SAWDUST PYROLYSIS AND PETROLEUM COKE CO2

GASIFICATION AT HIGH HEATING RATES

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Master of Science

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ABSTRACT

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Clean and efficient electricity can be generated using an Integrated Gasification Combined Cycle (IGCC). Although IGCC is typically used with coal, it can also be used to gasify other carbonaceous species like biomass and petroleum coke. It is important to understand the pyrolysis and gasification of these species in order to design commercial gasifiers and also to determine optimal conditions for operation.

High heating-rate (10^5 K/s) pyrolysis experiments were performed with biomass (sawdust) in BYU's atmospheric flat-flame burner reactor at conditions ranging from 1163 to 1433 K with particle residence times ranging from 23 to 102 ms. Volatile yields and mass release of the sawdust were measured. The measured pyrolysis yields of sawdust are believed to be similar to those that would occur in an industrial entrained-flow gasifier since biomass pyrolysis yields depend heavily on heating rate and temperature. Sawdust pyrolysis was modeled using the Chemical Percolation Devolatilization model assuming that biomass pyrolysis occurs as a weighted average of its individual components (cellulose, hemicellulose, and lignin). Thermal cracking of tar into light gas was included using a first-order kinetic model.

The pyrolysis and CO_2 gasification of petroleum coke was studied in a pressurized flatflame burner up to 15 atm for conditions where the peak temperature ranged from 1402 to 2139 K. The measured CO_2 gasification kinetics are believed to be representative of those from an entrained-flow gasifier since they were measured in similar conditions of elevated pressure and high heating rates (10^5 K/s). This is in contrast to the gasification experiments commonly seen in the literature that have been carried out at atmospheric pressure and slow particle heating rates. The apparent first-order Arrhenius kinetic parameters for the CO_2 gasification of petroleum coke were determined. From the experiments in this work, the ASTM volatiles value of petroleum coke appeared to be a good approximation of the mass release experienced during pyrolysis in all experiments performed from 1 to 15 atm. The reactivity of pet coke by CO_2 gasification exhibited strong pressure dependence.

Keywords: biomass pyrolysis, sawdust pyrolysis petroleum coke, gasification

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NOMENCLATURE

Variable	Definition
а	Acceleration
A_o	Pre-exponential factor
Α	Cross-sectional area
С	Concentration
C_d	Drag coefficient
d	Diameter
D_{AB}	Diffusion coefficient
E	Activation energy
f	Quadratic scaling factor used to predict HPFFB v_p profiles
F	Force
g	Gravity (9.81 m/s^2)
h	Height above HPFFB burner (from burner surface up to max height at which $v_{p,measured}$ was taken)
h_1	Height above HPFFB burner (from height L up to collection probe height)
h_c	Heat transfer coefficient
h_m	Mass transfer coefficient
ΔH_{pry}	Heat of pyrolysis
ΔH_{rxn}	Heat of reaction
k	Thermal conductivity
k _{rxn}	Reaction rate constant
L	maximum height above the burner at which $v_{p,measured}$ was taken in HPFFB

т	Mass
<i>m_{ratio}</i>	Ratio of $v_{p,measured}$ to $v_{p,theoretical}$ at height L in HPFFB
MW	Molecular weight
Nu	Nusselt number
Р	Pressure
R	Ideal gas constant
Re	Reynolds number
Sh	Sherwood number
t	Time
Т	Temperature
ν	Velocity
v_{∞}	Slip velocity
x	Mass fraction
Δz	Distance a particle traveled in a single time step
\mathcal{E}_b	Packing factor
\mathcal{E}_p	Emissivity of particle
θ	Blowing factor (correction of transfer coefficients during high mass transfer)
μ	Dynamic viscosity
v	Mass of Carbon that reacts per mole of reactant
ρ	Density
σ	Stefan-Boltzmann constant
χ	Chi factor (indication of effect of film diffusion)

1. Introduction

Developing countries and a growing world population place an ever-increasing demand for energy. The solution to meeting the energy needs of the future will most likely come from a combination of energy sources, two of which are biomass and petroleum coke. Biomass is a sustainable fuel source which allows energy generation from biological material such as sawdust, switchgrass, and yard clippings. Petroleum coke is a cheap and abundant by-product of oil refining that mainly consists of carbon. One way that biomass and petroleum coke can be transformed into useful energy is through gasification, which converts any carbon-containing material to hydrogen and carbon monoxide through partial oxidation.

Although the chemical reactions governing gasification are well understood, there is still much to be learned about gasification kinetics. This is especially true for the kinetics representative of those experienced in a commercial gasifier. In this research, petroleum coke was reacted with CO_2 in a high-pressure flat-flame burner (HPFFB) up to 15 atm at high heating rates. The measured CO_2 gasification kinetics are believed to be representative of those from an industrial setting since they were measured in similar conditions of elevated pressure and high heating rates (~ 10^5 K/s). This is in contrast to the gasification experiments commonly seen in literature that have been carried out at atmospheric pressure with slow particle heating rates. The operating conditions under which gasification rates are measured are important since operating conditions affect char structure and thus active surface area.

Pyrolysis precedes gasification or combustion and is the thermal decomposition of the solid fuel into permanent gases, tar (condensable vapors), and char (solid residue) (Ranzi et al., 2008). Studying pyrolysis is important since it precedes gasification and since the volatiles can be up to 90 wt% for some types of biomass (Jenkins et al., 1998). In this research, the pyrolysis yields of softwood sawdust were measured at varying reactor temperatures and particle residence times using an atmospheric flat-flame burner. The measured pyrolysis yields of sawdust are believed to be similar to those that would occur in an industrial entrained-flow combustor or gasifier. This is because the relative yields of gas, tar, and char depend heavily on heating rate and final temperature (Bridgwater, 1995), and the conditions in a flat-flame burner are comparable to those used in industry. Sawdust pyrolysis was modeled using the Chemical Percolation Devolatilization model (Fletcher et al., 1992) assuming that sawdust pyrolysis occurs as a weighted average of its individual components (cellulose, hemicellulose, and lignin). Tar cracking was taken into account by including 1st-order kinetics from literature.

2. Literature Review

This chapter gives background in several areas to better understand this research, and includes a review of pertinent literature. Some of the covered topics include the composition of biomass, primary and secondary pyrolysis, gasification, pet coke gasification experimental studies, and modeling of biomass pyrolysis.

2.1 Composition of Biomass

Interest in converting biomass to fuels and chemicals was sparked in the 1970s due to the oil crisis (Mohan et al., 2006). Although the heating value of biomass is less than that of coal, biomass has the advantages of being renewable, CO₂-neutral, and fairly abundant. Most biomass research for energy use has focused on wood, but the major components of any biomass are the same whether it be almond husks, corn stalks, wood, etc. All biomass is comprised mainly of cellulose, hemicellulose, and lignin as seen in Figure 2.1. Biomass also contains a significant amount of moisture, which can be as high as 30 to 40 wt%. Although present in lesser amounts, biomass also contains organic extractives and inorganic minerals.

Cellulose provides support to the primary cell wall with its strong, crystalline structure, making up about a third of all plant matter. Cellulose is made up of 5000 to 10,000 repeating glucose units (Crawford, 1981). Hydrogen bonding between strands and between molecules allows the cellulose network to lie flat (Mohan et al., 2006).



Figure 2.1. Representative chemical structures of cellulose, hemicellulose, and lignin (Internet1; Internet2).

Hemicellulose is a group of carbohydrates that surround the cellulose fibers in plant cells, and makes up about 25 wt% of dry wood (Rowell, 1984). Hemicellulose is composed of polymerized monosaccharides such as glucose, mannose, galactose, xylose, and arbinose (Mohan et al., 2006). Hemicellulose has a less rigid structure than cellulose, partially caused by hemicellulose containing 30 to 65 times fewer repeating saccharide monomers than cellulose (Soltes and Elder, 1981).

Lignin is found mostly between plant cell walls and makes up about 20 wt% of wood (Bridgwater, 2004). Although lignin lacks an exact structure, it is characterized by a branched, three-dimensional network containing many ether bonds (Mohan et al., 2006). Lignin has a very stable aromatic structure, slightly resembling that of a low-rank coal.

2.2 Petroleum Coke

Petroleum coke, or pet coke, is a by-product from oil refining. It results from the Coker process, which heats heavy 'bottom-of-the-barrel' oil until it cracks into more valuable gasoline components. Pet coke has a lower amount of ash, moisture, and volatiles when compared to coal (Yoon et al., 2007). Some of the advantages of pet coke are its cheap cost and high calorific value, although it has the drawbacks of higher sulfur and vanadium contents (Yoon et al., 2007).

Pet coke is increasingly used in gasifiers since its high sulfur content introduces environmental complications if combusted.

2.3 Background on Thermal Conversion

Combustion and gasification are commonly used to thermally convert both biomass and pet coke into useable energy. Although this research focuses on gasification, some discussion of combustion is given here due to the similarities of these processes, and to emphasize that pyrolysis research is important for both gasification and combustion. The first step that a particle passes through in either combustion or gasification is evaporation of any moisture from the particle. At higher temperatures, pyrolysis occurs, which means that the particle thermally decomposes into permanent gases, condensable vapors (tar), and solid residue (char) (Ranzi et al., 2008). Lastly, the primary pyrolysis products are either totally or partially oxidized depending on whether the process is combustion or gasification, respectively. Combustion and gasification mainly refer to the O₂-char and CO₂-char/H₂O-char heterogeneous reactions, respectively. Evaporation and pyrolysis are common to both combustion and gasification.

2.4 Primary Pyrolysis

Primary pyrolysis is defined as the initial thermal decomposition into gas, tar, and char upon heating, without secondary reactions in the gas phase. Pyrolysis is sometimes referred to as devolatilization. These terms will be used synonymously in this thesis, even though the technical difference between the two is whether or not the thermal decomposition of the particle takes place in the absence (pyrolysis) or presence (devolatilization) of oxygen. Typical primary pyrolysis yields of biomass and pet coke can be up to 90 and 13 wt%, respectively (Jenkins et al., 1998; Milenkova et al., 2003).

Studying pyrolysis is important since it precedes combustion or gasification, although pyrolysis can also be a stand-alone process. It is important in modeling to know when devolatilization has finished and also the relative amounts of the devolatilization products (i.e., gas, tar, and char).

2.5 Secondary Pyrolysis

Secondary pyrolysis refers to processes such as cracking, polymerization, condensation, or carbon deposition that result from the reaction of the primary pyrolysis products at high temperatures and sufficiently long residence times (Smoot and Smith, 1985). These reactions occur homogeneously in the gas phase and heterogeneously at the surface of the solid fuel or char particles (Wurzenberger et al., 2002). Generally speaking, secondary pyrolysis receives much less research attention than primary pyrolysis. However, secondary reactions have a very important influence on biomass product distribution and usability. The secondary pyrolysis of biomass will be addressed in this thesis.

It is necessary to understand how secondary pyrolysis reactions affect product utilization of biomass, especially wood. Thermal cracking of tar into light gas is a very important secondary reaction of wood due to the effect of this reaction on the product distribution of pyrolysis yields (i.e., gas, tar, and char) at relatively low temperatures. Although tar yields can be as high as 75 wt% following the primary pyrolysis of wood, tar cracking can cause light gas to be the major product of pyrolysis provided a sufficiently hot reactor temperature (Bridgwater, 2004). The tar-cracking reaction results in a gas yield that increases proportionately to the

destruction of tar. If bio-oil is the desired product from the thermochemical conversion of wood, then high liquid yields are desirable and the objective is to prevent any secondary reactions from occurring. In most other thermochemical processes, even low tar yields can cause problems by fouling and corroding equipment, causing damage to motors and turbines, lowering catalyst efficiency, and condensing in transfer lines (Vassilatos et al., 1992; Brage et al., 1996; Baumlin et al., 2005). No matter which thermochemical process is used to convert wood, it is important to know information about the thermal stability of pyrolysis tar since it can provide useful information about process design and operating conditions.

There is much literature that indicates wood tar begins to thermally crack into light gas near 500 °C. Scott et al. (1988) support that it is unlikely that a wood particle can still be in the primary pyrolysis phase at any temperature above 500 °C and that secondary reactions must occur above this temperature. Other researchers have studied the conditions at which maximum tar yields occur for use in making bio-oil from wood, and have concluded that these conditions involve short residence times with high heating rates at a maximum temperature near 500 °C (Scott and Piskorz, 1982, 1984; Bridgwater, 2003; Higman and Burgt, 2003; Li et al., 2004; Kang et al., 2006; Mohan et al., 2006; Zhang et al., 2007).



Figure 2.2. Silver birch tar yields from a fluidized bed reactor (Stiles and Kandiyoti, 1989).

Plots in literature such as the one shown in Figure 2.2 suggest that tar yields from wood pyrolysis pass through a maximum near 500 °C, and then decline at higher temperatures due to secondary tar-cracking reactions. Exposing wood tar to high temperatures at long residence times causes most of the tar to crack into light gas.

2.6 Biomass Pyrolysis Modeling

Pyrolysis reactions are extremely complex and result in a large number of intermediates. Since developing an exact reaction mechanism for each species would be extremely challenging, pyrolysis models simplify things by considering only the most important kinetics. These models are incorporated into large simulation models using commercial CFD packages, such as FLUENT, that aid in the design of industrial equipment by solving mass, momentum, and energy balances.

Prakash and Karunanithi (2008) wrote a review concerning the many biomass pyrolysis models available in literature. Di Blasi (2008) also authored an excellent review regarding the modeling of wood pyrolysis. Although many simple models have already been developed, additional research is needed since it would be beneficial to have a more generalized biomass pyrolysis model. Pyrolysis rate constants are available in literature, but they are often specific to a certain type of biomass in a particular reactor.

A more universal method of modeling biomass pyrolysis is representing biomass pyrolysis as a sum of its main components, namely cellulose, hemicellulose, and lignin (Koufopanos et al., 1989; Raveendran et al., 1996; Miller and Bellan, 1997; Pond et al., 2003). This method has successfully predicted primary pyrolysis yields (gas, tar, char) of biomass, but begins to fail when the parent material has a high ash content (Caballero et al., 1996; Biagini et

al., 2006). Couhert et al. (2009) found that the modeling the pyrolysis of biomass as the sum of its components also fails when trying to predict individual gas species. Nevertheless, representing biomass pyrolysis as a weighted average of its components is useful to predict yield distribution between light gas, tar, and char.

Several researchers have modeled biomass pyrolysis using the additivity law combined with the Chemical Percolation Devolatilization (CPD) model, which was originally developed to model the devolatilization yields of coal (Fletcher et al., 1992). The CPD model uses a description of coal structure, and models the rate of bridge breaking since coal has a chemical makeup of aromatic clusters connected by labile bridges. To use the CPD model for biomass, kinetic and structural parameters for cellulose, hemicellulose, and lignin must be determined. A weighted average of the pyrolysis yields of each component is then needed to obtain overall gas and tar yields. This approach of modeling biomass is used in this thesis to predict sawdust devolatilization.

Sheng and Azevedo (2002) reported kinetic and structural CPD parameters for cellulose, hemicellulose, and lignin based on a data fit of experiments in the literature. Their results do not take into account secondary reactions of tar cracking thermally into light gas. Although Sheng and Azevedo compared their model successfully with the pyrolysis yields of lignin, sawdust, and sugar cane bagasse, their results were not reproducible. However, they did provide very useful correlations to predict the fraction of cellulose and lignin of a particular biomass sample based on ultimate and proximate analyses.

Vizzini et al. (2008) provide CPD parameters for the three biomass components, but also included coefficients for the vapor pressure correlation for cellulose and hemicellulose that were different than the original CPD model. Vizzini's model also treated secondary tar cracking using

1st-order separate kinetics for cellulose, hemicellulose, and lignin. Lastly, their model used a population balance of side chains to differentiate between the side chains that leave the particle in the tar and ones that remain in the metaplast.

Pond et al. (2003) also developed kinetic and structural parameters for cellulose, hemicellulose, and lignin for use in the CPD model. Their parameters allowed a satisfactory prediction of volatile yields from black liquor, cellulose, and lignin. Pond's parameters enabled a prediction of volatile yields from primary pyrolysis since modeling secondary tar-cracking reactions were not attempted.

Most modeling of biomass pyrolysis in literature is specific to a particular type of biomass in a unique reactor. There is a lack of information on a generalized model of biomass pyrolysis that can handle different types of biomass and that includes thermal cracking of tar. This project will fill this gap in literature by presenting a model that can predict biomass pyrolysis yields as a function of biomass composition, pressure, heating rate, time, and temperature. Pyrolysis experiments of wood in a flat-flame burner will help evaluate the pyrolysis model, and will provide realistic pyrolysis yields of a biomass in conditions similar to a commercial entrained-flow reactor.

2.7 Gasification

Gasification is the process by which any carbonaceous species can be converted into a gaseous fuel called synthesis gas through partial oxidation. This process is preceded by pyrolysis and usually takes place commercially at 900-1500 °C and 25-40 bar (Higman and Burgt, 2003). Gasification is carried out at these high temperatures and pressures in order to speed along the relatively slow gasification kinetics. In a typical gasifier, roughly 20% of the

oxygen needed for stoichiometric combustion is provided (Smoot, 1993). The oxygen reacts with only a fraction of the available carbon, and is entirely consumed in about 10 ms (Batchelder et al., 1953). Although oxygen is present for only a short time in a gasifier, it is important since the exothermic combustion reaction provides the heat that drives the endothermic gasification reactions. These gasification reactions consume the remaining carbon through the reaction of the char with common gasifying agents like CO₂ and steam. These gases react with the char through dissociative chemisorption onto the carbon surface (Essenhigh, 1981). As long as the gasification reactions are not controlled by film diffusion, the internal surface area of the char plays an important role since it provides many more reacting sites than are available on the external char surface area.

The simplified global reactions that are important in a gasifier are listed in Table 2.1.

	ΔH _{rxn} ° (kJ/mol) (Higman and Burgt, 2003)	Relative Rate at 1073 K and 0.1 atm (Walker et al., 1959)	
$C + O_2 \rightarrow CO_2$	- 394	10^{5}	R2.1
$C + H_2O \rightarrow CO + H_2$	+ 131	3	R2.2
$C + CO_2 \rightarrow 2CO$	+ 172	1	R2.3
$C + 2H_2 \rightarrow CH_4$	- 75	0.003	R2.4

Table 2.1. Major global reactions of carbon combustion and gasification

This table also contains the relative rates of the global reactions from a review by Walker et al. (1959). These rates have been normalized by surface area and come from the reactions of various carbons with O_2 , H_2O , CO_2 , and H_2 . The sources of carbon from which the relative rates were calculated in Table 2.1 are coal char, graphite plates, graphitized carbon rods, electrode carbon, and carbon black. The char combustion reaction (R2.1 of Table 2.1) is about 10^5 times faster than the gasification reactions (R2.2 and R2.3) at 1073 K and 0.1 atm (Walker et al.,

1959). The gasification reaction with steam (R2.2) is about three times faster than the gasification reaction with CO_2 (R2.3) at the aforementioned conditions. The hydrogenation reaction (R2.4) is several orders of magnitude slower than the gasification reactions and is usually ignored in gasification studies (Smith et al., 1994). Note also that the combustion and hydrogenation reactions (R2.1 and R2.4) are exothermic, while the main gasification reactions (R2.2 and R2.3) are endothermic.

Although the gasification reactions and their thermodynamics are understood fairly well, there is still much room for improvement in predicting gasification kinetics, especially for industrial-like conditions. Modeling this heterogeneous reaction can become complicated very quickly when considering all the influencing factors. Some of these include diffusion of reactants, reactions with both H₂O and CO₂, particle size effects, pore diffusion, char ash content, temperature and pressure variations, and changes in surface area (Smoot and Smith, 1985). Predicting gasification kinetics therefore relies heavily on measured rate data.

As mentioned previously, the product of gasification is a gaseous fuel that is rich in both CO and H_2 . These products are valuable as fuels directly and can be used to fuel gas turbines in Integrated Gasification Combined Cycle (IGCC) systems to make clean and efficient electricity (Williams and Shaddix, 2007). The synthesis gas can also be used in many other ways such as intermediates to make chemicals. Figure 2.3 depicts the many uses of synthesis gas and illustrates the various areas that can benefit from this research.

2.8 Petroleum Coke Gasification

The most meaningful gasification kinetic data come from experiments carried out at similar heating rates, pressures, and temperatures as those from an industrial setting. A summary

of pet coke gasification experiments from the literature is included in Table 2.2. This summary focuses on research regarding CO_2 gasification of pet coke. The majority of experiments in the literature regarding pet coke gasification have been conducted at atmospheric pressure and low heating rates using a thermogravimetric analyzer (TGA). Although Wu et al. (2009) generated pet coke char at pressures as high as 30 bar, they still conducted their gasification experiments at atmospheric pressure in a TGA. Further experiments are needed to study the kinetics of pet coke gasification at high heating rates and elevated pressures in order to fill this gap in the literature and will ultimately aid in the design of more efficient gasifier designs.



Figure 2.3. Applications of synthesis gas (Bridgwater, 2003).

		Pressure	(atm)	1		1		1		1		1		1		1		> 1		1	
	Gasification	Reactor Type &	Gasifying Agent(s)	TGA	CO_2	TGA	H_2O, CO_2, H_2O-CO_2	TGA	CO_2	electric furnace	CO ₂	TGA	CO ₂	fixed bed	H_2O, CO_2	TGA	CO ₂	fixed bed	H_2O	TGA	CO ₂
		Pressure	(atm)	1		1		1		1		1		1		1-30		> 1		1	
J	Pyrolysis	Temperature	(K)	1223-1673		500-1520		1248-1323		1018-1178		1173-1573		923-1173		1223-1673		913		1273	
0		Heating Rate	(K/min)	30		10-20		25		not given		20		not given		6 (1 atm)	650 K/s (> 1 atm)	not given		30	
		Particle	Size (µm)	not given		250-355		85-125		220-2900		105-150		200		< 73		not given		61-74	
		Apparatus,	Sample Size	TGA, 8 mg		TGA, 40 mg		TGA, 10 mg		electric furnace		TGA, 30 mg		fixed bed		muffle furnace,	pressurized furnace	fixed bed, 500 mg		TGA, 8 mg	
		Reference		(Gu et al., 2009)		(Trommer and	Steinfeld, 2006)	(Zou et al., 2007)		(Tyler and Smith,	1975)	(Zamalloa et al.,	1995)	(Harris and	Smith, 1990)	(Wu et al., 2009)		(Ginter et al.,	1993)	(Zou et al., 2008)	

Table 2.2. Summary of petroleum coke gasification experiments in literature

3. Objectives and Approach

The objectives of this project are to improve the understanding of biomass pyrolysis and CO_2 gasification of petroleum coke in conditions similar to an industrial entrained-flow reactor, as well as to improve the modeling of both of these processes. This research will ultimately aid in more efficient gasifier design. This project is divided into the following tasks:

- Measure the pyrolysis yields of a softwood sawdust at 3 residence times at 3 temperatures. Pyrolysis tests of a single sawdust were performed on the atmospheric flat-flame burner (FFB) at 1 atm at peak temperatures of 1163, 1320, and 1433 K. The char was measured as the amount of solid remaining after the sawdust particles passed through the FFB, whereas the tar was taken as the mass which collected on water-cooled micropore filters. The gas yields were then calculated by difference. Mass release and volatile yields were measured as a function of temperature and residence time. Centerline gas temperatures were measured at each condition to calculate particle temperatures. Sawdust char structure was evaluated by SEM images.
- 2) Model biomass pyrolysis and include the thermal cracking of tar. Sawdust pyrolysis was modeled using the Chemical Percolation Devolatilization (CPD) model combined with a tar-cracking model. This model predicted well the sawdust devolatilization yields for 5 different sawdusts from 3 different reactors (FFB, fluidized bed, & drop-

tube). The model assumes that biomass devolatilization occurs as the weighted sum of its components (i.e., cellulose, hemicellulose, lignin).

- 3) Measure CO₂ gasification kinetics of pet coke at high heating rates up to 15 atm. Experiments were performed using a flat-flame burner at 5 pressures (1, 2.5, 5, 10, 15 atm) using conditions with peak temperatures ranging from 1402 to 2139 K. The mass release was measured to study the pyrolysis and CO₂ gasification of pet coke at conditions similar to those in a commercial entrained-flow gasifier. Characteristics of the char were tracked by measuring surface area, elemental composition, apparent density, and particle diameter. The extent of ash vaporization from the pet coke was also measured.
- Model high-temperature CO₂ gasification of pet coke at high pressure. Kinetic parameters were regressed for a first-order kinetic model in order to predict the CO₂ gasification of pet coke. Data collected from the HPFFB at 5 different conditions at 10 and 15 atm were used to determine the parameters.

The work is presented in the following order. Chapter 4 describes the experimental procedures used in this thesis project. Chapter 5 contains information regarding the sawdust pyrolysis experiments and associated modeling of biomass pyrolysis. Chapter 6 presents the pyrolysis and CO_2 gasification experiments of pet coke, as well as the related gasification modeling. Lastly, Chapter 8 contains the conclusions of this project as well as recommendations for future work.

4. Experimental Setup and Procedures

4.1 Softwood Sawdust Characterization

The ultimate and proximate analyses of the softwood sawdust used in this project are shown in Tables 4.1 and 4.2. Table 4.1 shows the results of the ultimate analyses obtained at BYU using a Leco TruSpec Micro and also obtained by Huffman Laboratories Inc. in Colorado. The values from the two analyses were within a fraction of a percent of each other, with the only exception being percent sulfur. The proximate analysis in Table 4.2 was performed at BYU following ASTM standard procedures as described by Zeng (2005).

	Huffman Analysis	BYU Analysis
C %	50.33	50.32
Н %	6.02	5.97
O % (by difference)	42.96	43.03
N %	0.07	0.07
S %	0.02	0.00

Table 4.1. Results of the ultimate analysis of sawdust used in BYU experiments (dry basis)

Table 4.2. Results of the proximate analysis of sawdust used in BYU experim	ients
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Sawdust	Wt%
Moisture (as received)	5.92
Ash (dry basis)	0.60
Volatiles (dry basis)	86.50
Fixed Carbon (dry basis)	12.90

The sawdust was ground using a wheat grinder (Blendtec Kitchen Mill) and then sieved in order to collect the 45-75 micron size fraction, which was used in all the experiments. The small size fraction was used in order to assume no temperature gradients within the particle for modeling purposes and to ensure a high particle heating rate. Figure 4.1 shows a SEM photo of the ground raw sawdust, which was taken at BYU using a FEI XL30 ESEM with a FEG emitter. The pits that can be seen on the raw sawdust in the SEM image are called 'tracheids' and are characteristic of softwood trees. As can be seen in Figure 4.1, a few long, skinny particles were able to pass through the sieve trays since their diameter was less than 75 microns, but the number of these particles was thought to be small. The size distribution of the sawdust particles was measured on a mass mean basis using a Coulter Counter instrument, and is included in Appendix A.



Figure 4.1. SEM photo of raw sawdust collected from the 45-75 micron sieve tray.

4.2 Petroleum Coke Characterization

The results of the ultimate and proximate analyses of the pet coke used in this project are shown Tables 4.3 and 4.4. Table 4.3 shows the results of the ultimate analyses that took place at BYU using a Leco TruSpec Micro and that were performed by Huffman Laboratories Inc. BYU's Leco TruSpec Micro did not perform as satisfactorily with pet coke as it did for sawdust,
assuming that the results of the ultimate analyses done by Huffman Laboratories are correct. The discrepancy with the analysis conducted by Huffman Laboratories would likely be lessened if BYU's instrument could achieve higher temperatures than 1050 °C.

	Huffman Analysis	BYU Analysis	
C %	87.62	88.10	
H %	1.81	2.01	
O % (by difference)	2.15	0	
N %	1.77	1.56	
S %	6.30	7.98	

Table 4.3. Results of the ultimate analysis of pet coke used in BYU experiments (dry basis)

In BYU's ultimate analysis of pet coke, the percentages of C, H, N, S and ash added to 101.1 so the values of C, H, N, and S were normalized so that the sum of these values with ash was 100. It was not possible to obtain a value for oxygen percent since oxygen percent is calculated by difference. The proximate analysis of the pet coke was performed at BYU following ASTM procedures.

Pet Coke	Wt%
Moisture (as received)	1.29
Ash (dry basis)	0.49
Volatiles (dry basis)	8.75
Fixed Carbon (dry basis)	90.76

Table 4.4. Results of the proximate analysis of pet coke used in BYU experiments

The pet coke was ground using a wheat grinder and then sieved in order to collect the 45-75 micron size fraction, which was used in all the experiments. Figure 4.2 shows SEM images of the sized pet coke. The average diameter of the pet coke particles was measured to be 62 μ m (see Appendix B). The small particles were used to represent the pulverized particle size used in industry and also to assume no temperature gradients within the particle for modeling.



Figure 4.2. SEM photo of raw pet coke collected from the 45-75 micron sieve tray.

4.3 Atmospheric Flat-Flame Burner

An atmospheric flat-flame burner (FFB) was used to study the pyrolysis of both sawdust and petroleum coke in a fuel-rich flame. Flat-flame burners are useful since they provide particle heating rates around 10^5 K/s, which nears particle heating rates of about 10^6 K/s which are common in commercial, entrained-flow combustors and gasifiers (Fletcher et al., 1997). Since the particular atmospheric FFB used in this research has been described previously in great detail (Ma, 1996), only a quick overview is given here. A schematic of the FFB appears in Appendix C.

The flat-flame burner used hundreds of small-diameter tubes to create many diffusion flamelets by feeding gaseous fuel through the tubes while introducing oxidizer in-between the tubes. The numerous small flamelets created a flat flame a few millimeters above the burner. Particles were entrained in nitrogen and carried to the middle of the burner surface through a small metal tube (0.053" ID). The particles then reacted while traveling upward in laminar flow in a quartz tower for a known residence time before the reacting particles were quickly quenched with nitrogen in a water-cooled collection probe. The volumetric flow rate of quench N₂ was about 2.5 times that of the hot gas. A virtual impactor and cyclone in the collection system separated the char aerodynamically while the soot/tar were collected on micropore filters. Permanent gases were pulled through the filters by a vacuum and released in a vent hood.

Particle residence time was controlled in the FFB by adjusting the height of the collection probe above the burner. Slow particle feeding rates near 1 g/hr were used to ensure single-particle behavior. The gaseous fuel supplied to the FFB was mainly CO with a trace amount of H_2 to stabilize the flame. A CO flame offered a wide temperature range (~1100 – 2000 K) and did not form soot, in contrast to a fuel-rich methane flame which had a more limited temperature range and formed soot in some conditions.

4.4 Pressurized Flat-Flame Burner

BYU's previous high pressure flat-flame burner (HPFFB) (Zeng, 2005) was shut down by a college safety officer since it had never been certified by the state of Utah. The design and troubleshooting of the new HPFFB was largely carried out by Randy Shurtz (In Progress 2011). The new reactor was used to study the CO_2 gasification kinetics of pet coke at pressures up to 15 atm. The HPFFB reactor operated much the same way as the atmospheric FFB. It had a similar diffusion flamelet burner (~1" OD) and collection system as the FFB, but differed by having these components enclosed in a pressurized vessel (see Figure 4.3).

The maximum reacting length (i.e., distance from burner to collection probe) of the HPFFB was ~16", which corresponded to a maximum particle residence time near 800 ms. The reactor was operated up to 15 atm, and its experimental variables were temperature, post-flame CO_2 mole fractions, particle residence time, and pressure. The primary fuel to the HPFFB was CO. Cylindrical heaters with a 2" inside diameter were used inside the HPFFB in order to

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maintain a hot environment beyond the near-flame region. These heaters were rated to a maximum temperature of 1200 °C, and were used when the collection probe was positioned more than 3" above the burner. Additional details of the HPFFB can be found in Appendix C.



Figure 4.3. External view of BYU's HPFFB (Shurtz, 2010).

4.4.1 Pressurized HPFFB Particle Feeder

A customized particle feeding system (see Figure 4.4) was designed and installed for use in the HPFFB lab since the previous HPFFB feeder (Mims et al., 1979; Solomon et al., 1982; Monson, 1992) could not reliably feed biomass particles. Although it was intended that the feeder be used exclusively for biomass, it also successfully fed coal, pet coke, and biphenyl at pressures up to 15 atm. The new particle feeder replaced the former system since its use resulted in far less frequent clogs. A detailed description of the feeder is presented in Appendix D.



Figure 4.4. HPFFB particle feeder.

4.5 Centerline Gas Temperature Measurements

Centerline gas temperature measurements were made in both the FFB and HPFFB using a B-type thermocouple. A specialized connection was attached to the HPFFB when the centerline temperature was measured in the pressurized HPFFB in order to maintain the pressure seal on the system. Additional details about measuring the centerline gas temperature profiles are included in Appendix E. A correction was applied to the raw temperature measurements in order to account for radiation losses from the thermocouple bead (see Appendix F).

4.6 Mass Release Tracer Analysis

Mass release refers to how much of the initial mass leaves the particle, and is an indicator of the extent of gasification or primary pyrolysis. For example, 35 wt% dry, ash-free (daf) mass release during pyrolysis means that 35 % of the initial particle's daf mass turned to volatiles. In this research, both ash and inorganic tracers (Al, Si, Ti) were used to calculate mass release. The general equation for daf mass release appears in Equation (4.1) where m_{char} , m_{ash} , and $m_{particle}^{0}$ are defined as the mass of the char, ash, and initial particle, respectively.

% mass release (daf) =
$$\left(\frac{m^{0}_{particle} - m_{char}}{m^{0}_{particle} - m_{ash}}\right) \cdot 100\%$$
 (4.1)

4.6.1 Mass Release by Ash Tracer

Ash tracer analysis assumes that the amount of ash in the unreacted particle is the same as that in the reacted particle, as shown in Equation (4.2)

$$m^{0}_{particle} \cdot x^{0}_{ash, particle} = m_{char} \cdot x_{ash, char} = m_{ash}$$
(4.2)

where $x^{0}_{ash,particle}$ and $x_{ash,char}$ are the mass fractions of ash in the unreacted particle and char, respectively. Substituting expressions for m_{char} and m_{ash} in terms of $m^{0}_{particle}$ back into Equation (4.1) and dividing by $m^{0}_{particle}$ yields:

% mass release (daf) =
$$\left(\frac{1 - \frac{x^0_{ash, particle}}{x_{ash, char}}}{1 - x^0_{ash, particle}}\right) \cdot 100$$
(4.3)

which allowed mass release to be calculated if the mass fractions of ash in the initial particle and char are known.

4.6.2 Mass Release by Inorganic Tracers

The derivation to calculate mass release by inorganic tracers is very similar to the derivation in Section 4.6.1, and assumes that certain inorganics (Al, Si, Ti) do not leave the reacting particle. Calculating mass release by using inorganic tracers was made possible in this study by analyzing both the sawdust char and raw sawdust using an inductively coupled plasma (ICP) instrument. The following derivation uses silicon as the tracer. Equation (4.4) assumes that the amount of silicon in the initial particle, char, and ash are all the same:

$$m^{0}_{particle} \cdot x^{0}_{Si,particle} = m_{char} \cdot x_{Si,char} = m_{ash} \cdot x_{Si,ash}$$
 (4.4)

where $x_{Si,particle}^{0}$, $x_{Si,char}$, and $x_{Si,ash}$ are the mass fractions of silicon in the initial particle, char, and ash, respectively. Using Equation (4.4), expressions for m_{char} and m_{ash} are determined in terms of $m_{particle}^{0}$ and substituted into Equation (4.1). The expression is then divided by $m_{particle}^{0}$ and yields:

% mass release (daf) =
$$\left(\frac{1 - \frac{x^{0}_{Si, particle}}{x_{Si, char}}}{1 - \frac{x^{0}_{Si, particle}}{x_{Si, ash}}}\right) \cdot 100$$
(4.5)

which allows mass release to be calculated from the mass fractions of silicon in the initial particle, char, and ash.

4.7 Determination of Particle Residence Times

It is very important to know the reaction time of a particle when determining particle kinetics. The particle reaction time in this thesis was taken as the time it took a particle to travel from the burner surface to the collection probe. A high-speed camera (Kodak EktaPro) was used to measure sawdust and pet coke velocities in the FFB and the HPFFB. The total particle residence time was then calculated using Equation (4.6) since the traveled particle distance was known as well as the particle velocity. This equation was a summation of small time steps of the particle as it traveled from the burner to the collection probe. The variable Δz is the distance a particle traveled in a single time step (Δt). Additional details about measuring particle velocities and calculating particle residence times are included in Appendix H.

$$\Delta t = \sum_{i=1}^{n} \frac{\Delta z}{v_{p_i}} \tag{4.6}$$

5. Sawdust Pyrolysis Experiments and Modeling

High-temperature pyrolysis experiments were conducted on a single softwood sawdust in an atmospheric flat-flame burner (FFB). This chapter focuses on the experimental results and addresses mass release, volatile yields, char and tar elemental composition, and char structure. Sawdust devolatilization modeling efforts using the CPD model are also discussed. Finelyground sawdust was used even though bigger biomass particles are typically used in industry. The results can be used to predict upper bounds on total volatile yields in larger-scale equipment.

5.1 Sawdust Experimental Conditions at Atmospheric Pressure

Sawdust was dried at 107 °C for a minimum of 1 hour before use. Sawdust experiments in the FFB were very time consuming due to the low ash content of the sawdust as well as frequent clogging problems in the feeder tube. The low ash content of the sawdust affects the amount of char required to perform an accurate ash test, which enabled the calculation of mass release by ash tracer (see Section 4.6.1). A slightly larger feed tube could have helped resolve this issue, but the tube's inner diameter was fixed with a maximum near 0.053". The average sawdust char collected in a given week was ~ 400 mg. Sawdust was fed to the atmospheric flat-flame burner (FFB) at a rate around 0.50 g/hr. Trying to increase the feed rate any further led to more frequent clogging problems.

Sawdust pyrolysis experiments were performed at atmospheric pressure in the FFB at peak temperatures of 1163, 1320, and 1433 K at three or four residence times per temperature. A CO flame was used for the experiments, although some hydrogen was added for flame stability. Figure 5.1 shows the centerline gas temperature profiles from these experiments, which have been corrected for radiation losses from the thermocouple bead (see Appendix F). A table of these measured temperatures is included in Table E.5 in the appendix. Table E.1 in the appendix contains the gas conditions for the sawdust pyrolysis experiments.



Figure 5.1. Centerline temperature profiles from sawdust pyrolysis experiments using FFB.

5.2 Sawdust Pyrolysis Mass Release

Figure 5.2 shows the daf mass release data from the FFB sawdust pyrolysis experiments at atmospheric pressure. The sawdust reached complete pyrolysis near 95 wt% daf at each of the three residence times at both 1320 K and 1433 K, but not at the earliest residence time at 1163 K. The particle residence time was simply not long enough at this low-temperature condition for the sawdust to reach full pyrolysis before it entered the collection probe. The higher temperatures

allowed the sawdust to reach complete pyrolysis quicker, but did not affect mass release. The mass release data in Figure 5.2 calculated by ash tracer (see Section 4.6.1) are summarized in Table A.1 in the appendix. The mass release calculated by mass balance (using weight of char collected and weight of raw sawdust fed) and ash tracer agreed within 5% at every condition, except the 1163 K 32 ms case which had an 11% discrepancy. The mass release observed from the sawdust FFB devolatilization experiments exceeded the ASTM volatiles value by 12% (see Table 4.2).



Figure 5.2. Mass release of FFB sawdust pyrolysis experiments at atmospheric pressure at peak temperatures from 1163 to 1433 K.

5.3 Sawdust Pyrolysis Yields

Tar and gas yields from the sawdust atmospheric experiments appear in Figures 5.3 and 5.4. The tar yields were calculated based on the mass that collected on the water-cooled micropore filters in the FFB collection system.

Note that the gas yields in Figure 5.4 were determined by difference, i.e., (100% – char yield% – tar yield% – ash%). The yields in both Figures 5.3 and 5.4 were calculated on a basis

of dry ash-free sawdust fed. The reported yields were based on a mass balance (i.e., tar yield = weight of collected tar/weight of daf sawdust fed), and are reported in Table A.3.



Figure 5.3. Tar yields from sawdust pyrolysis experiments in the FFB.

The high temperatures in the FFB resulted in very low tar yields, especially considering that sawdust tar yields can be as high as 75 wt% at certain conditions (Bridgwater, 2003). Thermal cracking of tar into light gas caused the low tar yields. Cracking becomes important above 800 K (Scott et al., 1988) for biomass tars. Corresponding elemental compositions are given in Appendix I.



Figure 5.4. Gas yields from sawdust pyrolysis experiments in the FFB.

It is interesting to note that the tar yields from the sawdust pyrolysis experiments level off near 1.5 wt% at each of the 3 temperature conditions in the FFB. It is suggested in the literature that there exists a small fraction of biomass tar that is or becomes refractory (Antal, 1983; Rath and Staudinger, 2001; Bridgwater, 2003; Di Blasi, 2008). Other researchers have shown that hotter reactor temperatures result in an increased fraction of aromatic compounds and condensed ring structures in the biomass tar (Stiles and Kandiyoti, 1989; Zhang et al., 2007). The sawdust tar collected in the FFB experiments was such a refractory tar since the hotter temperatures did not lower the tar yield.

The interested reader is directed to Appendix I for a discussion on the elemental composition of the sawdust tar and char collected from the FFB experiments.

5.4 SEM Images of Sawdust Char

SEM images of sawdust char collected at 1163, 1320, and 1433 K from BYU's FFB are shown in Figures 5.5 to 5.7. These images were taken at BYU using a FEI XL30 ESEM with a FEG emitter. Note that some of the images were taken at 100x magnification whereas others were taken at a magnification of 200x. Each of these figures shows the progression of char at increasing particle residence times at a single temperature.

The amount of char-like particles qualitatively increased with increasing particle residence time at each temperature condition, where char-like particles refer to those rounder particles that appear to have passed through a plastic stage. The fraction of wood-like particles qualitatively decreased with increasing residence time at each FFB condition, where wood-like particles refer to those particles with higher aspect ratios that resemble the raw sawdust (see Figure 4.1). The sawdust particles transformed to more sphere-like particles as they progressed

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to char. From a qualitative analysis, the ratio of char-like particles to wood-like particles appeared higher for the 1320 K condition than for the 1163 K condition at the ~50 ms particle residence time (see Figure 5.5 & Figure 5.6). This indicates that the sawdust transforms to char more quickly at higher temperatures. Further evidence of this can be seen by comparing the 1320 K and 1433 K chars at the ~40 ms particle residence time (see Figure 5.6 & Figure 5.7).



Figure 5.5. SEM images of sawdust char obtained in the FFB at the 1163 K condition. Note that the SEM image of the char collected at 102 ms is at a different magnification than the rest of the SEM images of char in this figure.

Mass release is essentially complete for all of these chars, except for the 1163 K 32 ms sawdust char (see Figure 5.2). This suggests that the shape of the sawdust continues to change even after

mass release is complete. Longer particle residence times would likely result in a higher fraction of rounded particles, but would not significantly affect mass release.

Figure 5.8 shows a close-up of sawdust char collected from the 1433 K FFB condition that was collected after 39 ms. Similar to the results found by Cetin et al. (2004), the original structure does not exist after devolatilization due to melting of the cell structure and plastic transformations. Just as is observed in Figure 5.8, both Zhang et al. (2006) and Dupont et al. (2008) pyrolyzed sawdust in drop-tube reactors and noticed that the sawdust char was spherical with many voids and pores.



Figure 5.6. SEM images of sawdust char obtained in the FFB at the 1320 K condition.

These morphological changes that occured to the sawdust are likely only characteristic of chars pyrolyzed at high heating rates since Cetin et al. (2004) did not observe any major structural changes of sawdust pyrolyzed at a low heating rate of 20 K/s.



Figure 5.7. SEM images of sawdust char obtained in the FFB at the 1433 K condition.

The fact that sawdust particles turn spherical after pyrolysis at high heating rates means that combustion or gasification of sawdust can be modeled assuming spherical particles.



Figure 5.8. Close-up view of sawdust char collected from 1433 K 39 ms in the FFB.

5.5 Sawdust Pyrolysis Modeling

The biomass devolatilization modeling efforts in this thesis stem from the work of Pond et al. (2003) and other researchers (Sricharoenchaikul, 2001; Sheng and Azevedo, 2002). Pond et al. proposed structural and kinetic parameters for the biomass components of cellulose, hemicellulose, and lignin for use in the Chemical Percolation Devolatilization (CPD) model (Fletcher et al., 1992), which was originally developed to predict coal devolatilization yields as a function of time, temperature, pressure, and heating rate. The CPD model assumes a base structural unit of biomass, and predicts pyrolysis yields based on how the initial structure breaks apart at high temperatures. Pond's proposed CPD parameters for biomass modeling are shown in Tables 5.2 and 5.3. The five structural parameters in the CPD model are molecular weight of the cluster (MW_I), molecular weight of side chains (M_{∂}), initial fraction of intact bridges (p_o), coordination number (σ +1), and initial fraction of char bridges (c_o). The definitions of the kinetic parameters of the CPD model are summarized in Table 5.1.

Pond et al. (2003) compared predicted primary pyrolysis yields (i.e., char, tar, and light gas) with experimental pyrolysis yields of cellulose, lignin, and black liquor. The work of this thesis evaluates the effectiveness of the model at predicting measured sawdust pyrolysis yields.

A tar-cracking model was added to account for the secondary reaction of tar thermally cracking into light gas.

E _b , kcal/mol	Bridge breaking activation energy
A_{b}, s^{-1}	Bridge frequency factor
$\sigma_{\rm b}$, kcal/mol	Standard deviation of E _b
Eg, kcal/mol	Gas formation activation energy
A _g , s-1	Gas frequency factor
σ_{g} , kcal/mol	Standard deviation of Eg
ρ	Char to gas kinetic ratio
E _c , kcal/mol	Difference in activation energy between
	bridge breaking and char formation
E _{cross} , kcal/mol	Cluster crosslinking activation energy
A_{cross}, s^{-1}	Cluster frequency factor

Table 5.1. Definition of the kinetic parameters for the CPD model

To predict sawdust pyrolysis yields, the CPD model was run separately for cellulose,

hemicellulose, and lignin using Pond's parameters (see Appendix J for a sample input file). This resulted in the predicted devolatilization yields from primary pyrolysis of pure cellulose,

hemicellulose, and lignin. The char, tar, and light gas yields of sawdust were then calculated as the weighted average of the individual components of cellulose, hemicellulose, and lignin in the unreacted sawdust. The vapor pressure parameters used for cellulose, hemicellulose, and lignin were the same as in the original CPD model.

Structural Parameter	MW ₁	M_{δ}	po	σ+1	C ₀
Cellulose	81	22.67	1.0	3.0	0.0
Hardwood hemicellulose	77.5	21.5	1.0	3.0	0.0
Softwood hemicellulose	81	22.67	1.0	3.0	0.0
Hardwood lignin	208	39	0.71	3.5	0.10
Softwood lignin	186	34	0.71	3.5	0.10

Table 5.2. Structural parameters to model biomass devolatilizationusing the CPD model (Pond et al., 2003)

Kinetic Parameter	Cellulose	Hemicellulose	Lignin	
E _b , kcal/mol	51.5	51.5	54.0	
A_{b}, s^{-1}	1.0E+18	1.0E+18	2.60E+15	
$\sigma_{\rm b}$, kcal/mol	3.0	3.0	3.972	
E _g , kcal/mol	42.0	42.0	66.0	
A _g , s-1	8.23E+12	8.23E+12	3.0E+15	
σ_{g} , kcal/mol	3.0	3.0	4.776	
ρ	5.0	5.0	3.9	
E _c , kcal/mol	0.0	0.0	0.0	
E _{cross} , kcal/mol	65.0	65.0	55.68	
A_{cross}, s^{-1}	3.0E+15	3.0E+15	3.0E+15	

Table 5.3. Kinetic parameters to model biomass devolatilizationusing the CPD model (Pond et al., 2003)

When the cellulose, hemicellulose, and lignin percentages of a particular biomass were not available in the literature, empirical equations were used in order to predict the cellulose and lignin percentages based on the ultimate and proximate analyses. Equations (5.1) and (5.2) were developed by Sheng and Azevedo (2002) from a large variety of biomass samples with molar ratios H/C from 1.26 to 1.69, O/C from 0.56 to 0.83, and volatile matter (VM) from 73 to 86% daf. The hemicellulose value cannot be determined simply as the difference between 100 and the sum of the percentages of cellulose and lignin, due to extractives. For wood, 10% is a good estimate for the extractives content. Thus, the percentage of hemicellulose could be found as the difference between 90 and the sum of the percentages of cellulose and lignin. The percentages of the 3 components were then normalized so the three values summed to 100 for use in the model.

% Cellulose =
$$-1019.07 + 293.81 (O/C) - 187.64 (O/C)^{2} + 65.14 (H/C) -19.30 (H/C)^{2} + 21.74 (VM) - 0.13 (VM)^{2}$$
 (5.1)

% Lignin =
$$612.1 + 195.37 (O/C) - 156.54 (O/C)^2 + 511.36 (H/C)$$

- $177.03 (H/C)^2 - 24.32 (VM) + 0.15 (VM)^2$ (5.2)

Thermal cracking of tar into light gas was very important to include since it significantly affects tar and gas yields above 500 °C (Scott et al., 1988). The tar-cracking kinetics of Vizzini

et al. (2008) were used when modeling sawdust devolatilization with the CPD model. Vizzini's model considers secondary tar cracking using 1st-order separate kinetics for the tar yields produced by cellulose, hemicellulose, and lignin. The tar-cracking model and kinetic parameters of Vizzini et al. appear in Equation (5.3) and Table 5.4, where A_o , E, and x_{tar} are defined as the pre-exponential factor, activation energy, and fraction of tar, respectively.

$$\frac{-dx_{tar}}{dt} = -k \cdot x_{tar} = \left[-A_o \cdot \exp\left(\frac{-E}{R \cdot T}\right) \right] \cdot x_{tar}$$
(5.3)

Biomass Component	A_o	E (kcal/mol)	
	(5)	(KCal/III0I)	
Cellulose	3.0E+06	26.17	
Hemicellulose	1.49E+06	26.17	
Lignin	1.49E+06	26.17	

Table 5.4. Kinetic parameters for predicting biomass tar-cracking

Vizzini's (2008) kinetics were applied to the primary pyrolysis tar yields of cellulose,

hemicellulose, and lignin from the CPD model. The resulting tar yields were then combined by the weighted average of cellulose, hemicellulose, and lignin. The thermally-cracked tar yields were then added to the weighted gas yields. The weighted CPD char yield remained unchanged when considering secondary tar-cracking reactions. The use of Vizzini's tar-cracking model maintained a very generalized biomass devolatilization model since both the primary and secondary pyrolysis yields were predicted based on a weighted average of the individual biomass components of cellulose, hemicellulose, and lignin. It is also possible to use tar-cracking kinetics specific to the biomass of interest by applying particular tar-cracking kinetics to the primary pyrolysis tar yields of the CPD model. For example, Fagbemi et al. (2001) proposed a model and reported kinetic parameters to predict tar-cracking specific to sawdust. Figure 5.9 shows a comparison between predicted yields from sawdust devolatilization and experimental yields obtained at BYU in the FFB at atmospheric pressure at conditions with peak temperatures of 1163, 1320, and 1433 K.



Figure 5.9. Comparison of sawdust yields between the CPD model's prediction with Vizzini's tar-cracking kinetics and BYU's FFB experiments at atmospheric pressure and peak temperatures of 1163, 1320, and 1433 K.

The maximum initial particle heating rates for the three temperature conditions were 2.5×10^5 ,

 3.8×10^5 , and 7.2×10^5 K/s, respectively. The fractions used for the cellulose, lignin, and

hemicellulose components were 0.461, 0.287, and 0.252.

The predicted sawdust yields in Figure 5.9 were performed using the CPD model with Pond's (2003) parameters combined with Vizzini's (2008) secondary tar-cracking model. The char prediction matches very well with experimental values in every case. The predictions using the simple 1st-order tar-cracking kinetics of Vizzini et al. (2008) matched the measured sawdust

pyrolysis yields in the FFB within 4.3 daf wt% upon complete pyrolysis at 1163, 1320, and 1433 K. There is room for improvement in the modeling of the shorter residence times of the 1163 K case (see Figure 5.9). The agreement between model and experimental gas and tar yields was improved in this case after tar-cracking kinetics specific to sawdust were used (see Figure 5.10). In Figure 5.10, the sawdust tar-cracking model of Fagbemi et al. (2001) was used. The values of the pre-exponential factor and activation energy were 4.28×10^6 s⁻¹ and 107.5 kJ/mole, respectively.



Figure 5.10. Comparison of sawdust yields between the CPD model's prediction with Fagbemi's (2001) tar-cracking kinetics and BYU's FFB experiments at 1163 K and atmospheric pressure.

Figure 5.11 is included for reference to show the predictions of the CPD model using

Pond's kinetic parameters <u>without</u> including a secondary tar-cracking model for the FFB 1163 K case. The modeled yields in the figure are the predicted sawdust yields resulting solely from primary pyrolysis. Note that in Figure 5.11 the predicted primary tar yield matches the measured gas yield, and vice versa. This figure clearly illustrates the need for a tar-cracking model since the measured tar and gas yields were so different from their predicted values.



Figure 5.11. Comparison of sawdust yields between the CPD model's prediction *without* Vizzini's tar-cracking kinetics and BYU's FFB experiments at 1163 K and atmospheric pressure.

5.5.1 Comparison of CPD Model with Experiments from Literature

Sawdust pyrolysis data were found in the literature in order to further evaluate how well the CPD model predicts sawdust devolatilization using Pond's (2003) kinetic parameters with Vizzini's (2008) secondary tar-cracking kinetics. The sawdust pyrolysis data in the literature with which the model was compared used particle sizes smaller than 250 µm; this allowed internal temperature gradients within the particle to be ignored.

5.5.1.1 Comparison of Model with Experiments of Scott et al.

Prediction of devolatilization yields compared with experimental data obtained from a fluidized bed at 1 atm using Maple, Poplar-Aspen, and Aspen bark at a residence time of 0.44 sec are shown in Figure 5.12. These experiments were carried out by Scott et al. (1985) at the University of Waterloo using wood with a mean diameter between 105-250 μ m. The kinetics of Vizzini et al. (2008) were used to estimate tar cracking.

Table 5.5 shows the percentages of cellulose, hemicellulose, and lignin for the woods modeled. As explained above, these component values were normalized in modeling so that they summed to 100. Model predictions including secondary tar cracking are shown as dotted lines in the figures, while solid lines denote the primary pyrolysis predictions without tar-cracking kinetics. Tar cracking does not affect char values, thus explaining why there is not a dotted line for char. The model over predicted char values below 500°C for each of the three woods, but agreed within 14.4 wt% with measured char yields above this temperature. The model correctly predicted tar cracking above 500°C, but it under predicted the tar yield below 500°C. The model showed promise at predicting devolatilization yields and trends for 2 kinds of wood and a wood bark.



Figure 5.12. Predicted devolatilization yields using the CPD model's prediction with Vizzini's tar-cracking kinetics compared with fluidized bed experiments for Poplar-Aspen, Maple, and Aspen bark at atmospheric pressure at 0.44 sec residence time (Scott et al., 1985). The solid lines indicate primary pyrolysis yields (i.e., no tar cracking).

The CPDCP version of the CPD code was used to model the sawdust yields in Figure 5.12 with an assumed 0.5 m/s particle velocity. A more correct way to model the experiments of Scott et al. would have been to use the original version of the CPD code which requires a particle temperature profile. However, the high tar yields (f_{tar}) of biomass caused numerical instability in the original CPD code as the following expression is used to estimate the fraction of gas (f_{gas}):

$$\mathbf{f}_{\text{gas}} = \mathbf{f}_{\text{gas}} \cdot (1 - \mathbf{f}_{\text{tar}}) \tag{5.4}$$

This problem will be resolved in the near future.

5.5.1.2 *Comparison of Model with Experiments of Nunn et al.*

Figure 5.13 compares the predicted devolatilization yields with sawdust pyrolysis data obtained from an electrical screen heater with a heating rate of 1000 K/s, a cooling rate of 200 K/s, and no hold time at the peak temperature. These experiments were obtained at 5 psig using Sweet Gum wood with a mean diameter between 45-88 µm (Nunn et al., 1985). Table 5.5 gives the percentage of cellulose, hemicellulose, and lignin for this wood. These values were normalized in modeling so that they summed to 100. Model predictions including secondary tar cracking are shown as dotted lines in Figure 5.13, while solid lines denote the primary pyrolysis predictions. Model predictions agreed within 6.7 wt% with experimental char yields, except at 800 K. Predicted tar yields were almost twice the experimental value at 800 K. At this temperature (but not above), tar cracking can generally be ignored. The reason for this discrepancy in tar yields is likely due to the fact that the kinetic parameters for biomass components in Table 5.3 were regressed from experiments with higher heating rates where maximum tar yields were higher (Bridgwater, 2004). Thus, the CPD model using the kinetic parameters in Table 5.3 under predicts biomass tar yields at lower heating rates, but agreed better

with tar yields from experiments conducted at higher heating rates (such as the FFB or fluidized bed experiments shown previously).

Name of Wood:	Aspen-Poplar	Maple	Aspen Bark	Sweet Gum
	(Scott et al.,	(Scott et al.,	(Scott et al.,	(Mok and
	1985)	1985)	1985)	Antal, 1992)
% Cellulose:	42.3	44.7	34.3	40.0
% Hemicellulose:	31.0	23.7	18.0	23.0
% Lignin:	16.2	24.0	13.7	19.0
Sum:	89.5	92.4	66.0	82.0

Table 5.5. Cellulose, hemicellulose, and lignin percentages of
woods modeledin Figures 5.12 and 5.13

Note that the tar yields in Figure 5.13 did not decrease to values near 0 wt% above 773 K because of tar cracking to light gas. Nunn et al. (1985) explained that the tar likely escaped the heated region of the heater before it reached a sufficient temperature to cause tar cracking.



Figure 5.13. Predicted devolatilization yields using the CPD model's prediction with Vizzini's tar- cracking kinetics compared with heated screen data for Sweet Gum wood at 5 psig using a 1000 K/sec heating rate and 200 K/s cooling rate with 0 sec residence time at the peak temperature. The solid lines indicate primary pyrolysis yields (i.e., no tar cracking).

5.5.1.3 Comparison of Model with Experiments of Wagenaar et al.

Figure 5.14 shows the CPD model's predictions of devolatilization yields of Pine sawdust (100-212 µm) from a drop-tube reactor (Wagenaar et al., 1993). Since the authors mentioned that tar cracking was avoided, the comparison of the model did not include secondary tar cracking, although it appears that a small amount of tar cracking occurred from 500 to 600 °C because tar yields decreased while gas yields increased. The fractions used for the cellulose, hemicellulose, and lignin components were 0.401, 0.323, and 0.276, respectively. Although the prediction of char yield was 12 wt% high at 450 °C, the discrepancy between predicted and measured yields decreased as pyrolysis temperature is increased.



Figure 5.14. Predicted devolatilization yields using the CPD model's prediction for a drop tube experiment.

5.6 Summary

Sawdust pyrolysis experiments were performed on an atmospheric FFB at peak temperatures of 1163, 1320, and 1433 K. Measured sawdust pyrolysis yields approached 95%. The low measured tar yields (< 3 wt%) were explained by secondary tar cracking that occurred above 500 °C. Sawdust volatile yields in the FFB exceeded the ASTM volatiles value by 12 wt%. From SEM images of the sawdust char, it was shown that the shape of the particles continued to change even after mass release was complete. The sawdust char particles were spherical with many voids and pores. The original structure of the sawdust did not exist after devolatilization due to melting of the cell structure and plastic transformations, which is typical of sawdust chars collected from high-heating-rate experiments.

Sawdust pyrolysis was also modeled using the CPD model combined with a tar-cracking model. This model satisfactorily predicted sawdust devolatilization yields for 5 different sawdusts from 3 different reactors (FFB, fluidized bed, & drop-tube). Since this model assumes that biomass devolatilization occurs as the weighted sum of its components (i.e., cellulose, hemicellulose, lignin), it is likely to fail when the parent biomass has high ash content (Caballero et al., 1996; Biagini et al., 2006). Also, the model performed better at predicting biomass pyrolysis yields from experiments with a high heating rate; otherwise, the predicted tar yields were too high.

6. Petroleum Coke Pyrolysis and CO₂ Gasification

High-temperature pyrolysis and CO_2 gasification experiments were conducted on a single pet coke sample using both an atmospheric flat-flame burner (FFB) and high-pressure flat-flame burner (HPFFB) up to 15 atm. This chapter focuses on the experimental results and addresses CO_2 gasification kinetics, ash release, char structure, and tar yields. There is also a discussion of changes in pet coke surface area, apparent density, particle diameter, and elemental composition during pyrolysis and gasification.

6.1 Pet Coke Experimental Conditions

Pet coke was typically fed to the atmospheric FFB and the HPFFB at a rate not exceeding 1.3 g/hr to ensure single particle behavior during the experiments. Similar to the sawdust experiments, a CO flame was used in all cases with a small amount of hydrogen for flame stability. The CO flame did not form soot, which was an advantage over a methane flame where soot formation was especially problematic at pressurized conditions. The pet coke was not dried before use in the experiments due to its very low moisture content (0.7 to 1.3 wt% depending on the season).

The centerline gas temperature profiles of the pet coke experiments performed in the atmospheric FFB are shown in Figure 6.1. A table of the centerline temperatures used to make Figure 6.1 is located in the appendix (see Table E.6). These temperatures have been corrected

for radiation losses from the thermocouple bead (see Appendix F), as have the HPFFB temperature profiles. Table E.2 in the appendix contains a summary of the gas conditions for the pet coke experiments in the atmospheric FFB.



Height Above Burner (inches)

Figure 6.1. Centerline gas temperature profiles in the atmospheric FFB for the pet coke experiments.

In the pressurized pet coke experiments in the HPFFB, the collection probe was positioned at different heights above the burner (3", 6", 10", 16.25") in order to vary particle residence time in the reactor. Even though the same gas condition was sometimes used with the collection probe at different heights above the burner, centerline temperature profiles were measured for each of the different collection heights. For example, it may seem logical to use the first 6" of measured temperatures from a 10" temperature profile in order to obtain a 6" profile of the same gas condition, but this would lead to erroneous temperatures for the 6" profile. This is explained by the power of the heaters used at each collection height and the different positions of the water-cooled collection probe. At heights of 3" and below, the heaters were not used. At the maximum height of 16.25", the heaters were operated at less than maximum power in order to keep the temperature of the heaters below their maximum rating of 1200 °C. The heaters could be utilized at a higher percentage of their maximum power when the

water-cooled collection probe was positioned at heights such at 6" and 10" above the burner since the probe was inserted further into the heater cavity and acted as a heat sink (see Figure C.2 in the appendix). Figure 6.2 shows three measured temperature profiles in the HPFFB at 15 atm with a peak temperature of 1918 K at differing positions of the collection probe above the burner. Note that both the 6" and 10" profiles began to drop in temperature at about 4" and 8", respectively. This is explained by the position of the water-cooled probe, which acted as a heat sink. Note that the 10" profile is about 30 K hotter than the 16.25" profile around 4-5" above the burner surface. This is explained due to the higher power of the heaters used in the 10" profile, as explained above.



Figure 6.2. Centerline temperature profiles of the 15 atm 1918 K HPFFB condition used for pet coke experiments with the collection probe positioned at 6", 10", and 16.25" above the burner.

Physically meaningful centerline-temperature measurements near the burner surface became more difficult to obtain as the probe height above the burner was increased. This was likely due to the problem of keeping the thermocouple bead in the centerline of the reactor as more of the thermocouple shaft was inserted into the reactor. When the gas temperature measurements near the burner were noisy, the first few inches of temperature measurements above the burner surface from a short profile were spliced with a longer temperature profile if the two profiles came from the same gas condition. The 20 measured gas temperature profiles in the HPFFB used for pet coke experiments, along with their associated gas conditions, are included in Appendix E.

6.2 Pyrolysis and CO₂ Gasification of Petroleum Coke

The pyrolysis and CO_2 gasification of pet coke was studied from 1 to 15 atm using both an atmospheric and pressurized flat-flame burner. All particle residence times during experiments were less than 1.06 seconds. The pet coke CO_2 gasification experiments at 10 and 15 atm were used to regress kinetic parameters for a 1st-order kinetic model. A comparison of the measured CO_2 gasification kinetics of pet coke with those in literature is also given.

6.2.1 Pyrolysis of Pet Coke

Figure 6.3 contains a summary of the data from all the pet coke pyrolysis experiments according to mass release values calculated by a mass balance (see Table B.1 in the appendix). A mass balance is obtained by weighing the collected char and comparing it to the weight of raw pet coke fed. Every pet coke experiment run at 1, 2.5, and 5 atm yielded pyrolysis data since no measurable amount of CO_2 gasification occurred at these conditions in the range of particle residence times of 23 to 753 ms. The pyrolysis data at 10 and 15 atm came from experiments at low particle residence times (< 104 ms) as CO_2 gasification occurred at higher residence times. The ASTM volatiles value (shown by the dashed line in Figure 6.3) for pet coke appeared to be a good approximation of the mass release experienced during pyrolysis in every case.

Other researchers found similar results when studying the pyrolysis of pet coke in a TGA at lower heating rates. Zamalloa et al. (1995) observed that 10 wt% of the pet coke turned to volatiles when heating it at 20 K/min under argon to a peak temperature of 1273 to 1473 K. Although the proximate analysis of the pet coke used by Zamalloa et al. was not provided, the ASTM voltatiles percent of 10 wt% is a good average value based on articles in the literature where this information has been provided (Yoon et al., 2007; Zou et al., 2007; Fermoso et al., 2009; Gu et al., 2009; Wu et al., 2009). Kocaefe et al. (1995) pyrolyzed 4 kinds of petroleum coke with ASTM volatile yields ranging from 7.2 to 12 wt% in a TGA under N₂ at a heating rate of 146 K/min. It was observed that the ASTM volatiles yield was a good approximation of the volatiles that escaped during pyrolysis in the TGA for each of the 4 varieties of pet coke. From these TGA experiments as well as the experiments performed at BYU, the ASTM volatiles yield of petroleum coke was a good estimate for the volatiles yield during both low and high heating-rate experiments for experiments from 1-15 atm.



Figure 6.3. Pet coke pyrolysis data.

6.2.2 CO₂ Gasification of Pet Coke Experiments

Experiments were conducted in the HPFFB to measure the gasification rate of pet coke by CO₂. A CO flame was used in all experiments with a small amount of hydrogen for flame stability. This allowed CO₂ gasification kinetics to be measured with only a minor presence of H₂O in the post-flame gas (< 1 mol%). This is important since H₂O is also a gasifying agent. Also, both CO and CO₂ were present in the post-flame gas (see Table E.4), which represents industrial conditions where CO inhibition of the CO₂ gasification reaction occurs (Walker et al., 1959; Revankar et al., 1987). CO strongly chemisorbs onto the pore surface of carbon and retards the CO₂ gasification rate (Turkdogan and Vinters, 1970).

CO₂ gasification kinetics were intended to be calculated with mass release data obtained by ash tracer analysis (see Section 4.6.1), which assumes that ash in the raw pet coke remains in the char. It was originally thought that using data from an ash test was more accurate than a mass balance (weighing char and how much pet coke was fed) because a mass balance can be easily thrown off by spilling, clogging in the feed line, and by char collecting in other parts of the reactor besides where it is intended. After a few months of pet coke experiments, it was noticed that there was a large discrepancy between the mass release calculated by ash tracer and that calculated by a mass balance at longer particle residence times. It was also noticed that the repeatability of the mass release of pet coke at a given condition was better when calculated by a mass balance than by ash tracer analysis. This is demonstrated in Figure 6.4, which was made using replicate mass-release data of pet coke during pyrolysis collected in the atmospheric FFB at a peak temperature of 1751 K. The average standard deviation between replicate runs at 1751 K was five times smaller (1.1% vs 5.4%) for the mass release values calculated by a mass balance than it was when mass release was calculated by ash tracer analysis. This was largely

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explained by ash leaving the char during the experiments. Vaporization of ash was a bigger problem when char was collected at longer residence times. The CO₂ gasification kinetics of pet coke were consequently determined from data obtained by a mass balance rather than ash-tracer analysis. Fortunately, this could be done because the weights of pet coke char had been recorded as well as the amount of raw pet coke fed. Although it can sometimes be difficult to obtain an accurate mass balance, it is believed that the mass release numbers calculated by a mass balance are fairly accurate since (1) many replicate experiments were performed, (2) special care was given to ensure the best mass balance possible, and (3) there was often good repeatability between duplicate experiments. The best mass balance possible was ensured by shutting down between different experimental conditions in order to clean out the collection system, and weighing the amount of pet coke fed as well as the collected char.



Figure 6.4. Percent mass release of pet coke at 1751 K that was collected in the atmospheric FFB.

Figure 6.5 shows a summary of the data from all the pet coke experiments where CO_2 gasification occurred based on mass release values determined by a mass balance (complete data summarized in Table B.1). CO_2 gasification of pet coke was only observed at 10 and 15 atm.

All pet coke experiments run at 1, 2.5, and 5 atm yielded pyrolysis data as no measurable amount of CO_2 gasification occurred at these conditions in the range of particle residence times of 23 to 753 ms. As can be seen in Figure 6.5, the mass release leveled off somewhere near a particle residence time of 350 ms since the temperature decreased below 1500 K after 6" above the burner in the majority of the HPFFB temperature profiles. Heaters were used in the HPFFB when char is collected at the longer residence times (> 3" above the burner), but they could not provide sufficiently hot temperatures for CO_2 gasification of pet coke to continue.



Figure 6.5. Percent mass release during pet coke CO₂ gasification experiments.

6.2.3 Modeling of Pet Coke CO₂ Gasification

The CO₂ gasification of pet coke was modeled using a simple first-order model, patterned similarly after a previous oxidation model (Sowa, 2009). The rate expression was:

$$-\frac{dm_p}{dt} \cdot \frac{1}{A_p} = -k_{rxn} \cdot P_{CO2,surf} = -\left[A_o \cdot \exp\left(\frac{-E}{R \cdot T_p}\right)\right] \cdot P_{CO2,surf}$$
(6.1)
where A_p is the external surface area of the assumed-spherical particle, k_{rxn} is the rate constant of CO₂ gasification, $P_{CO2, surf}$ is the partial pressure of CO₂ at the particle surface, A_o is the preexponential factor, E is activation energy, R is the ideal gas constant, and T_p is the particle temperature. The rate is negative since the particle lost mass during CO₂ gasification. Equation (6.1) was integrated using the Explicit Euler method for integration in an Excel spreadsheet. The kinetic parameters A and E were determined by minimizing the error between predicted and measured mass release of the pet coke particles. The measured mass release values of the pet coke came from experiments in the HPFFB where the rate of change in the mass of the particles were measured.

Although the model does not take pore diffusion into account, it does consider film diffusion, which allowed $P_{CO2,surf}$ to be solved for explicitly.

$$-k_{rxn} \cdot P_{CO2,surf} = \nu \cdot h_m \cdot \left(C_{CO2,\infty} - C_{CO2,surf}\right)$$
(6.2)

where *v* is the mass of carbon (in grams) that react per mole of reactant, h_m is the mass transfer coefficient (*Sh*·*D*_{*AB*}/*d_p*), and *C*_{*CO*2,∞} is the concentration of CO₂ in the bulk. In the case of CO₂ gasification, *v* was (12 g C/ mol CO₂) from the following reaction:

$$C + CO_2 \rightarrow 2 CO$$

The mass transfer coefficient (h_m) assumed a Sherwood number of 2, and used a Mitchell correlation (Mitchell, 1980) for the diffusion coefficient (D_{AB}) of CO₂ in N₂. The Sherwood number can be assumed to equal 2 for small spheres traveling close to the gas velocity (Fletcher, 1989). Using the ideal-gas law for the concentration terms in Equation (6.2) (i.e., $C_{CO2,\infty} = P_{CO2,\infty}$ /($R \cdot T_{gas}$) & $C_{CO2,surf} = P_{CO2,surf}/(R \cdot T_p)$) allowed $P_{CO2,surf}$ to be solved for:

$$P_{CO2,surf} = \frac{\nu \cdot h_m \cdot P_{CO2,\infty}}{R \cdot T_{gas} \left[k_{rxn} + \frac{\nu \cdot h_m}{R \cdot T_p} \right]}$$
(6.3)

where $P_{CO2,\infty}$ was calculated as the product of the total pressure and the mole fraction of CO₂ in the post-flame gases predicted by thermodynamic equilibrium. Substituting Equation (6.3) into Equation (6.1) allowed the rate per unit surface area to be solved as follows:

$$-\frac{dm_p}{dt} \cdot \frac{1}{A_p} = \frac{-P_{CO2,surf}}{\frac{R \cdot T_{gas}}{v \cdot h_m} + \frac{T_{gas}}{T_p \cdot k_{rxn}}}$$
(6.4)

Since only the gas temperature (T_{gas}) was measured during experiments, T_p was solved for each time step using an energy balance of the particle:

$$m_p \cdot C_p \cdot \frac{dT_p}{dt} = h_c \cdot A_p \cdot (T_{gas} - T_p) + \varepsilon_p \cdot \sigma \cdot A_p \cdot (T_{surr}^4 - T_p^4) + \frac{dm_p}{dt} \cdot \Delta H_{rxn}$$
(6.5)

where m_p is the mass of the particle, C_p is the heat capacity of the particle (Merrick, 1983), T_p is the particle temperature, *t* is time, h_c is the heat transfer coefficient ($Nu \cdot k_{gas}/d_p$), A_p is the external surface area of an assumed-spherical particle, ε_p is the emissivity of the char particle ($\varepsilon_p = 0.8$ with the assumption that it was similar to that of coal char) (Fletcher, 1989), σ is the Stefan– Boltzmann constant (5.67 x 10⁻¹² W/cm²/K), T_{surr} is the temperature of the surroundings (500 K), and ΔH_{rxn} is the heat of reaction for the CO₂ gasification reaction. The left-hand side of Equation (6.5) was set equal to zero since steady state was assumed during the small time steps. The first term on the right-hand side of Equation (6.5) represents the particle heating up from convective heat transfer. The second term in Equation (6.5) is the radiative heat transfer from the particle, which is negative since heat is leaving the particle. A more thorough analysis would have included radiative heat transfer to the particle, as was done when correcting the centerline gas temperature for radiation (see Appendix F). The last term in Equation (6.5) takes into account the heat from the reacting particle, which is negative (from the dm_p/dt term) due to the endothermic CO₂ gasification reaction. The Nusselt number (*Nu*) used in the heat transfer coefficient in Equation (6.5) was assumed to equal 2 due to the low Reynolds number of the small particle (~60 µm) traveling near the gas velocity. The thermal conductivity of the gas (k_{gas}) was assumed to equal that of N₂ since it made up about 70 mol% of the post-flame gases. The temperature dependence of the N₂ thermal conductivity was taken into account using the Mitchell correlation (Mitchell, 1980). The ΔH_{rxn} term for the CO₂ gasification reaction (C + CO₂ \rightarrow 2 CO) in Equation (6.5) was calculated at 25 °C as:

$$\Delta H^{25^{\circ}}{}_{rxn} = 2 \Delta H^{\circ}{}_{f,CO} - \Delta H^{\circ}{}_{f,CO2} - \Delta H^{\circ}{}_{f,char}$$
(6.6)

where H°_{f} is the heat of formation at 25 °C. The Dulong formula (Green and Perry, 1984) was used to calculate the heat of formation of the pet coke char ($H^{\circ}_{f,char}$). The Dulong formula is an empirical equation that allows the calculation of the heat of combustion of a char from its elemental composition for the reaction $C_{char} + O_2 \rightarrow CO_2$. Since $\Delta H_{combustion} = -\Delta H_{formation}$, the heat of formation of char at 25 °C can be solved for as:

$$\Delta H^{\circ}_{f,char} = \Delta H^{\circ}_{f,CO2} + \Delta H^{\circ}_{combustion,Dulong}$$
(6.7)

Substituting Equation (6.7) into Equation (6.6) allows the ΔH_{rxn} term for the CO₂ gasification reaction in Equation (6.5) to be calculated at 25 °C as:

$$\Delta H^{\circ}_{rxn} = 2 \Delta H^{\circ}_{f,CO} - 2 \Delta H^{\circ}_{f,CO2} - \Delta H^{\circ}_{combustion,Dulong}$$
(6.8)

The temperature dependence of the ΔH_{rxn} term in Equation (6.5) was included by including the $\int C_p dT$ terms in Equation (6.6) for CO, CO₂, and pet coke char using the Gordon McBride database (McBride et al., 2002). The $\int C_p dT$ term for the pet coke char was simply assumed to equal that of graphite using the temperature dependence of the Gordon McBride database. An

alternative would be to use $H^{\circ}_{f,graphite}$ as a good approximation for the heat of formation of pet coke char instead of using the Dulong formula to solve for it. The terms $\Delta H^{\circ}_{f,graphite}$ and $\Delta H^{\circ}_{f,char}$ (by the Dulong formula) are about 6% different from each other, and using $\Delta H^{\circ}_{f,graphite}$ instead of $\Delta H^{\circ}_{f,char}$ would have caused T_p values to increase anywhere from 6 to 30 K for the conditions used in the HPFFB at 10 and 15 atm.

The particle temperature (T_p) was solved using Equation (6.5) using the Secant method with 4 iterations. The time step (Δt) used in the spreadsheet was a function of a fixed change in distance (dx) traveled by the particle:

$$\Delta t = t_i - t_{i-1} = \frac{dx}{v_p}$$
(6.9)

where v_p is the particle velocity based on a measured particle velocity using a high speed camera (see Appendix H). The particle mass (*m*) of each time step was calculated as:

$$m_{i} = m_{i-1} + \Delta t \cdot \left(\frac{dm_{p,i-1}}{dt}\right) = m_{i-1} + \frac{dx}{v_{p}} \cdot \left(\frac{dm_{p,i-1}}{dt}\right)$$
(6.10)

using Equation (6.4) for the (dm_p/dt) term after multiplication by A_p . Gas temperature (T_{gas}) was input into the spreadsheet as a function of height above the burner using an empirical polynomial expression that fit the measured gas temperature. A changing particle diameter (d_p) was included using an empirical equation that was a function of height above the burner based on pet coke diameter measurements (see Appendix K).

It is important when measuring kinetics at high temperature to make sure that the measurements are not entirely controlled by film diffusion. The chi factor (Smith et al., 1994), χ , was calculated for all the conditions since it provides an indication of the effect of film diffusion. It is defined as the measured rate divided by the maximum rate under film-diffusion control (when $C_{CO2,surf}$ is zero in Equation (6.2)):

$$\chi = \left(\frac{k_{rxn} \cdot P_{CO2,surf}}{v \cdot h_m \cdot (C_{CO2,\infty})}\right) = \frac{k_{rxn} \cdot P_{CO2,surf}}{v \cdot h_m \cdot \left(\frac{P_{CO2,\infty}}{R \cdot T_{gas}}\right)}$$
(6.11)

where $P_{CO2,surf}$ had the same definition as in Equation (6.3). The surface reaction controls when χ is much less than 1. Film diffusion controls entirely when χ approaches 1. Mitchell et al. (1992) set this cutoff at 0.9. In the 10 atm and 15 atm pet coke HPFFB experiments, χ ranged from 0.2 to 0.35 and 0.55 to 0.7, respectively. These χ values mean that the measured kinetics took place under Zone II conditions (Smith et al., 1994), which is a transition region between surface-reaction control and film-diffusion control. The gasification pet coke kinetics measured in the HPFFB were likely similar to those in a commercial entrained-flow gasifier since these commercial reactors operate in Zone II conditions as well.

Five separate Excel worksheets were developed since there were 5 HPFFB conditions where a measurable amount of CO₂ gasification of pet coke occurred (10 atm: 1722K, 1967 K, 2139 K and 15 atm: 1681K, 1918 K). The pet coke experiments conducted at 1-5 atm were not used to regress the kinetic parameters for the CO₂ gasification reaction since no measurable amount of gasification occurred at these conditions in the range of particle residence times of 23 to 753 ms. Pyrolysis data were used as initial points for modeling, and were taken from the ASTM volatiles value when this information was not available. The experimental data that were used to solve for the gasification kinetic parameters were largely the pet coke mass release numbers calculated by mass balance. The mass release numbers calculated by ash tracer were only used if they were close to the mass release numbers calculated by mass balance. This is explained since ash sometimes vaporized from the pet coke char (see Section 6.2.2). Recall that the mass release of the pet coke leveled off because the temperature of the reactor above a certain point was not hot enough for continued CO₂ gasification (see Figure 6.5). This was the

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rationale for why experimental data of pet coke collected at 10" and 16.25" above the burner were not used directly to determine the kinetic rate coefficients. The values of mass release from the two aforementioned collection heights were still included to solve for the kinetic parameters, but were averaged with the mass release data of the 6" collection height since the mass release of pet coke at 6" above the burner was essentially the same as that of char collected at 10" or 16.25" above the burner. The data used for modeling are summarized in Table 6.1.

Pressure	Peak	Time of	Pyrolysis	Time of	Gasification	Gasification
(atm)	Temperature	Complete	Mass	Gasification	Collection	Mass
	(K)	Pyrolysis	Release	Points	Height	Release
		(ms)	(%)	(ms)	(inches)	(%)
10	1722	81	9.70	150	1.5	15.5
10	1967	91	8.78	373	6	38.8
10	2139	72	8.78	323	6	30.8
				104	2	13.9
15	1681	81	8.78	151	3	20.6
				318	6	54.8
15	1918	73	8.78	335	6	50.2

Table 6.1. Pet coke CO₂ gasification HPFFB data points used for modeling

The kinetic parameters were regressed using three data sets. The first data set included only the 10 atm data (3 conditions). The second data set included only the 15 atm data (2 conditions), while the third data set used both the 10 atm and 15 atm data. In these three cases, the pre-exponential factor varied while the activation energy was set to 140 kJ/mol based on CO_2 gasification experiments on a TGA with a reaction order of 1 (Kwon et al., 1988). The regressed rate parameters for the three data sets are summarized in Table 6.2. These parameters were regressed from experiments with peak temperatures in the range of 1722-2139 K at partial pressures of CO_2 from 1.7 to 3.2 atm (see Appendix E). Figure 6.6 and Figure 6.7 show the measured pet coke mass release data compared with that predicted by the gasification model using kinetic parameters regressed from the first and second data sets, respectively.

	\boldsymbol{E}	A_o
	(kJ/mol)	$\left[\frac{g \ Carbon}{cm^2 \cdot s \cdot atm \ CO_2}\right]$
10 atm	140	118.4
15 atm	140	4289.3
10 & 15 atm	140	333.2

Table 6.2. 1st-order kinetic rate coefficients for CO₂ gasification of pet coke



Figure 6.6. Comparison of 1st-order gasification model with measured pet coke data at 10 atm using $A_o = 118.4 \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{atm}^{-1}$. The percent mass release is based on the wt% of daf pet coke.

In Figure 6.6, the model under predicted the pet coke mass release at the 10 atm 1967 K condition at long residence times. The model also over predicted the mass release at 10 atm 2139 K at the long residence time. In Figure 6.7, the model behaved similarly where there was better agreement between the measured and predicted pet coke mass release values at low

residence times. At the longest residence times, the model under predicted the mass release at 15 atm 1681 K and over predicted the mass release at 15 atm 1918 K.



Figure 6.7. Comparison of 1st-order gasification model with measured pet coke data at 15 atm using $A_o = 4289.3 \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$. The percent mass release is based on the wt% of daf pet coke.

Figure 6.8 shows the measured pet coke mass release data compared with that predicted by the gasification model using kinetic parameters regressed from all the gasification experimental data from the HPFFB at once (10 <u>and</u> 15 atm). The 10 atm 1722 and 1967 K conditions showed good agreement in pet coke mass release between the model and that measured in the HPFFB. However, the model over predicted the mass release for the 10 atm 2139 K condition and under predicted the mass release for both conditions at 15 atm.

The discrepancy between predicted and measured pet coke mass release in Figures 6.6 to 6.8 is most likely caused by limitations of the model. For example, the simple 1st-order model did not take into account a changing pet coke pore structure. The model also did not address pore diffusion which becomes important in reactions that take place in Zone II. Thermal annealing (Hurt et al., 1998; Senneca and Salatino, 2002) and changing internal surface area of the particle were also not considered by the model. There may also be an error in the calculated particle temperatures (T_p). Fletcher (1989) measured temperatures of coal particles in entrained



flow and observed that they were hotter than predicted by the energy balance in Equation (6.5) near the injection point.

Figure 6.8. Comparison of 1st-order gasification model with measured pet coke data at 10 and 15 atm using $A_o = 333.2 \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$. The percent mass release is based on the wt% of daf pet coke.

An nth-order model (i.e., $P_{CO2,surf}$ ⁿ in Eqn 6.1) would likely allow an improved fit of the measured pet coke gasification data. Although an nth-order model requires iteration since $P_{CO2,surf}$ in Equation (6.3) cannot be solved for explicitly, it would allow all the pet coke data at

1-15 atm to be explained. The fact that no extent of pet coke gasification was measured below 10 atm suggests that the rate has strong pressure dependence, implying that the order of n would exceed unity in an nth-order model.

6.2.4 Comparison of Pet Coke CO₂ Gasification Kinetics with Literature

Zamalloa et al. (1995) studied CO_2 gasification kinetics from 1173 to 1573 K using a TGA where the partial pressure of CO_2 at the particle surface was 1 atm. The proposed rate that is stated to cover the transition region from chemical control to pore diffusion control is:

$$Rate(g/m^2 \cdot s) = 8 \cdot \exp\left(\frac{-143000}{R \cdot T}\right)$$
(6.12)

which uses a BET surface area and has units J/mol for the activation energy. The rate expression in Equation (6.12) predicted that pet coke gasification by CO_2 would not be observed in the short residence times (<1 sec) of the HPFFB or FFB. This is consistent with the BYU pet coke data that was measured at 1-5 atm (see Figure 6.3) since no measurable amount of gasification occurred in these runs. Although pet coke was observed to gasify at 10 and 15 atm in the HPFFB, this was not inconsistent with Zamalloa's reported rate since the operating conditions of the HPFFB at these cases were outside the range over which Zamalloa's rate can be considered valid (i.e., P_{CO2} in HPPFB > 1 atm).

The CO₂ gasification reactivity of pet coke was also compared to that of coal. Goetz et al. (1982) studied CO₂ gasification kinetics of different ranks of coal up to 1720 K using a drop tube furnace at atmospheric pressure with a CO₂ partial pressure of 0.3 atm. Goetz et al. also regressed kinetic parameters for a first-order CO₂ gasification model on a basis of external surface area, similarly as was done with the BYU pet coke data. The kinetic parameters of Goetz et al. appear in Table 6.3.

Coal Name	E	A_o
	(kJ/mol)	$\left[\frac{g \ Carbon}{cm^2 \cdot s \cdot atm \ CO_2}\right]$
Texas Lignite	165.34	660
Wyoming Wyodak	177.81	1040

Table 6.3. 1st-order kinetic rate coefficients for CO₂ gasification of coal

The kinetics of Goetz et al. predicted that lignite and Wyodak coals would experience a measurable amount (15 and 10 wt%, respectively) of CO₂ gasification given 100 ms reaction time at conditions similar to those run with pet coke in the BYU FFB reactor. This calculation assumed $P_{CO2,surf} = 0.3$ atm and a particle temperature of 1720 K. Since no CO₂ gasification was observed in the FFB pet coke experiments, it can be concluded that two ranks of coal are more reactive than pet coke at these conditions. This is consistent with the literature where other researchers have reported that the CO₂ gasification reactivity of pet coke is lower than that of coal based on experiments conducted at atmospheric pressure (Harris et al., 2006; Gu et al., 2009; Wu et al., 2009).

When comparing the reactivities of two fuels, it is ideal if the same experiments are performed on both fuels under identical conditions. Fortunately, Wyodak coal was run at some of the same conditions in the HPFFB reactor as the pet coke (Shurtz, 2011). Gasification experiments by CO_2 were performed using Wyodak coal at 5, 10, and 15 atm in the HPFFB. Unlike the pet coke which only pyrolyzed at 5 atm, the Wyodak coal experienced 64 wt% gasification by 371 ms (based on mass of coal remaining after pyrolysis). However, comparing the reactivities of pet coke and Wyodak coal solely based on the HPFFB experiments at 10 and 15 atm suggest that pet coke was more reactive. This conclusion assumed that no ash vaporized from the coal, since the mass release of the Wyodak coal was calculated using an ash tracer (see Section 4.6.1). The 1st-order CO_2 gasification rate constants of pet coke and Wyodak coal are

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plotted in Figure 6.9. The kinetic parameters in these rate constants were regressed as discussed in Section 6.2.3 using 10 and 15 atm data from the HPFFB. In Figure 6.9, the Wyodak rate constant used A_{ρ} and E values of 69.7 g/(cm²·s·atm) and 130 kJ/mol, respectively.



Figure 6.9. Comparison of 1^{st} -order rate constant for CO₂ gasification of pet coke and Wyodak coal based on 10 and 15 atm data in the HPFFB.

At partial pressures of CO_2 less than 1 atm, the CO_2 gasification reactivity of coal was higher than that of pet coke. However, the reactivities of pet coke and Wyodak coal were on the same order of magnitude from experiments with peak temperatures in the range of 1722-2139 K at partial pressures of CO_2 from 1.7 to 3.2 atm.

6.3 Pet Coke Ash Release

Ash was found to leave the pet coke, especially at longer residence times in the flat-flame burner reactors (see Section 6.2.2). Figure 6.10 was made by calculating a percent error in ash weight from a variety of conditions. This was done by calculating a percent error between the measured amount of ash in a particular char sample and the predicted amount of ash that would be present based on how much pet coke was fed. This method is only meaningful if a good mass balance was obtained, which explains why only certain experimental conditions were included in Figure 6.10. If pet coke char collected in other areas of the reactor besides the collection system, this would shift all the points in Figure 6.10 up and lead to lower ash release numbers at the longer residence times. A table of the data used to make this figure is included in Table B.2.



Particle Residence Time (ms)

Figure 6.10. Percent error in ash weight of pet coke samples collected from a variety of conditions. Negative values imply vaporization of ash.

If the percent error in ash weight was +/- 2%, then it was recorded as 0% since 2% is the accuracy of the scales at the low weights of ash measured (~8 mg of ash) after an ash test. The accuracy of the scale at weights near 8 mg (typical ash weight) was determined by a scale sensitivity experiment with the particular scale that was used to weigh ash samples. Figure 6.10 shows how much ash evaporated at a variety of conditions at all pressures from 1 to 15 atm in the FFB and HPFFB. These data are included since they can be used to estimate the percentage of ash that will leave the pet coke particle, thus allowing the design and/or operating conditions

of the gasifier to be adjusted accordingly. The evaporated ash may even be higher in an industrial setting because the temperature drops off below 1500 K after 6" above the burner in the majority of the temperature profiles of the HPFFB; this assumes that a hotter temperature would lead to a greater amount of ash leaving the pet coke particle. Data points in Figure 6.10 with a negative percent error in ash weight (data below the solid black line) are representative of chars that have experienced ash vaporization since this means that less ash was weighed than was predicted from a particular char. It is very noticeable in the figure that ash evaporates at longer residence times. The highest percentage of ash vaporization of the pet coke was observed at the 15 atm 1681 K condition (~42 %). Figure 6.10 can be used directly to estimate the amount of ash vaporization since -15% error in ash weight implies that 15% of the ash left the pet coke particle.

The explanation of why several pet coke chars contained more ash at the lower residence times than was predicted is left for further study, but may be explained by inhomogeneity of the ash distributed in the pet coke. On one particular ash test of a pyrolyzed char collected at 76 ms 1683 K 2.5 atm, four times the expected ash was observed. The char was put back in the furnace at 900 °C for another 5 hours, but the weight did not change. The appearance of this ash was different from all the other pet coke ash tests. After a typical ash test of pet coke, black flakes were found sticking to all sides of the crucible. The abnormal ash was light brown and collected at the bottom of the crucible. Two other ash tests were performed on chars collected on different days at 76 ms 1683 K 2.5 atm, but the very high ash content was not observed. This indicates that the condition at which the char was collected did not factor in the high ash content, but was more likely caused by ash inhomogeneity.

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6.4 SEM Images of Pet Coke

Several SEM pictures of pet coke char are included in Figure 6.11. Recall that SEM images of raw pet coke were included in Figure 4.2. In total, SEM images were taken of char collected from 12 operating conditions at all pressures (1 to 15 atm) that included fully pyrolyzed char as well as partially gasified char. There was no noticeable difference between fully pyrolyzed char and partially gasified char; the char in Figure 6.11 that was collected at 15 atm 1918 K represents a partially gasified char. Only 4 SEM images are shown in Figure 6.11 since all of the pet coke chars from the 12 different conditions closely resembled each other.



Figure 6.11. SEM images of pet coke char collected at various temperatures and pressures. The red circles are added to draw attention to the cracks in the pet coke.

The structure of the pet coke char appears to be very similar to that of raw pet coke, with the only difference being that the char contains small cracks in its surface. This observation is consistent with what other researchers have observed (Zamalloa and Utigard, 1995). The red circles in Figure 6.11 are included to draw attention to some of these cracks on the char that was collected at 2.5 atm; cracks are also present in the chars in Figure 6.11 that were collected at the two 15 atm conditions although they are more difficult to see. Every pet coke char that was observed under SEM contained these cracks; pressure was not believed to be an influencing factor since the cracks were observed in pet coke chars that were collected at every pressure condition (1 to 15 atm). Although the pet coke contains less than 10% volatiles, it is believed that the cracks are likely a result of the volatiles escaping the particle interior quickly, which is influenced by the high particle heating rates experienced in the flat-flame burner experiments. Evidence of the high particle heating rates causing the cracks on the pet coke char is provided by two observations. First, the char in Figure 6.11 that was collected at 15 atm 1431 K has less cracks than several other chars. Since the peak temperature of this operating condition was relatively cool, the particle heating rate was lower. This allowed more time for the volatiles to escape the particle, which resulted in less cracks in the char's surface. Second, pet coke char was collected at 1320 K from the atmospheric FFB with twice the carrier N₂ as usual in the feed tube. The low temperature combined with the high carrier N₂ were chosen to collect a char with a lower heating rate. The SEM of this particular char is shown in Figure 6.11 and does not contain any cracks. It is believed that the char collected at 1 atm 1320 K is fully pyrolyzed, although the mass balance of this experiment was corrupted because some of the char spilled.

6.5 CO_2 and N_2 Surface Area of Pet Coke

Changing surface area is one factor that complicates heterogeneous char reactions. The surface area affects gasification rates by influencing transport properties and the available particle surface area that is able to react with the gasifying or oxidizing agent (Smith et al., 1994). Chars with higher surface areas translate to higher gasification rates. Surface area data also provide insight into what is happening to the particle structure during devolatilization and gasification.

 N_2 and CO_2 adsorption isotherms were used to measure the surface areas of pet coke using a Micromeritics Tristar 3000 instrument. It is important to note that the N_2 and CO_2 surface area values are a measure of internal surface area, which is where most of the reactions take place since the internal surface area greatly exceeds the external surface area. This is true as long as the reaction is not film diffusion limited, which occurs at very high temperatures.

Nitrogen adsorption was conducted at 77 K (using liquid N₂) in the N₂ surface area measurements that follow, and provides information regarding the mesopore (radii from 1-20 nm) structure. N₂ surface areas that follow were calculated using the Brunauer-Emmett-Teller (BET) equation. Carbon dioxide adsorption was performed at 298 K (using an ice water bath), and provides insight regarding the micropores (radii < 1 nm) of the particle. CO₂ surface areas below were calculated using density functional theory (DFT), and represent the total area in the pores greater than or equal to 4.54 angstroms.

The dashed and solid lines in Figures 6.12 to 6.14 represent the average surface area value of raw pet coke and its corresponding 95% confidence interval of the population mean, respectively.

The CO₂ surface areas of pet coke char are shown in Figure 6.12 and Figure 6.13. Figure 6.12 shows CO₂ surface area measurements of fully pyrolyzed pet coke chars that were collected at 1, 2.5, and 5 atm. No CO₂ gasification occurred at these conditions. The 1 atm pet coke chars were collected from the atmospheric FFB, while the chars at the two higher pressure conditions were collected from the HPFFB. It appears that temperature is the most influential factor on surface area. The chars collected at the two lowest temperatures (2.5 atm 1683 K and 5 atm 1702 K) in Figure 6.12 had the highest surface area values, even slightly greater than that of raw pet coke. It is interesting that the char from 2.5 atm 1876 K had a higher CO₂ surface area than the char collected at 1 atm 1751 K. The gas temperature profile in the 2.5 atm 1876 K condition dropped off more quickly than the 1 atm 1751 K profile, which may explain the difference in CO₂ surface area. CO₂ surface area of the pet coke chars in Figure 6.12 decrease with longer residence time at the higher temperatures, leveling off to surface area values near 10% of that of unreacted pet coke.



Particle Residence Time (ms)

Figure 6.12. CO₂ surface area of fully pyrolyzed pet coke chars collected at 1, 2.5, and 5 atm. The 1 atm chars were collected from the FFB, whereas all other chars were from the HPFFB.

The surface areas of chars collected at 10 and 15 atm from the HPFFB are shown in Figure 6.13. The majority of these chars came from conditions where the char was partially gasified except where indicated by open symbols which represent pyrolysis data. Mass release data listed in Table B.1 (in the appendix) was used to distinguish between pyrolyzed char and gasified char. It appears that temperature is the most influential factor of CO₂ surface area from this figure as well. The lowest surface area measurement came from char collected at the hottest condition (10 atm 2139 K). CO₂ surface area decreased with increased residence time at 10 atm 1967 K and 15 atm 1918 K, but not for the 15 atm 1681 K condition. A summary of all the CO₂ surface area values of pet coke is located in Table B.3.



Figure 6.13. CO₂ surface area of pet coke chars collected at 10 and 15 atm. Open symbols indicate pyrolyzed chars.

Figure 6.14 shows a plot of N_2 surface area measurements taken from partially gasified chars collected at 10 and 15 atm, except for a single pyrolysis char from 10 atm indicated by an open symbol. At low residence times, the N_2 surface area values increased to several times higher than that of raw pet coke, but decreased with increasing residence time to values near or slightly below the surface area of raw pet coke. This implies that the mesopore region of the pet coke grows and then shrinks during CO_2 gasification. Nothing can be said with certainty concerning the mesopore region of the pet coke during pyrolysis since N_2 surface area measurements were not taken of the chars collected at 1 to 5 atm, but it is expected that a similar trend would be observed. A summary of all the N_2 surface area values of pet coke is located in Table B.4.

The changing values of internal surface area in the pet coke chars can be explained by growth and coalescence of pores. The internal surface area increases as the pores expand until the pores become so large that they coalescence, thus leading to a decrease in internal surface area (Dutta et al., 1977). The changing internal surface area of the pet coke chars is further evidence that the experiments did not take place in a regime limited by film diffusion. When a particle reaction is limited by film diffusion, the reaction takes place at the particle surface and leaves the interior of the particle unchanged.



Figure 6.14. N₂ surface area of partially gasified pet coke chars collected at 10 and 15 atm. The open symbol indicates a pyrolyzed char.

Tyler and Smith (1975) studied the CO_2 gasification of pet coke from 1030 to 1180 K in an atmospheric furnace using three different size fractions (2900, 900, 220 µm). They observed that the N₂ surface area of the pet coke had either remained unchanged or increased up to two times the original surface area. The pet coke in their study was reacted up to 5 hours so the effect of residence time was not known. The trend observed in Figure 6.14 is that longer residence times (up to ~1 sec) caused the N₂ surface area of the pet coke char to level off near values of the unreacted pet coke. The discrepancy in trends can be explained by the differences in reaction conditions. The experiments from the HPFFB were conducted at much lower particle residence times (< 1 s), but operated at higher heating rates, temperature, and pressure. Zamalloa and Utigard (1995) studied the CO₂ gasification of pet coke from 1173 to 1573 K using a heating rate of 20 K/min in an atmospheric TGA. The reaction time of these experiments was 30-40 minutes. The N₂ surface area of the pet coke decreased with increasing temperature, which is the same trend observed in by the experimental points near 350 ms of the 15 atm chars (1918 & 1681 K). Although no N₂ surface area analysis was performed on any of the pyrolyzed pet coke chars, Wu et al. (2009) found that a higher heating rate caused a decrease in the N₂ surface area of pyrolyzed pet coke. These experiments were conducted at 950 °C in an atmospheric furnace using heating rates of 6 K/min and 650 K/s. A comparison of the pet coke CO₂ surface areas with the experiments of other researchers was not possible due to the lack of this data in the literature.

A discussion of pet coke diameter ratios, apparent densities of pet coke chars, tar yields during pet coke pyrolysis and gasification experiments, and elemental composition of pet coke chars is given in Appendices K to N.

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6.6 Summary

The pyrolysis and CO₂ gasification of petroleum coke was studied from 1 to 15 atm using both an atmospheric FFB and a HPFFB at peak temperatures from 1402 K to 2139 K. The ASTM volatiles value of pet coke (8.78 % daf) appeared to be a good approximation of the mass release experienced during pyrolysis in all experiments performed from 1 to 15 atm. Pet coke CO₂ gasification was only observed to occur at the 10 and 15 atm experiments, but not at lower pressures. This suggests that the CO₂ gasification rate of pet coke has strong pressure dependence. Particle residence times in the reactor were less than 1.06 s in all experiments. The apparent first-order Arrhenius pre-exponential factor and activation energy determined for CO₂ gasification of pet coke were 333.2 g /cm²/s/atm and 140 kJ/mol, respectively. These parameters were regressed from experiments with peak temperatures in the range of 1722-2139 K at partial pressures of CO₂ from 1.7 to 3.2 atm.

The measured pet coke CO_2 gasification rates were compared with reported rates of pet coke and coal in the literature, and found to be consistent. The gasification rate of pet coke was also compared to Wyodak coal, since the two fuels were run separately in the HPFFB at the same operating conditions. At operating pressures up to 5 atm and where P_{CO2} was less than 1.15 atm, the CO_2 gasification reactivity of Wyodak coal was higher than pet coke. However, the reactivity of pet coke and Wyodak coal were on the same order of magnitude from experiments at 10 and 15 atm where the peak temperature and P_{CO2} ranges were 1722-2139 K and 1.7-3.2 atm, respectively.

Ash was found to vaporize from the char during experiments, especially at longer residence times. Up to 42 wt% of the ash in the pet coke was observed to leave the char, with ~20 wt% being an average value. SEM images of pet coke char revealed cracks in the char

surface at all pressures over a wide range of temperature conditions. These cracks are believed to be caused as a result of the high particle heating rates of the flat-flame burners and are thought to form as the volatiles quickly escape the interior of the pet coke particle. Besides these cracks, both pyrolyzed and partially gasified pet coke char closely resembled the structure of raw pet coke. Numerous surface area measurements (CO_2 and N_2) were taken of the pet coke chars collected over a variety of conditions. Temperature appeared to have the most influence on the surface area of the pet coke chars. A pet coke char collected from a hotter condition usually resulted in a char with decreased surface area. Increased particle residence time also was observed to lower the surface area of the pet coke chars. N_2 surface area was only obtained on partially gasified chars. At low residence times, the N_2 surface area increased several fold when compared to the N_2 surface area of raw pet coke, but would then drop back down to values close to the surface area of raw pet coke. This implies that the mesopore region of the pet coke grew and then shrunk during CO_2 gasification.

7. Error Analysis

The error analysis focuses on mass release since sawdust pyrolysis and CO_2 gasification of pet coke were the major research topics of this thesis. Recall that mass release was defined in Section 4.6.

For the pyrolysis of sawdust, replicate ash tests were performed using sawdust chars that had been collected from the FFB on different days in order to calculate replicate mass release values (see Section 4.6.1). The results are shown in Table 7.1.

Peak	Particle	% Mass Release (daf)	Standard
Temperature	Residence Time	by Ash Tracer	Deviation
(K)	(ms)		%
		97.8	
1163	55	96.8	0.6
		96.6	
		96.7	
1433	23	98.4	15
1155	23	96.4	1.5
1433	31	98.9	0.1
1 100	51	98.7	0.1

Table 7.1. Replicate ash-tracer mass release values during sawdust pyrolysis FFB experiments

The standard deviation (s) in Table 7.1 was calculated using N number of data points:

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$$
(7.1)

where the arithmetic mean (\bar{x}) of the individual data points (x_i) was defined as:

$$\overline{x} = \frac{1}{N} \sum_{i=1}^{N} x_i \tag{7.2}$$

There was very good repeatability in the sawdust mass release as indicated by the low standard deviations (< 1.5 %) of ash-tracer mass release in Table 7.1.

The error analysis of the sawdust pyrolysis experiments was further investigated by calculating the mass release using the inorganic tracers of Si, Al, and Ti (see Section 4.6.2) for a single sawdust char collected from the FFB. This value was then compared to the mass-release values obtained by ash tracer and a mass balance for the same condition (1163 K 55 ms), as shown in Table 7.2. Mass release by inorganic tracers and ash tracer agreed within 1%, while mass release by inorganic tracers and mass balance agree within 4%. This comparison was performed for only one condition due to the costly task of collecting enough sawdust char to perform an accurate ICP test.

% MR by Al,	Si, Ti Tracers	% MR by Ash Tracer	% MR by Mass Balance
Al	97.5%		
Si	99.1%	97.3%	94.2%
Ti	98.4%		

 Table 7.2. Mass release summary of the 1163 K 55 ms FFB sawdust case (daf basis)

The error analysis for the pet coke CO_2 gasification experiments relied on mass release values as determined by a mass balance (using weight of char collected and weight of raw pet coke fed). Mass release values could not be calculated by ash tracer and inorganic tracers for pet coke due to ash vaporization (see Section 6.3) and the absence of measurable quantities of Si, Al, and Ti in the pet coke, respectively. Fortunately, mass release values for the pet coke experiments could be calculated since the weights of pet coke char had been recorded as well as the amount of raw pet coke fed. The best mass balance possible was ensured by shutting down between different experimental conditions in order to clean out the collection system, and weighing the amount of pet coke fed as well as the collected char. A summary of the mass release pet coke CO_2 gasification data is shown in Table 7.3 as calculated by a mass balance.

Pressure (atm)	Peak Temperature (K)	Particle Residence Time (ms)	% MR (daf) * by mass balance	Standard Deviation %
10	1722	150	11.8 10.8	0.7
10	1967	663	34.8 36.6	1.3
10	1967	1061	26.2 48.1 43.3	11.5
15	1918	577	57.7 58.4	0.5
15	1918	994	38.0 44.5 52.6 50.0	6.5

Table 7.3. Mass release summary of the pet coke CO₂ gasification experiments in the HPFFB

The average standard deviation in pet coke mass release using all five experimental conditions where replicate experiments had been performed was 4.1%. The 10 atm 1967 K condition at 1061 ms and the 15 atm 1918 K condition at 994 ms had the highest standard deviations in mass release. Both of these conditions were run at the longest residence time possible for the condition (with the collection probe positioned 16.25" above the burner). It is possible that some pet coke char did not make it into the collection probe, but collected in other parts of the reactor during some of these replicate runs. The replicate experiments in Table 7.3 showed very good repeatability for mass release values determined by a mass balance. Mass release values determined by ash tracer or inorganic tracers are thought to be more accurate, but were not possible in this case.

8. Conclusions and Recommendations

8.1 Sawdust Pyrolysis Experiments

Sawdust pyrolysis experiments were performed on an atmospheric FFB at peak temperatures of 1163, 1320, and 1433 K. The conclusions for these experiments are:

- Sawdust mass release from devolatilization in the FFB exceeded the ASTM volatiles value by 12%.
- 2) The low tar yields (< 3 wt%) are explained by secondary tar cracking that occurs above 500 °C. Although tar yields can be as high as 75 wt% following the primary pyrolysis of wood, tar cracking caused the light gas to be the major product. The tar-cracking model of Fagbemi et al. (2001) well predicted the sawdust tar yields measured on the FFB. The pre-exponential factor and activation energy in Fagbemi's model were 4.28x10⁶ s⁻¹ and 107.5 kJ/mol, respectively.
- From SEM images of the sawdust char, it was shown that the shape of the particles continues to change even after mass release is complete.
- 4) The sawdust char particles were spherical with many voids and pores. The original structure of the sawdust did not exist after devolatilization due to melting of the cell structure and plastic transformations. The fact that sawdust particles turn spherical after

pyrolysis at high heating rates means that combustion or gasification of sawdust can be modeled assuming spherical particles.

8.2 Biomass Pyrolysis Modeling

Sawdust pyrolysis was modeled using the CPD model combined with a tar-cracking model. The conclusions for biomass modeling are:

- This model satisfactorily predicted sawdust devolatilization yields for 5 different sawdusts from 3 different reactors (flat-flame burner, fluidized bed, & drop-tube).
- 2) The biomass pyrolysis model is likely to fail when the parent biomass has high ash content since it assumes that biomass devolatilization occurs as the weighted sum of its components (i.e., cellulose, hemicellulose, lignin).
- 3) The model performed better at predicting biomass pyrolysis yields from experiments with a high heating rate. Otherwise, the predicted tar yields near 500 °C were too high.

8.3 Pet Coke Pyrolysis and CO₂ Gasification Experiments

The pyrolysis and CO_2 gasification of petroleum coke was studied from 1 to 15 atm using both an atmospheric FFB and a HPFFB. The conclusions follow:

- 1) The ASTM volatiles value of pet coke appeared to be a good approximation of the mass release experienced during pyrolysis in all experiments performed from 1 to 15 atm.
- 2) Ash was found to vaporize from the pet coke char during experiments, especially at longer residence times. Up to 42 wt% of the ash in the pet coke was observed to leave the char, with ~20 wt% being an average value.

- 3) SEM images of pet coke char revealed cracks in the char surface at all pressures over a wide range of temperature conditions. These cracks are believed to be caused as a result of the high particle heating rates of the flat-flame burners and are thought to form as the volatiles quickly escape the interior of the pet coke particle. Besides these cracks, both pyrolyzed and partially gasified pet coke char closely resembled the structure of raw pet coke.
- 4) Temperature appeared to have the most influence on the surface area $(CO_2 \text{ and } N_2)$ of the pet coke chars. A pet coke char collected from a hotter condition usually resulted in a char with decreased surface area. Increased particle residence time also was observed to lower the surface area of the pet coke chars. At low residence times, the N₂ surface area increased several fold when compared to the N₂ surface area of raw pet coke, but would then drop back down to values close to the surface area of raw pet coke. This implies that the mesopore region of the pet coke grew and then shrunk during CO_2 gasification.

8.4 Modeling of Pet Coke CO₂ Gasification

A first-order model was used to regress Arrhenius kinetic parameters for the CO_2 gasification of pet coke using measured mass release data from 10 and 15 atm HPFFB experiments. The results of the modeling efforts follow:

The apparent first-order Arrhenius pre-exponential factor and activation energy for CO₂ gasification of pet coke were 333.2 g Carbon/(cm²·s·atm CO₂) and 140 kJ/mol, respectively. These parameters were regressed from experiments with peak temperatures in the range of 1722-2139 K at partial pressures from 1.7 to 3.2 atm.

- 2) The measured pet coke CO_2 gasification rates were compared with reported rates of pet coke and coal char in the literature, and found to be consistent. The gasification rate of pet coke was also compared to Wyodak coal, since the two fuels were run separately in the HPFFB at the same operating conditions. At operating pressures up to 5 atm and where P_{CO2} was less than 1.15 atm, the CO_2 gasification reactivity of Wyodak coal was much higher than pet coke. However, the reactivity of pet coke and Wyodak coal were on the same order of magnitude from experiments at 10 and 15 atm where the peak temperature and P_{CO2} ranges were 1722-2139 K and 1.7-3.2 atm, respectively.
- 3) An nth-order model would likely allow an even better fit of the measured pet coke gasification data. The fact that no extent of pet coke gasification by CO_2 was measured below 10 atm suggests that the rate has strong pressure dependence, implying that the order of *n* would exceed unity in an nth-order model.

8.5 **Recommendations**

Listed below are several recommendations for future work based on knowledge gained during this thesis project:

Develop a new method to measure the gas temperature profiles in the HPFFB. There
 Improvements should be made to the safety of the HPFFB lab by changing the way
 centerline gas temperature profiles are measured (see Appendix E). A rubber stopper was
 used to maintain the pressure seal of the reactor up to 15 atm, but the danger of doing this
 is leaking high concentrations of CO into the room if the seal fails. The ceramic shaft of
 the thermocouple becomes a projectile if the seal between the rubber stopper and ceramic

shaft is compromised. It would be safer to develop a contraption where the thermocouple shaft was held in place and hooked to a moveable track.

- 2) Install hotter heaters in the HPFFB reactor. The heaters in the HPFFB were only rated to 1200 °C, which caused the temperature inside the reactor to level off near 1200-1300 °C during the experiments with long residence times (see Figure 6.2). These relatively low temperatures may be adequate for combustion studies, but are not highly suitable for gasification studies where the kinetics are orders of magnitude slower. The mass release of the pet coke reached an asymptote at a collection height about 6 inches above the burner (see Figure 6.5). Heaters rated to a higher temperature would allow a measurable difference in gasification reactivity above 6" above the burner.
- Increase the CO₂ concentrations in the HPFFB reactor. A higher extent of CO₂ gasification could have measured if a tank of CO₂ was plumbed into the line where oxidizer N₂ was introduced in this project.
- 4) Be hesitant about future biomass studies using the atmospheric FFB. Sawdust experiments in the FFB were very time consuming due to frequent clogging problems in the narrow feeder tube, which could not be widened. The biomass experiments were expensive in terms of man hours and costs of gases (mainly CO). Sawdust was fed at a low feed rate of 0.50 g/hr, and a typical char yield per week was only 400 mg.
- 5) *Study biomass tar cracking at higher temperatures*. It was noticed in the atmospheric FFB experiments that there was a small fraction of the sawdust tar that did not thermally crack into light gas (see Section 5.3). It would be interesting to see if sawdust tar cracks at a higher temperature since the peak temperature of the experiments of this thesis was only 1433 K. Cracking of tar is important since even low tar yields can cause problems

in industry by fouling and corroding equipment, causing damage to motors and turbines, lowering catalyst efficiency, and condensing in transfer lines.

- 6) Study *the char morphology changes during biomass pyrolysis for other types of biomass besides sawdust*. In this thesis, it was observed that the original structure of sawdust did not exist after devolatilization due to the melting of the cell structure and plastic transformations. It would be interesting to see if other types of biomass particles also turn spherical after devolatilization at high initial heating rates.
- 7) Study the pet coke CO₂ gasification reactivity at higher pressures in a TGA or drop tube reactor. Nearly all the pet coke CO₂ gasification studies in the literature have been conducted at atmospheric pressure where the pet coke CO₂ gasification reactivity is lower than coal. In this thesis, it was noticed that the CO₂ gasification reactivity of pet coke had a strong pressure dependence that caused the pet coke to be as reactive as coal. It would be interesting to find out if this same observation is true on other types of reactors besides a flat-flame burner.

9. References

- Antal, M. J., "Effects of Reactor Severity on the Gas-Phase Pyrolysis of Celulose-Derived and Kraft Lignin-Derived Volatile Matter," *Industrial & Engineering Chemistry Product Research and Development*, 22(2), 366-375 (1983).
- Bahlawane, N., U. Struckmeier, T. S. Kasper and P. Osswald, "Noncatalytic Thermocouple Coatings Produced with Chemical Vapor Deposition for Flame Temperature Measurements," *Review of Scientific Instruments*, **78**(1) (2007).
- Batchelder, H. R., R. M. Busche and W. P. Armstrong, "Kinetics of Coal Gasification," *Industrial & Engineering Chemistry* **45**, 1856 (1953).
- Baumlin, S., F. Broust, M. Ferrer, N. Meunier, E. Marty and J. Lede, "The Continuous Self Stirred Tank Reactor: Measurement of the Cracking Kinetics of Biomass Pyrolysis Vapours," *Chemical Engineering Science*, **60**(1), 41-55 (2005).
- Biagini, E., F. Barontini and L. Tognotti, "Devolatilization of Biomass Fuels and Biomass Components Studied by TG/FTIR Technique," *Industrial & Engineering Chemistry Research*, 45(13), 4486-4493 (2006).
- Bird, B., W. Stewart and E. Lightfoot, <u>Transport Phenomena</u>, New York, John Wiley & Sons, Inc. (2002).
- Brage, C., Q. H. Yu and K. Sjostrom, "Characteristics of Evolution of Tar from Wood Pyrolysis in a Fixed-Bed Reactor," *Fuel*, **75**(2), 213-219 (1996).
- Bridgwater, A. V., "The Technical and Economic-Feasibility of Biomass Gasification for Power-Generation," *Fuel*, **74**(5), 631-653 (1995).
- Bridgwater, A. V., "Renewable Fuels and Chemicals by Thermal Processing of Biomass," *Chemical Engineering Journal*, **91**(2-3), 87-102 (2003).
- Bridgwater, A. V., "Biomass Fast Pyrolysis," Thermal Science, 8, 21-49 (2004).
- Caballero, J. A., R. Font and A. Marcilla, "Comparative Study of the Pyrolysis of Almond Shells and Their Fractions, Holocellulose and Lignin. Product Yields and Kinetics," *Thermochimica Acta*, **276**, 57-77 (1996).

- Cetin, E., B. Moghtaderi, R. Gupta and T. F. Wall, "Influence of Pyrolysis Conditions on the Structure and Gasification Reactivity of Biomass Chars," *Fuel*, **83**(16), 2139-2150 (2004).
- Couhert, C., J. M. Commandre and S. Salvador, "Is It Possible to Predict Gas Yields of Any Biomass after Rapid Pyrolysis at High Temperature from Its Composition in Cellulose, Hemicellulose and Lignin?," *Fuel*, **88**(3), 408-417 (2009).
- Crawford, R. L., <u>Lignin Biodegradation and Transformation</u>, New York, John Wiley & Sons (1981).
- Di Blasi, C., "Modeling Chemical and Physical Processes of Wood and Biomass Pyrolysis," *Progress in Energy and Combustion Science*, **34**(1), 47-90 (2008).
- Dupont, C., J. M. Commandre, P. Gauthier, G. Boissonnet, S. Salvador and D. Schweich, "Biomass Pyrolysis Experiments in an Analytical Entrained Flow Reactor between 1073 K and 1273 K," *Fuel*, 87(7), 1155-1164 (2008).
- Dutta, S., C. Y. Wen and R. J. Belt, "Reactivity of Coal and Char .1. Carbon-Dioxide Atmosphere," *Industrial & Engineering Chemistry Process Design and Development*, 16(1), 20-30 (1977).
- Essenhigh, R. H., <u>Fundamentals of Coal Combustion</u>, in *Chemistry of Coal Utilization*, 2nd suppl. vol. (M.A. Elliot, ed.), pp.1153-1312, Wiley, New York (1981).
- Fagbemi, L., L. Khezami and R. Capart, "Pyrolysis Products from Different Biomasses: Application to the Thermal Cracking of Tar," *Applied Energy*, **69**(4), 293-306 (2001).
- Fermoso, J., B. Arias, M. G. Plaza, C. Pevida, F. Rubiera, J. J. Pis, F. Garcia-Pena and P. Casero, "High-Pressure Co-Gasification of Coal with Biomass and Petroleum Coke," *Fuel Processing Technology*, **90**(7-8), 926-932 (2009).
- Fletcher, T. H., "Time-Resolved Temperature-Measurements of Individual Coal Particles During Devolatilization," *Combustion Science and Technology*, **63**(1-3), 89-105 (1989).
- Fletcher, T. H., A. R. Kerstein, R. J. Pugmire, M. S. Solum and D. M. Grant, "Chemical Percolation Model for Devolatilization .3. Direct Use of C-13 NMR Data to Predict Effects of Coal Type," *Energy & Fuels*, 6(4), 414-431 (1992).
- Fletcher, T. H., J. L. Ma, J. R. Rigby, A. L. Brown and B. W. Webb, "Soot in Coal Combustion Systems," *Progress in Energy and Combustion Science*, **23**(3), 283-301 (1997).
- Gale, T. K., C. H. Bartholomew and T. H. Fletcher, "Decreases in the Swelling and Porosity of Bituminous Coals During Devolatilization at High Heating Rates," *Combustion and Flame*, **100**(1-2), 94-100 (1995).
- Ginter, D. M., G. A. Somorjai and H. Heinemann, "Factors Affecting the Reactivity of Chars and Cokes During Low-Temperature (640-Degrees-C) Steam Gasification," *Energy & Fuels*, 7(3), 393-398 (1993).
- Goetz, G. J., N. Y. Nsakala, R. L. Patel and T. C. Lao, "Combustion and Gasification Kinetics of Chars from Four Commercially Significant Coals of Varying Rank," Second Annual Contractors' Conference on Coal Gasification, Palo Alto, CA (1982).
- Green, D. W. and R. H. Perry, Perry's Chemical Engineers' Handbook, 6th Edition (1984).
- Gu, J., S. Wu, Y. Wu and J. Gao, "CO₂-Gasification Reactivity of Different Carbonaceous Materials at Elevated Temperatures," *Energy Sources Part A-Recovery Utilization and Environmental Effects*, **31**(3), 232-243 (2009).
- Guerrero, A., M. P. Ruiz, M. U. Alzueta, R. Bilbao and A. Millera, "Pyrolysis of Eucalyptus at Different Heating Rates: Studies of Char Characterization and Oxidative Reactivity," *Journal of Analytical and Applied Pyrolysis*, **74**(1-2), 307-314 (2005).
- Harris, D. J. and I. W. Smith, "Intrinsic Reactivity of Petroleum Coke and Brown Coal Char to Carbon Dioxide, Steam and Oxygen," Twenty-Third International Symposium on Combustion, The Combustion Institute: 1185-1190 (1990).
- Harris, D. J., D. G. Roberts and D. G. Henderson, "Gasification Behaviour of Australian Coals at High Temperature and Pressure," *Fuel*, **85**(2), 134-142 (2006).
- Higman, C. and M. v. d. Burgt, Gasification, London, Elsevier Science (2003).
- Hurt, R., J. K. Sun and M. Lunden, "A Kinetic Model of Carbon Burnout in Pulverized Coal Combustion," *Combustion and Flame*, **113**(1-2), 181-197 (1998).
- Hurt, R. H., D. R. Dudek, J. P. Longwell and A. F. Sarofim, "The Phenomenon of Gasification-Induced Carbon Densification and Its Influence on Pore Structure Evolution," *Carbon*, 26(4), 433-449 (1988).
- Incropera, F. P. and D. P. Dewitt, <u>Fundamentals of Heat and Mass Transfer</u>, Chicago, John Wiley & Sons (2002).
- Internet1, "Lignin Picture,"

http://images.google.com/imgres?imgurl=http://www.scq.ubc.ca/wpcontent/uploads/2007/01/lignin.gif&imgrefurl=http://www.scq.ubc.ca/biofuels-and-theprospect-of-converting-plant-fibres-into-gasoline-usingenzymes/&usg=__V2sfyE9PdaaJOT31Cz9isECKJ8o=&h=297&w=396&sz=4&hl=en&s tart=7&tbnid=pt2UZExb55OYcM:&tbnh=93&tbnw=124&prev=/images%3Fq%3Dligni n%26gbv%3D2%26hl%3Den Internet2, "Cellulose & Hemicellulose Pictures,"

http://images.google.com/imgres?imgurl=http://blogs.princeton.edu/chm333/f2006/biom ass/Hemicellulose.gif&imgrefurl=http://blogs.princeton.edu/chm333/f2006/biomass/bio_ oil/02_chemistryprocessing_the_basics/01_chemistry/&usg=__tnQkrNrvYfK39KpuG5Z RaI5BBU=&h=175&w=275&sz=2&hl=en&start=2&um=1&tbnid=ceGEmV21_qlXZM: &tbnh=73&tbnw=114&prev=/images%3Fq%3Dhemicellulose%26ndsp%3D18%26hl%3 Den%26sa%3DG%26um%3D1

- Jenkins, B. M., L. L. Baxter and T. R. Miles, "Combustion Properties of Biomass," *Fuel Processing Technology*, **54**(1-3), 17-46 (1998).
- Kang, B. S., K. H. Lee, H. J. Park, Y. K. Park and J. S. Kim, "Fast Pyrolysis of Radiata Pine in a Bench Scale Plant with a Fluidized Bed: Influence of a Char Separation System and Reaction Conditions on the Production of Bio-Oil," *Journal of Analytical and Applied Pyrolysis*, **76**(1-2), 32-37 (2006).
- Karunanithi, P. N. a. T., "Kinetic Modeling in Biomas Pyrolysis a Review," *Journal of Applied Sciences Research*, **4**(12), 1627-1636 (2008).
- Kaskan, W. E., "The Dependence of Flame Temperature on Mass Burning Velocity," Sixth Symposium (International) on Combustion (1957).
- Katsuki, M., Y. Mizutani and Y. Matsumoto, "An Improved Thermocouple Technique for Measurement of Fluctuating Temperatures in Flames," *Combustion and Flame*, **67**(1), 27-36 (1987).
- Kocaefe, D., A. Charette and L. Castonguay, "Green Coke Pyrolysis Investigation of Simultaneous Changes in Gas and Solid-Phases," *Fuel*, **74**(6), 791-799 (1995).
- Koufopanos, C. A., G. Maschio and A. Lucchesi, "Kinetic Modeling of the Pyrolysis of Biomass and Biomass Components," *Canadian Journal of Chemical Engineering*, **67**(1), 75-84 (1989).
- Koufopanos, C. A., N. Papayannakos, G. Maschio and A. Lucchesi, "Modeling of the Pyrolysis of Biomass Particles - Studies of Kinetics, Thermal and Heat-Transfer Effects," *Canadian Journal of Chemical Engineering*, **69**(4), 907-915 (1991).
- Kwon, T. W., S. D. Kim and D. P. C. Fung, "Reaction-Kinetics of Char-CO₂ Gasification," *Fuel*, **67**(4), 530-535 (1988).
- Li, S. G., S. P. Xu, S. Q. Liu, C. Yang and Q. H. Lu, "Fast Pyrolysis of Biomass in Free-Fall Reactor for Hydrogen-Rich Gas," *Fuel Processing Technology*, 85(8-10), 1201-1211 (2004).

- Ma, J., "Soot Formation During Coal Pyrolysis," PhD Dissertation, Brigham Young University (1996).
- McBride, B. J., M. Zehe and S. Gordon, "Nasa Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species," NASA TP-2002-215556 (2002).
- Merrick, D., "Mathematical-Models of the Thermal-Decomposition of Coal .2. Specific-Heats and Heats of Reaction," *Fuel*, **62**(5), 540-546 (1983).
- Milenkova, K. S., A. G. Borrego, D. Alvarez, J. Xiberta and R. Menendez, "Devolatilisation Behaviour of Petroleum Coke under Pulverised Fuel Combustion Conditions," *Fuel*, 82(15-17), 1883-1891 (2003).
- Miller, R. S. and J. Bellan, "A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicellulose and Lignin Kinetics," *Combustion Science and Technology*, 126(1-6), 97-137 (1997).
- Mims, C. A., M. Neville, R. Quann and A. Sarofim, "Laboratory Study of Trace Element Transformation During Coal Combustion," presented at the National 87th AIChE Meeting, August 19-22, Boston, MA (1979).
- Mitchell, R. E., "A Theoretical Model of Chemically Reacting Recirculating Flow," Livermore, CA. Sandia National Laboratory, SAND79-8236 (1980).
- Mitchell, R. E., R. H. Hurt, L. L. Baxter and D. R. Hardesty, "Compilation of Sandia Coal Char Combustion Data and Kinetics Analyses: Milestone Report", Sandia Technical Report, SAND92-8208, Sandia National Laboratory, Livermore, CA (1992).
- Mohan, D., C. U. Pittman and P. H. Steele, "Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review," *Energy & Fuels*, **20**(3), 848-889 (2006).
- Mok, W. S. L. and M. J. Antal, "Uncatalyzed Solvolysis of Whole Biomass Hemicellulose by Hot Compressed Liquid Water," *Industrial & Engineering Chemistry Research*, **31**(4), 1157-1161 (1992).
- Monson, C. R., "Char Oxidation at Elevated Pressure," PhD Dissertation, Brigham Young University (1992).
- Nunn, T. R., J. B. Howard, J. P. Longwell and W. A. Peters, "Product Compositions and Kinetics in the Rapid Pyrolysis of Sweet Gum Hardwood," *Industrial & Engineering Chemistry Process Design and Development*, 24(3), 836-844 (1985).
- Pond, H. R., T. H. Fletcher and L. L. Baxter, "Prediction of Tar and Light Gas During Pyrolysis of Black Liquor and Biomass," <u>3rd Annual Joint Meeting of the U.S. Sections of the</u> <u>Combustion Institute</u>, Chicago, IL (2003).

- Ranzi, E., A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci and S. Sommariva, "Chemical Kinetics of Biomass Pyrolysis," *Energy & Fuels*, **22**(6), 4292-4300 (2008).
- Rath, J. and G. Staudinger, "Cracking Reactions of Tar from Pyrolysis of Spruce Wood," *Fuel*, **80**(10), 1379-1389 (2001).
- Raveendran, K., A. Ganesh and K. C. Khilar, "Pyrolysis Characteristics of Biomass and Biomass Components," *Fuel*, **75**(8), 987-998 (1996).
- Revankar, V. V. S., A. N. Gokarn and L. K. Doraiswamy, "Studies in Catalytic Steam Gasification of Petroleum Coke with Special Reference to the Effect of Particle-Size," *Industrial & Engineering Chemistry Research*, 26(5), 1018-1025 (1987).
- Rowell, R. M., <u>The Chemistry of Solid Wood</u>, Washington D.C., American Chemical Society (1984).
- Rowley, R. L., W. V. Wilding, J. L. Oscarson, Y. Yang and N. F. Giles, "Dippr Data Compilation of Pure Chemical Properties, Design Institute for Physical Properties," Provo, Utah, Brigham Young University (2010).
- Scott, D. S. and J. Piskorz, "The Flash Pyrolysis of Aspen-Poplar Wood," *Canadian Journal of Chemical Engineering*, **60**(5), 666-674 (1982).
- Scott, D. S. and J. Piskorz, "The Continuous Flash Pyrolysis of Biomass," *Canadian Journal of Chemical Engineering*, **62**(3), 404-412 (1984).
- Scott, D. S., J. Piskorz and D. Radlein, "Liquid Products from the Continuous Flash Pyrolysis of Biomass," *Industrial & Engineering Chemistry Process Design and Development*, 24(3), 581-588 (1985).
- Scott, D. S., J. Piskorz, M. A. Bergougnou, R. Graham and R. P. Overend, "The Role of Temperature In the Fast Pyrolysis of Cellulose and Wood," *Industrial & Engineering Chemistry Research*, 27(1), 8-15 (1988).
- Senneca, O. and P. Salatino, "Loss of Gasification Reactivity toward O₂ and CO₂ Upon Heat Treatment of Carbons," *Proceedings of the Combustion Institute*, **29**, 485-493 (2002).
- Shaddix, C. R., "Correcting Thermocouple Measurements for Radiation Loss: A Critical Review," Proceedings of the 33rd National Heat Transfer Conference, Albuquerque, New Mexico (1999).
- Sheng, C. D. and J. L. T. Azevedo, "Modeling Biomass Devolatilization Using the Chemical Percolation Devolatilization Model for the Main Components," *Proceedings of the Combustion Institute*, 29, 407-414 (2002).

- Shurtz, R., "Pressurized Coal Pyrolysis and Gasification at High Initial Heating Rates," presented at the ACERC Conference, Feb. 25, Provo, UT (2010).
- Shurtz, R., "Effects of Pressure on the Properties of Coal Char and Soot under Gasification Conditions at High Initial Heating Rates," PhD Dissertation, Brigham Young University (In Progress 2011).
- Siegel, R. and J. Howell, <u>Thermal Radiation Heat Transfer</u>, New York, Hemisphere Publishing Corporation (1981).
- Smith, K. L., L. D. Smoot, T. H. Fletcher and R. J. Pugmire, <u>The Structure and Reaction</u> <u>Processes of Coal</u>, New York, Plenum Press (1994).
- Smoot, L. D. and P. J. Smith, <u>Coal Combustion and Gasification</u>, New York, Plenum Press (1985).
- Smoot, L. D., <u>Fundamentals of Coal Combustion for Clean and Efficient Use</u>, (Coal Science and Technology 20), Amsterdam, Elsevier (1993).
- Solomon, P. R., D. G. Hamblen, R. M. Carangelo and J. L. Krause, "Coal Thermal Decomposition in an Entrained Flow Reactor: Experiments and Theory," Nineteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA (1982).
- Soltes, E. J. and T. J. Elder, <u>Pyrolysis. In Organic Chemicals from Biomass</u>, Boca Raton, FL, CRC Press (1981).
- Sowa, J. M., "Studies of Coal Nitrogen Release Chemistry for Oxyfuel Combustion and Chemical Additives," M.S. Thesis, Chemical Engineering, Brigham Young University (2009).
- Sricharoenchaikul, V., PhD Dissertation, Georgia Institute of Technology (2001).
- Stiles, H. N. and R. Kandiyoti, "Secondary Reactions of Flash Pyrolysis Tars Measured in a Fluidized-Bed Pyrolysis Reactor with Some Novel Design-Features," *Fuel*, 68(3), 275-282 (1989).
- Sun, L. and B. X. Shen, "Microcrystallite Structural Changes of Petroleum Coke During the Course of Carbonization Analyzed by X-Ray Diffraction," *Petroleum Processing Section*, 20, 53-56 (2004).
- Trommer, D. and A. Steinfeld, "Kinetic Modeling for the Combined Pyrolysis and Steam Gasification of Petroleum Coke and Experimental Determination of the Rate Constants by Dynamic Thermogravimetry in the 500-1520 K Range," *Energy & Fuels*, **20**(3), 1250-1258 (2006).

- Tsai, C. Y. and A. W. Scaroni, "The Structural-Changes of Bituminous Coal Particles During the Initial-Stages of Pulverized-Coal Combustion," *Fuel*, **66**(2), 200-206 (1987).
- Turkdogan, E. T. and J. V. Vinters, "Effect of Carbon Monoxide on the Rate of Oxidation of Charcoal, Graphite and Coke in Carbon Dioxide," *Carbon*, **8**, 39-53 (1970).
- Tyler, R. J. and I. W. Smith, "Reactivity of Petroleum Coke to Carbon Dioxide between 1030 and 1180 K," *Fuel*, **54**(2), 99-104 (1975).
- Vassilatos, V., G. Taralas, K. Sjostrom and E. Bjornbom, "Catalytic Cracking of Tar in Biomass Pyrolysis-Gas in the Presence of Calcined Dolomite," *Canadian Journal of Chemical Engineering*, **70**(5), 1008-1013 (1992).
- Vizzini, G., E. B. A. Bardi, M. Calcitelli and L. Tognotti, "Prediction of Rapid Biomass Devolatilization Yields with an Upgraded Version of the Bio-CPD Model," 31st Meeting of the Italian Section of the Combustion Institute, Torino, Italy (2008).
- Wagenaar, M., W. Prins and W. P. M. Vanswaaij, "Flash Pyrolysis Kinetics of Pine Wood," *Fuel Processing Technology*, **36**(1-3), 291-298 (1993).
- Walker, P. L., F. J. Rusinko and L. G. Austin, "Gas Reactions of Carbon," *Advances in Catalysis*, **11**, 133-221 (1959).
- Williams, T. C. and C. R. Shaddix, "Contamination of Carbon Monoxide with Metal Carbonyls: Implications for Combustion Research," *Combustion Science and Technology*, **179**(6), 1225-1230 (2007).
- Wu, Y. Q., S. Y. Wu, J. Gu and J. S. Gao, "Differences in Physical Properties and CO₂ Gasification Reactivity between Coal Char and Petroleum Coke," *Process Safety and Environmental Protection*, 87(5), 323-330 (2009).
- Wurzenberger, J. C., S. Wallner, H. Raupenstrauch and J. G. Khinast, "Thermal Conversion of Biomass: Comprehensive Reactor and Particle Modeling," *Aiche Journal*, 48(10), 2398-2411 (2002).
- Yoon, S. J., Y. C. Choi, S. H. Lee and J. G. Lee, "Thermogravimetric Study of Coal and Petroleum Coke for Co-Gasification," (2007).
- Zamalloa, M., D. Ma and T. A. Utigard, "Oxidation Rates of Industrial Cokes with CO₂ and Air," *ISIJ International*, **35**(5), 458-463 (1995).
- Zamalloa, M. and T. A. Utigard, "Characterization of Industrial Coke Structures," *ISIJ International*, **35**(5), 449-457 (1995).
- Zeng, D., "Effects of Pressure on Coal Pyrolysis at High Heating Rates and Char Combustion," PhD Dissertation, Brigham Young University (2005).

- Zhang, H., "Nitrogen Evolution and Soot Formation During Secondary Coal Pyrolysis," PhD Dissertation, Brigham Young University (2001).
- Zhang, J., H. Toghiani, D. Mohan, C. U. Pittman and R. K. Toghiani, "Product Analysis and Thermodynamic Simulations from the Pyrolysis of Several Biomass Feedstocks," *Energy* & Fuels, 21(4), 2373-2385 (2007).
- Zhang, Y., S. Kajitani, M. Ashizawa and K. Miura, "Peculiarities of Rapid Pyrolysis of Biomass Covering Medium- and High-Temperature Ranges," *Energy & Fuels*, **20**(6), 2705-2712 (2006).
- Zou, J. H., Z. J. Zhou, F. C. Wang, W. Zhang, Z. H. Dai, H. F. Liu and Z. H. Yu, "Modeling Reaction Kinetics of Petroleum Coke Gasification with CO₂," *Chemical Engineering and Processing*, 46(7), 630-636 (2007).
- Zou, J. H., B. L. Yang, K. F. Gong, S. Y. Wu, Z. J. Zhou, F. C. Wang and Z. H. Yu, "Effect of Mechanochemical Treatment on Petroleum Coke-CO₂ Gasification," *Fuel*, 87(6), 622-627 (2008).

Appendix A. Tabulated Sawdust Pyrolysis Data

Figure A.1 shows a typical size distribution of the sawdust particles using a Coulter Counter LS series machine. The size distribution is on a mass mean basis. Sixteen sizing tests over 5 days yielded an average particle diameter of 88.2 microns with a standard deviation of 4.5 microns. There are two peaks in Figure A.1, indicating two separate size fractions of the sawdust particles. Additional sieving of the sawdust did not alleviate the problem of two size fractions. The Coulter Counter machine obtains a particle size distribution as suspended particles interrupt the flow path of a laser. The second peak in the figure can perhaps be explained by the orientation of the particles as they pass by the laser. If a particle interrupts the laser as it passes by length-wise, the interruption time of the laser will be lengthened, thus increasing the particle size distribution measured by the Coulter Counter machine.



Figure A.1. Typical size distribution of sieved sawdust on a mass mean basis.

Peak Temperature	Particle Residence	% Mass Release (daf)	% Mass Release (daf)
(K)	Time (ms)	by Ash Tracer	by Mass Balance
1163	32	94.98	84.41
		97.81	
1163	55	96.77	94.24
		96.58	
		96.74	
1163	78	98.21	93.88
1163	102	97.89	93.32
1320	29	97.42	94.33
1320	40	98.11	95.09
1320	51	98.40	94.70
1433	23	98.42	95 52
1455	25	96.37	<i>JJJJJ</i>
1433	31	98.85	94 89
1755	51	98.74	77.07
1433	39	98.24	95.28

Table A.1. Sawdust mass release data used to make Figure 5.2

Table A.2. Sawdust yields in atmospheric FFB at 1163, 1320, & 1433 K (basis of
daf sawdust fed) that were used to make Figure 5.3 and Figure 5.4

Peak Temperature	Residence Time (ms)	% Tar	% Gas
(K)			
1163	32	6.5	81.2
1163	55	3.1	91.5
1163	78	2.0	93.2
1163	102	1.5	93.5
1320	29	2.1	92.7
1320	40	1.2	94.7
1320	51	1.4	94.3
1433	23	0.8	94.7
1433	31	1.8	93.9
1433	39	1.6	94.3

Peak	Particle	Tar wt%	Gas wt%	Total Dry, Raw
Temperature	Residence Time		*determined by	Sawdust Fed
(K)	(ms)		difference	(g)
		6.48	74.88	1.227
		5.72	82.11	0.243
1163	32	7.52	82.57	0.222
		6.38	79.30	0.353
		6.25	82.60	0.272
		2.66	77.82	0.189
		3.04	91.49	0.255
1163	55	2.44	92.45	0.243
		2.72	93.95	0.284
		3.22	91.83	2.063
		1.09	92.29	0.672
1163	78	2.13	91.46	0.434
		2.48	91.28	2.064
		2.20	93.56	0.274
		2.00	92.60	0.277
		2.24	90.77	2.042
1163	102	1.36	92.71	0.266
		0.79	94.70	0.191
		1.80	91.56	0.257
1320	29	1.89	93.45	0.245
		1.89	91.69	0.245
		2.78	91.79	0.805
1320	40	1.20	94.79	1.550
1020	10	1.17	93.10	1.706
		1.25	92.79	0.872
1320	51	1.28	94.07	1.370
		1.54	92.83	0.926
		0.51	95.01	0.255
1433	23	0.36	96.18	0.225
		1.48	94.84	1.522
		2.05	91.27	1.810
		2.41	90.11	0.530
1433	31	1.94	95.21	0.873
		1.48	95.68	1.694
		1.22	89.82	0.246
		1.51	94.62	1.301
1433	39	1.77	93.19	1.637
		1.63	92.86	0.724

Table A.3. All tar and gas yields from sawdust pyrolysis experiments in the FFB
(basis of daf sawdust fed). Gas yield is determined by difference
(i.e., 100 - tar wt% - char wt%).

Appendix B. Tabulated Petroleum Coke Data

Figure B.1 shows a typical size distribution of the pet coke particles using a Coulter Counter LS series machine. The size distribution is on a mass basis. Three sizing tests yielded an average particle diameter of 62 microns with a standard deviation of 1 micron.



Figure B.1. Typical size distribution of sieved pet coke on a mass mean basis.

Table B.1.	Summary of mass	release for all	pyrolysis and	d gasification	experiments
	of pet coke	determined by	y a mass bala	nce and ash tr	acer.

Pressure (atm)	Peak Temperature (K)	Particle Residence Time (ms)	% MR (daf) * by mass balance	% MR (daf) * by ash tracer
1	1751	22	8.1	16.2
1	1751	55	9.3 8.4	8.3
1	1751	55	10.0 7.0	8.8 6.8
1	1751	98	9.3 8.6	5.5 17.6
1	1929	23	8.7	7.9

Table B.1 continued

Pressure	Peak	Particle	% MR (daf)	% MR (daf)
(atm)	Temperature	Residence	* by mass balance	* by ash tracer
	(K)	Time (ms)		
1	1929	60	9.6	7.9
1	1929	102	9.6	5.9
2.5	1683	43	26.5*	20.3
			6.28	11.94
			8.8	5.0
2.5	1683	76	11.5	18.1
			6.1	none
2.5	1683	111	6.5	8.8
			6.9	12.1
2.5	1683	369	11.4	12.2
2.5	1876	109	11.2	none
5	1702	44	15.8*	0.3
5	1702	56	29.4*	37.1
			6.03	13.57
5	1702	75	49.2*	none
			9.7	none
5	1702	96	6.93	4.52
5	1702	141	8.24	20.89
5	1702	467	9.59	21.00
5	1867	644	12.64	8.82
5	2110	753	11.41	17.15
10	1722	48	43.0*	11.2
10	1722	70	15.7*	29.9
10	1722	81	9.4	8.6
			5.2	15.7
			22.2*	17.4
10	1722	150	11.8	none
			10.8	none
10	1967	65	6.6	40.3
10	1967	373	43.6	none
10	1077	6(2)	24.9	15 7
10	1967	003	34.8	15./
10	1067	1061	30.0	none
10	1907	1001	20.2	none
			40.1	$\frac{1010}{24.4}$
10	0100	<i>F ()</i>	45.5	24.4
10	2139	563	30.8	18.9
15	1402	337	none	14.84
15	1681	50	27.9*	11.3
15	1681	104	11.66	16.21
15	1681	151	36.3	15.0
1.7	1.001	210	10.5	none
15	1681	318	52.78	6.12

Pressure (atm)	Peak Temperature	Particle Residence	% MR (daf) * by mass balance	% MR (daf) * by ash tracer
	(K)	1 ime (ms)		
15	1681	914	54.62	57.00
15	1918	335	50.12	22.06
15	1918	577	57.71	35.08
			58.41	none
			38.01	26.10
15	1918	994	44.54	36.53
			52.62	30.56
			50.04	none

Table B.1 continued

**More confidence should be given to the values determined by a mass balance in Table B.1 due to ash evaporation. The values followed by an asterisk are pyrolysis data that are unreasonably high, but that can be ruled out using explanations discussed in the paragraph below Figure B.2. The data in Table B.1 were used to make Figures 6.3 and 6.5.



Particle Residence Time (ms)

Figure B.2. Pet coke pyrolysis data.

Eight data points were left out of Figure 6.3 in the text for reasons discussed here. The circled points in Figure B.2 represent experiments that were ignored as pet coke pyrolysis data since the mass release values were unreasonably high. In every case, three good explanations could be used to explain why these 8 experimental points could be ignored. First, replicate data were sometimes available for these 8 outlying points where the mass release was much closer to that of an ASTM volatiles test. Second, data were often available from experiments that were performed at the same pressure and temperature for these 8 points, except at a higher residence time. In these cases, the data at the longer residence time was much closer to that of an ASTM volatiles test and could rule out some of the 8 points in question. Third, data were often available at a more extreme condition where the mass release was much lower than that of the 8 points. For example, there is a questionable experimental point that came from 2.5 atm 1683 K, but the data point from 2.5 atm 1876 K could be used to justify not using the earlier point since an equal or greater mass release would be expected at the higher temperature condition performed at the same pressure. In many instances, a combination of the aforementioned explanations could be used to rule out a single point. Spills, clogging in the feed line, and char not collecting in the desired location of the reactor explain the high mass release values of the 8 outlying points since the mass release numbers were calculated from a mass balance (weighing the amount of char collected and the amount of pet coke fed). This said, no measurable amount of CO₂ gasification was observed on any pet coke chars collected at 1, 2.5, and 5 atm.

	Particle	% Error in Ash	% Error in Ash	% Error in Ash
Description	Time (ms)	weight Experiment # 1	weight Experiment # 2	Weight Experiment # 3
1atm 1751K	33	0.0	15.8	0.0
1atm 1751K	55	3.2	0.0	-
1atm 1751K	98	-4.4	10.7	_
1atm 1929K	23	0.0	-	_
1atm 1929K	102	-4.0	-	-
2.5atm 1683K	43	6.4	-	-
2.5atm 1683K	76	-4.0	9.4	-
2.5atm 1683K	111	2.5	5.8	-
2.5atm 1683K	369	0.0	-	-
5atm 1702K	56	8.7	-	-
5atm 1702K	96	-2.5	-	-
5atm 1702K	141	15.9	-	-
5atm 1702K	467	-10.6	-	-
5atm 1867K	644	-4.2	-	-
10atm 1722K	81	0.0	12.4	-
10atm 1967K	65	56.3	-	-
10atm 1967K	663	-22.6	-	-
10atm 1967K	1061	-24.9	-	-
10atm 2139K	563	-14.6	-	-
15atm 1681K	318	-41.8	-	-
15atm 1918K	335	-33.6	-	-
15atm 1918K	577	-33.8	-	-
15atm 1918K	994	-16.1	-12.7	-31.7

Table B.2. Percent error in ash weight measurements of pet coke samples. Negative valuesimply ash evaporation. This data was used to make Figure 6.10.

Table B.3. CO₂ surface area measurements of raw pet coke and pet coke chars.

Description	Particle Residence Time (ms)	CO ₂ Surface Area (m ² /g) Experiment #1	CO ₂ Surface Area (m ² /g) Experiment #2	+ / - (if # Experiments ≥ 3) *95% conf. intervals
raw pet coke	-	187.3	-	10.3
1atm 1751K	33	126.9	-	6.8
1atm 1751K	55	51.2	50.3	-
1atm 1751K	98	31.2	-	-
1atm 1929K	23	115.1	-	-
1atm 1929K	60	28.3	27.6*	-
2.5atm 1683K	43	228.0	-	-
2.5atm 1683K	76	218.0	216.0	-

Table B.3 continued

Description	Particle Residence	CO ₂ Surface Area (m ² /g)	CO ₂ Surface Area (m ² /g)	+ / - (if # Experiments \geq 3)
2.5 . 1.0021	Time (ms)	Experiment #1	Experiment #2	*95% conf. intervals
2.5atm 1683K	111	217.0	-	-
2.5atm 1876K	73	116.1	-	-
2.5atm 1876K	109	76.9	-	-
5atm 1702K	56	235.0	-	-
5atm 1702K	75	216.9	-	-
5atm 1702K	96	215.4	-	-
5atm 1702K	141	213.2	-	-
5atm 1867K	644	19.8	-	-
5atm 2110K	753	16.6	-	-
10 atm 1722K	81	226.3	226.8	-
10 atm 1722K	150	159.6	-	12.2*
10 atm 1967K	65	170.7	-	-
10 atm 1967K	373	53.9	-	-
10 atm 1967K	663	200.3	68.6	-
10 atm 1967K	1061	76.5	-	-
10 atm 2139K	563	24.8	-	-
15 atm 1402 K	337	205.0	-	-
15 atm 1681 K	50	178.9	-	
15 atm 1681 K	104	209.7	-	-
15 atm 1681 K	151	159.3	184.9	-
15 atm 1681 K	318	189.1	-	-
15 atm 1681 K	914	185.8	-	-
15 atm 1918 K	335	56.3	-	-
15 atm 1918 K	577	94.4	90.9	-
15 atm 1918 K	994	58.6	-	33.0

* Measurements denoted with an asterisk in Table B.3 are replicate measurements of the same

char. The values in Table B.3 were used to make Figures 6.12 & 6.13.

Description	Particle Residence Time (ms)	N ₂ Surface Area (m ² /g) Experiment #1	N ₂ Surface Area (m ² /g) Experiment #2	+ / - (if # Experiments ≥ 3) *95% conf. intervals
raw pet coke	-	7.6	-	0.4
10atm 1967K	65	36.4	-	-
10atm 1967K	373	4.7	-	-
10atm 1967K	663	32.4	5.1	-
10atm 1967K	1061	9.6	-	-
15atm 1681K	151	21.4	-	-
15atm 1681K	318	12.9	-	-
15atm 1918K	335	4.3	-	-
15atm 1918K	577	6.8	-	-
15atm 1918K	994	10.6	-	3.4

Table B.4. N2 surface area measurements of raw pet coke and
pet coke chars used to make Figure 6.14.

** All replicate surface area data in Table B.4 came from char collected on different days.

Table B.5. Ratio of final particle diameter to initial particle diameter	of pet
coke chars used to make Figures K.1 & K.2	

Description	Particle	d/do	d/do	+/-	
	Residence	(Experiment #1)	(Experiment #2)	(if # Experiments \geq 3)	
	Time (ms)			*95% conf. intervals	
1atm 1751K	33	0.95	-	0.02	
1atm 1751K	55	0.94	-	0.02	
1atm 1751K	98	0.93	0.95	-	
1atm 1929K	23	0.95	-	-	
1atm 1929K	60	0.94	-	-	
1atm 1929K	102	0.94	-	-	
2.5atm 1683K	43	0.96	-	-	
2.5atm 1683K	76	0.95	-	0.03	
2.5atm 1683K	111	0.95	0.95	-	
2.5atm 1683K	369	0.92	-	-	
2.5atm 1876K	109	0.93	-	-	
5atm 1702K	44	0.95	-	-	
5atm 1702K	56	0.95	-	-	
5atm 1702K	75	0.96	-	-	

Description Particle		d/do	d/do	+/-
Residence		(Experiment #1)	(Experiment #2)	(if # Experiments \geq 3)
	Time (ms)			*95% conf. intervals
5atm 1702K	96	0.95	-	-
5atm 1702K	141	0.95	-	-
5atm 1702K	467	0.93	-	-
5atm 1867K	644	0.92	-	-
5atm 2110K	753	0.93	-	-
10atm 1722K	48	0.94	-	-
10atm 1722K	70	0.92	-	-
10atm 1722K	81	0.95	0.96	-
10atm 1722K	150	0.92	-	0.05
10atm 1967K	65	0.94	-	-
10atm 1967K	373	0.79	-	-
10atm 1967K	663	0.83	0.84	-
10atm 1967K	1061	0.81	-	0.12
10atm 2139K	563	0.85	-	-
15atm 1681K	50	0.94	-	-
15atm 1681K	104	0.92	-	-
15atm 1681K	151	0.87	0.94	-
15atm 1681K	318	0.75	-	-
15atm 1681K	914	0.75	-	-
15atm 1918K	335	0.76	-	
15atm 1918K	577	0.71	0.71	-
15atm 1918K	994	0.78	-	0.05

Table B.5 continued

Description	Particle	Particle Tap Density Tap Density		+/-	
	Residence	(g/cm^3)	(g/cm^3)	(if # Experiments \geq 3)	
Time (ms)		(Experiment #1)	(Experiment #2)	*95% conf. intervals	
raw pet coke	N/A	0.874		0.009	
1atm 1751K	33	0.931		0.021	
1atm 1751K	55	0.934	0.976		
1atm 1751K	98	0.955		0.038	
1atm 1929K	23	0.931			
1atm 1929K	60	0.959			
1atm 1929K	102	0.957			
2.5atm 1683K	43	0.916	0.892		
2.5atm 1683K	76	0.945		0.068	
2.5atm 1683K	111	0.921	0.936		
2.5atm 1683K	369	0.996			
2.5atm 1876K	73	0.933			
2.5atm 1876K	109	0.982			
5atm 1702K	44	0.854			
5atm 1702K	56	0.900	0.907		
5atm 1702K	75	0.950	0.906		
5atm 1702K 96		0.940			
5atm 1702K	141	0.936			
5atm 1702K	467	0.989			
5atm 1867K	5atm 1867K 644				
5atm 2110K	753	0.976			
10atm 1722K	48	0.922			
10atm 1722K	70	0.948			
10atm 1722K	81	0.918	0.929		
10atm 1722K	150	0.951		0.042	
10atm 1967K	65	0.973			
10atm 1967K	373	1.011			
10atm 1967K	663	0.999	0.950		
10atm 1967K	1061	0.993		0.024	
10atm 2139K	563	0.997			
15atm 1402K	337	0.893	0.897		
15atm 1681K	50	0.950			
15atm 1681K	104	0.972			
15atm 1681K	151	0.970	0.938		
15atm 1681K	318	0.968	0.970		
15atm 1681K	914	0.931			
15atm 1918K	335	1.014			
15atm 1918K	577	1.015	1.000		
15atm 1918K	994	0.998		0.016	

Table B.6. Bulk densities (or tap densities) used to calculate the apparent
densities of pet coke used to make Figures L.1 & L.2 by
the calculations described in Appendix L.

Description	Particle	Tar wt%	Tar wt%	+/-
	Residence	(Experiment # 1)	(Experiment # 2)	(if # Experiments \geq 3)
1atm 1751K	1 Ime (ms)	0.38	_	° 95% com. Intervais
1 atm 1751K	55	0.30		0.30
1 atm 1751K	08	0.42	-	0.20
	96	0.35	-	0.20
1atm 1929K	23	0.34	-	-
1atm 1929K	60	0.18	-	-
1atm 1929K	102	0.61	-	-
2.5atm 1683K	43	0.42	0.67	-
2.5atm 1683K	76	0.39	-	0.43
2.5atm 1683K	111	0.18	0.38	-
2.5atm 1683K	369	0.98	-	-
2.5atm 1876K	73	0.36	-	-
2.5atm 1876K	109	0.31	-	-
5atm 1702K	56	0.47	-	0.04
5atm 1702K	75	0.94	0.22	-
5atm 1702K	96	0.50	-	-
5atm 1702K	141	0.67	-	-
5atm 1702K	467	0.57	-	-
5atm 1867K	644	0.74	-	-
10atm 1722K	70	0.59	-	-
10atm 1722K	81	0.25	0.41	-
10atm 1722K	150	0.82	-	1.07
10atm 1967K	65	0.52	-	-
10atm 1967K	373	0.35	-	-
10atm 1967K	663	0.51	0.38	-
10atm 1967K	1061	0.31	0.72	-
15atm 1681K	104	0.57	-	-
15atm 1681K	151	0.76	0.44	-
15atm 1681K	318	0.52	-	-
15atm 1681K	914	0.35	-	-
15atm 1918K	335	0.68	1.55	-
15atm 1918K	577	0.75	-	0.60
15atm 1918K	994	0.57	-	0.36

Table B.7. Tar yield values of pet coke on a basis of daf pet coke fed.This data was used to make Figure M.1.

The maximum particle heating rates for all the pet coke conditions are summarized in Figure B.3. These heating rates (dT_p/dt) were calculated using the following energy balance for a particle in entrained flow (Fletcher, 1989):

$$\frac{dT_p}{dt} = \frac{\theta \cdot h_c \cdot A_p \cdot (T_{gas} - T_p) - \sigma \cdot \varepsilon_p \cdot A_p \cdot (T_p^4 - T_{surr}^4) + \frac{dm_p}{dt} \cdot \Delta H_{pyr}}{m_p \cdot C_p}$$
(9.1)

(0 1)

where T_p is the particle temperature, *t* is time, θ is the blowing factor that corrects for high mass transfer rates (Bird et al., 2002), m_p is the mass of the particle, A_p is the external particle surface area, C_p is the heat capacity of the particle (Merrick, 1983), h_c is the heat transfer coefficient ($Nu \cdot k_{gas}/d_p$), ε_p is the emissivity of the char particle ($\varepsilon_p = 0.8$ with the assumption that it was similar to that of coal char) (Fletcher, 1989), σ is the Stefan–Boltzmann constant (5.67 x 10⁻¹² W/cm²/K), T_{surr} is the temperature of the surroundings (500 K), and ΔH_{pyr} is the heat of pyrolysis (assumed -100 cal/g, which is slightly endothermic). Most of the heating rates in the pet coke experiments were very close to 10⁵ K/s.

Pressure	Peak Temperature	Maximum Heating Rate
(atm)	(K)	(K/s)
1	1751	1.21×10^{5}
1	1929	$1.07 \text{x} 10^5$
2.5	1683	1.12×10^5
2.5	1876	1.52×10^5
5	1702	$1.04 \mathrm{x} 10^5$
5	1867	$1.14 \mathrm{x} 10^5$
5	2110	1.72×10^5
10	1722	$9.74 \mathrm{x10}^4$
10	1967	1.18×10^5
10	2139	1.27×10^5
15	1402	6.62×10^4
15	1681	8.89×10^4
15	1918	1.06×10^5

Figure B.3. Maximum particle heating rates of pet coke for all conditions.

Excluded Pet Coke Data Point:

Something likely went wrong with one of the replicate experiments performed at 10 atm 1967 K 663 ms. There were peculiarities in this char, as it did not follow trends in surface area, char density, and elemental composition. This particular experimental point was therefore left out of the figures in the thesis. The peculiar char could be explained by an incorrectly-set mass flow controller or a mislabeled jar of char.

To elaborate further, there was a large discrepancy between replicate surface area measurements of the pet coke char collected at 10 atm 1967 K with a particle residence time of 663 ms (see Tables B.3 & B.4). Both the CO_2 and N_2 surface areas are significantly higher for one of the chars. Although the surface area measurements came from chars collected over a month apart, it is believed this in an anomaly since replicate surface area measurements of all other chars had much better repeatability. The lower CO_2 and N_2 surface area measurements of char collected at 10 atm 1967 K 663 ms are believed to be more accurate based on surface area measurements of char collected at lower and higher residence times at this same condition.

The density of this same char did not follow density trends when compared to chars collected at earlier and later residence times from this same condition (see Table B.6). This same char did not follow the elemental compositional trends of the other chars collected at different residence times from this same condition (10 atm 1967 K). Even though the elemental composition of the 663 ms point is included in Table N.1, it was not used in Figures N.1 to N.3.

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Appendix C. Additional FFB and HPFFB Information



Figure C.1. Atmospheric flat-flame burner with separation system (Ma, 1996).

Additional HPFFB Information

The burner and the collection probe of the HPFFB (see Figure 4.3) could easily be moved up and down since they were clamped to moveable tracks. It was very important that these two pieces of the reactor be securely fastened to prevent them from becoming projectiles from the pressurized vessel. Nitrogen-entrained particles were fed to the middle of the burner surface in the HPFFB through a steel tube (0.042" ID). The particles then passed through a quartz tube (1" ID) until they were collected by a water-cooled nitrogen-quenched collection probe. The volumetric flow rate of quench N₂ was about 2 times that of the post-flame gas. Just as in the atmospheric FFB, the collection system separated char aerodynamically in a virtual impactor and cyclone system. Filters collected any tar/soot while gases passed through the filters and were released in a fume hood. Water cooling was used on both of the filter flanges as well as an insert in the bottom cap through which the burner passed. A pressure controller was used to ensure constant pressure during an experiment. Cylindrical heaters with a 2" inside diameter (see Figure C.2) were used inside the HPFFB in order to maintain a hot environment beyond the nearflame region. These heaters were rated to a maximum temperature of 1200 °C, and were used when the collection probe was positioned more than 3" above the burner. Two quartz tubes were used inside the HPFFB reactor. The longer quartz tube extended from the bottom cap to the top of the heaters. The other shorter quartz tube sat between the longer quartz tube and the flatflame burner. The length of this shorter tube depended on the collection height of the experiment since this tube extended from the bottom vessel cap to just below the collection probe. The use of this shorter quartz tube greatly increased collected char yields since the only flow path it offered to the particles was directly into the collection probe. Five K-type thermocouples were positioned at different heights above the burner, and were situated between the heaters and long quartz tube.

A variable power supply along with both copper and platinum wire comprised the HPFFB's custom ignition system. Together these components acted as a glow plug, and made

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ignition possible up to 15 atm. Prior to ignition, the vessel was pressurized slightly higher than the desired operating pressure with N_2 in order to detect any leaks.



Figure C.2. Cutaway view of HPFFB reactor (not drawn to scale).

After any possible leaks were addressed, current was passed through the ignition system, causing the platinum wire to glow. A flammable mixture of gases was then introduced into the pressurized vessel. The ignition occurred near the top of the reactor, but dropped down to the burner after a few seconds. After the burner was lit, the ignition power supply was turned off and the water-cooled, nitrogen-quenched collection probe was lowered further into the vessel to its final position. The reactor was then allowed to warm up until it reached steady temperatures before particles were fed to the HPFFB. The warm up time was as long as 80 minutes after ignition. Two viewports (9/16" diameter) provided the only optical access into the HPFFB reactor. The top viewport allowed the operator to view the brightness of the platinum wire

during ignition, since too much current would have caused it to melt. The top viewport also allowed the operator to know when ignition occurred, signaling him/her to change from ignition settings to operating settings. The bottom viewport allowed optical access to the bottom of the vessel, where both the flat flame and feeding particles could be seen.

The pressure seal on the HPFFB reactor was made possible by gaskets, o-rings, and the use of compression, NPT, and Conax[®] Buffalo fittings. Gaskets were used at the interfaces where the top and bottom caps meet the main body of the reactor. Both the collection probe and the burner passed through double o-rings as they entered the HPFFB vessel through the top and bottom caps, respectively. Compression, NPT, and Buffalo fittings were used elsewhere to maintain the pressure seal on the system and allowed reactor access to thermocouples and power leads.

Nitrogen-entrained particles were carried from the feeding system to the middle of the burner surface through a single, continuous metal tube (0.042" ID). The tube which carried particles to the burner was surrounded by a larger metal tube (1/8" OD). The bigger tube served two purposes. It protected the smaller tube from being easily bent, and it also allowed compression fittings to be used without clamping down on the inside tube. Epoxy was used to fill the annulus created by the two tubes. Otherwise, the carrier gas would have followed the path of least resistance and traveled through the annulus without carrying any particles.

The primary fuel to the HPFFB was CO. The CO passed through a 'carbonyl trap' on its way to the burner, where iron and nickel carbonyls were captured using activated charcoal (20-40 mesh) and a small amount of iodine. The aforementioned contaminants are common in pressurized CO cylinders, and can cause a red deposit in the post-flame regions of the reactor if unaddressed (Williams and Shaddix, 2007).

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Appendix D. Development of HPFFB Particle Feeder

The new pressurized particle HPFFB feeder was a plunger-type feeder, similar to the atmospheric FFB particle feeder (Ma, 1996). A stepper motor pushed a plunger forward into a bed of particles, which caused the particles to dropped down into a funnel. From the funnel, particles dropped into a stainless-steel feed tube (0.042" ID) where they were entrained in N_2 until they were released in the middle of the burner inside the HPFFB.

In order to make the feeder, a hole was drilled into a piece of cast acrylic tubing at an angle. A tap was then used to make ¹/₂" NPT threads through the drilled hole. A connector (¹/₂" NPT, ¹/₂" Swagelok) was then screwed into the acrylic tubing. The connector in the acrylic tubing was made permanent by putting epoxy at the interface between the connector and tubing walls. The use of epoxy ensured that the connector would not unscrew and also created a pressure seal. The cast acrylic tubing was chosen to have a ¹/₂" wall thickness since a thinner wall would not have engaged as many threads of the connector, which is a major concern in a pressurized system. It is also important to note that <u>cast</u> acrylic tubing was used instead of cheaper extruded acrylic tubing since it is easily machined and performs better at high pressures. The central unit of the feeder consists of the acrylic tubing inserted between a custom-machined top and bottom (see Figure D.1). The metal top contains 6 holes. Fittings (1/8" NPT, 1/8" Swagelok) were screwed into 2 of these holes. The 2 holes allow carrier N₂ to be plumbed in, and also permit a metal wire to be inserted in the feeder line during operation in case of a clog

(see Figure D.2). The use of a separate metal tube, Swagelok fittings, and a septum maintained the pressure seal on the system when a metal wire is inserted for clogs. The other 4 holes on the metal top are for threaded metal rods. The metal bottom also has 4 holes for the same threaded rods. Nuts are used at the ends of the threaded rods to clamp down on the feeder unit (see Figure D.2). O-rings are used between the acrylic tubing and the metal top and bottom in order to maintain the pressure seal on the system. The metal bottom also contains one additional hole in the center into which was screwed a fitting (1/8" NPT, 1/8" Swagelok). This center hole provides a channel by which the feed tube enters the central feeder unit. The feed tube sits slightly inside the bottom of the glass funnel, which provides support for the funnel to stand upright (see Figure D.1).



Figure D.1. HPFFB particle feeder.

The axial hole in a metal tube ($\frac{1}{2}$ "OD) was made larger by drilling it out and then using a reamer to smooth the inside of the tube. This was done in order that a plunger could pass through the tube since this is where particles are housed prior to being entrained in carrier N₂. Swagelok nuts ($\frac{1}{2}$ ") and ferrules were used on separate ends of the metal tube (see Figure D.3). One of the nuts screwed onto the $\frac{1}{2}$ " connector sticking out of the cast acrylic tubing, while the other nut screwed onto a separate connector ($\frac{1}{2}$ "Swagelok, $\frac{1}{2}$ " Swagelok).



Figure D.2. Top view of the HPFFB particle feeder.

The plunger was made using a 3/8" aluminum shaft, and contained a Teflon[®] head taken from a Gastight[®] plunger. A commercial plunger could not be used since none was found of sufficient length. The plunger passes through o-rings in order to maintain the pressure seal as it progresses forward inside the metal tube where particles are stored (see Figure D.3). Metal washers act as a space filler between the o-rings and ½" Swagelok nut that screws onto the connector attached to the metal tube.



Figure D.3. Close-up view of the metal tube and plunger of the HPFFB particle feeder.

A stepper motor is used to progress the aluminum plunger forward through the particle bed, thereby allowing particle feeding. The stepper motor is controlled using a VBA program. A small metal shaft was inserted into a hole that was drilled into the stepper motor lead screw (see Figure D.4) since the screw only progresses forward if it is kept from rotating. The metal shaft rides along a PVC track as the lead screw progresses forward, thus preventing the screw from turning (see Figure D.1 and Figure D.4). A connecting piece was made which serves as the union between the stepper motor lead screw and the aluminum plunger (see Figure D.4). This custom part is made of a flat piece of metal that is joined to a cylindrical piece of aluminum by a screw. It provides a large, flat surface for the lead screw to press against, but also houses roughly ¹/₂" of the plunger.



Figure D.4. Side view of the HPFFB feeder stepper motor in operation.

An alpha ionizer (NRD Staticmaster) is used to control static on the inside of the cast acrylic tubing to prevent particles from clinging together. Also, a pneumatic vibrator as well as several CPU fans of various sizes were used to provide vibration to the particle feeding system. A CPU fan easily became a vibrator after a metal nut was glued to a single fan blade (see Figure D.1).

Appendix E. Gas Temperature Measurements and Gas Conditions

The centerline gas temperature profiles of the atmospheric FFB and the HPFFB were measured using a B-type thermocouple with a 0.005" wire diameter. The thermocouple bead diameter was measured under a microscope. A 602 micron silica-coated bead was used in the temperature profiles in the atmospheric FFB. Multiple thermocouples were used to measure the temperature profiles of the HPFFB since they often broke due to damage sustained by the fragile bead or ceramic shaft. The typical alumina-coated (see Appendix G) bead diameter used in the HPFFB reactor was near 400 microns.

For the atmospheric FFB temperature profiles, a ring stand and clamp were used to position the thermocouple in the center of the quartz tower (see Figure C.1) above the burner after the collection system had been removed. The first measured temperature was taken at 7" above the burner surface. The burner was then raised incrementally while temperatures were recorded until the thermocouple bead was directly over the burner surface. The burner was then incrementally lowered, and replicate temperature data were recorded. The final uncorrected temperature profile was then calculated as the average of the two recorded temperatures at each height above the burner. A radiation correction (see Appendix F) was then applied to the raw temperature measurements to calculate the gas temperature.

Measuring the centerline temperature in the HPFFB was more complicated since it required the pressure seal to be maintained as the ceramic shaft of a thermocouple was lowered

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further into the pressurized vessel. HPFFB temperature profiles were measured after the top filter and cyclone of the separation system were removed (see Figure 4.3). A water-cooled plate with a hole running through its center was bolted in place of the collection system (see Figure E.1).



Figure E.1. Cutaway view of the water-cooled plate used while measuring temperature profiles on the HPFFB (not drawn to scale).

The ceramic shaft of the thermocouple was fed through a small metal disk, a drilled-out rubber stopper, and the water-cooled plate. Note that this method is not recommended since it poses a safety risk if the ceramic shaft becomes a projectile from the pressurized vessel. The rubber stopper sat snugly in the plate's middle hole and was held in place after the metal disk was tightened down using screws into the water-cooled plate. Friction between the ceramic shaft and rubber stopper held the thermocouple in place. After the HPFFB reactor had been lit sufficiently long to achieve a steady reactor temperature, the operator pushed the thermocouple shaft down further into the reactor so that the thermocouple bead was no longer positioned inside the collection probe, where it resided during reactor warm up. Marks on the ceramic shaft allowed

the operator to know the height of the thermocouple bead above the burner. Temperatures were recorded at incremental heights above the burner until the bead was directly over the burner. The thermocouple shaft was then pulled away from the burner incrementally as temperatures were again recorded. The final uncorrected temperature profile was then calculated as the average of the two recorded temperatures at each height above the burner, and a radiation correction (see Appendix F) was then used to calculate the gas temperature.

Below are all the gas conditions used for both pet coke and sawdust experimentation (see Tables E.1 to E.4). In addition, all the measured temperature gas temperature profiles are listed (see Tables E.5 to E.10).

Deals Town on true	11(2 V	1220 IZ	1422 IZ	
Peak Temperature	1103 K	1320 K	1433 K	
Gas flow (kg/s)	$4.898 \cdot 10^{-4}$	$5.048 \cdot 10^{-4}$	5.739·10 ⁻⁴	
Φ (Equivalence Ratio)	1.59	1.43	1.29	
Carrier N ₂ (SLPM)	0.0367	0.0367	0.0367	
O_2 (SLPM)	1.49	2.05	2.58	
Oxidizer N ₂ (SLPM)	7.75	7.8	12.5	
CO (SLPM)	10.2	9.75	8.85	
H_2 (SLPM)	0.6	0.3	0.45	
Fuel N ₂ (SLPM)	5.93	6.5	5.7	
Quench N ₂ (SLPM)	60	60	60	
Equilibrium Post-Flame Gas Compositions				
CO ₂ mol%	11.39	16.14	17.56	
H ₂ O mol%	0.77	0.67	1.21	
CO mol%	30.18	23.84	14.58	
H ₂ mol%	1.72	0.56	0.42	
N ₂ mol%	55.93	58.80	66.23	

Table E.1. Gas conditions for sawdust FFB pyrolysis experiments

Peak Temperature	1751 K	1929 K		
Gas flow (kg/s)	$8.015 \cdot 10^{-4}$	7.730·10 ⁻⁴		
Φ (Equivalence Ratio)	1.16	1.10		
Carrier N ₂ (SLPM)	0.0367	0.0367		
O_2 (SLPM)	4.47	5.09		
Oxidizer N ₂ (SLPM)	18.5	19.16		
CO (SLPM)	11.82	12		
H_2 (SLPM)	0.36	0.32		
Fuel N ₂ (SLPM)	6.5	3.5		
Quench N ₂ (SLPM)	60	60		
Equilibrium Post-Flame Gas Compositions				
CO ₂ mol%	23.12	27.40		
H ₂ O mol%	0.89	0.83		
CO mol%	8.64	6.74		
H ₂ mol%	0.07	0.04		
N ₂ mol%	67.26	64.47		

Table E.2. Gas conditions for pet coke FFB experiments at 1 atm

Table E.3. Gas conditions for pet coke HPFFB experiments at 2.5 & 5 atm

Pressure &	2.5 atm	2.5 atm	5 atm	5 atm	5 atm		
Peak Temperature	1683 K	1876 K	1702 K	1867 K	2110 K		
- ··· ···- F ······ ··	peak	peak	peak	peak	peak		
Gas flow (kg/s)	$1.544 \cdot 10^{-4}$	$1.551 \cdot 10^{-4}$	$2.229 \cdot 10^{-4}$	$2.232 \cdot 10^{-4}$	$2.255 \cdot 10^{-4}$		
Φ (Equivalence Ratio)	1.27	1.19	1.26	1.17	1.17		
Carrier N ₂ (SLPM)	0.06	0.06	0.075	0.075	0.075		
Air (SLPM)	3.15	3.75	4.55	5.45	6.15		
Oxidizer N ₂ (SLPM)	2.75	2.12	3.99	3.08	1.96		
CO (SLPM)	2.08	2.08	3.0	3.0	3.44		
$H_2(SLPM)$	0.17	0.17	0.17	0.17	0.17		
Quench N ₂ (SLPM)	18	18	25	25	25		
]	Equilibrium Post-Flame Gas Compositions						
CO ₂ mol%	15.7	19.19	16.3	20.0	23.04		
H ₂ O mol%	1.8	2.07	1.3	1.5	1.49		
CO mol%	11.9	8.95	11.4	8.2	9.72		
H ₂ mol%	0.4	0.23	0.3	0.1	0.13		
N ₂ mol%	70.2	69.08	70.7	70.2	65.06		
Pressure &	10 atm	10 atm	10 atm	15 atm	15 atm	15 atm	
--------------------------------	-----------------------	-----------------------	-----------------------	-----------------------	-----------------------	-----------------------	
Peak Temperature	1722 K	1967 K	2139 K	1402 K	1681 K	1918 K	
	peak	peak	peak	peak	peak	peak	
Gas flow (kg/s)	$3.625 \cdot 10^{-4}$	$3.660 \cdot 10^{-4}$	$3.664 \cdot 10^{-4}$	$4.889 \cdot 10^{-4}$	$4.854 \cdot 10^{-4}$	$4.863 \cdot 10^{-4}$	
Φ (Equiv. Ratio)	1.25	1.16	1.16	1.43	1.24	1.15	
Carrier N ₂ (SLPM)	0.1	0.1	0.1	0.15	0.15	0.15	
Air (SLPM)	7.4	8.9	10	8.0	9.9	11.9	
Oxidizer N ₂ (SLPM)	6.5	5.0	3.2	9.49	8.7	6.69	
CO (SLPM)	4.9	4.9	5.6	7.72	6.56	6.56	
H ₂ (SLPM)	0.17	0.17	0.17	0.42	0.17	0.17	
Quench N ₂ (SLPM)	40	40	40	52	52	52	
	Equilib	rium Post-Fla	ame Gas Con	npositions			
CO ₂ mol%	16.9	20.78	23.76	12.86	17.1	21.0	
H ₂ O mol%	0.8	0.91	0.93	1.06	0.6	0.7	
CO mol%	11.1	7.72	9.25	19.18	10.9	7.5	
H_2 mol%	0.2	0.08	0.07	0.69	0.1	0.0	
N_2 mol%	71.0	70.03	65.43	65.91	71.3	70.8	

Table E.4. Gas conditions for pet coke HPFFB experiments at 10 & 15 atm

Table E.5. Centerline gas temperature profiles from <u>sawdust</u> pyrolysisexperiments in FFB used to make Figure 5.1

Height Above	1163 K Peak	1320 K Peak	1433 K Peak
Burner (inches)			
0	1003	1163	1314
0.25	1128	1287	1401
0.5	1152	1312	1419
0.75	1160	1318	1429
1	1162	1320	1433
1.5	1163	1316	1430
2	1158	1309	1425
2.5	1152	1300	1418
3	1146	1293	1408
3.5	1140	1283	1400
4	1133	1274	1389
4.5	1123	1264	1376
5	1117	1256	1363
5.5	-	1244	1352
6	1103	1233	1339
7	1087	1213	1311

Height	1751 K	1929 K
Above Burner (")	peak	peak
0	1552	-
0.25	1699	1893
0.5	1733	1918
0.75	1749	1923
1	1751	1929
1.5	1745	1925
2	1731	1911
2.5	1716	1890
3	1697	1869
3.5	1677	1846
4	1658	1822
4.5	1638	1796
5	1620	1770
6	1582	1721
7	1543	1673
8	1499	1620

Table E.6. Centerline gas temperature profiles of Figure 6.1 for pet coke experiments in atmospheric FFB

Table E.7. Centerline gas temperature profiles for HPFFB pet coke experimentswith a collection height up to 3" above the burner

Height	2.5 atm	2.5 atm	5 atm 1702 K	10 atm 1722 K	10 atm	15 atm
Above Burner (")	peak	peak	peak	peak	peak	peak
0	1448	1876	1590	1722	1961	1643
0.25	1616	1820	1691	1713	1967	1681
0.5	1667	1860	1702	1672	1952	1655
0.75	1683	1870	1698	1655	1937	1643
1	1675	1855	1687	1653	1919	1637
1.25	1664	1835	1669	1646	1896	1632
1.5	1642	1807	1651	1630	1869	1613
1.75	1613	1771	1635	1605	1827	1608
2	1582	1730	1613	1576	1788	1590
2.25	1556	1694	1588	1578	1763	1559
2.5	1528	1660	1507	1519	1708	1521
2.75	1500	1626	1467	1499	1669	1487
3	1468	1570	1442	1464	1631	1388

Height Above	10 atm	15 atm	15 atm	15 atm
Burner (")	1967 K peak	1402 K peak	1681 K peak	1918 K peak
0	1962	1323	1654	1841
0.25	1974	1400	1683	1883
0.5	1962	1402	1654	1898
0.75	1948	1402	1640	1918
1	1929	1390	1634	1906
1.25	1906	1376	1630	1854
1.5	-	1362	1610	1836
1.75	1867	1344	1605	1810
2	1863	1336	1587	1777
2.25	-	1307	1557	1744
2.5	1813	1286	1518	1742
2.75	-	1245	-	1697
3	1703	1222	1484	1606
3.5	1616	-	-	-
4	1513	1198	1315	1419
4.5	1483	-	-	-
5	1473	1147	1264	1367
5.5	1466	1123	1231	1347
6	1351	996	1096	1169

Table E.8. Centerline gas temperature profiles for HPFFB pet coke experimentswith a collection height of 6" above the burner

Table E.9. Centerline gas temperature profiles for HPFFB pet coke experimentswith a collection height of 10" above the burner

Height Above Burner ('')	2.5 atm 1683 K	5 atm 2110 K	5 atm 1702 K	5 atm 1867 K	10 atm 1967 K	10 atm 2139 K	15 atm 1918 K
/ /	peak	peak	peak	peak	peak	peak	peak
0	1448	2026	1590	1735	1962	2139	1841
0.25	1618	2079	1691	1845	1974	2068	1883
0.5	1671	2110	1702	1864	1962	2030	1898
0.75	1688	2098	1698	1867	1948	2019	1918
1	1681	2067	1687	1858	1929	2012	1906
1.25	1670	2032	1669	1843	1906	1977	1854
1.5	1648	1995	1651	1824	1879	1970	1836
1.75	1618	1945	1635	1773	1835	1935	1810
2	1586	1785	1613	-	-	1868	1777
2.25	1561	1761	-	-	-	1838	1744
2.5	1532	1670	-	-	-	1791	1742
2.75	-	1633	-	-	-	1731	1697
3	-	1597	-	1617	1703	1703	1606
3.5	-	-	-	-	1616	-	-
4	1507	1617	1479	1591	-	1680	1510
5	1478	1619	1479	1584	1517	1576	1464
6	-	1609	1476	1576	1468	1547	1407
7	1431	1602	1472	1563	1421	1492	1370

Table E.9 continued

Height Above Burner ('')	2.5 atm 1683 K peak	5 atm 2110 K peak	5 atm 1702 K peak	5 atm 1867 K peak	10 atm 1967 K peak	10 atm 2139 K peak	15 atm 1918 K peak
8	1416	1593	1465	1550	1376	1441	1316
9	1399	1576	1455	1533	1346	1408	1285
9.5	-	1563	-	1522	1332	1395	1269
10	1251	1540	1428	1501	1307	1357	1227

Table E.10. Centerline gas temperature profiles for HPFFB pet coke experimentswith a collection height of 16.25" above the burner

Height Above Burner (")	10 atm	15 atm	15 atm
	1967 K peak	1681 K peak	1918 K peak
0	1962	1643	1841
0.25	1974	1681	1883
0.5	1962	1655	1898
0.75	1948	1643	1918
1	1929	1637	1906
1.25	1906	1632	1854
1.5	1879	1613	1836
1.75	1835	1608	1810
2	1796	1590	1777
2.25	1770	1559	1744
2.5	-	1521	1742
2.75	1728	-	1697
3	1725	1487	1606
3.25	1710	-	-
3.75	1675	-	1488
4.25	1628	-	1471
4.75	-	1315	1442
5.25	1562	1293	1421
6.25	1519	1267	1377
7.25	1505	1245	1349
8.25	1478	1225	1319
9.25	1460	1212	1297
10.25	1461	1208	1288
11.25	1463	1205	1281
12.25	1452	1208	1278
13.25	1464	1210	1278
14.25	1461	1215	1276
14.75	1456	-	-
15.25	1449	1218	1277
15.75	1441	1219	1275
16.25	1414	1214	1275

Appendix F. Radiation Correction for Gas Temperature Measurements

The centerline gas temperature profiles of the atmospheric FFB and the HPFFB were measured using a B-type thermocouple with a 0.005" wire diameter. The measured temperature is actually the temperature of the thermocouple bead, and thus calculations are required to solve for the gas temperature. It is very important to obtain an accurate gas temperature, especially when trying to obtain kinetic rate constants. Many important topics about correcting thermocouple measurements for radiation loss are covered in the review article by Shaddix (1999).

The gas temperature is solved using an energy balance of the thermocouple bead. The bead is heated by convection and is cooled by radiating heat away to the cooler reactor walls. Conduction through the thin, relatively long wires coming off from the thermocouple bead is ignored. Assuming that the thermocouple bead is at equilibrium, the following energy balance is used:

$$Q_{convection} = Q_{radiation} \tag{F.1}$$

$$h \cdot A_{bead} \cdot (T_{gas} - T_{bead}) = A_{bead} \cdot \sigma \cdot \varepsilon \cdot (T_{bead}^{4} - T_{wall}^{4})$$
(F.2)

where *h* is the convective heat transfer coefficient, A_{bead} is area of the thermocouple bead (this cancels out), T_{gas} is the gas temperature, T_{bead} is the temperature of the thermocouple bead, T_{wall} is the wall temperature of 500 K, σ is the Stefan-Boltzmann constant (5.67·10⁻⁸ W/m²/K⁴), and ε

is the emissivity of the thermocouple bead. Equation (F.2) was used to solve for the gas temperature in the atmospheric FFB and in the HPFFB when heaters were not used (when collection probe was positioned ≤ 3 " above the burner). Heaters were not used at the low collection height since the temperature in the first 3 inches above the burner is hotter than the maximum heater temperature. View factors were used in the temperature correction when HPFFB heaters were utilized, which is addressed further on in this appendix.

Solving for the gas temperature using Equation (F.2) requires iteration because the transport properties (heat capacity, viscosity, & thermal conductivity) of the gases surrounding the thermocouple bead are calculated at the film temperature (average of T_{gas} & T_{bead}), which is not known beforehand. The transport properties of the gases were calculated using DIPPR equations (Rowley et al., 2010) and were determined as the molar average of the three most prevalent post-combustion gases of N₂, CO₂, and CO as determined from a thermodynamic equilibrium program. The three aforementioned gases typically comprised at least 97% of the post-combustion gases. The temperature profiles from the atmospheric FFB and HPFFB were measured using a silica-coated and an alumina-coated thermocouple bead, respectively. The thermocouple bead coatings provide a protective layer around the bead to minimize catalytic heating of the bead during temperature measurements. The emissivity (ε) of a silica-coated bead was taken as 0.22 (Kaskan, 1957), and the emissivity of an alumina-coated bead was calculated by the following equation:

$$\varepsilon = 1.74 \cdot (-0.1 + 3.24 \cdot 10^{-4} T - 1.25 \cdot 10^{-7} T^2 + 2.18 \cdot 10^{-11} T^3)$$
(F.3)

where T is the temperature in K. The part of the formula in Equation (F.3) that is enclosed in parentheses is an empirical fit of the emissivity of an S-type thermocouple, and the 1.74 factor

accounts for the alumina coating of the thermocouple bead (Shaddix, 1999; Bahlawane et al., 2007).

Determining the values to use in Equation (F.2) is fairly straight forward, except for h which requires many calculations and is defined by:

$$h = \frac{Nu \cdot k_{gas}}{D_{bead}} \tag{F.4}$$

where D_{bead} is the diameter of the thermocouple bead, k_{gas} is the thermal conductivity of the gases surrounding the bead at the film temperature, and Nu is the Nusselt number. The diameter of the thermocouple bead was measured under a microscope, and was typically around 400 microns. Multiple thermocouples were used to measure the temperature profiles of the HPFFB since they often broke due to damage sustained to the fragile bead or ceramic shaft. The Nusselt number was calculated using the following falling drop correlation that is applicable to convection past the assumed-spherical thermocouple bead:

$$Nu = 2 + 0.6 \cdot \text{Re}^{1/2} \cdot \text{Pr}^{1/3}$$
(F.5)

where Re is the Reynolds number and Pr is the Prandtl number. The Reynolds number is defined as:

$$\operatorname{Re} = \frac{\rho_{gas} \cdot v_{gas} \cdot D_{bead}}{\mu_{gas}}$$
(F.6)

where ρ_{gas} is the gas density, v_{gas} is the gas velocity past the thermocouple bead, and μ_{gas} is the gas viscosity at the film temperature. The gas density was calculated as:

$$\rho_{gas} = \frac{P}{R \cdot T_{gas}} \cdot MW_{gas} \tag{F.7}$$

where *P* is pressure, *R* is the ideal gas constant, and MW_{gas} is the molecular weight of the postcombustion gases. The gas velocity (v_{gas}) was taken as the measured particle velocity if this information was available, but was calculated using the following formula in other cases:

$$v_{gas} = \frac{m_{gas}}{Area_{CS} \cdot \rho_{gas}}$$
(F.8)

where m_{gas} is the mass flow rate of the post-combustion gases (which is the same as the precombustion gases), and $Area_{CS}$ is the cross-sectional area of the flow path. The measured centerline particle velocity was believed to be a more accurate prediction of the gas velocity than that obtained when using Equation (F.8). Developed flow explains why measured velocities were always faster than that predicted by Equation (F.8) since velocity along the centerline is faster than the average velocity. The Prandtl number is defined as:

$$\Pr = \frac{C_{pGAS} \cdot \mu_{gas}}{k_{gas}}$$
(F.9)

where C_{pGAS} is the gas heat capacity at the film temperature.

As discussed above, view factors were used to solve for the local gas temperature in the HPFFB when heaters were utilized (when collection probe was positioned ≥ 6 " above the burner). The method of combining appropriate view factors to solve for the radiation-corrected gas temperature in the non-elementary geometry of the HPFFB was largely developed by Randy Shurtz, a fellow BYU graduate student. This said, the sole difference to the temperature correction compared to the above discussion is a small change to the energy balance of the thermocouple bead:

$$h \cdot (T_{gas} - T_{bead}) = \sum [F_{ij} \cdot \sigma \cdot \varepsilon \cdot (T_{bead}^{4} - T_{surroundings}^{4})]$$
(F.10)

where F_{ij} is the appropriate view factor, which is also referred to as a configuration or shape factor. The view factor is defined as the fraction of the radiation leaving surface *i* that is intercepted by surface j (Incropera and Dewitt, 2002). F_{13} is the fraction of the radiation that leaves the thermocouple bead and is intercepted by the collection probe if 1 and 3 are represented by the thermocouple bead and collection probe, respectively. $T_{surroundings}$ in Equation (F.10) is the temperature of the surroundings, which was assumed to be 500 K except when accounting for radiation of the thermocouple bead to the heater walls. In this case, the $T_{surroundings}$ was taken as the measured temperature of the heater wall provided by six K-type thermocouples placed at various heights above the burner positioned between the quartz tube and the heaters (refer to Figure F.2). There were four view factors used, referred to as F₁₂, F₁₃, F₁₄, and F₁₅. Figure F.2 is provided as a visual aid for the following definitions. F₁₂ refers to bead-to-burner view factor (between pink dotted lines in Figure F.2); F_{13} refers to the bead-to-probe view factor (between turquise dotted lines); F_{14} refers to the view factor from bead to vessel walls and insulation in the lower HPFFB chamber (between pink & black dotted lines depicted by red arrows); and F₁₅ refers to the view factor of the bead to everywhere else, but mostly is the bead-to-heater wall view factor (between turquoise & black dotted lines depicted by blue arrows).

Sphere-to-disk view factors (Siegel and Howell, 1981) were used to solve for F_{12} , F_{13} , and F_{14} while F_{15} was determined by difference since view factors sum to unity in an enclosure. Figure F.1 and Equation (F.11) are provided as further explanation of the sphere-to-disk view factors in the generic situation where r_A is the sphere radius (thermocouple bead) and r_B is the disk radius (burner, collection probe, or heaters in the case of the HPPFB geometry).



Figure F.1. Sphere-to-disk view factor schematic that relates to Equation (F.11).

$$F_{AB} = \frac{1}{2} \left(1 - \frac{1}{\sqrt{1 + \left(\frac{r_B}{h}\right)^2}} \right)$$
(F.11)

The calculation of F_{14} requires further explanation since this view factor is calculated differently when the thermocouple bead is lower than $\frac{1}{2}$ " from the burner surface since the thermocouple bead is below the heaters. For ease in explaining, F_{16} is defined as the view factor of the thermocouple bead to the bottom portion of the HPFFB through the imaginary disc created by the bottom portion of the heaters (between black dotted lines in Figure F.2), and F_{17} is the view factor of the bead to the upper portion of the HPFFB through the imaginary disc created by the bottom portion of the heaters when the thermocouple bead is less than $\frac{1}{2}$ " from the burner. If the bead is positioned above the heaters ($\geq \frac{1}{2}$ " above the burner), F₁₄ is calculated by the difference between F_{16} and F_{12} . If the thermocouple bead is below the heaters ($\leq \frac{1}{2}$ " above the burner), F_{14} is calculated as the summation of F_{17} and F_{12} subtracted from unity since view factors sum to one in an enclosure. Figure F.3 is included since it helps to easily visualize which view factors are important at different heights above the burner. For example, F₁₃ (bead-to-probe view factor) becomes important when the thermocouple bead is about 2.5" away from the collection probe, but otherwise is essentially zero. F₁₂ (bead-to-burner view factor) is important only when the thermocouple bead is less than 2" away from the burner, and so on.



Figure F.2. HPFFB during temperature measurements with an assumed-spherical thermocouple bead. Dotted lines aid in the explanation of the sphere-to-disc view factors used in correcting the measured temperature for radiation losses from the thermocouple bead (see above text).



Figure F.3. View factors in the HPFFB when the probe is situated 16.25" above the burner.

Appendix G. Coating Thermocouple Beads by Vapor Deposition

Platinum-based thermocouples are very common in combustion/gasification experiments due to their stability in high temperatures, and their resistance to attack in both reducing and oxidizing environments (Shaddix, 1999). The problem that arises is that platinum is catalytic and the energy balance used to correct thermocouple measurements for radiation loss in Appendix F becomes more difficult due to the effects of catalytic heating. Catalytic heating is more prevalent near the flame since catalytic activity is expected in the chemically nonequilibrium part of a reactive flow (Katsuki et al., 1987). Silica, alumina, and BeO/Y₂O₃ are the typical non-catalytic coatings used on thermocouple beads to alleviate the aforementioned problem.

Temperatures were measured in the HPFFB using an alumina-coated thermocouple bead. The method of coating the bead involved an apparatus that allowed alumina to be deposited on the bead through chemical vapor deposition based on a recent article by Bahlawane et al. (2007). The basic idea was to get AlCl₃ to react with oxygen in the air to form an alumina coating on the thermocouple bead. The experimental setup and the inner workings of BYU's thermocouple bead coating apparatus are shown in Figure G.1 and Figure G.2, respectively. To coat a thermocouple bead, a heated cord was wrapped around the metal housing that contained the AlCl₃ in order to raise the AlCl₃ vapor pressure by increasing its temperature. A K-type thermocouple was placed between the heated cord and surrounding insulation in order to measure the AlCl₃ temperature. A variable power supply allowed control of the heated cord, and was adjusted until the K-type thermocouple read values near 135 °C. A vacuum pulled a controlled amount of air from the inlet through a needle valve, while another variable power supply allowed control of the deposition temperature of alumina on the thermocouple bead. The electrical current through the thermocouple bead was adjusted until the bead glowed brightly through the viewport. A deposition time up to 2 hours can be required to ensure a good coating on the thermocouple bead.

Although the apparatus was made out of PVC, it could have easily been made out of metal. This change would have allowed a higher vacuum to be drawn on the system, thus increasing both the partial pressure of AlCl₃ and alumina deposition on the thermocouple bead.



Figure G.1. Apparatus used to coat thermocouple beads with an alumina coating by chemical vapor deposition. 'A' is the variable power supply used to pass current though the thermocouple bead; 'B' is a K-type thermocouple reader that measured the temperature of the AlCl₃; 'C' is the power supply to the heating cord wrapped around the metal housing that contained the AlCl₃; 'D' is the outlet line hooked to a vacuum; 'E' is the viewport that allowed optical access to the glowing thermocouple bead; 'F' is a pressure gauge; 'G' is where the AlCl₃ was encased in a metal housing surrounded by heating cord & insulation; and 'H' is the needle valve which controlled the amount of air pulled into the system.

The apparatus also allowed a thermocouple bead to be coated after it had become part of a finished thermocouple through the top T-fitting. In this scenario, a rubber stopper with a center hole was placed around the ceramic shaft of the thermocouple and was held down by a nut in order to maintain a vacuum on the system.



Figure G.2. Inside workings of the thermocouple bead coater. The red line represents where thermocouple bead would be positioned during the coating process.

A simple electrolysis test was performed to ensure the coating of a thermocouple bead, as displayed in Figure G.3. The bead of a finished thermocouple was placed in a water and NaOH solution in a beaker. An electrical circuit was created using wire, two 1.5-volt batteries, and the thermocouple. A proper coating of the thermocouple bead was ensured if no bubbles formed on the bead. Note that the schematic in Figure G.3 is not drawn to scale.



Figure G.3. Experimental setup to test if a thermocouple bead was successfully coated.

Appendix H. Measured Particle Velocities in FFB and HPFFB Reactors

Measuring particle velocities allowed the calculation of particle residence time, which was used to determine gasification kinetics and also to evaluate pyrolysis models. A high-speed camera (Kodak EktaPro) was used to measure sawdust and pet coke velocities in the FFB and the HPFFB. The camera allowed particles to be filmed up to 1000 frames per second (fps), but particles were typically only filmed up to 250 fps since the lower frame speeds allowed dimmer particles to be measured while also enabling longer record times. After filming, the recorded particle movement was played on a monitor and the distance a particle traveled in one frame was measured on the screen. The relationship between apparent distance traveled and actual distance traveled was obtained by measuring an object of known length on the monitor, and calculating accordingly. The particle velocity was then obtained by dividing the distance traveled by the time of a single frame (1/50, 1/125, or 1/250 sec). Particle velocities at a single height above the burner were taken as the average of at least 5 different particles.

Theoretical calculations were necessary to obtain particle residence times since the particles could not be filmed over the entire particle path. In the HPFFB, a 9/16" viewport offers the sole optical access into the reactor. In the FFB, the first measured particle velocities were obtained about 1" above the burner surface. Thus theoretical calculations were necessary to bridge the gap where particle velocities could not be measured.

Theoretical Particle Velocity Model

A simple model was used to predict particle velocities when particles could not be filmed. The model was based on the assumption that all particles were spherical, whether they were pet coke or sawdust. Particle interactions were ignored, justified by the slow feed rate (0.5 to 1.3 g/hr) that ensured single particle behavior. Lastly, the model assumed that there was no change in particle mass or diameter. A quadratic scaling factor was used in order to transition from a purely theoretical particle velocity at the burner inlet to a measured particle velocity, typically about 1 inch above the burner surface.

The equations used to predict particle velocities begin with a simple force balance on the particle taking into account the forces due to gravity, buoyancy, and drag (see Figure H.1).



Figure H.1. Depiction of the forces on a single particle as the particles travel from the burner to the collection probe.

Equation (H.1) gives the definition of force, while Equation (H.2) is simply the rearrangement of Equation (H.1) in order to solve for acceleration (*a*), where v_p is the particle velocity, *t* is time, F_{drag} is the drag force, $F_{buoyancy}$ is the buoyancy force, $F_{gravity}$ is the force on the particle due to gravity, m_p is the particle mass, d_p is the particle diameter, and ρ_p is the particle

density. The diameters of sawdust and pet coke used in the model were 75 and 60 microns, respectively. Densities of sawdust and pet coke were taken as 650 kg/m^3 (Koufopanos et al., 1991) and 1750 kg/m³ (measured), respectively.

$$\sum Force = mass \times acceleration \tag{H.1}$$

$$a = \frac{dv_p}{dt} = \frac{\left(F_{drag} + F_{buoyancy} - F_{gravity}\right)}{m_p} = \frac{\left(F_{drag} + F_{buoyancy} - F_{gravity}\right)}{\left(\frac{\pi \cdot d_p^3}{6}\right) \cdot \rho_p}$$
(H.2)

The general drag force correlation used was (Bird et al., 2002):

$$F_{drag} = \left(\frac{1}{2} \cdot \rho_{gas} \cdot v_{\infty}^{2}\right) \cdot \left(wetted \ surface \ area\right) \cdot \left(C_{d}\right) \tag{H.3}$$

where ρ_{gas} is the gas density, C_d is the drag coefficient, and the *wetted surface area* is taken as the area obtained when projecting the solid onto a plane perpendicular to the fluid flow $(\pi \cdot d_p^2/4)$. The term v_{∞} is the slip velocity between the entrainment gas and the particle and is defined as:

$$v_{\infty} = v_{gas} - v_p \tag{H.4}$$

where v_{gas} is the gas velocity and v_p is the particle velocity. The gas velocity was predicted as:

$$v_{gas} = \frac{\dot{m}_{gas}}{\rho_{gas} \cdot A_{burner}} \tag{H.5}$$

where \dot{m}_{gas} is the gas mass flow rate, and A_{burner} is the cross-sectional area of the flow path through which the post-combustion gases travel before entering the collection probe. The gas density, ρ_{gas} , is defined using the ideal-gas law as:

$$\rho_{gas} = \frac{P}{R \cdot T} \cdot MW_{gas} \tag{H.6}$$

where *P* is pressure, *R* is the ideal-gas constant, *T* is temperature, and MW_{gas} is the average gas molecular weight of the post-combustion products predicted by thermodynamic equilibrium. The correlation used for C_d in Equation (H.3) is:

$$C_d = \left(\sqrt{\frac{24}{\text{Re}}} + 0.5407\right)^2$$
 (H.7)

which is for a sphere up to a Reynolds number ($Re = \rho_{gas} \cdot d_p \cdot v_{\infty} / \mu_{gas}$) of 6000 (Bird et al., 2002). The dynamic gas viscosity (μ_{gas}) was calculated using the following empirical correlation:

$$\mu_{gas} = \left[2.25 \times 10^{-8} (T) + 1.95 \times 10^{-5}\right] Pa \cdot \sec$$
(H.8)

where the temperature is in Kelvin. The correlation in Equation (H.8) was developed after plotting the gas viscosity from several conditions from both the HPFFB and the FFB and noticing a linear trend (see Figure H.2). The gas viscosity at a given condition in Figure H.2 was calculated using DIPPR correlations (Rowley et al., 2010) to predict the viscosity of individual post-combustion gas products (N₂, CO₂, CO, H₂O, H₂, Ar) and then calculating the molar weighted average as determined by the predicted products from thermodynamic equilibrium.



Figure H.2. Visual comparison of how well Equation (H.8) predicts gas viscosity at experimental conditions from the FFB and the HPFFB.

The equations for the forces of buoyancy and gravity are:

$$F_{buoyancy} = \left(\frac{\pi \cdot d_p^{-3}}{6}\right) \cdot \rho_{gas} \cdot g \tag{H.9}$$

$$F_{gravity} = \left(\frac{\pi \cdot d_p^{-3}}{6}\right) \cdot \rho_p \cdot g \tag{H.10}$$

where g is taken as 9.81 m/s² and all other terms carry the aforementioned definitions. Substituting Equations (H.3), (H.4), (H.7), (H.9), and (H.10) into (H.2) yields Equation (H.11) after simple rearrangement.

$$a = \frac{dv_p}{dt} = \left(\frac{\rho_{gas}}{\rho_p} \cdot \left(v_{gas} - v_p\right)^2\right) \left(\frac{3}{4 \cdot d_p}\right) \left(\sqrt{\frac{24}{\text{Re}}} + 0.5407\right)^2 + g \cdot \left(\frac{\rho_{gas}}{\rho_p} - 1\right)$$
(H.11)

Equation (H.11) would be simpler if Stoke's flow was assumed, but this assumption was not made since the Reynolds number of the particle was greater than 0.1 (Bird et al., 2002). Equation (H.12) is the definition of particle velocity where z is the distance above the burner.

$$\frac{dz}{dt} = v_p \tag{H.12}$$

Equations (H.11) and (H.12) were plugged into Polymath, a program capable of solving differential equations. A Runge-Kutta-Fehlberg ODE solver was used to solve for the theoretical particle velocity profiles. Calculating particle velocity required an initial velocity at the burner surface, which was taken as the terminal velocity in the feed tube which runs from the feeder to the burner. This velocity was solved for by equating Equation (H.11) to zero and solving for v_p using N₂ gas properties (carrier gas in feed tube) and using the cross-sectional area of the feed tube when solving for v_{gas} . The FFB and HPFFB feed tube inside diameters were 0.053" and 0.041", respectively.

Separate Polymath files were created for each experimental condition by entering the appropriate operating pressure, measured temperature profile, gas mass flow rate, and post-combustion gas molecular weight. Each individual temperature profile from the FFB and the HPFFB was entered into its respective Polymath file as a function of z after fitting the measured temperature profile in Excel to a polynomial equation.

HPFFB Particle Velocity Measurements

The entire particle velocity profile in the HPFFB could not be measured since a small viewport (9/16" diameter) about 1" above the burner surface provided the sole optical access into the HPFFB. A high-speed camera was used to measure particle velocities through this viewport at a maximum of two different heights above the burner surface. These particle velocity measurements in the HPFFB were taken at a maximum height about ³/₄" above the burner surface and are included near the end of Appendix H.

A method was developed to predict the entire HPFFB particle velocity profile with a single velocity measurement. The scheme used a quadratic scaling factor to transition from a theoretical particle velocity to a measured particle velocity, and then scaled by the centerline gas temperature to predict the particle velocity beyond the height at which the maximum particle velocity had been measured.

The quadratic scaling factor, f, was a function of the height above the burner and was multiplied by the theoretical particle velocity to estimate the true particle velocity up to the maximum height above the burner at which a particle velocity measurement had been taken (usually $\sim \frac{3}{4}$ "):

$$v = f(h) \cdot v_{p, \text{theoretical}} \tag{H.13}$$

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where $v_{p,theoretical}$ is the predicted particle velocity from using Equations (H.11) and (H.12). The equation for *f* took the form:

$$f(h) = a_1 \cdot h^2 + b_1 \cdot h + c_1 \tag{H.14}$$

where *h* is the height above the burner up to the maximum height at which a particle velocity had been measured in the HPFFB. The constants a_1 , b_1 , and c_1 could be solved using two boundary conditions, assuming that the maximum particle velocity occurred about ³/₄" off the burner surface. This was the height at which particle velocity was measured and was also near the maximum measured centerline temperature. The boundary conditions and definition of maximum *f* follow:

$$f(0) = 1$$
 (H.15)

$$f(L) = m_{ratio} = \frac{v_{p,measured}}{v_{p,theoretical}}$$
(H.16)

$$\frac{df}{dh}\Big|_{L} = 0 = 2a_1 \cdot L + b_1 \tag{H.17}$$

where *L* is the maximum height above the burner at which a particle velocity was measured, and m_{ratio} is the ratio of the measured particle velocity to the theoretical particle velocity (see Eqns (H.11) & (H.12)) at height *L*. The average value of m_{ratio} over the many different HPFFB conditions was 2.06, but ranged from 1.03 to 3.45. The first boundary condition suggests that the theoretical particle velocity was used at the burner surface, which was taken as the theoretical, terminal particle velocity in the feed tube. The second boundary condition defines m_{ratio} , and Equation (H.17) resulted from assuming that the maximum particle velocity took place at height *L*. The constants *a*, *b*, and *c* could be solved using the two boundary conditions and definition of maximum as:

$$a_1 = \frac{1 - m_{ratio}}{L} \tag{H.18}$$

$$b_1 = \frac{2 \cdot \left(m_{ratio} - 1\right)}{L} \tag{H.19}$$

$$c_1 = 1$$
 (H.20)

where all terms retain their aforementioned definitions. Equations (H.18) through (H.20) provided a closed-form solution to the quadratic scaling factor (see Eqn (H.14)).

The particle velocity beyond the height where the particle velocity had been measured in the HPFFB was scaled by temperature. This originated from a simple derivation based on the ratios of gas mass flow rate from 2 conditions, assuming that v_{gas} was a good approximation of v_p :

$$\dot{m}_{gas} = \rho_{gas} \cdot v_{gas} \cdot Area_{flowpath} \approx \rho_{gas} \cdot v_p \cdot Area_{flowpath}$$
(H.21)

$$\frac{\dot{m}_{gas1}}{\dot{m}_{gas2}} \approx \frac{\rho_{gas1} \cdot v_{p1} \cdot A_{flowpath1}}{\rho_{gas2} \cdot v_{p2} \cdot A_{flowpath2}}$$
(H.22)

where $A_{flowpath}$ is the cross-sectional area of the flow path and all other terms carry their aforementioned definitions. Using the definition of density from the ideal gas law and assuming that the cross-sectional area terms from the 2 conditions were equal, Equation (H.23) results.

$$v_{p2} \approx v_{p1} \cdot \frac{T_2}{T_1} \cdot \frac{\dot{m}_{gas2}}{\dot{m}_{gas1}} \cdot \frac{MW_1}{MW_2}$$
(H.23)

The following equation was used to predict the velocity profile beyond the maximum height above the HPFFB burner at which a particle velocity had been measured and is the result of Equation (H.23) when the 2 reference points came from the same operating condition:

$$v_{p}(h_{1}) = v_{p,ref} \cdot \frac{T(h_{1})}{T_{ref}}$$
 (H.24)

where h_I is the height above the burner from *L* to the collection probe height, and *T* is the measured centerline gas temperature. The reference point ($v_p \& T$) for each condition was the measured particle velocity at the maximum measured height above the burner (< 1") and the associated centerline gas temperature at this height. Equation (H.24) scaled the remaining particle velocity profile by gas temperature.

A lens effect also had to be taken into account for particle velocity measurements taken through the HPFFB viewport. Filming particles through the viewport glass and two quartz tubes (see Figure H.3) caused the particles to appear to travel significantly slower than they actually were. To solve for the lens correction, a ruler was placed in the unpressurized HPFFB along the centerline while the reactor was not in operation. A $\frac{1}{2}$ mark on the ruler was measured on the monitor screen. The $\frac{1}{2}$ scale was calculated as only 0.19" long after accounting for the fact that distances on the monitor appeared larger than they actually were (determined by measuring the 9/16" viewport on the monitor screen). A lens correction was thus applied by multiplying the measured particle velocities by 2.58 after first addressing the magnifying effect of the monitor screen.



Figure H.3. Experimental setup to measure particle velocities in the HPFFB.

Figure H.4 shows two representative particle velocity profiles from the HPFFB that were obtained by using velocity measurements obtained at a single height above the burner and following the method described above. The predicted velocity profile was always was within the error of the second particle velocity measurement when a second measurement was made.



Figure H.4. Two representative particle velocity profiles determined by one experimental v_p point from the HPFFB. Note how the profiles are always within the uncertainty of the second velocity measurement that was <u>not</u> used to develop the velocity profile.

The x-error bars in the particle velocity measurement came from the viewport diameter of 9/16", which gave an uncertainty of ± 0.28 " on the height above the burner at which the particle velocity was actually measured. The y-error bars represent the 95% confidence interval of the population mean from the measurements of at least 5 different particle velocities. Particle velocity profiles of pet coke at all the conditions are included at the end of Appendix H.

FFB Particle Velocity Measurements

The atmospheric FFB provided much more optical access of the particle (see Figure H.5) than available in the HPFFB. The first particle velocities were measured in the FFB about 1" above the burner surface. The model discussed above was therefore used to predict particle velocity profiles for both sawdust and pet coke in the FFB up to the first measured height. The same quadratic scaling factor (see Eqn (H.14)) discussed above was used in conjunction with the

model in order to transition from a purely theoretical velocity at the burner surface to the first measured particle velocity. The theoretical particle velocity at the burner surface was taken as the calculated terminal particle velocity in the feed tube (ID = 0.053"). Measured particle velocities were then used to complete the remaining velocity profile to the collection probe, and are included near the end of Appendix H.



Figure H.5. Sawdust particle in FFB. Note that the atmospheric FFB facility allows optical access of the particle over a wide range.

Particle velocity measurements at a single height above the burner were taken as the average of at least 5 different particles. No lens effect was used to correct the FFB velocity measurements since filming through the quartz pane with the high-speed camera did not skew the particle velocity measurements.

The sawdust velocities at the 1163 K condition in the FFB could not be measured since the particles were not sufficiently bright at this low temperature to be filmed by the high-speed camera. In this case, the sawdust velocity profile was estimated by Equation (H.23) using the sawdust velocity profile from the 1433 K condition as a reference (Zhang, 2001). The particle velocity profiles of sawdust are included near the end of Appendix H.

Particle Residence Time Calculation

Particle residence times were calculated after particle velocity profiles had been measured and merged with theoretical calculations as discussed previously. Equation (H.25) was then used to calculate the total particle residence time, which was a summation of small time steps of the particle as it traveled from the burner to the collection probe. The variable Δz is the distance a particle traveled in a single time step (Δt).

$$\Delta t = \sum_{i=1}^{n} \frac{\Delta z}{v_{p_i}} \tag{H.25}$$

The particle residence times for both sawdust and pet coke in the FFB and the HPFFB at various collection heights are conveniently located in Tables H.1 to H.3. Note that the theoretical initial particle velocities (i.e., terminal particle velocity in feed tube) are included in these tables since an initial velocity condition is required to solve Equation (H.11). Complete particle velocity profiles for both sawdust and pet coke are included in Tables H.4 to H.7.

Height Above Burner ('')	1163 K sawdust	1320 K sawdust	1433 K sawdust	1751 K pet coke	1929 K pet coke
v _o (m/s)	0.33	0.33	0.33	0.13	0.13
1	32	29	23	-	23
1.5	-	40	31	-	-
2	55	51	39	33	-
3	78	-	-	-	-
4	102	-	-	55	60
8	-	-	-	98	102

Table H.1. Sawdust and pet coke residence times (ms) in FFB at various collection heights

Height Above Burner ('')	2.5 atm 1683 K	2.5 atm 1876 K	5 atm 1702 K	5 atm 1867 K	5 atm 2110 K
v _o (m/s)	0.19	0.19	0.09	0.09	0.09
0.75	-	-	44	-	-
1	43	-	56	-	-
1.5	-	-	75	-	-
2	76	73	96	-	-
3	111	109	141	-	-
6	-	_	_	_	_
10	369	-	467	644	753

Table H.2. Pet coke residence times (ms) in HPFFB at various collection heights at 2.5 & 5 atm

Table H.3. Pet coke residence times (ms) in HPFFB at variouscollection heights at 10 and 15 atm

Height Above Burner ('')	10 atm 1722 K	10 atm 1967 K	10 atm 2139 K	15 atm 1402 K	15 atm 1681 K	15 atm 1918 K
v _o (m/s)	0.04	0.04	0.04	0.05	0.05	0.05
0.75	48	-	-	-	50	-
1	-	65	-	-	-	-
1.5	81	-	-	-	-	-
2	-	-	-	-	104	-
3	150	-	-	-	151	-
6	-	373	-	337	318	335
10	-	663	563	-	-	577
16.25	-	1061	-	-	914	994

1163 K	1163 K	1320 K	1320 K	1433 K	1433 K
Height Above	V _p (cm/s)	Height Above	V _p (cm/s)	Height Above	V_p (cm/s)
Burner (mm)		Burner (mm)		Burner (mm)	
0	35.5	0	35.5	0	35.5
1.65	53	1.65	57.7	1.2	65.4
3.3	63.1	3.3	69.1	2.4	79
4.95	69.7	4.95	77.4	3.6	91.9
6.6	76.2	6.6	84.2	4.8	102.3
8.25	82.2	8.25	90.7	6	111.7
9.9	87.9	9.9	96.7	7.2	120.5
11.55	93.5	11.55	102.4	8.4	128.5
13.2	99.1	13.2	108.3	9.6	136.7
14.85	104.6	14.85	114	10.8	144.5
16.5	110.3	16.5	119.7	12	152.4
20	110.3	20	119.7	16	152.4
40	110.3	24	119.7	20	152.4
45	109.9	28	119.7	25	152.4
60	109.9	32	119.7	30	152.4
75	108.8	36	119.7	35	152.4
85	108.8	40	119.7	40	152.4
90	108.8	42	119.7	42	152.4
95	107.5	45	119.7	45	158
102	107.5	51	119.7	51	158

Table H.4. Sawdust particle velocities at various heights above
the FFB at 1163, 1320 and 1433 K

Table H.5. Pet coke particle velocity profiles in the FFB at 1 atm

1 atm; 1751 K peak	1 atm; 1751 K peak	1 atm; 1929 K peak	1 atm; 1929 K peak
Height Above	$\mathbf{V_p}$	Height Above	$\mathbf{V}_{\mathbf{p}}$
Burner (mm)	(cm/s)	Burner (mm)	(cm /s)
0.0	12.7	0.0	12.7
1.2	52.2	1.5	63.5
2.1	67.2	2.6	79.9
3.3	83.9	4.0	97.2
5.0	102.6	4.9	106.1
6.0	112.7	7.0	124.4
8.4	134.1	8.3	133.5
9.8	144.9	11.2	151.1
11.2	155.2	12.8	158.8
14.2	173.8	14.4	165.8
15.8	181.9	16.0	172.0
17.4	189.2	19.3	182.0
19.0	195.6	21.0	185.9

1 atm; 1751 K peak	1 atm; 1751 K peak	1 atm; 1929 K peak	1 atm; 1929 K peak
Height Above	$\mathbf{V_p}$	Height Above	$\mathbf{V}_{\mathbf{p}}$
Burner (mm)	(cm/s)	Burner (mm)	(cm /s)
22.4	205.4	22.7	188.9
24.1	208.7	24.4	191.2
25.8	211.0	27.9	194.1
38.1	211.3	38.1	200.6
50.8	211.3	50.8	207.6
63.5	211.3	63.5	213.0
76.2	211.3	76.2	218.4
88.9	211.3	88.9	219.2
101.6	235.4	101.6	220.0
114.3	235.4	114.3	226.9
127.0	235.4	127.0	233.9
139.7	244.7	139.7	237.4
152.4	244.7	152.4	240.9
165.1	244.7	165.1	240.1
177.8	233.5	177.8	239.3
190.5	233.5	190.5	245.9
203.2	233.5	203.2	252.5

Table H.5 continued

Table H.6. Pet coke particle velocity profiles in the HPFFB at 2.5 and 5 atm

Height	2.5 atm	2.5 atm	5 atm	5 atm	5 atm
Above	1683K peak	1876K peak	1702 K peak	1867 K peak	2110 K peak
Burner (mm)	V_{p} (cm/s)	V_{p} (cm/s)	V_{p} (cm/s)	V _p (cm/s)	V _p (cm/s)
0.0	19.1	19.1	9.3	9.3	19.1
2	35.2	42.0	28.6	27.8	32.0
4	45.6	52.9	37.8	33.8	36.6
6	54.0	60.3	44.7	37.6	39.0
8	60.9	65.9	50.2	40.2	40.5
10	66.8	70.4	54.6	42.2	41.4
12	71.5	73.8	58.0	43.8	42.0
14	75.2	76.5	60.6	44.9	42.4
15.6	77.4	78.1	61.9	45.6	42.6
16	77.9	78.4	62.2	45.8	42.7
18	79.5	79.7	63.1	46.3	42.7
19.5	80.2	80.2	63.2	46.4	42.7
Particle velocities are obtained for distances of $x > 19.5$ mm above the burner using the equation					
$v_p = v_p(19.5 \text{ mm}) \cdot T(x) / T(19.5 \text{ mm})$ where T is the centerline gas temperature at x. T(19.5 mm) values are given					
below for each of the conditions.					
$T(\overline{19.5 mm})$	1687 K	1869 K	1697 K	1866 K	2096 K

Height Above Burner (mm)	10 atm 1722K peak V _n (cm/s)	10 atm 1967K peak V _n (cm/s)	10 atm 2139K peak V _n (cm/s)	15 atm 1402K peak V _n (cm/s)	15 atm 1681K peak V ₂ (cm/s)	15 atm 1918K peak V _n (cm/s)
0.0	4.2	4.2	4.2	4.7	4.7	4.7
2	27.1	27.8	29.4	20.0	26.0	25.9
4	36.4	34.8	37.9	28.0	36.4	34.4
6	42.9	39.3	43.7	34.5	44.1	40.8
8	48.0	42.5	48.0	40.1	49.9	45.8
10	52.0	45.0	51.5	44.8	54.1	50.0
12	55.0	46.9	54.1	48.6	56.9	53.3
14	57.2	48.2	56.1	51.6	58.2	55.7
15.6	58.4	48.9	57.1	53.3	58.4	57.1
16	58.6	49.0	57.3	53.6	-	57.3
18	59.3	49.4	57.9	54.7	-	58.2
19.5	59.3	49.4	58.0	55.0	-	58.3
Particle velocities are obtained for distances greater than the last given value by scaling by temperature						
using the equation: $v_p = v_p(last measured value) \cdot T(x) / T(last measured value)$ where T is the centerline gas						
temperature at x. T(last measured value) is given below for each of the conditions.						
T(last measured	1655 K	1936 K	2018 K	1401 K	1648 K	1917 K
value)						

Table H.7. Pet coke particle velocity profiles in the HPFFB at 10 and 15 atm

The measured pet coke particle velocities in the HPFFB reactor appear in Table H.8. These measurements already include the lens effect correction. All the velocity measurements in the HPFFB were taken at a maximum height of 0.77" above the burner, except for the 15 atm 1681 K condition. There is no particular reason why this measurement was taken at a different height except that the measurements were taken over several days and this was simply overlooked.

The heights listed in Table H.8 have an uncertainty of ± 0.28 " since particle velocity measurements were not all taken from the middle of the 9/16" viewport. Both the sawdust and pet coke measured particle velocities in the atmospheric FFB reactor appear in Table H.9. The 95% confidence intervals of the population mean are given in the table for the velocity measurements, except for a single height from the 1751 K condition since this value is the average of only 2 measurements. All other velocities in the table are the average from at least 5 measurements.

Pressure	Peak Temperature	Height Above Burner	Particle Velocity
(atm)	(K)	(")	(m/s)
2.5	1683	0.06	0.54 ± 0.06
		0.77	0.80 ± 0.07
5	1702	0.27	0.59 ± 0.05
		0.77	0.63 ± 0.09
5	1867	0.77	0.46 ± 0.07
5	2110	0.77	0.43 ± 0.06
10	1722	0.34	0.53 ± 0.05
		0.77	0.59 ± 0.03
10	1967	0.77	0.49 ± 0.09
10	2139	0.77	0.58 ± 0.11
15	1402	0.77	0.55 ± 0.06
15	1681	0.62	0.58 ± 0.03
15	1918	0.03	0.28 ± 0.05
		0.77	0.58 ± 0.07

Table H.8. Measured velocities of pet coke in HPFFB

Table H.9. Measured velocities of sawdust and pet coke in FFB

Peak Temperature	Particle Type	Height Above	Particle Velocity
(K)		Burner (")	(m/s)
1320	sawdust	1.5	1.20 ± 0.06
		1.5	1.52 ± 0.08
1433	sawdust	2	1.58 ± 0.09
		3	1.44 ± 0.04
		4	1.45 ± 0.05
		1	2.11 ± 0.15
1751	pet coke	1.5	2.04 ± 0.07
		3	2.35 ± 0.08
		6	2.45 ± 0.05
		8	2.34
		1	1.94 ± 0.03
		2	2.08 ± 0.12
		3	2.18 ± 0.14
1929	pet coke	4	2.20 ± 0.09
		5	2.34 ± 0.03
		6	2.41 ± 0.02
		7	2.39 ± 0.11
		8	2.52 ± 0.05

Appendix I. Elemental Composition of Sawdust Tar and Char

The elemental composition of the sawdust tars appears in Table I.1, and was measured using BYU's Leco TruSpec Micro. The tar composition was taken as the average of 3 replicates of the same sample, except for the 1163 K 32 ms condition, which did not have any replicates due to lack of sample. Note in Table I.1 that the carbon percentage increased with severity of conditions, which is indicative of increasing aromaticity. Fagbemi et al. (2001) measured the C, H, O composition of sawdust tar collected from 770 K in a drop-tube reactor to be 53.9, 6.8, 39.3 wt%, respectively. This tar composition reported from literature is closest in composition to the tar collected in BYU's FFB at 1163K at the shortest residence time. The higher carbon content and lower oxygen content of the BYU tar at 1163 K is explained since it was collected from a condition about 400 K hotter.

Nunn et al. (1985) measured the elemental composition of tar from the pyrolysis of Sweet Gum sawdust from an electrical screen heater reactor at peak temperatures of 770, 895, and 1355 K. Although their measured tar composition was fairly constant for all three temperatures, the authors mention that the tar may have escaped the region of the heated screen before secondary tar-cracking reactions could occur. The tar escaping the heated region would also affect the tar composition, which explains why the sawdust tar collected by Nunn et al. (1985) did not vary with temperature. This is in contrast to the tar composition trends observed from the BYU FFB sawdust experiments, where increased temperatures were observed to cause a higher C content and lower O and H content.

Figure I.1 show the fraction of the initial amount of C, H, O, and N that end up in the sawdust tar from the 1163, 1320, and 1433 K FFB experiments. The shapes of the curves in the figure are largely determined by the amount of tar that was formed at each condition. Sulfur was not included in the figures since sulfur was only detected on the sample without any replicates, which may have been an anomaly. If there was any sulfur in the other 9 soot samples, it was outside the detection limits of the instrument. The mass fraction of the original C, H, and O that remain in the tar are all below 8.5 wt% while that of N is about 5 to 35 wt%. The tar from the 1163 K 32 ms condition is the only sample with such a high fraction of N that remained in the tar, and is also the sole sample that did not have a replicate elemental composition run. Excluding this single point, the mass fraction of the original N that remained in the tar was 5 to 16%.

Peak	Residence	% C	% H	% N	% S	% O
Temperature	Time					(by difference)
(K)	(ms)					
1163	32	65.29	5.05	0.39	0.04	29.23
1163	55	73.99	4.68	0.27	not detected	21.06
1163	78	77.22	4.53	0.29	not detected	17.96
1163	102	80.79	4.57	0.26	not detected	14.38
1320	29	77.45	4.95	0.53	not detected	17.07
1320	40	80.15	4.46	0.55	not detected	14.84
1320	51	81.34	4.53	0.60	not detected	13.53
1433	23	80.92	3.95	0.70	not detected	14.43
1433	31	82.43	2.88	0.38	not detected	14.31
1433	39	89.97	3.64	0.26	not detected	6.13

Table I.1. Ultimate analysis of the sawdust tar from pyrolysis FFB experiments (dry basis)

The ultimate analysis of the sawdust char is included in Table I.2. The values come from the analysis performed on BYU's Leco TruSpec Micro and are the average of 3 replicates of the
same sample. If the chars contained any sulfur, it was below the detection levels of the instrument. Nunn et al. (1985) measured the elemental composition of char from the pyrolysis of Sweet Gum sawdust from an electrical screen heater reactor at peak temperatures of 610 and 810 K. The elemental composition of Nunn's char was 50% C, 6% H, and 40 wt% O, which is similar to the elemental composition of the char collected at the 1163 K 32 ms condition in the FFB.



Figure I.1. Fraction of the initial amount of C, H, O, and N that remain in the tar in the 1163, 1320, and 1433 K FFB sawdust experiments.

Guerrero et al. (2005) measured the Eucalyptus sawdust char composition after pyrolyzing sawdust for 1 hr in a fixed bed reactor at 1173 K. The composition of Guerrero's char contained roughly 90, 0.5, and 9 wt% for C, H, O values, respectively. Both Guerrero's results and the

trends observed Table I.2 suggest that increased residence time lead to a decrease in percentages of O and H in the sawdust char, with an associated increase in carbon content. Note that the values in Table I.2 were presented on a dry, ash-free (daf) basis, except for the ash percent.

Peak Temperature	Residence Time	% C	% H	% N	% O (by difference)	% S	% Ash (dry basis)
(K)	(ms)						
1163	32	58.58	4.98	0.20	36.24	-	10.74
1163	55	61.32	3.54	0.22	34.92	-	18.30
1163	78	68.66	2.57	0.27	28.50	-	25.22
1163	102	73.25	3.37	0.25	23.13	-	22.21
1320	29	66.07	5.35	0.17	28.42	-	18.95
1320	40	69.01	3.59	0.30	27.10	-	24.17
1320	51	70.04	3.07	0.31	26.58	-	27.43
1433	23	61.48	3.28	0.24	35.01	-	20.93
1433	31	65.39	2.76	0.28	31.57	_	33.40
1433	39	72.48	2.52	0.26	24.74	_	25.50

Table I.2. Ultimate analysis of the sawdust char from pyrolysis FFB experiments (daf basis)

Figure I.2 shows the effect of temperature on the O/C, H/C, and N/C atomic ratios by comparing sawdust chars that were collected at roughly the same residence time (within 3 ms or less). The H/C atomic ratio decreases with increasing temperature, and is the most sensitive to temperature in the 1163-1433 K range. A decreasing H/C ratio means that H leaves the char more quickly than C, which is expected.

The O/C atomic ratio also decreases with increasing temperature, but its decrease is less drastic than the H/C ratio. This means that the O leaves the char more quickly than C, which is also expected. The N/C ratio appears to decrease with increasing temperature, except for the point at 1433 K at 30 ms in Figure I.2. It is difficult to determine the trend of the N/C ratio since the very low nitrogen values in the sawdust char are approaching the lower detection limits of the instrument. Note that the N/C ratio is multiplied by 100 in the Figure I.2 in order to graph all the atomic ratios on the same scale.



Figure I.2. Atomic ratio of sawdust chars as a function of temperature at particle residence times of 30 and 40 ms.



Figure I.3. Fraction of the initial amount of C, H, O, and N that remain in the char in the 1163, 1320, and 1433 K FFB sawdust experiments.

Figure I.3 shows the fraction of the initial amount of C, H, O, and N that end up in the sawdust char from the 1163, 1320, and 1433 K FFB experiments. The mass fraction of C, H, and O that remain in the sawdust char are all below 6 wt% while that of N is about 5 to 14 wt%.

Figure I.4 shows how the composition of the sawdust char changes as a function of temperature and residence time in the FFB. The composition of raw sawdust is included as a reference. As discussed above, increasing particle residence time in the FFB reactor led to a decrease in H and O content in the sawdust char with an associated increase in carbon content.



Figure I.4. Compositional progression as sawdust transforms into char at 1163, 1320, and 1433 K in FFB.

Appendix J. Sample Input File for CPD Code

Included below is a sample input file for cellulose that was run using the CPDCP version of the CPD model. The only change to the CPD Fortran code when using it to model biomass pyrolysis was to not subtract '7' from the mass of the side chains, i.e., the line of Fortran code that used to read "mdel=mdel-7" now reads "mdel=mdel." The "7" was used when modeling coal and accounted for a methyl group remaining after a bridge was broken during devolatilization.

The CPDCP version of the code is useful for entrained flow experiments and requires a particle velocity profile and gas temperature profile. The only change that would be made to run this code for hemicellulose or lignin would be to change the structural and kinetic parameters (see Tables 5.2 & 5.3). Other versions of the model are CPD and CPD heat, whose input files are similar enough that they are not included here. The particular sample input file included below was used to model the sawdust pyrolysis experiments in the atmospheric FFB reactor at a peak temperature of 1433 K.

Input file for cellulose

Sawdust_vel_1433.dat Sawdust_temp_1433.dat Cell_1433K_1.txt Cell_1433K_2.txt Cell_1433K_3.txt ! Name of Particle Velocity Profile file (included below)
! Name of Gas Temperature Profile file (included below)
! Name of first output file
! Name of second output file
! Name of third output file

1.0		TIMAX !maximum time (seconds)
300.		TG0
72.		VG0 !cm/s
0.6		RHOP !G/CM**3
0.0090		DP !CM
0.0		swell !(df-d0)/d0
-106		DELHV !CAL/G (- MEANS ENDOTHERMIC)
0.0		Omegaw
0.004		OMEGAA
0.75		EMIS
500.		TWALL
1200		THTR (1700 for high T, 1200 for Low T)
300.		TTUBE
1.e-5,5.e	-5,10	dt,dtmax,iprint
1.0	!p0	! structural parameters of cellulose (See Table 5.2 of this thesis)
0.0	!c0	
3.0	!sig-	+1
81	!mw	,
22.67	!mc	lel
1.0e18	!ab	! kinetic parameters of cellulose (see Table 5.3 of this thesis)

- 65000 !Ecr (activation energy for crosslinking rate)
- 0 !arad (pre-exponential factor for N attack by free radical)
- 0 !erad (activation energy for N attack by free radical, cal.)
- 0 !fstable (initial frac. of MW decay with no radical N attack)

!Acr (pre-exponential factor for crosslinking rate)

- 0 !an (high T slow N release pre-exponential factor)
- 0 !en (high T slow N release activation energy, calories)
- 0 !ensig (deviation bound for distribution of en)

- .444 %Carbon (DAF) !Composition of Cellulose
- .062 %H

51500

3000

5.0

0.0

8.23e12

42000

3000

3.e15

!eb

!ec

!ag

leg!

legsig!

!ebsig

!ac=rho

- .00 %N
- .494 %O
- .00 %S

^{1.0 !}pressure (atm)

Sawdust_vel_1433.dat file

c 45-75 micron velocities, 1433 K c z(mm) vp (cm/s)

0	35.5
0.3115	45.3
0.6334	52.9
0.919	58.5
1.2	65.4
2.4	79
3.6	91.9
4.8	102.3
6	111.7
7.2	120.5
8.4	128.5
9.6	136.7
10.8	144.5
12	152.4
25.4	152.4
38.1	152.4
50.8	158
63.5	158

Sawdust_temp_1433.dat file

c BYU Flat Flame Burner Temperature profile for Sawdust 1433K pyrolysis c z(mm) Tg (K)

0.00	300
1	1314
6.35	1401
12.70	1419
19.05	1429
25.40	1433
38.10	1430
50.80	1425
63.50	1418
76.20	1408
88.90	1400
101.60	1389
114.30	1376
127.00	1363
139.70	1352
152.40	1339
177.80	1311

Appendix K. Diameter Ratio for Pet Coke Chars

The diameter ratios of pet coke may prove useful for modeling purposes for both pyrolysis and gasification of pet coke since the particle diameter affects gasification rates, effective diffusivities, and fragmentation behavior (Hurt et al., 1988). The ratio of final pet coke diameter to initial pet coke diameter was calculated using mass release information of a particular experiment as well as density of the raw pet coke and pet coke char. A discussion follows concerning the calculations used to determine the particle diameter ratios of pet coke.

Assuming a spherical particle, the mass of pet coke char was divided by that of unreacted pet coke:

$$\frac{m_1}{m_0} = \frac{\rho_1}{\rho_0} \cdot \left(\frac{d_1}{d_0}\right)^3 \tag{K. 1}$$

where m, ρ , d refer to the mass, apparent density, and diameter of the particles, respectively. The subscripts '1' and '0' refer to the char and unreacted pet coke, respectively. The ratio of m_1 to m_0 was determined using mass release numbers as follows:

$$\frac{m_1}{m_0} = 1 - \frac{\% \ mass \ release}{100}$$
(K. 2)

where % *mass release* carries the same definition as in Section 4.6. The apparent density is the mass of the particle divided by the volume of the particle, and includes voids inherent in the material. The bulk density was much easier to measure, and is related to the apparent density through Equation (K. 3):

$$\rho = \frac{\rho_{bulk}}{1 - \varepsilon_b} \tag{K. 3}$$

where ρ_{bulk} and ε_b are defined as the bulk density and inter-particle void fraction or packing factor. The bulk density of pet coke and its char were measured using a technique similar to that used by Tsai and Scaroni (1987), where particles were added to a graduated cylinder of known volume. The bulk density was then calculated by dividing the mass of particles added by the volume of the bed. The graduated cylinder was also tapped repeatedly to ensure the minimum volume of the bed. The value for ε_b was taken as 0.45 (Tsai and Scaroni, 1987; Gale et al., 1995). Assuming that the packing factor for the raw pet coke and the pet coke char were the same, ($\rho_{1/}\rho_0$) in Equation (K. 1) is then equal to ($\rho_{bulk1/}\rho_{bulk0}$). The ratio of d_1 to d_0 was then calculated using a combination of Equations (K. 1) to (K. 3) as:

$$\frac{d_1}{d_0} = \left[\left(1 - \frac{\% \text{ mass release}}{100} \right) \cdot \frac{\rho_{bulk0}}{\rho_{bulk1}} \right]^{1/3}$$
(K. 4)

with an estimated error of 10-20% (Tsai and Scaroni, 1987).

Figures K.1 and K.2 show the ratio of final particle diameter to initial particle diameter from experiments at a wide variety of conditions. Particle swelling was not observed in any of the FFB and HPFFB pet coke experiments. The data shown in Figure K.1 came solely from pyrolysis experiments since CO_2 gasification was not observed at 1, 2, or 5 atm. Figure K.2 contains data at 10 and 15 atm where CO_2 gasification of pet coke was observed. Table B.5 in the appendix summarizes the data found in these two figures.

The tap technique (which is used to obtain $\rho_{bulk0}/\rho_{bulk1}$) was performed at least twice and often 3 times for each char collected from a single experiment. The average of these replicate tap densities was then used in Equation (K. 4). A table of all the tap densities of pet coke is included in Table B.6. The value for m/m_o in the d/d_o calculation came from mass release data in

Table B.1 preferring the mass release value calculated by mass balance over that obtained by ash tracer for reasons discussed in Section 6.2.2. If a good mass balance was unattainable from an experiment because of spilling or forgetting to weigh the feed plunger, d/d_o values were not calculated since it would have led to erroneous values.





Figure K.1. Ratio of final particle diameter to initial particle diameter of pyrolyzed pet coke chars collected at 1, 2.5, and 5 atm.



Figure K.2. Ratio of final particle diameter to initial particle diameter of partially gasified pet coke chars collected at 10 and 15 atm.

Appendix L. Density of Pet Coke Char

The apparent densities of pet coke chars from a variety of conditions were calculated using the measured bulk density by the tap technique and a packing factor as discussed in Appendix K. The apparent density is the mass of the particle divided by the volume of the particle, and includes voids inherent in the material. The apparent density of raw pet coke using the tap technique was 1.59 ± 0.02 g/cm³, which is very close to reported values in literature (1.64 and 1.66 g/cm³) for 2 different kinds of pet coke (Tyler and Smith, 1975). The literature values were measured by mercury displacement, whereas the density of the pet coke used at BYU was calculated by the tap technique which has an estimated error of 10-20% (Tsai and Scaroni, 1987). Based on the comparison of the pet coke densities from literature, the error of obtaining the pet coke density using the tap technique was lower than 4%.

The apparent densities of the pet coke chars appear in Figure L.1 and Figure L.2. The bulk densities of all the pet coke chars that were used to calculate the apparent densities are located in Table B.6. Density of the pet coke chars was higher than that of the raw pet coke in every case, except at the 5 atm 1702 K 44 ms condition. The calculated mass release percent of this particular condition was 0.3%, which means that this particular sample did not pyrolyze. The density of this char was within the error of the density of the raw pet coke, which was expected.

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Figure L.1. Apparent density of pet coke chars from the 1, 2.5, and 5 atm conditions.



Particle Residence Time (ms)

Figure L.2. Apparent density of pet coke chars from the 10 and 15 atm conditions. The circled data points did not experience gasification.

It is interesting that the density of the gasified particles increased (see Figure L.2) since this is contrary to what is predicted by the different heterogeneous char reaction regimes. For example, a decreasing particle density is assumed as long as the reaction is not controlled by film diffusion since the reactive gases are able to diffuse into the interior of the porous char particle before they are consumed (Smith et al., 1994). When the heterogeneous char reaction is controlled by film diffusion, a constant density is assumed since the reaction only occurs on the particle surface. Harris and Smith (1990) observed that that the particle density of pet coke decreased linearly during CO₂ gasification, which is consistent with the theory just described. Their experiments took place over the temperature range 920-1170 K in a fixed bed reactor at atmospheric pressure. In contrast, Hurt et al. (1988) found that the gasification reaction resulted in densification of a variety of carbon particles by gasification-induced atomic rearrangements. The chars of Hurt et al. were prepared by placing different kinds of carbon in a furnace at 1000 °C for 1 hour, and then evaluating their reactivity in a TGA over the temperature range 370-990 °C. Hurt et al. concludes that measuring particle density is a faulty test for determining the reaction regime of gasification since carbon particles became more dense during gasification. The increased densities of gasified pet coke chars in Figure L.2 may be caused partially by gasification-induced atomic rearrangements, but probably is also a result of atomic rearrangements that take place spontaneously at high temperatures in carbon structures (Hurt et al., 1988). Note that the circled data points in Figure L.2 did not experience gasification, based on their mass release numbers in Table B.1.

It is interesting to note that the density of the pet coke chars also increased in the pyrolyzed pet coke chars where gasification did not occur (see Figure L.1 and circled data points in Figure L.2). This is consistent with the findings of Kocaefe et al. (1995). They observed that

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increasing pyrolysis temperature caused the pet coke particles to become more dense over the temperature range from 500-1200 °C for experiments conducted in a TGA using a 150 °C/min heating rate. Kocaefe et al. also observed that increased residence time caused the pet coke chars to more dense until their density reached an asymptote. Wu et al. (2009) examined the x-ray diffraction (XRD) spectra of pyrolyzed pet coke chars that had been prepared in an atmospheric furnace at a heating rate of 6 °C/min at maximum temperatures ranging from 950-1400 °C. They observed that higher pyrolysis temperature resulted in a more ordered carbon crystalline structure. Sun and Shen (2004) also found that the carbon structure of pet coke became more ordered with an increase in temperature. Wu et al. also tracked the effect of pyrolysis pressure on carbon crystalline structure of pet coke chars that had been prepared at 650 °C at 1-30 atm in a pressurized furnace, and found the crystalline structure of the pet coke char was hardly affected by pressure. The results of other researchers are similar to those observed from pet coke experiments performed from 1 to 15 atm in the FFB and HPFFB. The density of the pet coke chars in Figure L.1 is likely the result of a more ordered carbon structure that occurs at high temperatures. Also, pyrolysis pressure appears to have almost no effect on pet coke particle density (see Figure L.1).

Appendix M. Tar Yields of Pet Coke

Tar yields of pet coke are included in Figure M.1 for experiments carried out from 1 to 15 atm. The tar yields represent the weight percent of daf pet coke fed that was collected on the water-cooled glass-fiber filters. Following an experiment, the filters were allowed to dry overnight before they were weighed. The tar yield is usually less than 1 wt%, and the average daf tar yield using every experimental point is 0.51 wt%. There are no definite trends of tar yields based on operating temperature or pressure. To the author's knowledge, no tar yields from pet coke pyrolysis or gasification experiments have been reported in the literature. The values used to make Figure M.1 are included in Table B.7 in the appendix.



Figure M.1. Tar yields of pet coke on a daf basis.

Appendix N. Elemental Analysis of Pet Coke

The ultimate analysis of the pet coke chars and a single pet coke tar are included in Table N.1. The values come from the analysis performed on BYU's Leco TruSpec Micro and are the average of at least 3 replicates of the same sample, except for the tar because there was only enough sample to perform the elemental analysis twice. Only a single tar sample was analyzed for composition since insufficient tar collected on the filters during typical experiments as to allow the scraping of tar from the filters. The particular condition at which the tar was collected was a preliminary condition, and thus the only information known about this condition was that it was collected from a fuel-rich condition with a peak temperature near 1500 K with a particle residence time near 25 ms at 1 atm.

Ultimate analyses from the BYU TruSpec Micro instrument compared well with that performed by Huffman Laboratories, Inc (see Table 4.3). From Table 4.3, it is seen that the BYU instrument slightly over predicts the percentages of C, H, and S when analyzing the composition of raw pet coke. This creates a slight problem because the percentage of oxygen is determined by difference, and is unattainable if the sum of C, H, N, S, and ash is 100 or greater. In the normalized cases, the ash percentage of the char was left alone while the percentages of C, H, N, and S were normalized so that C, H, N, S, and ash summed to 100. The ash percentage was not manipulated since it was measured separately during an ash test. To obtain an idea for the correction, the percentages of C, H, N, and S values from the analysis of raw pet coke from BYU's TruSpec Micro were 89.08%, 2.03%, 1.57%, and 8.02%, respectively before these values were normalized to give the values listed in Table 4.3. A 0% oxygen value in Table N.1 indicates that the elemental composition values of a particular char were normalized. This issue prevents the percentage of oxygen in the char from being obtained in about half of the pet coke char samples, thus explaining why oxygen is not included in any of the figures below.

Description	Particle Residence Time (ms)	%С	%H	%N	%S	%O by difference	Ash wt%
Tar 1atm ~1500K	~25	83.09	1.26	1.68	6.09	7.88	none
Char 1atm 1751K	33	90.78	0.42	1.24	7.15	0	0.42
Char 1atm 1751K	55	91.17	0.06	1.18	7.21	0	0.38
Char 1atm 1751K	98	91.09	0.15	1.16	7.17	0	0.43
Char 1atm 1929K	102	90.58	0	1.21	6.91	0.93	0.37
Char 2.5atm 1683K	76	86.68	0.97	1.52	7.55	2.86	0.43
Char 2.5atm 1683K	369	91.12	0.08	1.21	7.18	0	0.40
Char 5atm 1702K	75	88.98	1.23	1.48	7.88	0	0.43
Char 5atm 1702K	141	88.60	1.14	1.50	6.27	2.05	0.45
Char 5atm 1702K	467	89.26	0.40	1.22	8.62	0.06	0.45
Char 5atm 1867K	644	87.50	0	1.11	7.10	3.91	0.39
Char 5atm 2110K	753	91.34	0	1.00	7.24	0	0.43
Char 10atm 1722K	81	87.85	1.41	1.49	6.92	1.91	0.42
Char 10atm 1722K	150	89.49	0.69	1.31	8.08	0	0.43
Char 10atm 1967K	65	88.58	0.55	1.19	7.86	1.24	0.59
Char 10atm 1967K	373	88.13	0.09	1.13	7.86	2.37	0.42
Char 10atm 1967K	663	89.06	0.89	1.38	8.26	0	0.42
Char 10atm 1967K	1061	90.59	0.09	1.12	7.74	0	0.47
Char 15atm 1402K	337	87.13	2.03	1.62	8.01	0.81	0.41
Char 15atm 1681K	151	89.45	0.62	1.38	8.14	0	0.41
Char 15atm 1681K	318	87.49	0.81	1.31	7.99	2.03	0.38
Char 15atm 1681K	914	87.26	0.69	1.28	8.06	2.29	0.42
Char 15atm 1918K	335	90.76	0.15	1.09	7.56	0	0.45
Char 15atm 1918K	577	89.32	0.55	1.11	7.86	0.62	0.54
Char 15atm 1918K	994	90.04	0	1.14	7.80	0.50	0.51

Table N.1. Ultimate analysis of pet coke chars and a single tar fromFFB and HPFFB experiments (dry basis)

If BYU's TruSpec Micro behaves similarly for pet coke char as it does for raw pet coke, the composition of C, H, N, and S could be slightly off, but probably not enough for concern. Figures N.1 to N.3 depict the initial amount of H, N, and S that end up in the pet coke char. The values in the aforementioned figures were computed using elemental compositions of both the char and raw pet coke as well as mass release values from that same condition (see Table B.1).



Figure N.1. Fraction of the initial amount of H that remained in the pet coke char for experiments carried out at 1 to 15 atm. The chars in the left figure were fully pyrolyzed, but did not undergo gasification. The chars in the right figure experienced gasification, except where noted by circled data points.

Separate figures were made for the pet coke char collected at 1, 2.5, and 5 atm because these fully pyrolyzed chars did not experience gasification, while the chars collected at 10 and 15 atm did gasify, except where denoted by circled data points in the figures. Care should be taken when comparing the 1 atm experimental chars with the chars collected at higher pressures since these chars were collected on different facilities.

It appears that temperature has the biggest effect on the fraction of H, N, and S that remains with the char. Char collected from a higher peak temperature loses H, N, and S more quickly when compared to chars with similar residence times. Pressure does not appear to be a large influential factor in the composition of H, N, and S in the pet coke chars. The chars collected at 1 atm lost H, N, and S more quickly than chars from higher pressures, but this also may be attributed to temperature differences since the temperature drops off more quickly in the HPFFB than in the atmospheric FFB. A comparison of the elemental composition of pet coke char was not possible due to the lack of this data in the literature.



Figure N.2. Fraction of the initial amount of N that remained in the pet coke char for experiments carried out at 1 to 15 atm. The chars in the left figure were fully pyrolyzed, but did not undergo gasification. The chars in the right figure experienced gasification, except where noted by circled data points.



Figure N.3. Fraction of the initial amount of S that remained in the pet coke char for experiments carried out at 1 to 15 atm. The chars in the left figure were fully pyrolyzed, but did not undergo gasification. The chars in the right figure experienced gasification, except where noted by circled data points.