experiments a conical quench section was interposed between the bottom of the vertical column and the catch pot, shown in Figure 3. At the bottom of the quench section, cold nitrogen gas at approximately  $-196^{\circ}\text{C}$  was injected to quickly cool the solids and prevent further devolatilization. In this case, the solids heating time at the reactor temperature was essentially the free-fall time in the vertical column, about 2 seconds.

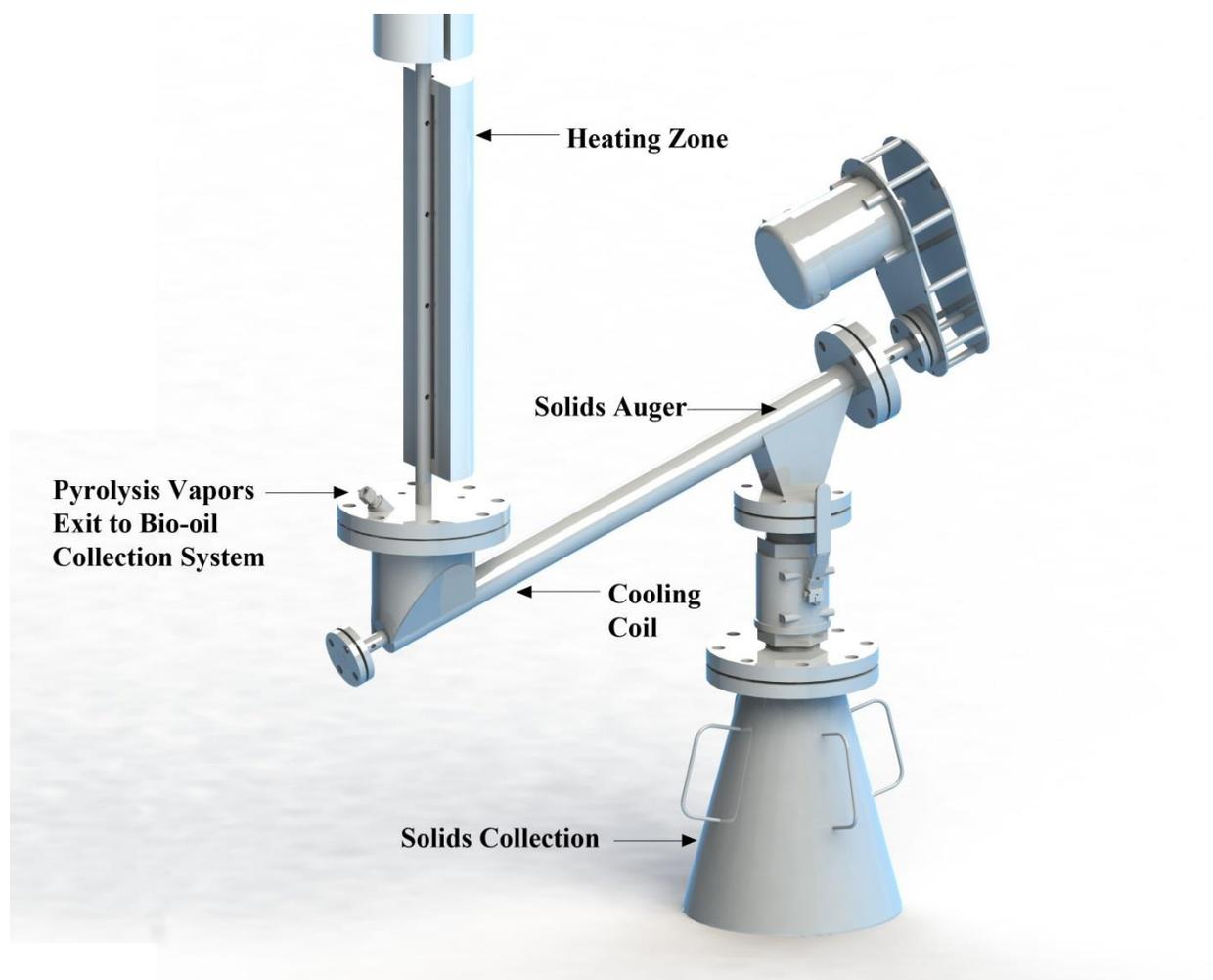
An alternative solids collection system allowed control of solids heating time at the bottom of the vertical reactor. This was accomplished by interposing a cooled auger between the bottom of the heated vertical reactor and the unheated catch pot. By controlling the rotational speed of the auger, the heating time of the solids could be controlled, ranging from five to forty seconds. This configuration is illustrated in Figure 4.



**Figure 2: Static solids collection system with heated catch pot.**



**Figure 3: Static solids collection system with interposed conical section to allow cold nitrogen gas injection for rapid solids quenching.**



**Figure 4: Conveyed solids collection system with interposed auger to allow control of solids heating time.**

#### Experimental Trials and Product Analysis

Six reactor experiments were performed to understand the relationship between the yields of pyrolysis products from lignocellulosic biomass and the solids heated time (See Table 1). The biomass chosen for these experiments was ground red oak sieved to 250-850  $\mu\text{m}$  (average of 500  $\mu\text{m}$ ). One experiment was conducted with both the heated and cooled static solids catch systems

and four tests were performed using the conveyed solids catch system operating at different auger speeds.

**Table 1: Experiment conditions**

<b>Solids Collection Method</b>	<b>Operation</b>	<b>Solids Heating Time (Seconds)</b>
Static solids catch	Cooled	1.4
Conveyed solids catch	1200 RPM	6.4
Conveyed solids catch	600 RPM	11
Conveyed solids catch	250 RPM	21
Conveyed solids catch	100 RPM	41
Static solids catch	Heated	>2000

Pyrolysis operating conditions were identical for the six tests, the only variable altered in the tests being the particle heating time. The lower 2.77 m of the 3.05 m reactor was heated to 550°C wall temperature. Nitrogen gas at a flow rate of 18 L/min was used as a sweep gas. The feedstock was injected into the reactor 3.05 meters above the exit of the heated column. This produced a particle residence time in the heated section of 1.4 s [11]. These conditions produced a vapor temperature of 542° C and an average particle temperature of 509°C. This measurement was acquired by using a system of thermocouples that measured the average temperature of the solid particles.

Pyrolysis products included the condensed phase (bio-oil), solid residue (referred to as bio-char, although it may contain unreacted biomass), and non-condensable gases. After exiting the reactor tube, the majority of the solid particles (>99% by mass) were disengaged from the

sweep gas and fell into the catch pot. The remainder of the char along with produced vapors and sweep gas passed through a gas cyclone where >99% of the entrained char was removed. The sweep gas and produced vapors then entered a quench system where they were rapidly cooled by mixing the produced vapors with cold nitrogen gas cooled by a liquid nitrogen heat exchanger. The cooled vapors entered an electrostatic precipitator (ESP) operated at 15 kV. The walls of the ESP were maintained at 150°C to facilitate the flow of bio-oil into a collection bottle. The liquid collected at this stage is known as Stage Fraction 1 (SF1). Vapors that did not condense in SF1 were passed into a cyclone surrounded by a coolant jacket followed by a tube condenser, both held at 0°C using a chiller. This process removed the majority of condensable products, referred to as SF2. The vapor stream passed through a glass wool filter to remove any remaining aerosols followed by a desiccant filter to collect residual moisture remaining in the gas stream. At this point the volumetric flow of the nitrogen used as sweep gas or quenching gas and non-condensable gases (NCG) produced during pyrolysis was measured by a wet test meter (WTM). A slip stream of this exit flow was analyzed by a micro gas chromatograph (micro GC) while the rest of the gases were vented.

The mass of the solid and liquid products were determined gravimetrically. The mass of NCG was calculated based on the average density of the gas, excluding nitrogen gas used for sweep and quenching, as determined from the micro GC data and the average volumetric flow rate measured by the WTM.

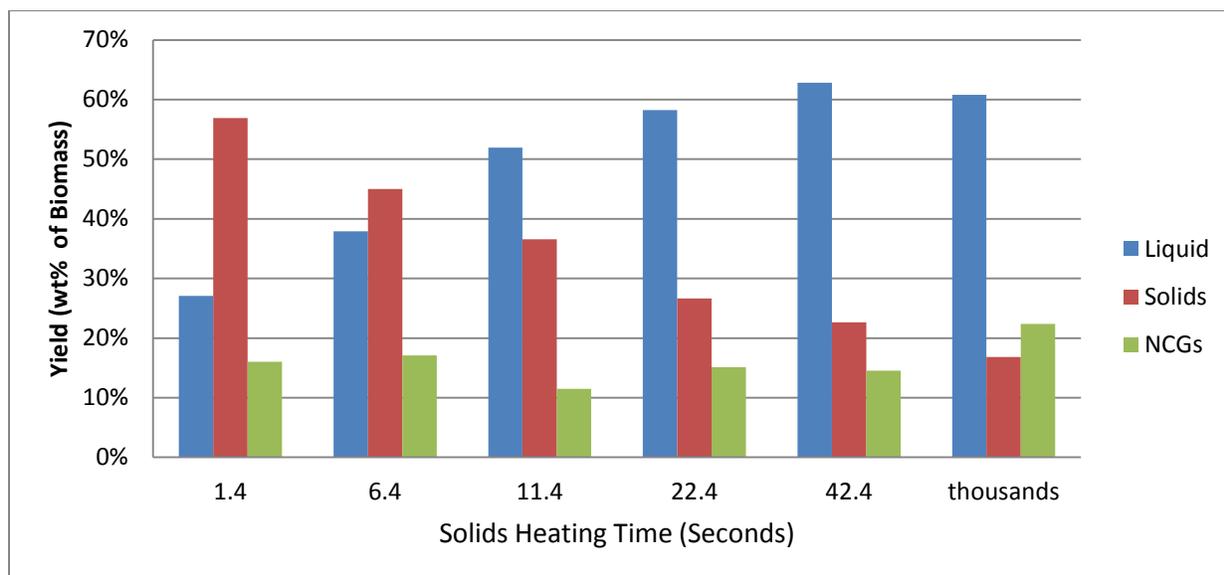
Proximate analysis of the solid products was performed using a Thermo-gravimetric analysis (TGA) on a Metler Toledo TGA/DSC1 STAR system. Each sample was weighed into a ceramic crucible and loaded into the instrument. Each sample weighed approximately 20 mg, with a variability of less than 5 mg. Each sample was heated in nitrogen gas to 105°C and held for 48

minutes to drive off any moisture in the sample. The mass was recorded before heating the sample to 950°C and held for 100 minutes to drive off any volatiles in the sample. The mass loss equaled the volatiles content of the biochar. The nitrogen sweep gas was replaced with air and the sample held for an additional 30 minutes to burn off any fixed carbon in the sample. The remaining residue equaled the ash content of the biochar. Each sample was tested in duplicate. The bio-oil was analyzed for water-soluble sugars and carboxylic acids. Water-soluble sugars were analyzed using a Dionex UltiMate 3000 High-Performance Liquid Chromatograph (HPLC). Sugars quantified include cellobiose, cellobiosan, xylose, galactose, mannose and levoglucosan. 500mg of bio-oil were measured into a centrifuge tube with 5 mL of deionized water. The centrifuge tube was heated to 50° C and vortexed to mix the contents. The sample was then transferred to a sample vial. This vial was then analyzed twice via HPLC. This was repeated for each stage fraction of bio-oil and reported on a biomass basis.

Acids were analyzed using a Dionex Ion Chromatography (IC) Model 3000. Acids quantified included: glycolate, formate, acetate, and propionate. One hundred milligrams of bio-oil was measured into a centrifuge tube and 1.5 mg of methanol and 6 mL of deionized water added. The centrifuge tube was heated to 50° C and vortexed to mix the contents. After it was sufficiently mixed a sample was taken from the centrifuge tube and filtered into a sample vial. This vial was analyzed twice with the IC. This was repeated for each stage fraction and reported on a biomass basis.

## Results and Discussion

Yields for liquid, solids, and NGC products for the six experiments are shown in Figure 8. Liquid yields ranged from 27 wt% to 63 wt%. Liquid yield increased as solids heating time increased. Non-condensable gases remained relatively stable around 15 wt% except for the longest solids heating time for which NGS increased to 22 wt%. On the other hand, the amount of solid residue dropped from 58 wt% to less than 20 wt% as solids heating time increased. These results indicate that so-called ‘biochar’ can continue to release volatiles recoverable as liquid well beyond the few seconds usually assumed for fast pyrolysis.

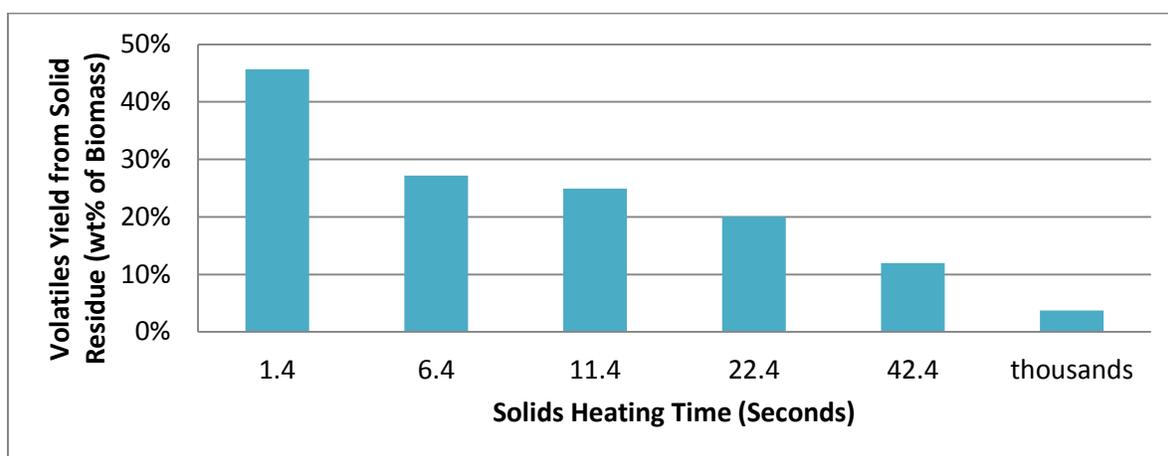


**Figure 5: Effect of solids heating time on yields of liquid, solids, and non-condensable gases (NCG) from the pyrolysis of red oak.**

The system did not have enough range of control over solids heating time to determine the optimal time for maximum liquid yield, but it is clearly greater than 40 s, much longer than some configurations of pyrolysis allow. The much longer solids heating time of the heated catch

could have actually produced a higher yield, but because of its larger volume the other methods potential liquid products could have be reduced into non-condensable gases.

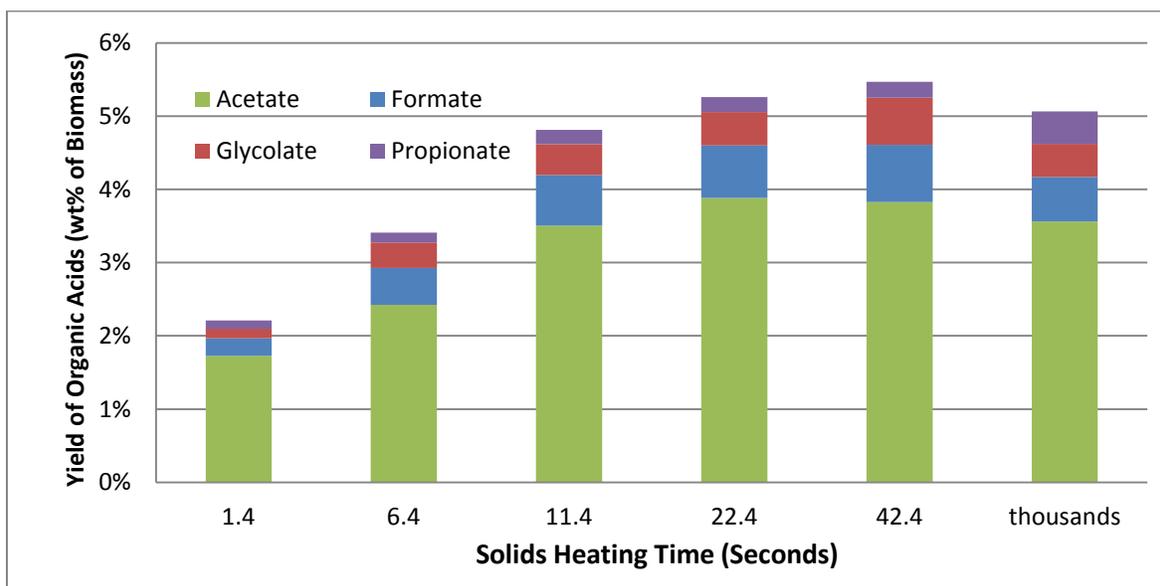
Proximate analysis of the residual solids also illustrates the potential of solids residue to release additional volatiles with increased solids heating time (Figure 9). In the cooled static char catch experiment approximately 45 wt% volatiles remained in the solids after the 1.4 s that the particles were heated while falling through the reactor. Even after 40 s of heating, the solids contained 12 wt% volatiles (very long heating times reduced this to 3 wt%.



**Figure 6: Effect of solids heating time on volatile content of residual solids for the pyrolysis of red oak.**

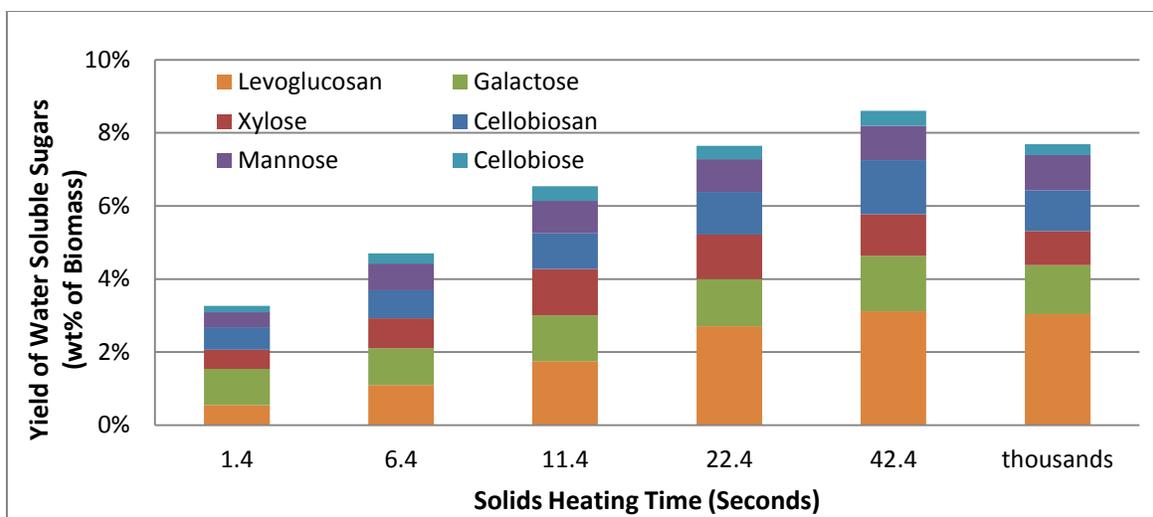
The composition of liquids as a function of solids heating time gives some indication as to the origin of the increased liquid yields. Figure 10 shows the yields of carboxylic acids as a function of solids heating time. The yield of acetic acid, which arises predominately from acetyl groups in hemicellulose, is about 1.8 wt% for the baseline case of 1.4 s solids heating time and represents about 82% of the acids [15]. Increasing solids heating time to 40 s almost doubles acetic acid yield, which suggests that even hemicellulose has not substantially pyrolyzed after

1.4 s. On the other hand, the proportionally greater increases in formate, propionate, and glycolate acids, which can derive from cellulose as well, suggests that cellulose has pyrolyzed even less than hemicellulose at the shortest heating time evaluated [16].



**Figure 7: Effect of solids heating time on yields of organic acids.**

Analysis of water soluble sugars, shown in Figure 11 also provides information as to which components of biomass contribute most to the gains in liquid yield with increasing solids heating time. Total water soluble sugars increase substantially over the solids heating times evaluated, from about 3 wt% to around 8 wt%. Of the six sugars measured, only xylose comes exclusively from hemicellulose. It increased from 0.52 wt% to around 1.14% from baseline heating time to 40 s, a 140% increase. The other sugars (levoglucosan, mannose, galactose, cellobiosan, and cellobiose), which can come from either cellulose or hemicellulose but predominately the former, showed a 180% increase over the same range [17]. These observations indicate that neither hemicellulose nor cellulose has pyrolyzed within 1.4 s but pyrolysis of the cellulose in particular benefits from longer solids heating time.



**Figure 8: Effect of solids heating time on yields of water-soluble sugars.**

Yields of phenolic oligomers, derived from lignin were not explicitly measured in these experiments. However, its contribution to increased liquid yields can be estimated from the yields of carboxylic acids and water soluble sugars, which are other major products of pyrolysis. Whereas overall yield of liquid increased by almost 35 wt%, the carboxylic acids and sugars combined account for only about one-third of this increase, suggesting that most of the increase came from pyrolysis of lignin.

## Conclusions

The results of this study indicate that solids heating time during pyrolysis of lignocellulosic biomass needs to be greater than the few seconds usually assumed and extends beyond 40 s to achieve the maximum yield of liquid product. Analysis of carboxylic acids and water soluble sugars gives evidence that even hemicellulose requires substantially longer time than usually assumed to completely pyrolyze although cellulose benefits even more from longer times. Although changes in lignin-derived compounds were not explicitly analyzed, the very large increases observed in overall liquid yields appears to derive from increased efficiency in pyrolyzing lignin as solids heating time was increased.

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## CHAPTER 4 GENERAL CONCLUSIONS

### Conclusions

Iowa State University's freefall reactor has proven to be a valuable research tool because of its ability to operate in wide ranges of many different process variables which include but are not limited to feedstock composition, biomass feedrate, sweep gas composition and volumetric flowrate, heated reactor length, reactor wall temperature, bio-oil collection methods, and solids collection methods. The ability to test these variables at such wide ranges has proven to be very helpful in identifying the relationships between the variables and final pyrolysis products.

Without these testing abilities, we would not have been able to identify the previously unforeseen impact that solids heating time had on bio-oil yields in our studies. Detailed lab analysis of our products has given us even further insight to kinetics of pyrolysis and helped us understand that by manipulating reaction temperature and duration, we are getting even closer to achieving optimum bio-oil yields. As a whole, this research has proven that that while rapidly heating particles is important, retaining particles so that they have time to break down and volatilize is just as important. An ideal solids heating time for the freefall has been confirmed to be over 40 seconds, and could possibly be as long as a minute.

### Recommendations for future work

Further research should be performed to better understand the relationship between typical process variables. This would be best performed as part of a multi-variable design of experiment (DOE). This DOE should again include solids heating time as one of the tested

variables. Particle size is another variable that would likely influence the effect of solids heating time on pyrolysis products. This variable could be tested using the char quench to identify the rate at which different particle sizes are pyrolyzing. The free fall reactor could also be fitted with a new char catch vessel to allow for continuous operation while also allowing for a longer solids heating time. Other important research could be performed to understand the effect of sweep gas composition. In research reactors nitrogen is typically utilized to provide a non-reacting environment. Sweep gas composed of the typical non-condensable gases or hydrogen gas could prove interesting and may change pyrolysis products considerably. One of the major downfalls of the freefall reactor design is its limited heat transfer ability; this could be minimized by preheating sweep gas or by utilizing enough oxygen to complete auto-thermal pyrolysis, reducing the amount of heat input into the reactor to the amount required to replace heat lost to heat loss from the reactor. Both of these would also increase the scalability of a freefall reactor.

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