

## **ABSTRACT**

LONG, JOHN MICHAEL. Development of a Charcoal Slurry for Compression Ignition Internal Combustion Engines. (Under the direction of Michael D. Boyette).

Alternative fuels research has been at the forefront of current energy research in recent years. Many different research pathways have developed to produce alternative fuels. This research focuses on the thermal pathway which uses heat to break down biomass into useable compounds and/or energy. Charcoal is one of the useable compounds produced and is currently used throughout the world as a solid fuel for heating and cooking. Charcoal is an alternative fuel for the fossil fuel coal. Coal dust and coal slurries have been studied as alternative fuels for compression ignition internal combustion (IC) engines or diesel engines. This research investigated the use of charcoal in the form of a liquid slurry as a renewable alternative to coal slurries and diesel fuel in compression ignition IC engines. Charcoal was successfully micronized using a multi-step milling process. Different charcoal sources were used and analyzed to develop charcoal slurries that were successfully tested in a diesel engine platform. Virgin charcoal was produced under controlled conditions and analyzed to calculate energy density for comparison of charcoal slurries with other liquid fuels. The addition of charcoal particles to biodiesel increases the overall energy density per unit volume. Displacing less than 20% of the

volume of 100% biodiesel with charcoal creates a slurry with an energy density equal to or greater than diesel fuel.

© Copyright 2014 John Michael Long

All Rights Reserved

Development of a Charcoal Slurry for Compression Ignition Internal  
Combustion Engines

by  
John Michael Long

A dissertation submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

Biological and Agricultural Engineering

Raleigh, North Carolina

2014

APPROVED BY:

---

Michael D. Boyette  
Committee Chair

---

Larry F. Stikeleather

---

Grant H. Ellington

---

Tiegang Fang

## **DEDICATION**

I'd like to dedicate this dissertation to my family. Thank you for your love and support throughout the years.

## **BIOGRAPHY**

John Michael Long was born in High Point, NC on January 25, 1983 to Michael and Patricia Long. He is the oldest of two children. John grew up in the community of Midway in Davidson County, North Carolina on a family farm raising tobacco and beef cattle. He graduated North Davidson Senior High School in May of 2001 where he continued his education at North Carolina State University that fall. He graduated with a Bachelor's of Science in Biological Engineering with agricultural and environmental concentrations in 2005. After graduation, he became actively involved with tobacco research during which he completed his Masters of Science in Biological Engineering in 2008. John continued his education at North Carolina State University upon becoming a doctoral candidate in the fall of 2010 focused on renewable energy fuels for diesel engines.

## **ACKNOWLEDGMENTS**

I would like to take the opportunity to thank everyone that has helped me achieve this life-long goal.

First and foremost I would like to take the opportunity to acknowledge my Lord and Savior for giving me the strength and sometimes courage to accomplish my dreams.

I would like to thank Dr. Michael Boyette, my committee chair, for his years of encouragement and support. Thank you for believing in me and pushing me to be my best.

## TABLE OF CONTENTS

<b>LIST OF TABLES</b> .....	vii
<b>LIST OF FIGURES</b> .....	viii
<b>1 INTRODUCTION</b> .....	1
1.1 INTERNAL COMBUSTION ENGINES .....	2
1.2 BIOMASS DERIVED FUELS .....	3
1.3 RESEARCH QUESTIONS .....	8
<b>2 LITERATURE REVIEW</b> .....	10
2.1 COAL-WATER SLURRIES .....	11
2.1.1 General Electric .....	11
2.1.2 Arthur D. Little/Cooper-Bessemer .....	15
2.1.3 General Motors/Southwest Research Institute .....	16
2.2 CHARCOAL SLURRIES .....	17
<b>3 MATERIALS AND METHODS</b> .....	22
3.1 WASTE WOOD CHARCOAL .....	22
3.1.1 Size Reduction .....	23
3.1.2 Particle Analysis .....	27
3.1.3 Slurry Analysis .....	28
3.1.3.1 Viscosity .....	29
3.1.3.2 Diesel Engine Testing .....	30
3.2 VIRGIN WOOD CHARCOAL .....	32
3.2.1 Biomass Preparation .....	32
3.2.2 Carbonization .....	38
3.2.3 Size Reduction .....	42
3.2.4 Physical Property Analysis .....	44
3.2.4.1 Moisture .....	44
3.2.4.2 Ash .....	46
3.2.4.3 Density .....	47
3.2.4.4 Energy Content .....	49
<b>4 RESULTS AND DISCUSSION</b> .....	51
4.1 WASTE WOOD CHARCOAL .....	51
4.1.1 Size Reduction .....	51
4.1.2 Particle Analysis .....	55
4.1.3 Slurry Analysis .....	68
4.1.3.1 Viscosity .....	70
4.1.3.2 Diesel Engine Testing .....	72
4.2 VIRGIN WOOD CHARCOAL .....	74
4.2.1 Carbonization .....	74
4.2.2 Size Reduction .....	79
4.2.3 Physical Property Analysis .....	80
4.2.3.1 Moisture .....	81

4.2.3.2 Ash.....	83
4.2.3.3 Density.....	85
4.2.3.4 Energy Content.....	87
<b>5 CONCLUSIONS</b> .....	90
<b>REFERENCES</b> .....	97

## LIST OF TABLES

Table 4.1	Weight distribution of sieved particles after processing through the Wiley mill.....	80
Table 5.1	Theoretical energy values (Higher Heating Value) for fuels used in this research.....	95

## LIST OF FIGURES

Figure 1.1	Major research branches for the thermal processing of biomass .....	6
Figure 3.1	Inside the Wiley mill used for initial charcoal size reduction .....	24
Figure 3.2	Burr mill setup for further particle size reduction .....	25
Figure 3.3	Ball mill setup for micronizing charcoal.....	26
Figure 3.4	Freshly cut yellow poplar logs.....	33
Figure 3.5	Using a drawknife to begin the bark removal process.....	34
Figure 3.6	Separating the bark.....	35
Figure 3.7	Yellow poplar logs with bark removed .....	36
Figure 3.8	Yellow poplar wood prepared for drying .....	37
Figure 3.9	Yellow poplar wood packed in the chamber.....	39
Figure 3.10	Chamber installed in high temperature furnace.....	40
Figure 3.11	Exhaust pipes installed for gases exiting the chamber .....	41
Figure 4.1	Ground charcoal particles after one pass through the burr mill .....	53
Figure 4.2	Charcoal after processing through the ball mill.....	55
Figure 4.3	Charcoal particle size distribution histogram for run 1 .....	56
Figure 4.4	Charcoal particle size distribution histogram for run 2 .....	58
Figure 4.5	Charcoal particle size distribution histogram for run 3 .....	59
Figure 4.6	Charcoal particle size distribution histogram for run 4 .....	60
Figure 4.7	Charcoal particle size distribution histogram for run 5 .....	61
Figure 4.8	400X image of larger ground charcoal particle structure.....	62
Figure 4.9	400X image of ground charcoal with ash .....	64
Figure 4.10	Energy dispersive X-ray spectrometry of ground charcoal sample .....	65
Figure 4.11	Ground charcoal particles mixed with a biodiesel blend at 25%(v/v) .....	69
Figure 4.12	Viscosity measurements of 25%(v/v) charcoal-biodiesel slurry .....	71
Figure 4.13	Furnace temperature data during carbonization .....	75
Figure 4.14	Flammable gases exiting the chamber during carbonization .....	77
Figure 4.15	Comparison of dried yellow poplar and the charcoal produced.....	78
Figure 4.16	Wet-basis moisture percentage of ground yellow poplar charcoal .....	82
Figure 4.17	Ash percentage by mass of ground yellow poplar charcoal ...	84
Figure 4.18	Absolute density of ground charcoal.....	86
Figure 4.19	Caloric values for yellow poplar charcoal samples.....	88

## **1 INTRODUCTION**

Development of alternative energy sources has been the focus of research in the scientific community for a number of years. Novel sources of energy or techniques to harvest energy in nature such as wind, solar, geothermal, and hydropower systems are continually being developed by researchers. The ultimate goal is the development of an integrated energy system that provides clean, renewable energy for a variety of applications.

Technology generated through the research of novel energy systems has been limited in wide application due to many socioeconomic factors. Further, the economics of new technology can be cost prohibitive when employed to convert existing systems. Novel energy systems typically use little of the existing infrastructure which requires their application to require significant capital investments often with long-term returns on that investment. The question of economic viability fuels the inherent nature of society to resist rapid large-scale change in the status quo.

Overcoming these socioeconomic factors requires gradual integration of novel energy systems into existing infrastructure. Biomass derived fuels provide the necessary first step towards an integrated renewable energy system. The development of renewable fuels such as those derived from biomass can directly replace or reduce fossil fuel consumption. Fortunately, these biomass derived fuels can be adapted to current infrastructure

requirements for storage, handling and usage. Since few changes to the current infrastructure are necessary, the initial capital investment required to utilize biomass derived fuels is minimal and money can be gradually invested in novel energy systems and technology. Biofuels are able to reduce or replace the fossil fuels used in the current energy infrastructure allowing gradual investment in the capital necessary to implement a novel energy system. In this way, biofuels can serve as the necessary bridge between current energy systems and future energy systems independent of fossil fuels.

## 1.1 INTERNAL COMBUSTION ENGINES

The availability of inexpensive fossil fuels during the 20<sup>th</sup> century spurred the research and development of infrastructure and industries centered on their use as the sole energy source. The research and development of the internal combustion engine is one example. The internal combustion (IC) engine is used as the prime source of mechanical power for vehicles, equipment, generators, and many other applications used throughout the world. Extensive time and money has been invested in the development of various types of internal combustion engines operating primarily on liquid fossil fuels. An important subset of IC engines,

compression-ignition IC engines, commonly referred to as diesel engines, were the main focus of the research described in this dissertation.

The engineer, Rudolph Diesel, is credited with developing the first high pressure, self-ignition IC engine with his 1892 German patent (Diesel 1892). The patent outlined the use of liquid, gaseous, and solid fuels in his compression-ignition IC engine. In addition to liquid fuel oils, Diesel tested dry coal dust in his engine prototype to support his patent's claim that any type of combustible material could be used to fuel his IC engine (Soehngen 1976). The flexibility of the diesel engine to accept various fuel types makes it an excellent platform for alternative fuel research.

## 1.2 BIOMASS DERIVED FUELS

Biomass encompasses biological materials that are derived from living or recently living organisms. In most cases, biomass refers to biological materials harvested from plants; therefore, the vast majority of biomass derived fuels or biofuels are produced from biomass harvested from plant materials. Biofuels can be generated through a number of different pathways depending on feedstocks and intended products.

The first pathway utilized to generate biofuels from biomass is the biochemical pathway. Biomass is converted to usable fuels or fuel feedstocks using known chemical pathways found within living organisms.

In many cases, microorganisms are used to convert biomass into compounds that can be used directly as a fuel source. Two of the most prevalent bioconversion areas utilizing the biochemical pathway are fermentation (fuel alcohol) and anaerobic digestion (methane).

Fermentation allows the conversion of simple sugars into alcohol. The alcohol produced can then be used directly as a liquid fuel. Biomass must be broken down into these simple sugars before the microorganisms can produce the alcohol fuel. Breaking down plant starches into glucose is a simple process, but the conversion of cellulose into useable sugars requires an involved sequence of steps. Because of the prevalence of cellulose, much of the research in the last 20 years has been focused on simplifying the conversion of cellulosic biomass into alcohol fuels (Lin and Tanka 2006).

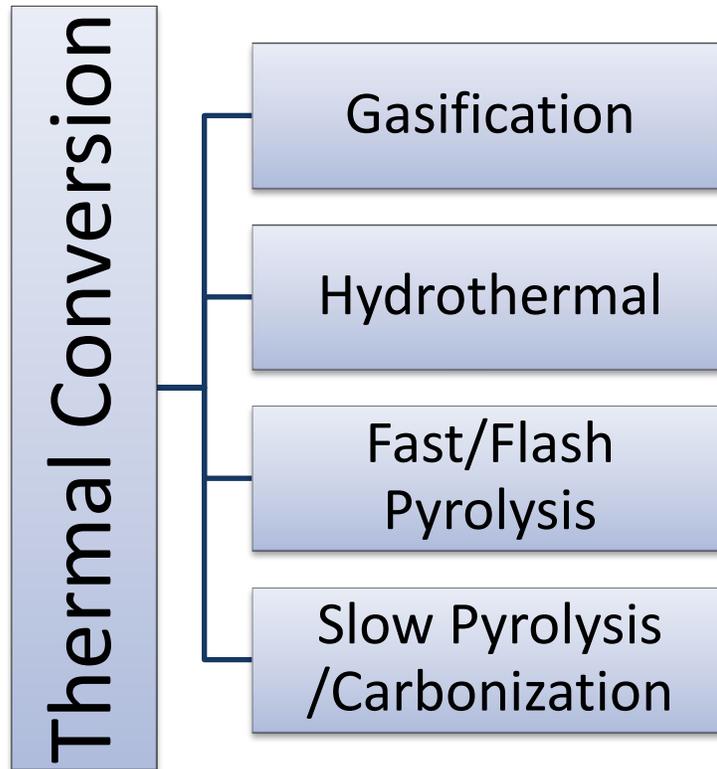
Anaerobic digestion utilizes microorganisms to break down organic materials such as biomass in the absence of oxygen. The microorganisms consume the biomass and produce a biogas mixture that contains flammable methane gas. Much of the current research is focused on the use of waste products such as animal manures as energy sources for digesters, but any type of biomass could be used given the correct combination of microorganisms and conditions.

The second major pathway for converting biomass into useable biofuels is the chemical pathway. Biomass is converted to usable fuels

through the application of various chemical processes. The major difference between this pathway and the biochemical pathway is that these chemical processes occur without the aid of microorganisms. The transesterification of oils derived from plant materials into methyl and ethyl esters or biodiesel is one example.

The third major pathway for converting biomass into usable biofuels is the thermal pathway where heat is used to break down the biomass. The simplest form of thermal conversion is the direct combustion of the biomass to generate heat and is man's oldest known method for extracting energy from a fuel source. This method of extracting energy from biomass was used and perfected centuries before the discovery and use of fossil fuels for cooking and heating homes.

The thermal conversion of biomass can also generate usable liquid, gaseous, and solid fuels. Figure 1.1 presents the four different research branches pursued within the thermal pathway to produce useable biofuels.



**Figure 1.1** Major research branches for the thermal processing of biomass

Gasification is the first research branch pursued to generate usable biofuels from biomass. During gasification, biomass is subjected to temperatures generally in excess of 800°C with little to no oxygen present. The biomass is completely altered to produce a flammable syngas as the primary product. This syngas is composed of carbon dioxide, carbon monoxide, and some hydrogen gases. A small amount of organic tar can be present depending on the feedstock, gasification method and conditions.

Hydrothermal processing is another method that may be used to generate a usable biofuel from biomass. Biomass is subjected to

temperatures ranging from 300°C to 350°C in a very high pressure steam environment (approximately 30-50MPa). A partially deoxygenated liquid oil is produced as the main product of this process. Additionally, a small amount of flammable gases and charcoal are produced as a byproduct.

Fast or flash pyrolysis is still another research branch commonly pursued in current biofuel research. Biomass is quickly heated (>1000°C/sec) with no oxygen to temperatures ranging from 450°C to 550°C. A highly oxygenated pyrolysis oil is generated as the main product of the process with a small amount of flammable gases and charcoal produced as byproducts.

Slow pyrolysis or carbonization is another research branch pursued in current biofuel research. Biomass is heated slowly with little oxygen to a temperature ranging from 350°C to 800°C. The major product of this process is a low oxygen charcoal solid. Some syngas and pyrolysis oils are produced as byproducts of this process.

The majority of research conducted on the thermal processing of biomass focuses on the first three research branches. The main reason for this focus is because the first three research branches result in a product that exists in either the gas or liquid phase at room temperature. Most of the current fossil fuel infrastructure is based around the fuel being in either a gaseous or liquid phase. Due to the lack of current research on the topic,

this research focuses on the production of a liquid fuel from an admixture of finely reduced charcoal produced by carbonization and liquid petroleum as a carrier. The ultimate results would be to offset some portion of fossil fuel with renewable fuel.

Since charcoal is a solid fuel, this research was conducted to adapt the charcoal fuel to the current infrastructure by introducing it into a liquid fuel. The most direct method for liquefying any solid material is by producing a slurry. The addition of charcoal particles to a liquid renewable fuel such as biodiesel produces a potentially useful liquid fuel slurry.

### 1.3 RESEARCH QUESTIONS

The goal of this research was to develop and analyze charcoal as part of a liquid fuel slurry and answer the following questions:

- Can charcoal be effectively milled to produce micronized particles (<1mm diameter) that might remain suspended in biodiesel?
- How does the size of the charcoal particle affect the shape, structure and physical properties?
- What is the ash content of a typical wood charcoal used in a slurry?
- How does the addition of charcoal particles affect the liquid fuel's viscosity and other physical and chemical properties?

- How does the addition of charcoal particles affect the liquid fuel's energy density, physical, chemical and economic viability?

Laboratory experiments were developed and performed to address these questions and are reported in the following sections.

## **2 LITERATURE REVIEW**

The use of a solid fuel in a diesel engine is not a new idea. Dr. Rudolph Diesel, the inventor of the diesel engine first envisioned his engine to be a multi-fuel engine (Diesel, 1892). Researchers such as Pawlikowski explored the use of solid fuels such as powdered coal in diesel engines during the early 20<sup>th</sup> century (McMillian, 1989). During World War II, diesel fuel oil supplies were strained which created demand for research on alternate fuels. Germany, with their abundant natural coal resources, pursued research that resulted in several low speed diesel engines successfully running on coal dust.

During the 1960's in the US, several research groups continued this work to solve some of the issues plaguing the use of coal dust in diesel engines (Ryan, 1994). Despite much work in the early 20<sup>th</sup> century on solid fuel combustion, the dry coal dust particles have many issues with carburation and injection in to the cylinders (Ryan, 1994). The use of air as the carrier of the particles also presented safety concerns due to the mixture's extreme flammability at the correct proportions. Unlike pre-mixed liquid-fueled engines, the oxidizer was used to transport the fuel from storage to the combustion chamber. The early premixing of the fuel and air presented a safety concern and resulted in many premature detonations of the fuel/air mixture before entering the combustion chamber of the engine.

## 2.1 COAL-WATER SLURRIES

Research conducted within the last thirty years has sought to alleviate carburation issues by removing the coal from the air intake stream and injecting it directly into the cylinder. The most prevalent method has been to mix the coal particles with water to produce a coal-water slurry (CWS). The bulk of this research was conducted in the 1980's and continued into the early 1990's. The US Department of Energy (DOE) funded several research grants centered on the development of liquid fuel slurries of coal particles (Caton and Hsu, 1994). The ultimate goal of this research was the development of a coal-water slurry that could replace No. 2 diesel fuel oil used in compression-ignition IC engines. Many prominent research institutions and universities worked simultaneously on different components of this research initiative as outlined in the following sections.

### 2.1.1 General Electric

General Electric Transportation Systems (GE-TS) invested a great deal of time and resources in the development of coal-water slurry fueled diesel engines (Caton and Hsu, 1994). During preliminary testing of coal-water slurries, GE-TS outlined five issues that had to be overcome for a successful coal-water slurry system. These issues, in order of significance, are as follows:

1. Formulation of acceptable engine-grade coal-based fuels
2. Successful injection
3. Successful ignition/combustion
4. Minimizing engine/injector wear
5. Minimizing engine emissions

After years of research, GE-TS determined that an optimum coal-water slurry was composed of (percent by mass) 48 percent coal, 2 percent additives, and the balance water (Caton, 1994). This formulation was found to be optimal when the coal used had less than one percent ash content and was ground to an average particle size of three microns. GE-TS found that this formulation would auto-ignite with proper in-cylinder temperatures and pressures, but they suggested a three to five percent by mass pilot injection of #2 diesel fuel oil to insure consistent ignition characteristics (Caton, 1994).

Initial injector testing determined that the initial jet velocity measured was 15% greater for coal-water slurries than diesel fuel due to differences in physical properties. The higher jet velocity of the CWS caused the fuel stream to impinge upon the piston crown and walls before ignition. Hsu et al. determined that impingement was unavoidable and injector hole number and shape had little effect on combustion characteristics (1992). Ignition delay was determined to be highly dependent on secondary atomization of

the fuel from in-cylinder surfaces which increased ignition delay up to five times that of diesel fuel (Caton, 1994). At full load conditions, the piston crown temperatures were found to be high enough to cause immediate vaporization of the slurry and less dependence on secondary atomization. At partial load conditions, lower in-cylinder temperatures resulted in ignition delay due to fuel stream impingement. Pilot injections of diesel fuel were used to decrease ignition delay under partial load conditions. These diesel fuel pilot injections were used to increase in-cylinder temperatures before the main CWS injection event.

Most of the research conducted by GE-TS utilized jerk pump type, positive displacement injector systems, but a few of their tests used electronically controlled accumulator injector systems. These higher pressure systems (85 MPa) were shown to have increased atomization and improved combustion (Caton, 1994). The highest combustion efficiency or carbon burn out achieved was 99.5% at full load conditions (Hsu et al. 1990 and 1991). Combustion characteristics were affected more by injection parameters than coal-water slurry variations in properties and compositions. Hsu determined that combustion characteristics were a function of inlet air temperature, inlet air pressure, amount of pilot fuel injected, and the pressure of the coal-water slurry injection (1988). It was

concluded that average in-cylinder gas temperatures were above 890°K for successful combustion to occur (Hsu and Flynn, 1989).

Wear was a major issue for any of the engine components that came in contact with the coal-water slurry. The accelerated wear was attributed to the abrasiveness of the coal particles and the ash produced during combustion. Steel and cast iron components commonly used by internal combustion engine makers at the time of this research were highly susceptible to wear. GE-TS determined that engines fueled by coal-water slurries had component wear, such as rings and cylinder liners, exceeding acceptable tolerances in a matter of 2 to 20 times faster than similar engines fueled by #2 diesel fuel alone (Caton, 1994). GE-TS experimented with various alloys and coatings on components experiencing excessive wear to increase life. As a result of this research, GE-TS determined that the use of novel materials and coatings, in combination with a low ash fuel, would decrease wear enough to reduce the time between engine overhauls to acceptable levels.

Engine emissions were measured throughout the course of the GE-TS program. Initial measurements determined that carbon monoxide (CO) and nitrogen oxide emissions (NO<sub>x</sub>) were 50% lower for engines running on coal-water slurry versus diesel fuel. Even after using cleaner “engine grade” coal, sulfur present in the coal created issues with sulfur dioxide emissions.

Many different catalysts and processes were used to reduce emissions. Cyclones were used to remove particles in the exhaust stream greater than five microns. Excess hydrocarbons and carbon monoxide were reduced by passing the exhaust stream through granular beds of copper oxide. Injection of ammonia into the exhaust stream along with a barrier filter with sorbent, removed greater than 85% of the NO<sub>x</sub> and 90% of the sulfur dioxide produced (Caton, 1994). The emission reduction equipment was tested during the full scale locomotive test conducted on a GE-TS test track.

#### 2.1.2 Arthur D. Little/Cooper-Bessemer

Arthur D. Little, Inc. and Cooper-Bessemer Corporation worked together as part of the DOE research initiative to develop stationary coal-water slurry engines for modular power generation (10 to 100MW). Arthur D. Little managed the research project while Cooper-Bessemer was responsible for engine design and testing. A significant portion of the research was dedicated to the adaptation of currently available diesel fuel injection technology to coal-water slurry fuels. Little/Cooper refined a high-pressure injection system for the Cooper-Bessemer industrial low and medium speed engines. The majority of the wear experienced during their testing was found to be a result of coal particle erosion and cavitation of the fuel mixture. Ignition issues were resolved using a novel natural gas jet cell

as opposed to a pilot injection of #2 diesel fuel used by other research groups (Rao, 1989). The natural gas jet cell was a separate chamber in the cylinder head that connected to the combustion chamber by a narrow passage. During the compression stroke, air was forced into the jet cell chamber through this passage mixing with the natural gas that entered the chamber at the beginning of the stroke. The compressed air/gas mixture was ignited with a spark plug and the hot combustion gases were forced into the main combustion chamber as a jet. This jet provided the heat needed to ignite the CWS main injection event. The natural gas jet cell was able to successfully ignite the CWS with an amount of natural gas equivalent to three percent of the total fuel energy content injected each cycle (Rao, 1989).

### 2.1.3 General Motors/Southwest Research Institute

General Motors Corporation (GM) partnered with the Southwest Research Institute (SwRI) to investigate the use of a coal-water slurry in medium speed diesels from their Electro-Motive Division in 1982. This research paralleled other work at the time to develop a coal-water slurry fueled locomotive engine and found similar issues when converting from diesel fuel to a coal-water slurry, but most of their work concluded that the Electro-Motive engines would require much cleaner coals to be a feasible

fuel (Ryan, 1994). GM/SwRI also investigated the use of coal-water slurries in high speed diesels utilizing the Detroit Diesel 71 series of engines. The increased temperature of these two-cycle engines was shown to have an advantage when burning coal-water slurries (Urban, 1988). Previous research determined that a theoretical limit of 1000 rpm could not be exceeded due to the residence time of the coal-water slurry fuel, but GM/SwRI was able to successfully run a two-cycle diesel engine on coal-water slurry at 1900 rpm. GM/SwRI determined that by increasing intake temperatures and in-cylinder turbulence, higher engine speeds could be reached than were previously calculated (Ryan, 1994).

## 2.2 CHARCOAL SLURRIES

Building upon the work conducted on coal slurries, N'kpomin et al. investigated the use of charcoal as part of a ternary mixture for fueling diesel engines (1995). A charcoal-oil-water slurry was produced using (percent mass) 40% charcoal, 10% fuel oil, 49.2% water, and 0.8% surfactant. The charcoal-oil-water slurry had a dynamic viscosity of 2000 cP at a shear rate of  $100 \text{ s}^{-1}$ . Charcoal particles initially used in the slurry had an average particle size of four microns. These ultrafine charcoal particles were collected using a filter to capture the dust escaping a hammer mill loaded with ground charcoal. N'kpomin et al. discovered that once the

average charcoal particle size was four microns or less, the viscosity of the slurry was much higher for a particular suspended solids loading. This increase in viscosity was determined to be a result of interparticle forces trapping the liquid phase within charcoal structures. These particle structures are formed as a result of the increased effect surface forces have on the ultrafine charcoal particles (N'kpomin et al. 1995).

Ellem and Mulligan reviewed the possibilities of a liquid fuel composed of micronized biochar slurry (2011). The process began with the slow pyrolysis of a biomass to produce a biochar or charcoal. The biochar could then be micronized and washed to remove soluble ash in a variety of processes. Ellem and Mulligan suggested that micronizing and washing was an established process for coal water fuels and could be applied to biochar (2011). Micronization of biochar is less energy intensive than coal due to the structural differences. Lignocellulosic biomass consists of cell walls that are less than two microns thick, resulting in a biochar that consists of a porous structure composed of many small void spaces separated by thin walls rather than a solid structure. Coal structure ranges from that of a sedimentary rock (bituminous) to a metamorphic rock (anthracite). This structural difference means that biochar is much more brittle than coal and would require less energy input to micronize.

Ash most commonly found in biomass consists of oxides: silicon ( $\text{SiO}_2$ ), aluminum ( $\text{Al}_2\text{O}_3$ ), iron ( $\text{Fe}_2\text{O}_3$ ), calcium ( $\text{CaO}$ ), magnesium ( $\text{MgO}$ ), sodium ( $\text{NaO}_2$ ), potassium ( $\text{K}_2\text{O}$ ) and phosphorus ( $\text{P}_2\text{O}_5$ ) (Ellem and Mulligan 2011). The percentage of each of these compounds varies significantly among different sources of biomass. For example, grasses and crop residues tend to have higher proportions of silicates than biomass derived from a woody plant. Ellem and Mulligan noted that during the formation of the biochar by slow pyrolysis, the ash component of the biomass would form discrete structures on the surface of the biochar (2011). These concentrated formations of ash suggest that the use of mechanical separation and leeching would be effective in removing much of the ash present in the biochar.

Charcoal slurries formed from biochar will need to vary in composition based on the type of diesel engine fueled by the slurry. Due to resonance time within the combustion chamber and engine tolerances, high speed diesels require slurries with particle sizes less than two microns, medium speed diesels will tolerate particle sizes up to ten microns, and low speed diesels can tolerate particle sizes up to thirty microns. Ellem and Mulligan also noted that a multimodal distribution of charcoal particle sizes produced higher suspended solids loadings at the same viscosity as a unimodal distribution of charcoal particle sizes (2011).

Soloiu et al. analyzed the combustion of a charcoal slurry and its impact on injection system performance (2011). The charcoal was produced from slow pyrolysis of cedar wood chips. The charcoal had an ash content of 1.77% by mass and had a calorific value of 29,209 kJ/kg. Charcoal particles were milled to an average particle size of 10.33 microns. The slurry consisted of (percent mass) 25% charcoal, 72.2% diesel fuel, and 2.8% water. A single cylinder diesel engine was instrumented to compare in-cylinder conditions between the charcoal slurry and diesel fuel. Maximum combustion pressure was found to be comparable to diesel fuel, but ignition delay at full load was 0.4 ms slower than diesel fuel. Heat release was 35 joules per crank angle degree more than diesel fuel and the maximum combustion temperature was 30°K higher than diesel fuel. The increased temperatures translated to higher exhaust temperatures by 40-50°K. The smoke Bosch number was lower for the charcoal slurry at any load and Soloiu et al. theorized that this was due to the presence of oxygen in the fuel (2011). NO<sub>x</sub> emissions were higher for the charcoal slurry, but could be improved by optimizing injection timing. Changes in injection timing affected NO<sub>x</sub> emissions and soot formation in a manner different from diesel fuel. Increases in injection timing did not sharply increase soot formation, but did decrease NO<sub>x</sub> formation as expected (Soloiu et al. 2011).

Soloiu et al. experienced several issues with the injection system while operating on charcoal slurry (2011). The stock injection system initially had sticking issues due to deposits forming on the injector seat and needle. These issues were solved by reducing the particle size of the charcoal and modifying the injector design. The new design incorporated an auxiliary high pressure lubricating oil system that prevented the charcoal particles from entering the space between the needle's stem and holder. Injector wear was the other issue while operating the engine on charcoal slurry. After a 50 hour test run, the injector needle and seat exhibited four to eight times more wear than a similar run length on diesel fuel (Soloiu et al. 2011).

### **3 MATERIALS AND METHODS**

The research methodology developed during this investigation was based upon the production of a charcoal slurry composed of micronized charcoal particles and a biodiesel B20 fuel blend. Charcoal used in this process was derived from two different sources. The first source was a separate research project designed to produce charcoal from commercially available wood chips. The second source of charcoal was produced from woody biomass under controlled conditions, micronized and then analyzed further.

#### **3.1 WASTE WOOD CHARCOAL**

The initial phase of this research concentrated on the production of a charcoal slurry using readily available charcoal. The charcoal used for this portion of the research was produced using wood chips as the feedstock. The wood chips were a waste product of the logging industry. Limbs and other unmarketable portions are chipped and hauled offsite after harvesting timber. Charcoal was produced in conjunction with a research study focused on utilizing a Top-lit updraft (TLUD) gasifier as a simple and convenient means of generating biochar. By using readily available charcoal, the initial research could be focused more on developing methods

to produce micron-sized charcoal particles and slurries containing those particles.

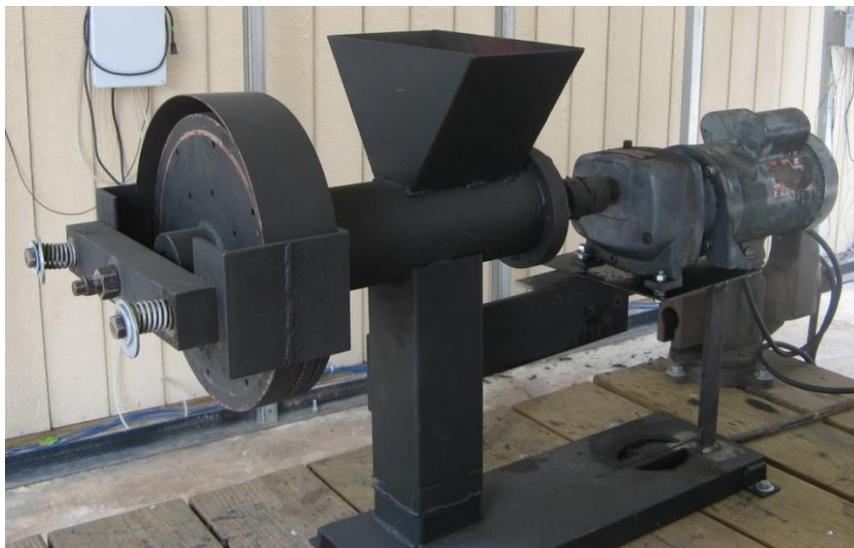
### 3.1.1 Size Reduction

The first step in the production of a charcoal slurry was to produce a micronized charcoal particle. Micronized charcoal particles were achieved through a multi-step milling sequence. The charcoal produced was initially very similar in size and shape to the parent biomass before the carbonization process. The larger pieces of charcoal were broken by hand into smaller pieces and placed in the hopper of a Wiley mill (Model 4, Thomas Scientific, Swedesboro, NJ) (Figure 3.1).



**Figure 3.1** Inside the Wiley mill used for initial charcoal size reduction

A 1 mm screen was installed in the bottom of the Wiley mill to produce fine charcoal particles. All of the charcoal chips were processed through the Wiley mill and stored in sealable plastic bags. The ground charcoal was then sieved using a no. 100 sieve (149 micron). Charcoal particles that passed through the sieve were placed back in sealable plastic bags to be used in the next step of the process. The larger particles that did not pass through the sieve were ground further using the custom-made burr mill pictured in figure 3.2.



**Figure 3.2** Burr mill setup for further particle size reduction

The burr mill featured adjustable burr plates that set the desired grind. Charcoal particles were processed through the burr mill until they were able to pass through the no. 100 sieve. All of the ground charcoal that was able to pass through a no. 100 sieve from either the Wiley mill or burr mill, was then processed using a custom ball mill (Figure 3.3).



**Figure 3.3** Ball mill setup for micronizing charcoal

The lab scale ball mill was constructed using a 3 liter polypropylene bottle (Nalgene Round Wide-Mouth Mason Jar, Thermo Fisher Scientific Inc., Waltham, MA) as the tumbling cylinder and two electric conveyor rollers custom mounted to an elevated frame. The bottle was loaded half-full of the ground charcoal that passed through the no. 100 sieve and a dozen  $\frac{1}{2}$ " steel ball bearings. After sealing the lid, the bottle was placed on its side on the rollers. The rollers were powered and the ball bearings inside the bottle tumbled and rolled on the charcoal particles. The ball mill jar rotated at a constant speed of 64 RPM for varying time durations ranging from 24 hours to 2 weeks.

At the end of each run, the ground charcoal was removed, the ball bearings were separated and the ground charcoal was sieved using a no. 325 sieve (44 micron). Any charcoal that would not pass through this sieve was placed back into the ball mill for further processing. This process was repeated until the ground charcoal would readily pass through the no. 325 sieve. The ground charcoal was then stored in plastic bags for further analysis.

### 3.1.2 Particle Analysis

Samples were collected from the ground charcoal after it had been successfully processed through all three milling stages and passed through the no. 325 sieve. Particle composition, size, and size distribution for the ground charcoal was measured. Two separate methods were used to collect this data.

The first method utilized a scanning electron microscope to capture images of the charcoal particles in high resolution. These highly magnified images were recorded to provide physical characteristics of the charcoal such as the shape, size and relative distribution of particles produced. The scanning electron microscope also incorporated an energy-dispersive X-ray detector. The elemental composition of a selected portion of the sample was analyzed while the images were being generated.

The second method utilized a laser diffraction system (Spraytec, Malvern Instruments Ltd, Malvern, Worcestershire, United Kingdom) to measure the size and distribution of the sample particles. The device was calibrated to measure particles from 0.1 microns to 1000 microns. The sample charcoal particles were entrained in an air stream that passed between the laser emitter and receiver. Particle size histograms over the calibrated range were produced and recorded by the laser diffraction system. These histograms are presented in the next chapter.

### 3.1.3 Slurry Analysis

A liquid charcoal slurry was produced using the ground charcoal generated from the micronization process during the initial stages of the research. For initial testing, a slurry composed of 25% by volume charcoal particles was produced. The liquid carrier for this particular slurry was a commercially available B20 (20% by vol. biodiesel) diesel fuel blend. A small amount of the ground charcoal was added slowly to a known volume of B20 diesel fuel blend (750mL) and then the slurry was agitated. This process was repeated until the total slurry mixture volume was reached (1000mL).

### *3.1.3.1 Viscosity*

One of the concerns of this research was how the addition of charcoal particles affected the viscosity of the mixture compared to no. 2 ultra-low sulfur diesel (ULSD) fuel oil. The viscosity of the 25% by volume charcoal slurry was measured using a viscometer (DV-II+, Brookfield Engineering, Middleboro, MA) and compared to ULSD fuel oil. Viscosity measurements were recorded for both the 25% by volume charcoal slurry and the ULSD fuel oil. Two different spindle sizes were selected and viscosity was measured at three different spindle speeds of 20, 50 and 100 rpm. The test sample was thoroughly agitated before each test. Measurements were performed at a room temperature of 21°C where all samples were allowed to equilibrate with this temperature. A 600mL beaker was filled with roughly 500mL of the charcoal slurry and the viscometer spindle was lowered into the beaker until the surface of the liquid met the immersion groove on the spindle's shaft. The spindle speed was set and the viscosity was manually recorded once the viscometer's measurement stabilized. This process was repeated until a measurement had been recorded for each spindle speed and type of spindle. This same procedure was repeated using a 600mL beaker filled with 500mL of ULSD fuel oil.

### *3.1.3.2 Diesel Engine Testing*

The 25% by volume charcoal slurry was also tested in an inline, three cylinder, indirect-injected diesel engine (3TNE68, Yanmar Co., Ltd, Osaka, Japan). An indirect injection engine was selected due to the larger injector orifice of 0.040 inches (1016 microns). This larger injection orifice was roughly 23 times the diameter of the No. 350 (44 micron) sieve mesh used to process the charcoal particles.

Few modifications were made to the engine system. The engine fuel system was plumbed with a manifold and cutoff valving. Depending on the fuel valve position, the engine's high pressure injection pump would be supplied with either the formulated 25% by volume charcoal slurry or a B20 diesel fuel oil blend. The B20 diesel fuel oil blend tank utilized the engines stock lift pump and filter system. The charcoal slurry tank was plumbed in such a way that an electric fuel pump supplied slurry to the high pressure injection pump while bypassing the stock fuel filter system. There was no filtration of the charcoal slurry to prevent removal of charcoal particles which would alter the percentage of charcoal contained in the slurry injected in the cylinder. A portion of volume pumped by the electric fuel pump was continually returned to the charcoal slurry tank. This recirculation of the charcoal slurry provided the needed agitation to prevent settling and separation of the solid phase from the liquid phase. A chemical

dispersant, as mentioned in the literature for solid particle slurries, was not utilized since the agitation was sufficient to maintain particle suspension.

The testing procedure followed was to start the engine and bring it to operating temperature using only the B20 diesel fuel oil blend. During the warm-up period, the electric fuel pump would recirculate the charcoal slurry and disperse any settled charcoal particles throughout the liquid phase of the slurry. After reaching operating temperature, the valving was then switched to draw only from the charcoal slurry tank. The engine was then run only on the charcoal slurry for the testing period. Before shutdown of the engine, the valving would be switched back to the B20 diesel fuel blend tank. Clear connectors and other “sight glasses” throughout the plumbing allowed for visual inspection of the fuel lines. The engine was run on the B20 diesel fuel blend until all of the slurry remaining in the fuel line was consumed. The purpose of flushing the injection system of the charcoal slurry was to prevent any issues that may result from settling of charcoal particles in these systems. After the initial startup sequence, the engine could be started on the charcoal slurry if the slurry tank was still sufficiently agitated.

## 3.2 VIRGIN WOOD CHARCOAL

One of the goals of this research was the production of micronized charcoal particles from a woody biomass feedstock. The first stage of this research focused on the production of micronized charcoal particles using charcoal that was readily available as a product of TLUD gasifier. The biomass feedstock for this charcoal was woodchips produced from logging residue and waste wood pieces. The wood chips contained various species of woody biomass and the possibility of ash contaminants entrained during the collection and chipping process. The focus of this next portion of the research is on the analysis of charcoal produced using a known feedstock under controlled conditions.

### 3.2.1 Biomass Preparation

A yellow poplar or tulip poplar tree (*Liriodendron tulipifera*) was chosen as the species for the biomass feedstock. Yellow poplar is one of the largest, fast growing hardwood species found east of the Mississippi river from Florida to New York. Yellow poplar trees grow tall (70-100 ft) with most of the branches concentrated near the top of the trunk. This characteristic allows harvesting of long, smooth logs without the labor of limb removal as seen in figure 3.4. The yellow poplar tree has the potential

to produce a greater volume of dry wood per acre than much denser species such as oak (Beck 1990).



**Figure 3.4** Freshly cut yellow poplar logs

A yellow poplar tree was harvested on 4 June 2011 at Fishel Family Farms (Clemmons, North Carolina). Three logs were cut from the lower half of the trunk (Figure 3.4). The fresh cut logs were hauled back to D. S. Weaver Laboratories (Raleigh, North Carolina) for processing. The three logs were then allowed to lay in direct sunlight outdoors for three hours with an average temperature of 39.7°C (89°F) during this time period. The logs were

then brought indoors and secured in a vice. This short warming period increases the ease in separating the bark from the wood by heating the sap and tissue in the cambium layer found between the bark and wood. The purpose of removing the bark is to remove much of the windblown silicates which would otherwise end up in the ash. Silicate ashes are much harder to remove than water-soluble ashes in the final charcoal product.



**Figure 3.5** Using a drawknife to begin the bark removal

A drawknife was used to carefully remove a one inch wide section of bark the length of the log (Figure 3.5). Material was carefully removed until

only bare wood is exposed. A small flat edge such as a putty knife was then inserted between the wood and bark along the exposed cambium layer. Slowly working down the length of the log, the bark was separated from the wood underneath (Figure 3.6).



**Figure 3.6** Separating the bark

Once the separation was started, the bark was completely removed by peeling the bark away from the wood using one's bare hands. This method of bark removal works well for logs cut during late spring to early summer because of the abundance of sap moving to the extremities of the tree

during new leaf growth. This sap is conducted mostly through the cambium and nearby layers. The added moisture between the bark and wood decreases the effort needed to destroy the connecting tissues. This method of bark removal on yellow poplar trees has been utilized by people of the Appalachian Mountains to harvest bark for various uses such as baskets, siding and shingles. The bark was removed using this method for all three logs harvested. The resulting log is a smooth yellow wood (Figure 3.7).



**Figure 3.7** Yellow poplar logs with bark removed

The logs were then cut to roughly 17" lengths using a vertical bandsaw. These shorter sections were then either quartered or halved depending on their initial diameter to create pieces of similar volume. In figure 3.8 the final prepared wood pieces are stacked on a hand truck to be carried to the dryer.



**Figure 3.8** Yellow poplar wood prepared for drying

The moisture content of freshly cut wood is too high for charcoal production and must be dried prior to conversion. The cut wood pieces were placed in a custom built forced air dryer at 108°C for 16 hours. The cut wood pieces were then allowed to equilibrate with the ambient

temperature until it was cool enough to handle. The cut wood was then removed from the dryer and the total mass was recorded.

### 3.2.2 Carbonization

The cut and dried yellow poplar wood was placed in a custom stainless steel chamber designed for lab-scale charcoal production (Figure 3.9). The chamber measured 406 mm (16 in) wide by 406 mm (16 in) deep by 457 mm (18 in) tall and had a 330 mm (13 in) diameter round opening at the top. Eight stud bolts welded around the opening secured a flat round lid.



**Figure 3.9** Yellow poplar wood packed in the chamber

This arrangement allowed the lid to seal the chamber opening using a high temperature gasket material (3300, Deacon Industries Inc., Washington, PA). This seal reduced gas exchange with the inside of the oven and prevented oxygen from entering the chamber near this opening. Two 1/8 NPT couplers were welded in one of the vertical faces of the chamber that allowed the insertion of 1/8 NPT pipe nipples through the wall of the chamber. These exhaust pipes allowed the gases evolving from the wood during the carbonization process to exit the chamber.

The total mass for the cut wood pieces was recorded and the cut wood pieces were placed into the chamber with all of the pieces oriented so that the longest edge of each piece was vertical. Pieces were packed tightly to reduce the amount of open space within the chamber. Then the chamber lid was placed onto the vessel and all eight bolts were tightened to provide an even seal. The chamber was then placed into a high temperature furnace (Iguana, Paragon Industries, L.P., Mesquite, Texas) as shown in figure 3.10 and the furnace door was secured. The furnace was rated at 10.8 kW with a maximum furnace temperature of 1287°C.



**Figure 3.10** Chamber installed in high temperature furnace

The exhaust pipes were threaded through the wall of the furnace and into the 1/8" NPT couplers on the side of the chamber (Figure 3.11). A

stainless steel drip pan was placed below the two pipes to catch any tars that would condense as the gases exit the pipes.



**Figure 3.11** Exhaust pipes installed for gases exiting the chamber

The high temperature furnace followed a specific programmed heating rate schedule for the duration of the carbonization process. The heating rate schedule consisted of an initial heating at full rate until a temperature of 250°C was reached. Then the furnace followed a heating rate of 100°C per hour from 250°C to 700°C. The furnace was then programmed to cut off once a temperature of 700°C was reached.

Once the high temperature furnace completed the heating schedule, the oven doors were immediately opened to stop the carbonization process and the chamber was allowed to cool to room temperature overnight. Internal furnace temperatures were measured and recorded for the duration of the carbonization process. The chamber was disassembled and removed from the high temperature furnace the following day. The resulting charcoal was then removed from the chamber and the total mass produced was measured and recorded. The charcoal was placed in a plastic tub and sealed until it could be processed further.

### 3.2.3 Size Reduction

The charcoal produced from the yellow poplar was processed using the same milling process developed earlier in the research. The yellow poplar charcoal was removed from the storage tubs and broken by hand into smaller pieces that fit in the Wiley mill hopper. All of the charcoal was processed through the Wiley mill and stored in sealable plastic bags.

A small sample of the charcoal particles was chosen at random to obtain a quick evaluation of the Wiley milling process. Two readily available sieve sizes were chosen (#35-500micron and #100- 149micron) to determine approximately how small of particles were ground. The two sieves were stacked with the no. 35 sieve on top and both were placed on a catch pan or

receiver. The sample was placed in the top of the no. 35 sieve and the entire column was shaken by hand for approximately one minute. Each sieve and the receiver was weighed individually and recorded. The mass fraction of the original sample remaining on each sieve was determined using equation 3.1.

$$\omega_i = \frac{m_i}{m_{tot}} \quad (3.1)$$

where

$\omega_i$  = mass fraction of charcoal sample remaining on sieve  $i$

$m_i$  = mass of charcoal remaining on sieve  $i$ , g

$m_{tot}$  = total mass of charcoal sample sieved, g

The ground charcoal that was produced from the Wiley mill was all processed through a no. 100 sieve. Ground charcoal particles that did not pass through the no. 100 sieve were processed through the burr mill previously described until they were able to pass through the no. 100 sieve. The charcoal particles that passed through the no. 100 sieve were then processed through the ball mill for a minimum of 24 hours. All of the ground charcoal processed through the ball mill was placed in a no. 325 sieve (44 microns). Ground charcoal that passed through the no. 325 sieve was placed in sealable plastic bags and charcoal that remained on the no. 325 sieve was processed through the ball mill again. Smaller 10 gram samples were then selected from the charcoal that passed through the no.

325 screen and placed into separate labeled bags to be used in the analysis portion.

### 3.2.4 Physical Property Analysis

Determining several of the quantitative physical characteristics of the charcoal was one of the goals of this research. Analysis of the ground yellow poplar charcoal provided moisture content, ash content, absolute density and energy content. The moisture and ash content provide quantitative insight into the composition of the charcoal particles. As a fuel source, the amount of water present affects the combustion of the particle. The amount of ash present can affect wear on fuel and engine systems and produce crystalline-like structures of the fused ash under high combustion temperatures. Ground charcoal absolute density and energy content values can be combined with known values for fuel oils to determine slurry energy densities for specific charcoal particle loadings. Data collection and measurement methodologies for each physical property are discussed in the following sections.

#### *3.2.4.1 Moisture*

Four empty crucibles were placed upside down in a muffle furnace (Isotemp Muffle Furnace 10-550-126, Thermo Fisher Scientific, Waltham,

MA) at a temperature of 750°C for one hour. This initial firing removed any moisture, oil or other combustible material remaining on the crucible from previous usage and handling. The empty crucibles were moved to a desiccator and allowed to cool for an hour. The empty crucibles' mass,  $m_c$ , was recorded to the nearest 0.0001 gram and the crucibles were returned to the desiccator.

The muffle furnace temperature was then set to 105°C and allowed to reach equilibrium. Each crucible was filled with one gram of ground charcoal selected from one of the ten gram charcoal sample bags. A new mass value,  $m_{cs}$ , was recorded for each crucible containing ground charcoal. All four crucibles were placed in the muffle furnace and remained for 24 hours at 105°C. The crucibles were then removed and placed in the desiccator to cool for one hour. A new mass value,  $m_{csd}$ , was recorded for each crucible containing the oven-dry ground charcoal. The moisture percentage on a dry basis was calculated using equation 3.2.

$$M_{dry} = \frac{(m_{cs} - m_{csd})}{m_{cs} - m_c} \times 100 \quad (3.2)$$

where

$M_{dry}$  = dry-basis moisture content, %

$m_{cs}$  = mass of crucible with air dry sample, g

$m_{csd}$  = mass of crucible with sample dried at 105°C, g

$m_c$  = mass of crucible, g

The dry-basis moisture content,  $M_{dry}$ , was calculated and recorded for each crucible. Samples were returned to the desiccator to await ash content analysis.

#### 3.2.4.2 Ash

The four crucibles containing oven-dry charcoal samples from the moisture content analysis were removed from the desiccator and placed back into the muffle furnace at 750°C for 20 hours. The crucibles were then removed and placed immediately into the desiccator and allowed to cool for one hour. Cooled crucibles were removed from the desiccator and a new mass value,  $m_{ca}$ , was recorded. The percentage of ash on a dry-basis was calculated using equation 3.3.

$$\% \text{ Ash} = \frac{m_{ca} - m_c}{m_{csd} - m_c} \times 100 \quad (3.3)$$

where

$\% \text{ Ash}$  = percentage of ash on an oven-dry basis, %

$m_{ca}$  = mass of crucible with ash residue, g

$m_{csd}$  = mass of crucible with sample dried at 105°C, g

$m_c$  = mass of crucible, g

Each crucible was then wiped clean and added back to the muffle furnace at 750°C for one hour. Crucibles were removed from the muffle furnace and allowed to cool. These crucibles were then ready to be used again in the

moisture content analysis. The moisture and ash content analysis was performed for each of the sample bags collected for the ground yellow poplar charcoal produced for this research.

#### 3.2.4.3 Density

The absolute density of the ground yellow poplar charcoal was calculated using a helium pycnometer (Accupyc 1330, Micromeritics, Norcross, GA) to measure the sample particle volume and balance to measure the sample mass. The helium pycnometer was calibrated using a 10cc sample volume chamber and two stainless steel spheres with a total calibrated volume of 6.371937cc. The helium pycnometer was placed in manual mode and the stainless steel sphere volume was measured and calculated by hand using equation 3.4 to compare to the automatic calculation.

$$V_s = V_c + \frac{V_r}{1 - \frac{P_1}{P_2}} \quad (3.4)$$

where

$V_s$  = absolute volume of sample, cc

$V_c$  = volume of sample chamber, cc

$V_r$  = volume of reference chamber, cc

$P_1$  = initial pressure in sample chamber, psi

$P_2$  = pressure after equilibration with the reference chamber, psi

After calibration of the helium pycnometer, the automatic mode was set to purge the sample chamber and reference chamber with helium and zero the internal pressure transducer before each volumetric measurement. The mass of the sample chamber insert was then recorded,  $m_{ins}$ , to the nearest 0.0001 gram. The chamber insert was then filled with air-dry ground charcoal from the sample bags collected previously and a new mass,  $m_{ins+sam}$ , was recorded. The mass of the sample was calculated using equation 3.5.

$$m_{sam} = m_{ins+sam} - m_{ins} \quad (3.5)$$

where

$m_{sam}$  = mass of the charcoal sample in the 10cc chamber insert, g

$m_{ins+sam}$  = mass of the 10cc chamber insert filled with ground charcoal, g

$m_{ins}$  = mass of the 10cc chamber insert, g

For each run, the pycnometer was set to perform ten volumetric measurements. The average volume over these ten measurements was recorded as the absolute volume for the sample run. Absolute density was calculated for each run using the sample mass and the average absolute volume for the run. All seals and sealing surfaces were wiped clean and properly greased after each run to prevent gas leakage from the sample

chamber. Three runs were performed for each sample bag. The process was then repeated for each sample bag.

A bulk density was calculated by taking a sample of the original yellow poplar charcoal before the milling process. A small section of the charcoal was cut into a 1 cm by 1cm by 1cm cube using a saw. This cube of charcoal was weighed using a mass balance to the closest 0.0001 gram. The bulk density for this 1 cc cube of charcoal was equal to the mass measured. This measurement allowed comparison of the ground charcoal particle density to the original parent charcoal density.

#### *3.2.4.4 Energy Content*

The energy contained within the ground poplar charcoal was determined using a bomb calorimeter (CAL-2KECO, Digital Data Systems Pty Ltd., Johannesburg, Gauteng, South Africa). A new steel crucible was fired in the muffle furnace at 800°C for 10 minutes. After cooling, the empty crucible mass,  $m_c$ , was recorded to the nearest 0.0001 gram. A 0.5 gram sample of ground poplar charcoal from one of the sample bags was added to the empty crucible and a new mass,  $m_{cs}$ , was recorded. The crucible and sample was placed in the bomb vessel's holder. The vessel firing wire and seals were examined for damaged and replaced if necessary. A cotton string was tied to the firing wire with the end of the string touching the ground

charcoal sample inside the crucible. The vessel was then sealed and charged with 300 psi of pure oxygen. The exact sample mass,  $m_s$ , as calculated using equation 3.6, was entered into the bomb calorimeter and the vessel was fired.

$$m_s = m_{cs} - m_c \quad (3.6)$$

where

$m_s$  = mass of sample, g

$m_{cs}$  = mass of crucible and sample, g

$m_c$  = mass of empty crucible, g

The energy content per unit mass measured by the bomb calorimeter was recorded for each run. The process was repeated for each replication and additional sample bag.

## **4. RESULTS AND DISCUSSION**

This research analyzed the potential of a charcoal slurry utilizing micronized charcoal particles and a biodiesel blend. The research was conducted using two different sources of charcoal. A multi-step milling process was used to generate micronized charcoal. Charcoal particle properties were analyzed and evaluated for potential impacts to slurry production and usage. A charcoal slurry was produced using a biodiesel blend and tested in a commercially available diesel engine.

### **4.1 WASTE WOOD CHARCOAL**

The charcoal used for the initial phase of research was produced using wood chips as the parent biomass. This charcoal was a product of a separate research project that generated batches of charcoal chips for soil incorporation. These readily available charcoal chips were the source of solid charcoal for this phase the research.

#### **4.1.1 Size Reduction**

The multi-step milling process described previously in chapter 3 was developed through an iterative process. The charcoal chips initially varied in size and shape, averaging one inch across their major dimension. These chips were small enough that they could be hand loaded into the hopper of

the custom burr mill pictured in figure 3.2. The burr mill used a tapered auger that carried the charcoal chips into the center of the stationary plate and forced the chips between the rotating burr plates.

The burr mill was able to reduce the overall particle size of the charcoal chips, but there were a few issues that had to be addressed during the milling process. Larger charcoal chips had to be manually removed because they would lodge inside the auger housing and prevent charcoal from entering the burr mill. By adjusting the gap between the stationary and rotating burr plates, the size of the ground charcoal particles exiting the mill could be adjusted. The burr mill worked best when the material was passed through the mill multiple times. Subsequently smaller ground particles exited the mill as the burr plate gap was reduced each time. The initial product exiting the burr mill contained ground charcoal particles varying in size from a few millimeters to over 10 millimeters as pictured in figure 4.1.



**Figure 4.1** Ground charcoal particles after one pass through the burr mill

After multiple passes through the burr mill, the ground charcoal was reduced to a fine powder that was similar in consistency to wheat flour. At this point, the burr mill was no longer able to reduce the ground charcoal size further and the ball mill was used.

The larger charcoal pieces were handled much easier by the Wiley mill and therefore processed through the Wiley mill first. The Wiley mill, as pictured in figure 3.1, used a rotating blade with multiple fixed blades in the housing wall. A replaceable screen allowed particles of the desired size to exit out the bottom of the mill and into the collection chamber. Particles

that were too large to pass through the screen remained inside the mill until the blades were able reduce their size further. Utilizing the one millimeter screen, all of the ground charcoal particles that exited the mill were less than one millimeter on average in a single pass. The Wiley mill was setup to be a small batch laboratory mill so it could only handle processing the charcoal chips in small batches which slowed down the milling speed overall compared to the burr mill.

The ball mill was the last step in the milling process for the ground charcoal particles. The custom ball mill reduced the particle size further by constantly allowing steel balls to roll and tumble over the finely ground charcoal powder produced earlier in the milling process. The impact and weight of the steel balls crushed the fine charcoal particles over a long period of time into micronized charcoal particles. The ball mill is a time consuming batch process. The fine charcoal particles were processed by the ball mill for various run times ranging from a few days to a week in length. The longer the run time, more charcoal particles were successfully micronized. The micronized charcoal removed from the ball mill was then ready to be used further in the slurry and particle analysis as pictured in figure 4.2

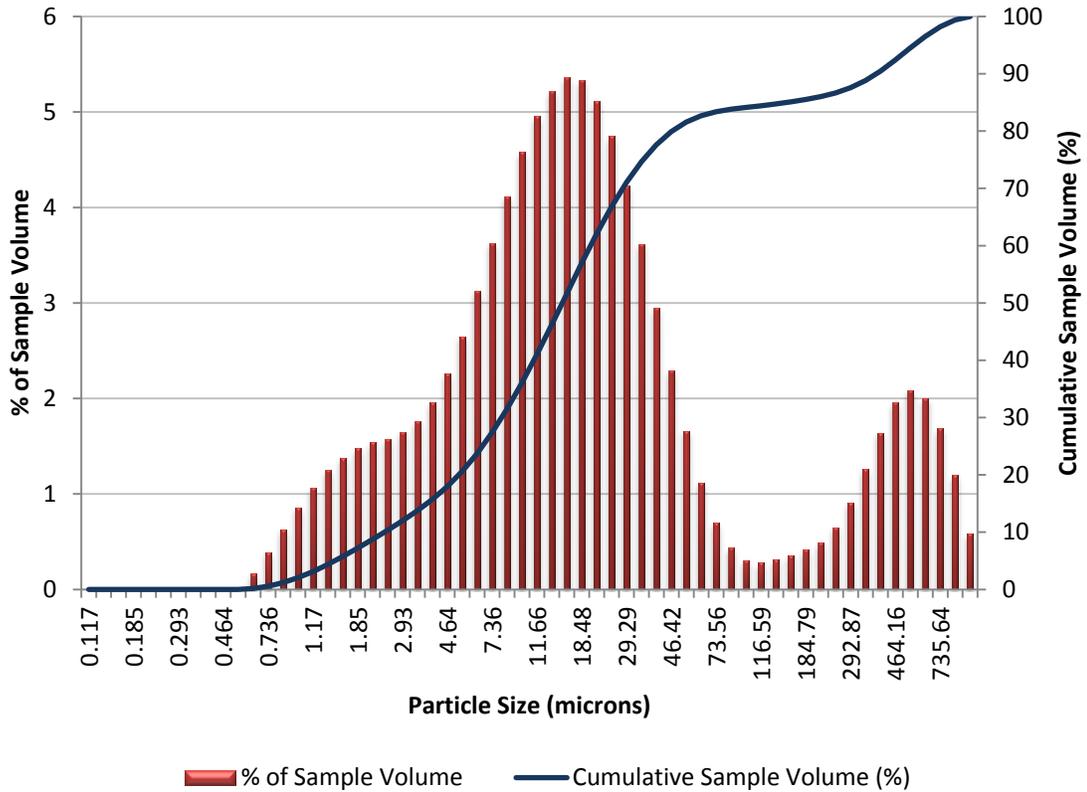


**Figure 4.2** Charcoal after processing through the ball mill

#### 4.1.2 Particle Analysis

Ground charcoal particle samples were analyzed using the laser diffraction system (Spraytec, Malvern Instruments Ltd, Malvern, Worcestershire, United Kingdom) described in the previous chapter. Charcoal particles that passed between the laser and detector were measured. Particles were sized from zero to 1000 microns in discrete steps and the frequency of particles within each step size was recorded. Histograms were generated for each run using the data collected to represent the percentage of the total sample for each step size. These

histograms were then overlaid by a curve representing the percentage of the total sample volume for a particle of x size or smaller.

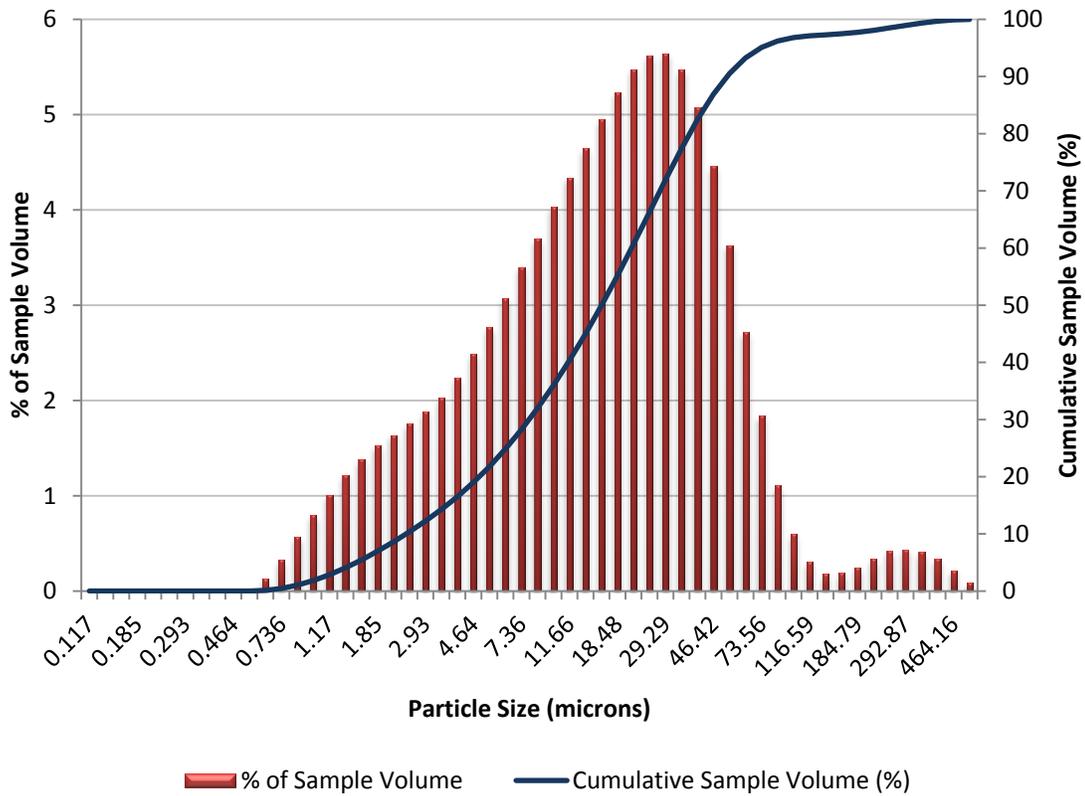


**Figure 4.3** Charcoal particle size distribution histogram for run 1

Figure 4.3 presents the data collected during the first sample run. One can clearly see that there are two peaks in the histogram. The first peak occurs around 16 microns and the second around 600 microns. The laser diffraction system is designed to analyze liquid sprays and other materials with a spray pattern. This requires that the particles be entrained

in an air stream so that they pass between the laser emitter and detector. Without sufficient time to disperse in the air stream, the ground charcoal particles tended to remain close together as agglomerations. These particle agglomerations would be measured as much larger particles by the laser diffraction system. The second peak in the histogram at 600 microns is assumed to be a measurement of these agglomerated particles.

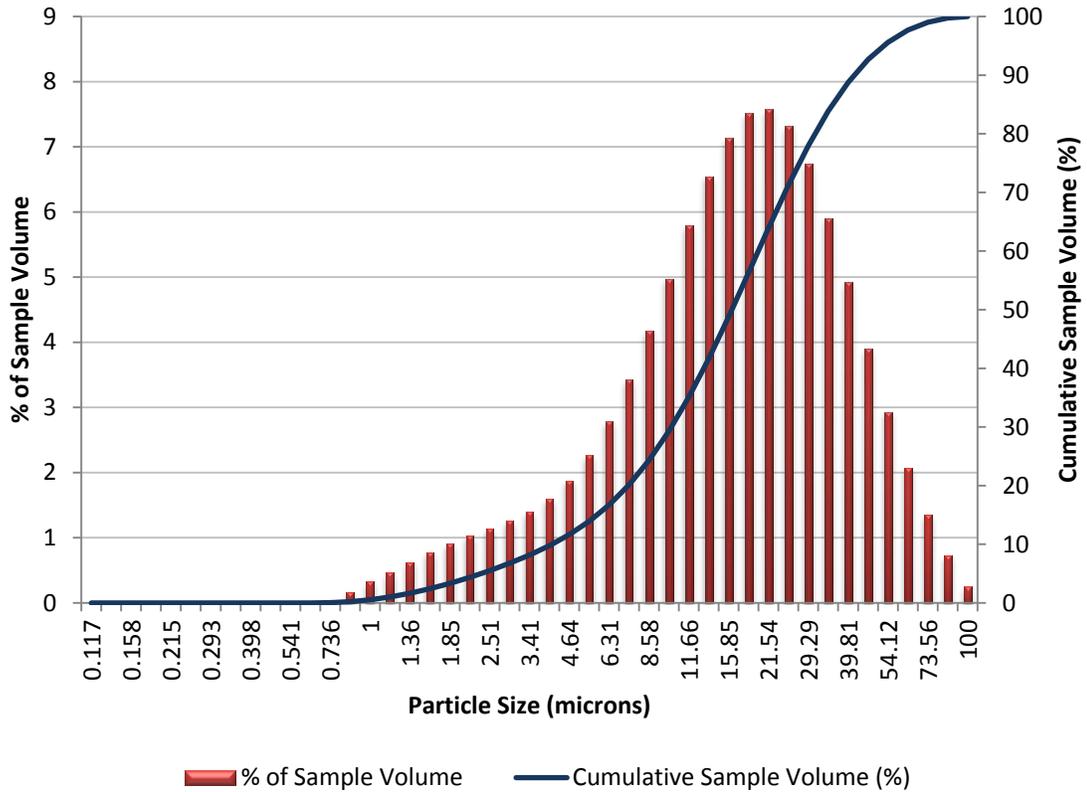
Even with the agglomeration of ground charcoal particles, over 80% of the sample volume is composed of particles that are less than 50 microns and over half of the particles are less than 15 microns. Based upon these measurements, the multi-step milling process was able to successfully produce micronized charcoal particles.



**Figure 4.4** Charcoal particle size distribution histogram for run 2

Adjusting the processes by which the ground charcoal particles were dispersed across the laser diffraction system sensors, the secondary peak in the histogram for the second run was much smaller as presented in figure 4.4. The charcoal particles were entrained in the air much further from the sensor, which allowed the particles time to separate further. The secondary peak occurred around 300 microns for this run and only 3% of the total sample volume was included in this peak. The primary histogram peaked at 30 microns. Similarly to the first run, 82% of the sample volume were

ground charcoal particles of 50 microns or smaller and half of the sample volume was 16 microns or smaller.

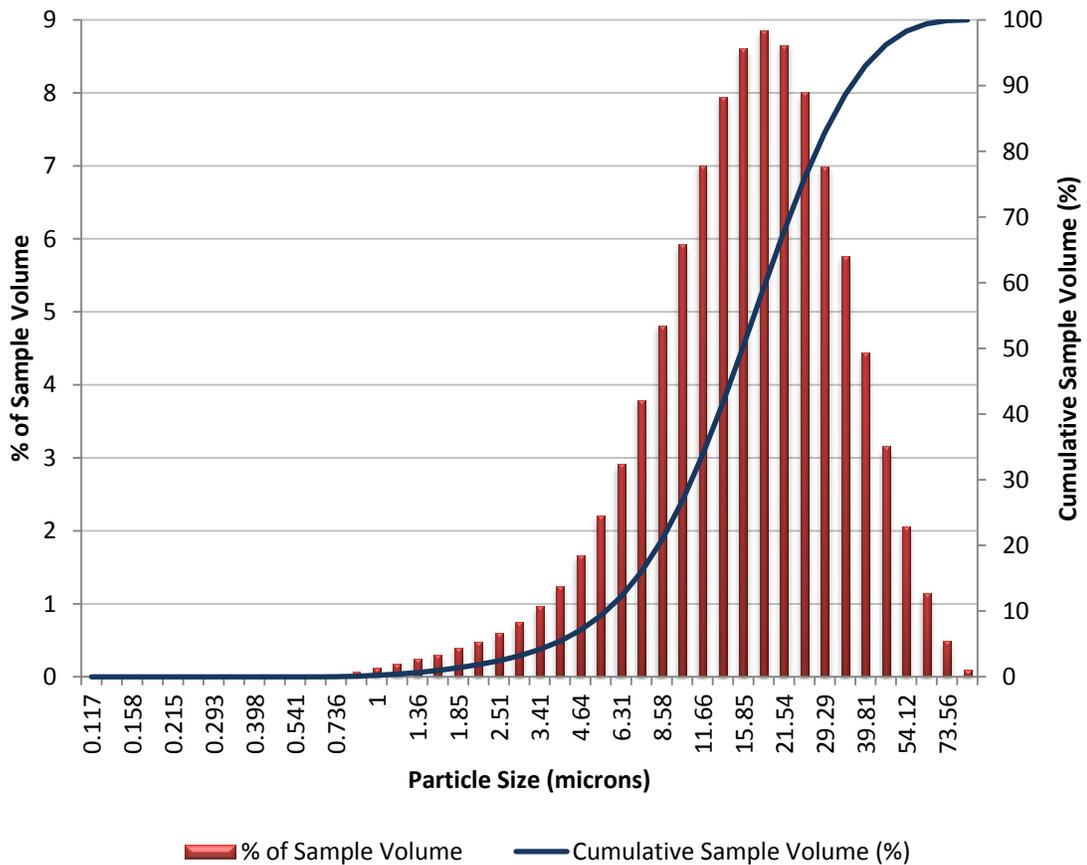


**Figure 4.5** Charcoal particle size distribution histogram for run 3

On the third run, the process by which the ground charcoal particles were entrained in the air stream passing through the laser diffraction system sensors was optimized. Figure 4.5 presents the data for this run. The secondary peak was eliminated by eliminating the issues with particle agglomeration during the measurement. Comparing the single peak

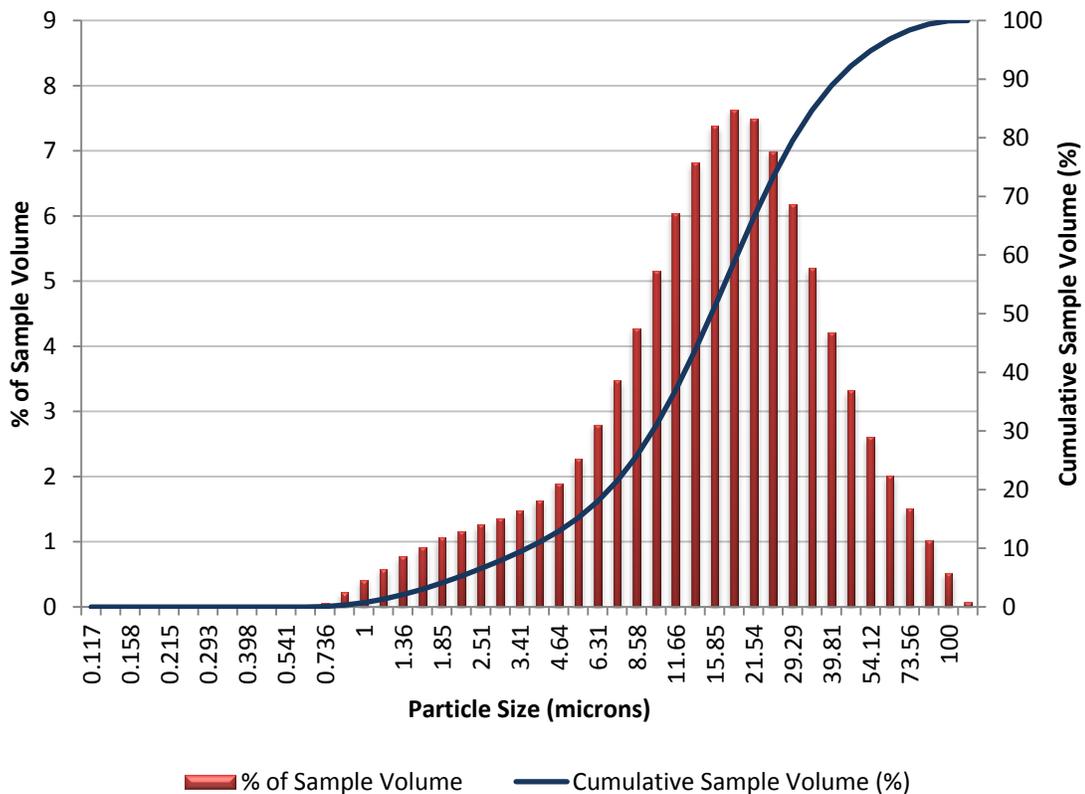
histogram to the first peak in the previous two figures, one can quickly see that the data range consists of particles measured to be approximately 1 micron to 100 microns.

The median particle size for the third run was 22 microns with half of the sample volume consisting of 16 microns or smaller. With the elimination of particle agglomeration, close to 95% of the particles were 50 microns or less for this run.



**Figure 4.6** Charcoal particle size distribution histogram for run 4

The fourth run was similar to the previous run (Figure 4.6). The ground charcoal particle sizes ranged from approximately 1 to 86 microns. The median particle size was 19 microns with half of the sample volume measuring 16 microns or smaller. Ninety-seven percent of the total sample volume consisted of particles measuring 50 microns or less.

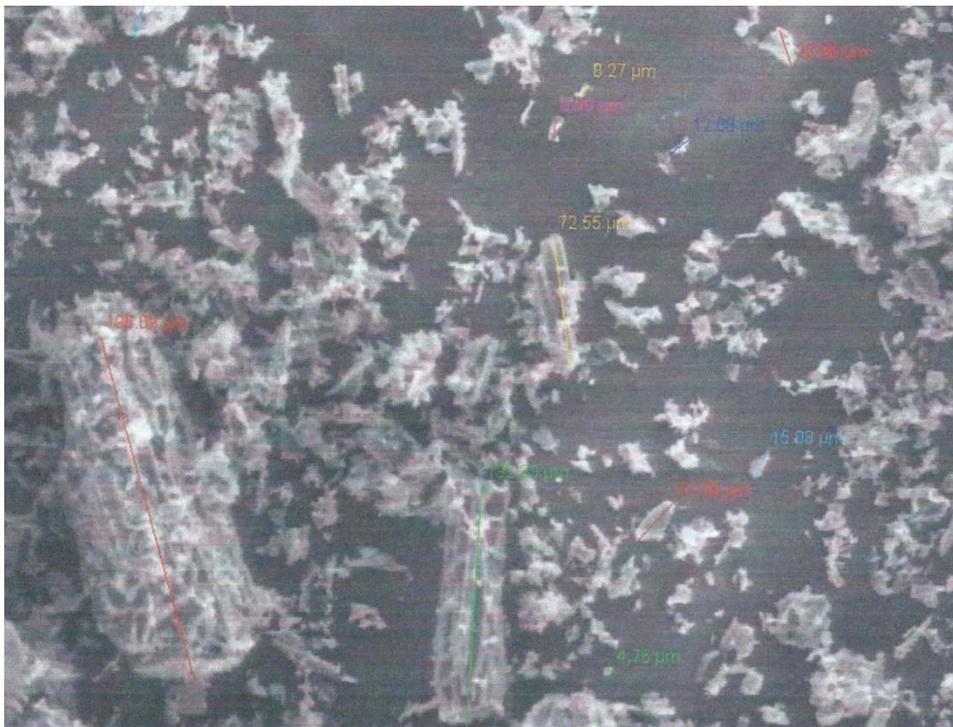


**Figure 4.7** Charcoal particle size distribution histogram for run 5

The fifth and final run is presented by figure 4.7. Again, the range of measured ground charcoal particle sizes for this run varied from

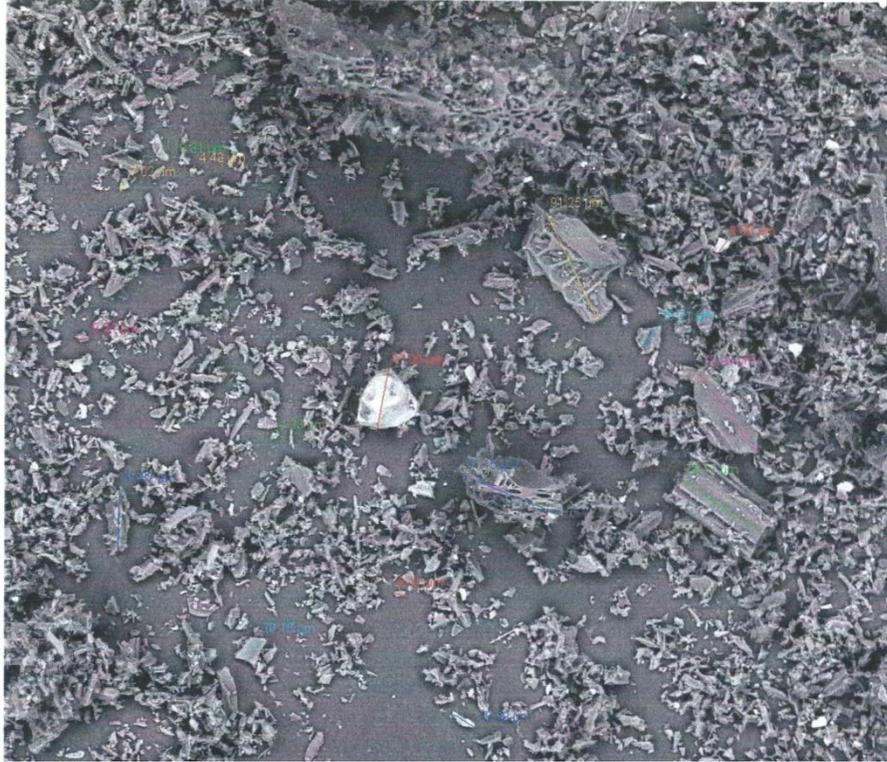
approximately 1 to 100 microns. The median particle size for this run was 19 microns with half of the sample volume consisting of ground charcoal particles that were 16 microns or less. Ninety-three percent of the total sample volume for this run consisted of ground charcoal particles that measured 50 microns or less.

Several images of the ground charcoal sample were collected using a scanning electron microscope. The purpose of this process was to examine the size and shape of the ground charcoal particles. Figure 4.8 is an image of the ground charcoal sample under a magnification of 400X.



**Figure 4.8** 400X image of larger ground charcoal particle structure

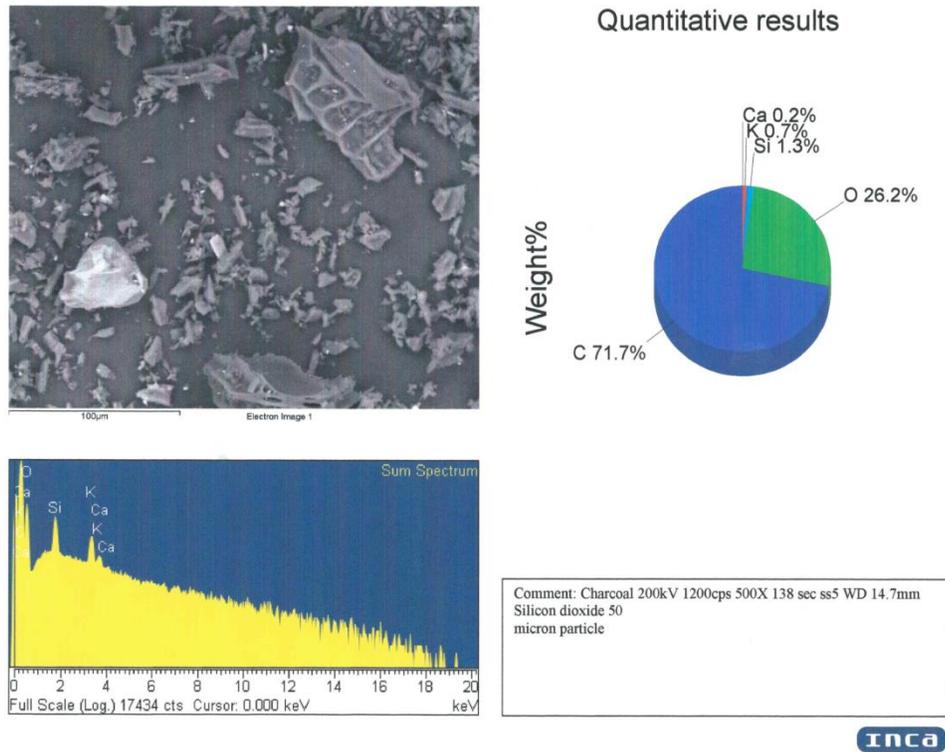
The porous structure of the charcoal is evident in the larger particles of this image. The larger particles tend to have a long cylindrical shape overall, but as the particle size is reduced the particle shape becomes more irregular. The largest particle in the lower left of figure 4.8 with a length of almost 200 microns has a width to length aspect ratio of 0.4. Since the larger particles tended to have small aspect ratios, the sieving method used would allow these particles to pass through a sieve mesh that was much smaller than their largest dimension. The resulting ground charcoal would contain a larger percentage of charcoal particles that were larger than the mesh size. The particles in this sample that were around 50 microns or less tended to be more irregularly shaped with aspect ratios much closer to unity.



**Figure 4.9** 400X image of ground charcoal with ash

One of the advantages of collecting images using the scanning electron microscope is that ash particles that would be seemingly invisible to the naked eye can be distinguished from charcoal particles. Figure 4.9 is an image of the ground charcoal sample that contained several ash particles as distinguished by the lighter colored particles in the image. The largest ash particle near the center of the picture is 50 microns across. Several smaller ash particles (7 microns and smaller) can also be found in this image. The scanning electron microscope that was used to collect these

images was also equipped with an X-ray detector that could conduct an energy dispersive X-ray analysis of the sample.



**Figure 4.10** Energy-dispersive X-ray spectrometry of ground charcoal sample

The complete elemental analysis of the sample image containing the visible ash particles can be found in figure 4.10. The sum spectrum graph in the lower left section of figure 4.10 contains peaks that correspond with the elements carbon, calcium, oxygen, silicon, and potassium. The only other element that can be assumed to be present in the sample is hydrogen.

The energy dispersive X-ray spectrometer is unable to measure elements as small and light as hydrogen atoms.

According to the elemental analysis, 2.2% of the total sample mass can be attributed to the ash elements Ca, K, and Si. These ash elements can occur in several different molecular forms, but most commonly they would be found as an oxide. The elemental silicon would be most commonly present as silicon dioxide ( $\text{SiO}_2$ ), but other silicates such as dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ) and tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ) are possible. Although, the high ratio of elemental silicon to calcium in the overall mass percentage for this analysis suggests that the majority of the elemental silicon is present as silicon dioxide.

Elemental calcium can also be present in two additional molecular forms for this sample analysis: calcium oxide ( $\text{CaO}$ ) and calcium carbonate ( $\text{CaCO}_3$ ). Calcium carbonate is the most probable form considering that calcium oxide will react with the excess carbon dioxide ( $\text{CO}_2$ ) present during the charcoal production process to form calcium carbonate. Calcium carbonate ashes can be removed from the charcoal by rinsing the charcoal sample with water saturated with carbon dioxide. The calcium carbonate will react with the carbonated water to form a water soluble calcium bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ ).

Elemental potassium can be present in several different molecular forms. The simple oxide, potassium oxide ( $K_2O$ ), is highly reactive and would quickly form potassium hydroxide (KOH) with any moisture present. Potassium hydroxide would then react with the excess carbon dioxide present during the charcoal production process to form potassium bicarbonate ( $KHCO_3$ ) and potassium carbonate ( $K_2CO_3$ ). Potassium bicarbonate decomposes at temperatures greater than  $100^\circ C$  into potassium carbonate. Taking all of these reactions into consideration the potassium would most likely occur in the form of potassium carbonate. All of these molecular forms of elemental potassium are water soluble compounds and could be rinsed from the charcoal sample using water only.

The removal of ash compounds containing elemental silicates requires a more energy intense mechanical separation process. The best way to reduce ash compounds containing silicates is to minimize contamination of the parent biomass by silicate compounds. One of the concerns of silicate ash in a carbon fuel is the possibility of forming glass slag under high combustion temperatures. Pure silicon dioxide will only melt to produce glass at very high temperatures exceeding  $2000^\circ C$  which is well above the melting point of most metals. With the addition of calcium oxides and potassium oxides (commonly called ceramic fluxes), the melting temperature required to form glass is reduced by almost 75%. This lower melting

temperature suggests that the ash found in the sample analyzed could possibly form glass slag on surfaces or create other issues in a combustion system if used without removing the ash first.

#### 4.1.3 Slurry Analysis

A charcoal slurry was produced using the micronized charcoal and a biodiesel blend. A commercially available B20 blend was used as the liquid phase of the slurry. The slurry was prepared using the method discussed in the previous chapter. The slurry contained a 25% by volume (38% by mass) mixture of ground charcoal particles with the remainder of the slurry consisting of the B20 biodiesel blend. The use of the volumetric fraction allowed comparison to other forms of diesel fuel blends. The mass fraction allowed comparison to various coal and charcoal slurries found in the literature. A sample vessel of the slurry is pictured in figure 4.11.



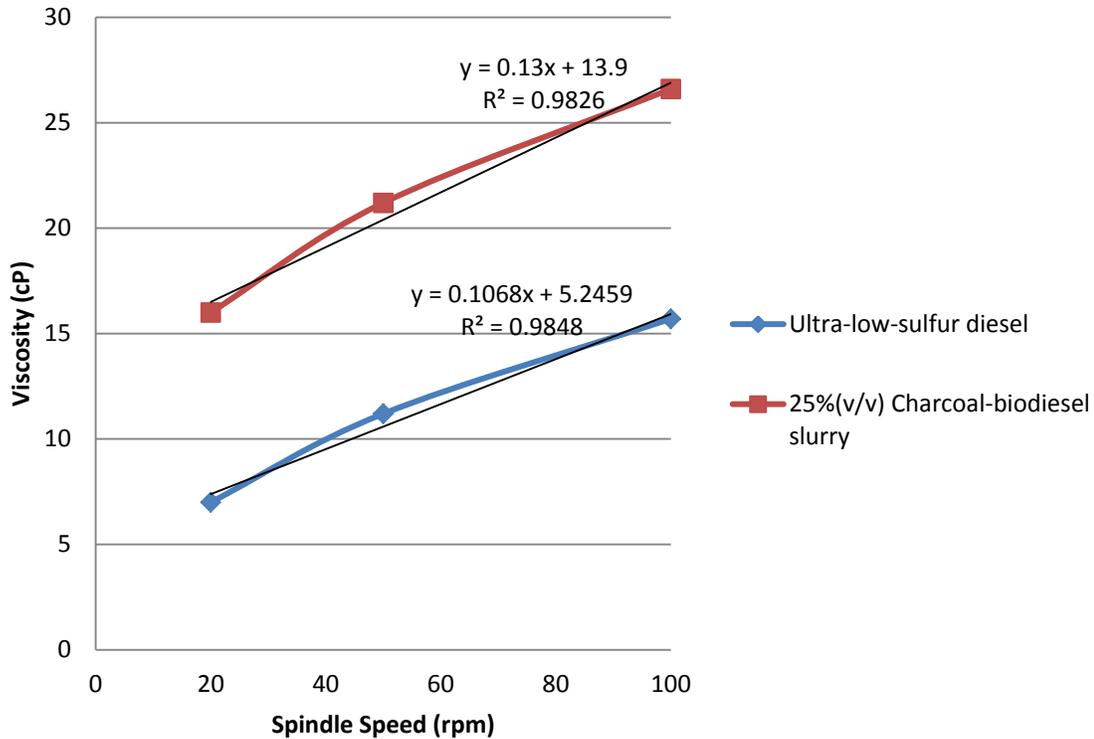
**Figure 4.11** Ground charcoal particles mixed with a biodiesel blend at 25%(v/v)

Once the ground charcoal particles were dispersed throughout the liquid phase of the slurry, the slurry became a very dark black liquid. If the charcoal slurry was allowed to remain stagnant, the ground charcoal particles would settle to the bottom of the vessel. The solid and liquid phases were easily reintegrated by simply mixing after the settling occurred. Settling time was affected by the size of the ground charcoal particles used in preparing the slurry. As the average size of the ground charcoal particles was reduced, the settling time of the slurry was increased. The micronized charcoal produced from the multi-step milling process generated charcoal

slurries that would require 24 hours of stagnation to settle. This settling time was acceptable for the purposes of this research. For this fuel to be used as formulated in a commercial application, an electric agitation pump or specially designed in-tank pumping system would be required for engine systems that have long periods between constant use.

#### *4.1.3.1 Viscosity*

One of the questions proposed during the course of this research was how the addition of ground charcoal particles to a liquid fuel, such as biodiesel or no. 2 diesel fuel oil, affected the viscosity. Liquid fuels are typically considered to be Newtonian fluids that have viscosities that are independent of the amount of shearing stress applied at a constant temperature. This property of liquid fuels allows for pumping and agitation during necessary processes such as mixing, transportation or high pressure injection without extreme viscosity changes. Data were collected using a rotational viscometer to measure and compare the viscosity of the prepared 25% by volume ground charcoal slurry and a commercially available no. 2 ULSD fuel oil. The viscosity data were plotted versus the spindle speed in figure 4.12.



**Figure 4.12** Viscosity measurements of 25%(v/v) charcoal-biodiesel slurry

The ULSD fuel oil exhibited non-Newtonian properties according to the data presented in the plot. A Newtonian fluid would have a constant viscosity over all spindle speeds. This is inconsistent with other studies found in the literature that conclude that diesel fuel, biodiesel, and biodiesel blends act as Newtonian fluids at temperatures above their cold filter plugging point (Boshui 2010). There are two possibilities for this result. The first possibility is that the temperature of the fluid measured varied enough throughout the measurement process to cause a change in viscosity. Temperature was not maintained with certainty using a water

bath or other temperature control method. The second possibility is that the viscometer precisely measured the viscosity at each spindle speed, but was not accurate enough at the lower viscosities measured.

By comparing the two curves, one can reason that the charcoal slurry exhibits characteristics similar to the ULSD fuel oil. The difference between the viscosities of the ULSD fuel oil and the charcoal slurry at each spindle speed was 10 centipoise on average. The two curves are close to parallel to one another. The linear equation beside each curve is the result of a linear regression of the data points along the curve. The slopes of these two lines support the idea that the curves are almost parallel and the linear regression for both curves has a coefficient of determination ( $R^2$ ) that is very close to unity. Using these facts, one could reason that the charcoal slurry would handle changes in shear stress similarly to the ULSD fuel oil and would also be considered a Newtonian fluid.

#### *4.1.3.2 Diesel Engine Testing*

The 25% by volume charcoal slurry prepared previously was successfully tested by fueling a three cylinder, indirect injected diesel engine. Several different non-working 3TNE68 Yanmar diesels were combined to create a single working engine. The engine used a custom fuel plumbing system described in the previous chapter that allowed the

selection of fuel from either of two different tanks. One of the tanks contained a B20 biodiesel fuel blend as the control while the other tank contained the 25% by volume charcoal slurry. An electric fuel pump was used to provide constant agitation to the charcoal slurry tank to prevent any settling of the charcoal particles. Clear plastic tee fittings and unions were used throughout the fuel system plumbing to operate as fuel sight glasses. These sight glasses provided a way to positively identify which fuel was entering the injection system of the engine.

The diesel engine was started and warmed up to operating temperature using the B20 biodiesel blend fuel tank. The fuel valving was then switched to only allow the engine to draw fuel from the charcoal slurry tank. The engine was allowed to run until half of the fuel in the charcoal slurry tank was consumed. The fuel valving was then switched back to the B20 biodiesel blend. The sight glasses were monitored to confirm that all of the charcoal slurry had been consumed by the engine before shutdown.

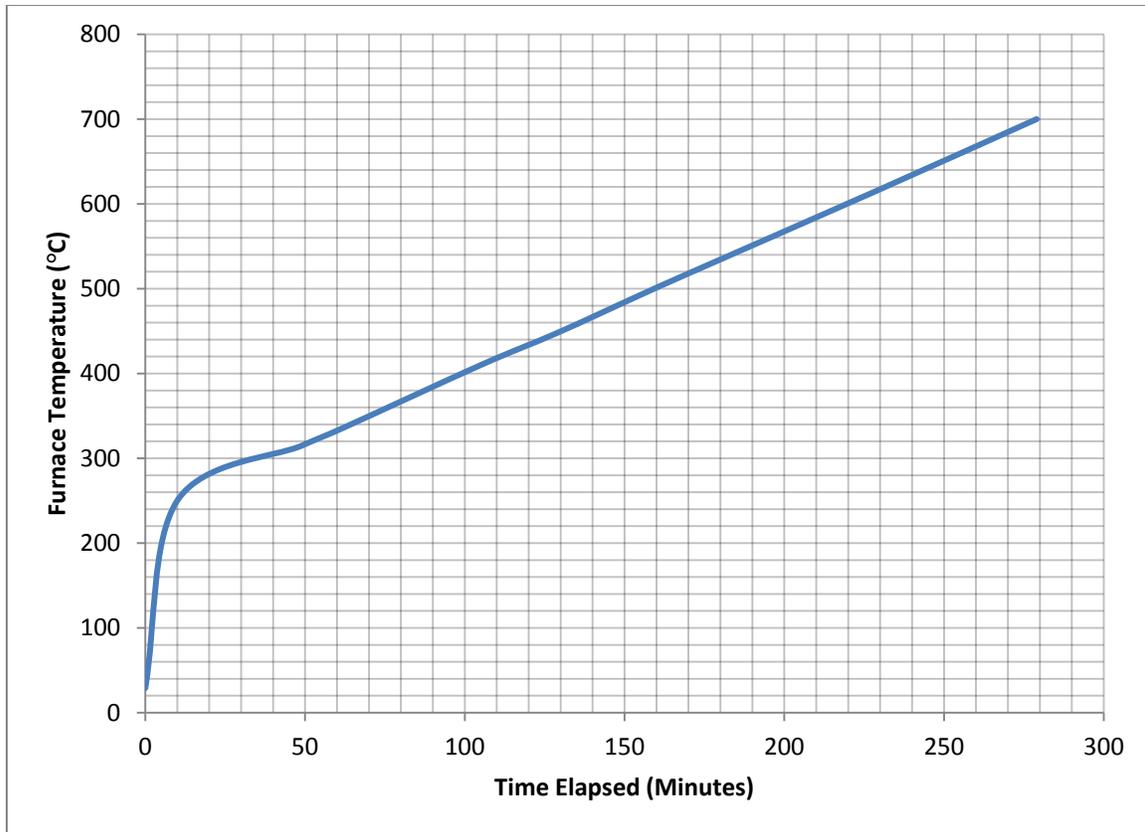
During the operating period, there were no visual differences in the exhaust gases exiting the engine. Also there were no easily noticeable differences in engine sound between the two fuels. All of the engine testing occurred at low idle under no-load conditions.

## 4.2 VIRGIN WOOD CHARCOAL

The latter phase of this research focused on the analysis of charcoal produced from a woody biomass that was freshly harvested. The charcoal was produced under controlled laboratory conditions to insure repeatability. This charcoal was then analyzed to provide quantitative data for physical characteristics affecting its use in a charcoal slurry fuel.

### 4.2.1 Carbonization

The yellow poplar biomass was freshly harvested and prepared for the charcoal production process using the method presented in the previous chapter. The chamber was loaded with 14.8 kg of dried yellow poplar wood pieces and placed in the furnace. Temperature data were collected during the carbonization of the dried yellow poplar wood. Figure 4.13 presents this temperature data over the total elapsed time of 279 minutes.



**Figure 4.13** Furnace temperature data during carbonization

The furnace was programmed to increase the temperature to 250°C at full rate and then increase the temperature at a rate of 100°C per hour until 700°C. The furnace was then cut off and opened to allow the chamber containing the charcoal to cool. The furnace was able to reach 250°C after 10 minutes had elapsed. The desired rate of 100°C per hour was slightly overshoot until 50 minutes had elapsed. For the remainder of the heating time, the recorded temperature increased at a steady rate of 100°C per hour.

Light organic molecules evolved from the yellow poplar wood pieces during the carbonization process. These light organics were forced to exit the chamber through the exhaust pipes as more of these gases were generated. The majority of these light organic molecules are collectively known as wood gas which is a syngas composed of varying mixtures of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), methane (CH<sub>4</sub>), and hydrogen (H<sub>2</sub>). This gas is flammable and was flared throughout the carbonization process to reduce atmospheric emissions. Figure 4.14 demonstrates these gases exiting the chamber during carbonization of the yellow poplar wood pieces. The top exhaust pipe in the figure was not yet flared to provide a comparison to the flared lower exhaust pipe.



**Figure 4.14** Flammable gases exiting the chamber during carbonization

The other light organic compounds exiting the chamber were organic tar vapors. These vapors condensed on the cooler inside walls of the exhaust pipes. The liquid tar was gradually forced to the end of the exhaust pipe by the constant flow of syngas exiting the pipe. A stainless steel drip pan and beaker was used to collect as much of the liquid tar as it dripped from the ends of the exhaust pipes. A metal funnel was modified and inserted on the end of the lower exhaust pipe to collect the liquid organic tar exiting the chamber.

After the furnace and chamber were allowed to cool overnight, the chamber was removed. The charcoal was removed from the chamber and the total charcoal mass measured was 3.5 kg. Comparing this mass to the original biomass, 76% of the original weight was lost during the carbonization process.

The charcoal produced from the yellow poplar retained much of the biomass' original structure. The overall size and shape are similar as seen in figure 4.15.



**Figure 4.15** Comparison of dried yellow poplar and the charcoal produced

The calculated loss in mass with little loss in overall size supports the hypothesis that this charcoal would also exhibit the hollow honeycomb structure examined previously in the waste wood charcoal. These charcoal pieces were stored in sealable plastic containers until they were ready to be processed further.

#### 4.2.2 Size Reduction

The charcoal produced from the yellow poplar required some additional steps in the milling process compared to the charcoal chips. The larger charcoal pieces, as pictured in figure 4.15, were much larger than the charcoal chips used previously and had to be broken into smaller pieces by hand. These larger pieces were then processed through the Wiley mill due to their size before they were processed further.

One of the goals of this research was to determine if charcoal particles could be successfully produced that were small enough to be suspended in a liquid carrier. The yellow poplar charcoal was used to evaluate the multi-step milling process since the charcoal was consistent in structure. A sample was collected from the charcoal after the initial processing through the Wiley mill. Mechanical sieves were used to separate particles by size and remove larger particles. Mechanical sieving of particles became more difficult the smaller the particles became. Table 4-1 presents the weight

data collected after sieving the sample. Almost 80% of the sample mass is composed of particles that pass through a no. 100 (152 micron) sieve.

**Table 4.1** Weight distribution of sieved particles after processing through Wiley mill

<b>Sieve</b>	<b>Total Mass (g)</b>	<b>Empty Mass (g)</b>	<b><math>\Delta</math> Mass (g)</b>	<b>Mass%</b>
<b>No. 35</b>	397.9	397.5	0.4	0.9
<b>No. 100</b>	439.9	431.1	8.8	20.6
<b>Receiver</b>	395.8	362.2	33.6	78.5

The screen on the Wiley mill is 1 mm or 1,000 microns. A material that is difficult to grind would produce more particles that were close to 1,000 microns. Very little was left on the no. 35 sieve which is less than half of the size of the Wiley mill screen. This analysis suggests that the charcoal produced was brittle and would be easier to mill into smaller particle sizes.

#### 4.2.3 Physical Property Analysis

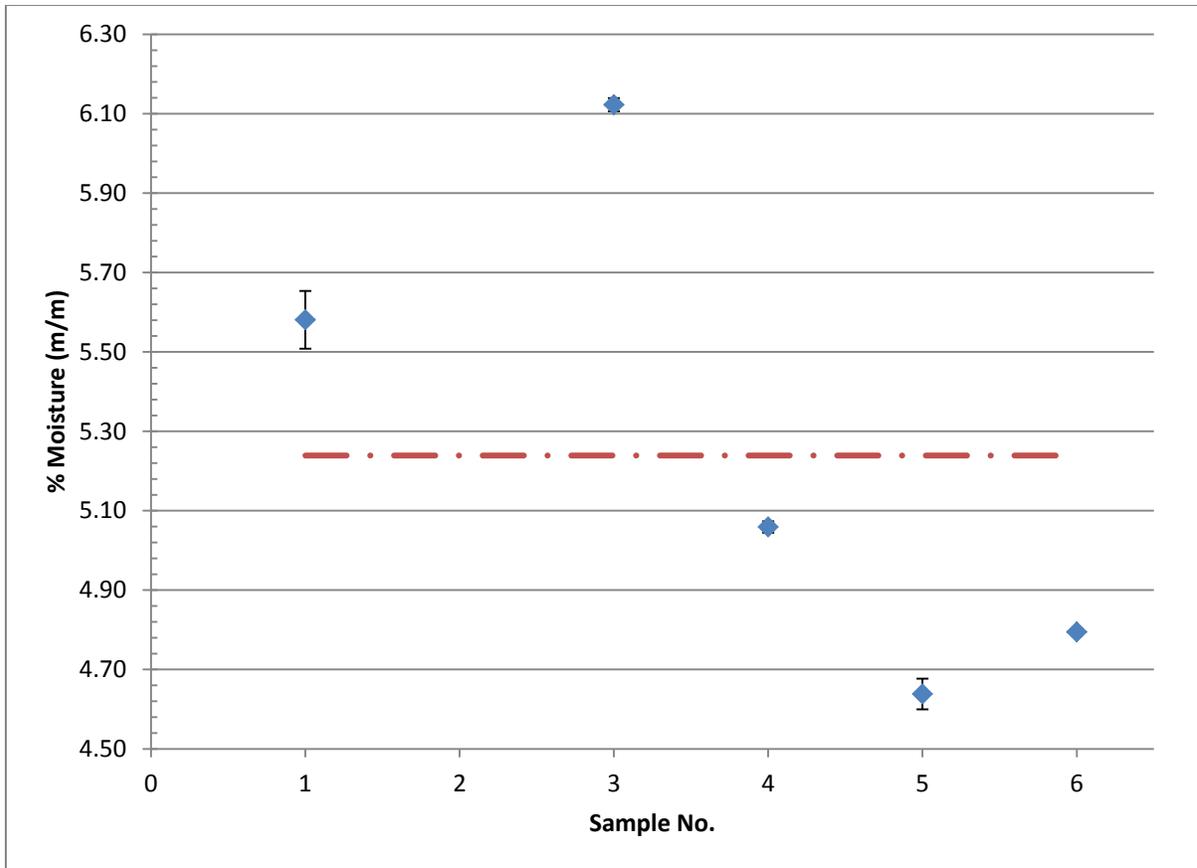
Charcoal slurries are directly affected by the physical characteristics of the charcoal and the liquid phase used to carry the charcoal particles. The charcoal slurries prepared during the course of this research utilized a commercially available B20 biodiesel blend. The physical properties of this

liquid fuel are well documented. Through the determination of the physical characteristics of the ground charcoal, one can predict the qualities of charcoal slurries prepared with the B20 biodiesel blend.

#### *4.2.3.1 Moisture*

The moisture content of the ground yellow poplar charcoal was the first physical property quantified. The amount of moisture retained in the ground charcoal would affect the combustion characteristics of the charcoal particles. Energy would be consumed by the water molecules retained by the charcoal particles for phase change during combustion of the charcoal slurry.

The ground charcoal moisture was measured and calculated using an oven drying method presented previously. The moisture content was calculated using a dry-basis calculation and then converted to a wet-basis percentage. The wet-basis percentage has a potential range of 0 to 100%. The calculated moisture content for the ground yellow poplar charcoal is presented in figure 4.16.



**Figure 4.16** Wet-basis moisture percentage of ground yellow poplar charcoal

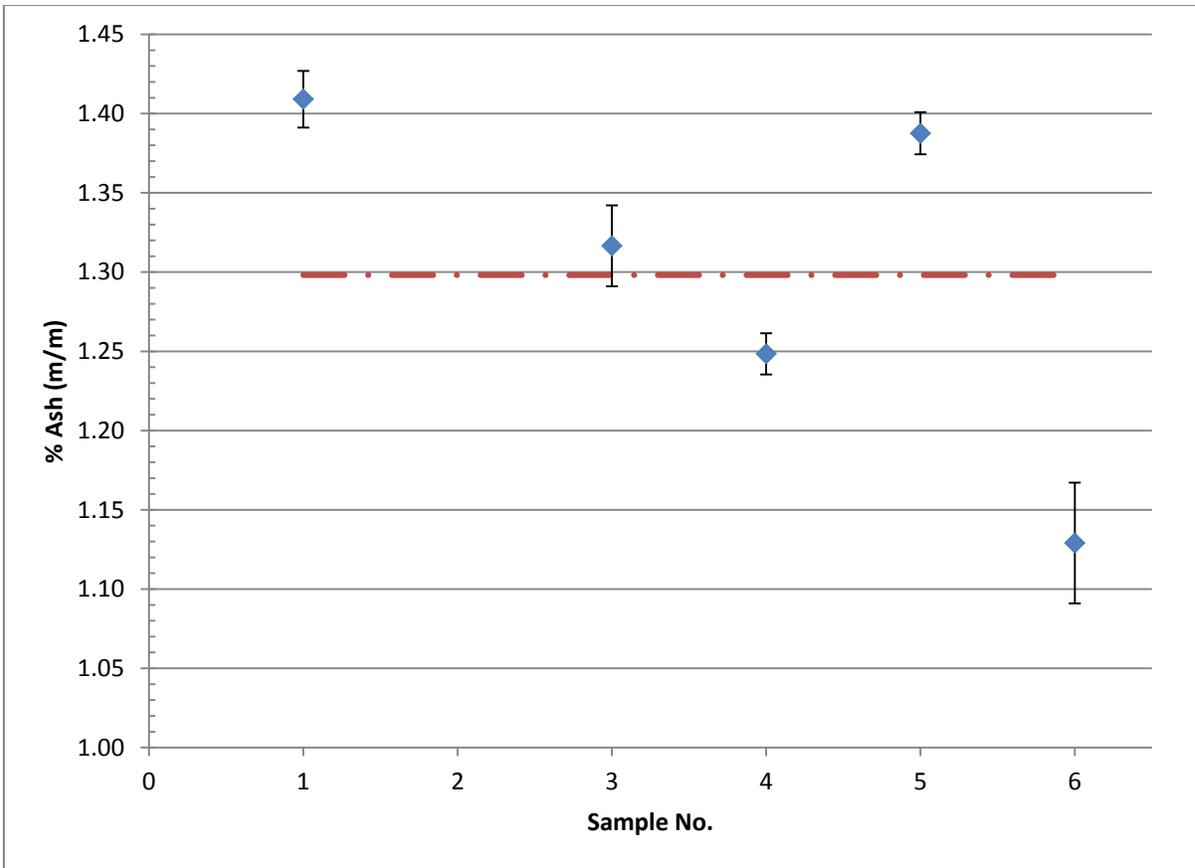
The moisture content of the ground yellow poplar charcoal averaged 5.24% (m/m) over all samples and replications. This mean is depicted by the dashed horizontal line in figure 4.16. The calculated standard error for each sample is shown by the error bars. Sample number two is left intentionally blank. The measurement of this sample was unavailable due to measurement issues. The first sample had the greatest variability between replications as supported by the standard error calculated for this

sample. Assuming a normal distribution for the entire population, a t-distribution was assumed for the sample population. Based upon a 95% confidence level, the wet-basis moisture content mean for the yellow poplar charcoal used in this research will fall within the range of 4.48% (m/m) to 6.00% (m/m) moisture content on a wet-basis or  $5.24 \pm 0.76\%$  (m/m).

#### *4.2.3.2 Ash*

The ash content of the charcoal directly affects the amount of ash present in the charcoal slurry. The closer to zero the percentage of ash present in the prepared charcoal slurry, the higher quality the fuel. Internal combustion engines require that the liquid fuel used is very low in ash content. The close tolerances between internal mechanisms necessary for operation cannot afford the erosion created by a fuel source high in ash. High combustion temperatures can cause slagging of certain ash materials as mentioned previously.

The ash content percentage for the ground yellow poplar charcoal was quantified by combusting the ground charcoal particles in a muffle furnace until all combustible material had been consumed. The method for this analysis was presented in the previous chapter. The ash content percentage was calculated using the oven-dry mass of the ground charcoal and presented in figure 4.17 for each sample.



**Figure 4.17** Ash percentage by mass of ground yellow poplar charcoal

The average ash content over all of the samples and replications was 1.30% (m/m) as depicted by the dashed line in figure 4.17. The standard error calculated for each sample is depicted by the error bars. The fifth sample had the highest variance among the sample replications measured as shown by the largest standard error. Again, the second sample was unavailable for this analysis and was intentionally left blank in figure 4.17. Assuming a normal distribution for the overall population, a t-distribution

was used to describe the sample population. Based upon a 95% confidence level, the mean ash content for the ground yellow poplar charcoal analyzed will lie within the range of 1.16% (m/m) to 1.44% (m/m) ash content or  $1.30 \pm 0.14\%$  (m/m).

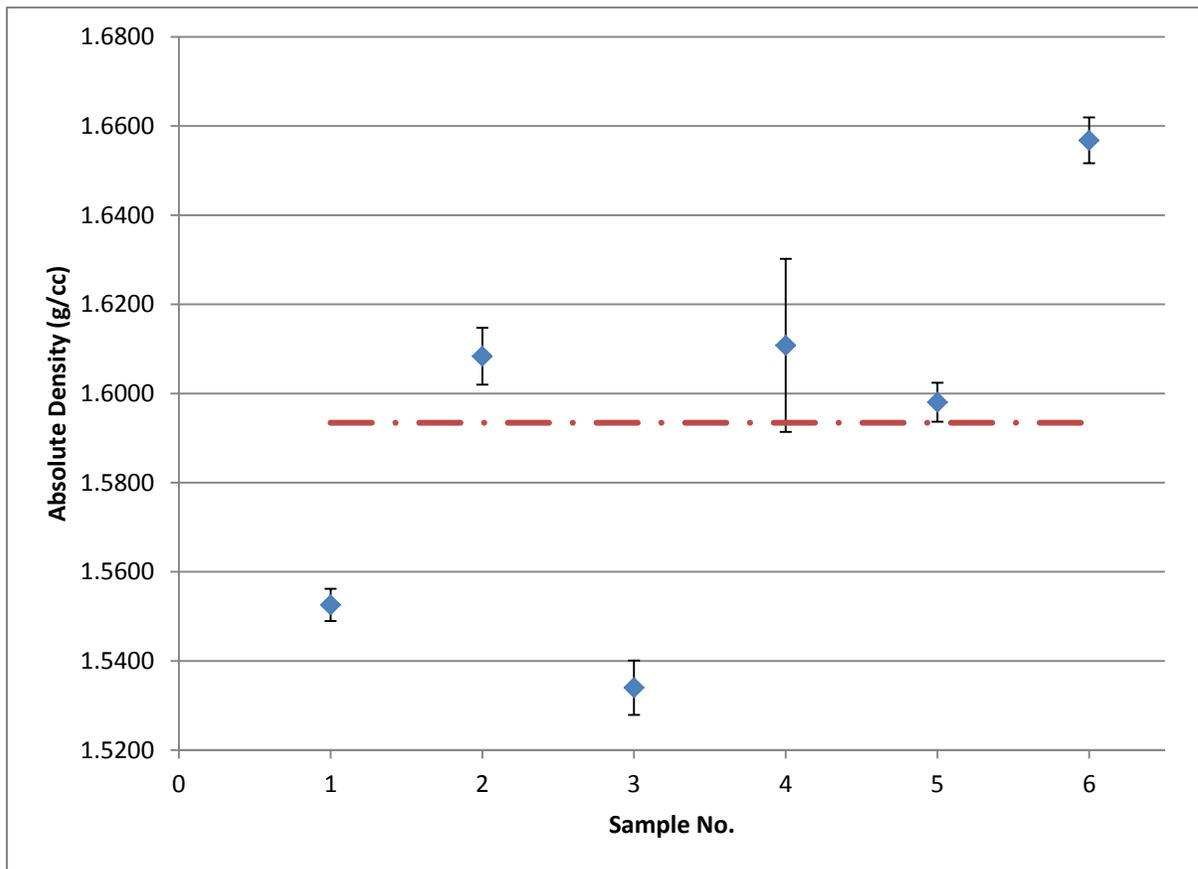
#### *4.2.3.3 Density*

Most liquid fuels are measured on a volumetric basis. Energy density in liquid fuels is based upon the amount of energy per unit volume. Solid fuels are based upon mass. When using a solid fuel such as charcoal in a liquid suspension, the energy density of the liquid fuel slurry is directly affected by the volume of liquid fuel replaced by the solid fuel. The density of the solid fuel is necessary to calculate the volume displaced by adding a solid particle such as charcoal to a liquid fuel. The energy density (energy per unit volume) for the charcoal slurry can then be calculated and compared to energy density for existing liquid fuels.

The density of a material composed of many smaller particles can be calculated in many ways. The bulk density includes the pore space between each particle in the overall material volume. This value can vary depending on how the material is handled. The absolute density includes only the cumulative volume of the solid particles. Since the particles will be

dispersed throughout the liquid fuel, the absolute density is the most appropriate measure.

The absolute density of the ground yellow poplar charcoal was quantified using a helium pycnometer to measure the volume of the solid particles for a known sample mass. Data were collected using the method discussed in the previous chapter. The absolute density of the ground charcoal is presented by sample in figure 4.18.



**Figure 4.18** Absolute density of ground charcoal

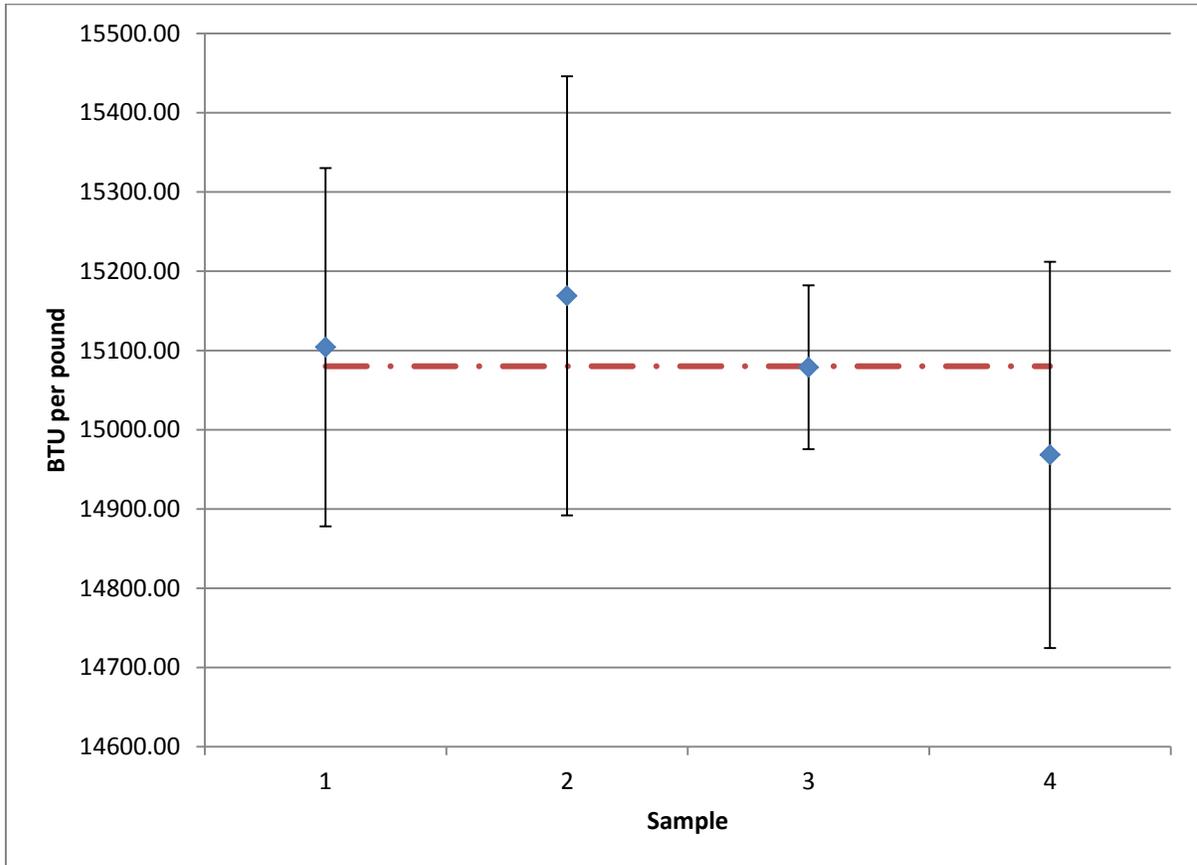
The mean density calculated for all of the samples and replications was 1.59 g/cc. The overall sample mean is depicted by a dashed horizontal line in figure 4.18. The standard error calculated for each sample is depicted by the error bars. The fourth sample exhibited the greatest variance among its sample replications as represented by the largest standard error calculated for all the samples. Assuming a normal distribution for the overall population, the sample population was described through the use of a t-distribution. Based upon a 95% confidence level, the mean absolute density of the ground poplar charcoal used in this research would fall within the range of 1.54 g/cc to 1.64 g/cc or  $1.59 \pm 0.05$  g/cc. Using this absolute density, the mass of ground charcoal can be converted to determine the displacement volume of liquid fuel in the charcoal slurry.

#### *4.2.3.4 Energy Content*

The purpose of any combustion system is the conversion of chemical energy stored in a fuel source to another usable form. The energy density of a fuel source is determined by the amount of energy contained per unit quantity. For solid fuel sources, the energy content is typically calculated based upon a per unit mass basis.

The energy content per unit mass for the ground poplar charcoal was quantified using a bomb calorimeter. Data were collected using the method

discussed in the previous chapter. The energy content of ground charcoal was calculated and presented in figure 4.19.



**Figure 4.19** Calorific values for yellow poplar charcoal samples

The overall mean calorific value for the samples measured is represented by the horizontal dashed line with a value of 35,076 kJ/kg (15,080 BTU/lb). Samples 1, 2 and 4 all have similar variance among their respective replications as represented by the similarity in the standard error

calculated for each of these samples. Assuming a normal distribution for the overall population, a t-distribution was used to approximate the sample population. Based upon a 95% confidence interval, the mean energy content for the ground poplar charcoal used in this research will lie within the range of 34,767 kJ/kg (14,947 BTU/lb) to 35,385 kJ/kg (15,213 BTU/lb) or  $35,076 \text{ kJ/kg} \pm (15,080 \pm 309 \text{ BTU/lb})$ .

## **5. CONCLUSIONS**

This research focused on the development of a charcoal slurry for fueling compression-ignition IC engines. The slurry was produced through the addition of ground charcoal particles to a commercially available B20 biodiesel blend. Several research questions were identified previously and experiments were developed to address these questions.

A multi-step milling process was developed using two different charcoal sources as the input feedstock. Charcoal pieces were ground using a combination of a lab scale Wiley mill and a burr mill. The ground charcoal was then processed through a custom-built ball mill. The resulting ground charcoal was then analyzed to determine if the milling process was able to successfully generate micronized charcoal particles.

The success of the milling process was quantified using several different testing methods. The ground charcoal particles were sieved and weighed to determine the general distribution of particles. Also a laser diffraction system measured the exact distribution of ground charcoal particle sizes. All of these methods supported the conclusion that micronized charcoal particles can be generated from even large charcoal pieces with relative ease.

A scanning electron microscope was used to magnify the ground charcoal particles to provide insight into the charcoal particle shape and

structure. Images were captured of ground charcoal samples under a 400X magnification. The shape and structure of the ground charcoal particles observed in the imagery could be categorized into two categories.

Particles that were larger than 50 microns exhibited a visible porous structure with many long, narrow pores. Much of this structure can be attributed to the anatomy of the parent biomass. The cellular structure of wood is composed of elongated tracheid cells in softwoods or fibre cells in hardwoods (Gibson 2012). The porous structure was produced by the remaining walls of these elongated cells after the wood was converted to charcoal. Since the larger ground charcoal particles were composed of long empty cells, these larger ground charcoal particles tended to have long cylindrical shapes with aspect ratios of 0.5 and less. The elongated shape of these larger particles posed an issue for some methods used to mechanically size the particles such as sieving. With the correct orientation, these larger particles could pass through a sieve screen designed to retain particles half the size.

The porous structure was less evident for the particles less than 50 microns. These smaller particles were more irregularly shaped with aspect ratios close to unity. One can conclude that this change in structure was directly related to the size of the elongated cells within the porous structure. Once particles were less than 50 microns, they only contained a portion of

the long carbonized cell wall that composed the overall porous structure of the charcoal piece before milling.

Engine wear was a major issue with coal slurries in the literature. Piston rings and injector orifices were the two major wear parts while running on a coal slurry. The majority of the orifice wear was created by the impingement of coal particles upon the injector seat during injection events. The combination of silicate ashes in the coal particle and the overall hardness of the coal structure, allowed the coal particles to slowly wear away the metal injector seat. Piston ring wear was a result of slurry impingement on the cylinder walls. This impingement trapped coal particles in the oil film, allowing coal particles to enter the close tolerances between the piston rings and cylinder. Charcoal, from a structural standpoint, would be much more brittle and would tend to fail under stress from a much harder material like the steel found in engine internal parts. This property of wood charcoal would decrease the wear caused by contact with engine parts when compared to coal.

The ash content of a fuel used by IC engines is important for the overall longevity of the engines. The amount of ash present in the final slurry must be minimized to not increase engine wear beyond what is considered acceptable. The charcoal used in this research was analyzed to determine the amount and types of ash present. Through the use of an

energy-dispersive X-ray spectrometer, the measured elemental ash consisted of silicon, potassium and calcium for the wood chip charcoal. Of these elements, the silicon would be the hardest ash to remove. The percentage of silicon present in the overall ash content for the charcoal was considerably less than what was found in coal used for slurry fuels in the literature. The lower percentage of silicates would reduce the amount of wear caused by to engine and fuel system parts. The potassium and calcium ash can be converted to molecular forms that are water soluble and easily removed by flushing the ground charcoal with water as discussed in the previous section. Further research would be required to determine the best method for removing the water soluble ashes and also if the overall process would be economical and energy efficient. The ash content measured for the yellow poplar charcoal averaged 1.30% which was significantly lower than the ash found in coal. With proper handling and cleaning, one could produce micronized charcoal with less than 1% ash content by mass. One could generalize that overall engine wear due to ash alone should be much less than what was found for coal slurries in the literature, but quantitative studies would be necessary for definitive results. Such a study was beyond the scope of this research.

The viscosity of a charcoal slurry prepared from the ground charcoal particles and a biodiesel blend was compared to commercial diesel fuel.

Although the viscometer used in this analysis was unable to provide accurate enough results to determine actual viscosity values, a comparison between the two fuels could still be made using known facts about diesel fuel from the literature. The charcoal slurry was consistently more viscous than the diesel fuel, but both fuels reacted similarly to changes in shear rate.

One of the most pressing questions of this research was: “Does the addition of charcoal particles improve the energy density of the liquid fuel?”. Since the addition of a single charcoal particle to a liquid fuel displaces a volume of liquid fuel equal to the volume of the charcoal particle, the energy content of the charcoal particle must be greater than the liquid fuel to improve the overall energy density from a theoretical standpoint. Empirically, the energy contained within a liquid fuel is never fully extracted by a combustion system. The combination of different fuel types can lead to synergism between the two fuels which could result in a higher combustion efficiency than each could achieve separately. The theoretical energy values for no. 2 diesel fuel, biodiesel, charcoal and the 25% (v/v) charcoal slurry can be found in table 5.1.

**Table 5.1** Theoretical energy values (Higher Heating Value) for fuels used in this research

<b>Property</b>	<b>No. 2 Diesel Fuel</b>	<b>Biodiesel</b>	<b>Charcoal</b>	<b>Charcoal Slurry 25%(v/v)</b>
<b>Energy Content (BTU per gallon)</b>	137,380(b)	127,960(b)	200,564(a)	151,763(a)
<b>Density (lb/gal)</b>	6.98(a)	7.41(a)	13.3	8.62(a)
<b>Energy Content (BTU per pound)</b>	19,673(b)	17,266(b)	15,080	17,597(a)

(a) Calculated values

(b) Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model, version 1.7. 2007. Input Fuel Specifications. Argonne National Laboratory. Chicago, IL

The energy content per unit volume is the metric by which energy density in liquid fuels is measured. Although the energy content per unit mass is much lower for the charcoal when compared to the liquid fuels, the energy content per unit absolute volume is much higher due to the charcoal's greater density. The displacement of liquid fuel with an equal volume of charcoal would increase the overall energy content per unit volume.

One of the drawbacks of replacing no. 2 diesel fuel with biodiesel is the lower energy density of biodiesel. Almost 7.5% more biodiesel must be consumed to generate the same amount of energy as no. 2 diesel fuel. Using 100% biodiesel as the basis for a slurry, a portion of the biodiesel could be displaced by micronized charcoal particles. A fully renewable

biodiesel-charcoal slurry could be produced with the same energy density as no. 2 diesel fuel. Using the energy data from table 5.1, displacing 13% (v/v) of the volume of biodiesel with micronized charcoal would produce a charcoal slurry with an energy content per unit volume equivalent to no. 2 diesel fuel. Even if a very conservative value for both the measured energy content and density of the charcoal was used (34,767 kJ/kg and 1.54 g/cc), only 15% (v/v) of the biodiesel would need to be replaced by micronized charcoal to create a slurry equivalent to the energy density of no. 2 diesel fuel.

A charcoal biodiesel slurry has potential to be a completely renewable liquid fuel replacement for no. 2 diesel fuel. This research has shown that charcoal slurries can be successfully produced on the laboratory scale and have the potential to be an energy dense liquid fuel. There are several future research areas that can be conducted to determine the commercial viability of a charcoal biodiesel slurry. Emissions could be analyzed and compared to no. 2 diesel fuel during combustion. The long term suspension of charcoal particles in biodiesel should be explored. Also the economic and energy costs of producing a charcoal slurry fuel should be analyzed for viability.

## REFERENCES

- Beck, D. E. 1990. *Liriodendron tulipifera* L., yellow-poplar. In *Silvics of North America, Volume 2, Hardwoods*. Agriculture Handbook 654, 406-416. R. M. Burns and B. H. Honkala, eds. Washington, D.C.: USDA-Forest Service.
- Boshui, C., S. Yuqiu, F. Jianhua, W. Jiu, and W. Jiang. 2010. Low-temperature properties of biodiesel: rheological behavior and crystallization morphology. *China Petroleum Processing and Petrochemical Technology*. 12(1): 29-33.
- Caton, J. A., and B. D. Hsu. 1994. The General Electric coal-fueled diesel engine program (1982-1993): a technical review. *Journal of Engineering for Gas Turbines and Power* 116(4): 749-757, doi: 10.1115/1.2906882.
- Diesel, R. 1892. Arbeitsverfahren und ausföhrungsart für verbrennungsmaschinen. German Patent No. RP67207 (in German).
- Ellem, G. K., and C. J. Hsu. 2012. Biomass char as a fuel for internal combustion engines. *Asia-Pacific Journal of Chemical Engineering* 7(5): 769-776, doi: 10.1002/apj.636.
- Gibson, L. J. 2012. The hierarchical structure and mechanics of plant materials. *Journal of The Royal Society Interface* 9(76): 2749-2766, doi: 10.1098/rsif.2012.0341.

- Hsu, B. D. 1988. Progress on the investigation of coal-water slurry fuel combustion in a medium speed diesel engine: part 1—ignition studies. *Journal of Engineering for Gas Turbines and Power* 110(3): 415-422, doi: 10.1115/1.3240137.
- Hsu, B. D., and G. L. Confer. 1990. Coal-fueled diesel engine performance—fuels effect. In *Proc. 7th Annual Coal-Fueled Heat Engines and Gas Stream Cleanup Systems Contractors Review Meeting*, 262-271. Morgantown, WV: U.S. Department of Energy Morgantown Energy Technology Center
- Hsu, B. D., and G. L. Confer. 1991. Progress on the investigation of coal-water slurry fuel combustion in a medium speed diesel engine: part 4—fuels effect. In *Coal Fueled Diesel Engines*, 1-8. J. A. Canton and H. A. Webb, eds. ASME-ICE.
- Hsu, B. D., and P. L. Flynn. 1989. Preliminary study of using coal-water slurry fuel in GE-7FDL medium speed diesel engine. In *Proc. 18th International Congress on Combustion Engines*. Tianjin, China: CIMAC.
- Hsu, B. D., G. L. Confer, Z. J. Shen. 1992. Progress on the investigation of coal-water slurry fuel combustion in a medium-speed diesel engine: part 5—combustion studies. *Journal of Engineering for Gas Turbines and Power* 114(3): 515-521, doi: 10.1115/1.2906619.

- Lin, Y., and S. Tanaka. 2006. Ethanol fermentation from biomass resources: current state and prospects. *Applied Microbiology and Biotechnology* 69(6): 627-642, doi: 10.1007/s00253-005-0229-x.
- McMillian, M. H., and H. A. Webb. 1989. Coal-fueled diesels: systems development. *Journal of Engineering for Gas Turbines and Power* 111(3): 485-490, doi: 10.1115/1.3240279.
- N'kpomin, A., A. Boni, G. Antonini, and O. François. 1995. The deashed charcoal-oil-water mixture: a liquid fuel for biomass energetical valorization. *The Chemical Engineering Journal* 60: 49-54, doi: 10.1016/0923-0467(95)02986-9.
- Rao, A. K., R. P. Wilson, M. H. McMillian, J. A. Kimberley, E. N. Balles, and R. A. Mayville. 1989. Cooper-Bessemer coal-fueled engine system – progress report. *Journal of Engineering for Gas Turbines and Power* 111(3): 498-506, doi: 10.1115/1.3240281.
- Ryan, T. W. 1994. Coal-fueled diesel development: A technical review. *Journal of Engineering for Gas Turbines and Power* 116(4): 740-748, doi: 10.1115/1.2906881.
- Soehngen, E. E. 1976. The development of coal-burning diesel engines in Germany: a state-of-the-art review. Washington, D.C.: Energy Research and Development Administration.

Soloiu, V., J. Lewis, Y. Yoshihara, and K. Nishiwaki. 2011. Combustion characteristics of a charcoal slurry in a direct injection diesel engine and the impact on the injection system performance. *Energy* 36(7): 4353-4371, doi: 10.1016/j.energy.2011.04.006.

Urban, C. M., B. T. Jett, H. E. Mecredy, T. W. Ryan III, and M. N. Ingalls. 1988. Coal-water slurry operation in an EMD diesel engine. *Journal of Engineering for Gas Turbines and Power* 110(3): 437-443, doi: 10.1115/1.3240140.