

Production, Characterization, and Applications of Activated Carbon

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Master of Science

by

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The undersigned, appointed by the Dean of the Graduate School, have examined the thesis entitled

**PRODUCTION, CHARACTERIZATION, AND
APPLICATIONS OF ACTIVATED CARBON**

presented by Eric Paul Leimkuehler

a candidate for the degree of Master of Science

and hereby certify that in their opinion it is worthy of acceptance.

Dr. Galen Suppes

Dr. Peter Pfeifer

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Thesis Format

This thesis is a four chapter series detailing the production and characterization of activated carbon. The first chapter gives an introduction to the history, production processes, and applications of activated carbon. The second chapter introduces a production process used to generate activated carbons with proven characteristics and details a mass balance on this process. The third chapter explores variations on the process used in the second chapter and the use of screening methods to analyze different activated carbons produced using varying conditions and materials. The fourth chapter summarizes the conclusions made in the first three chapters and gives suggestions for future research. The first and fourth chapters are overview sections while the second and third chapters each have their own abstract, introduction, methods and materials, and results and discussion sections as well as figures and tables.

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Chapter 1: Introduction

1.1: Introduction and Definition

The following thesis investigates the production of activated carbon, an environmentally friendly adsorbent which is used in many industries. Activated carbon can be derived from many different sources and produced in varying production processes. The raw materials used, activation process, and process parameters determine the physical properties and performance characteristics of the resulting carbon. Modifying these activation properties determines the porosity and pore volume distribution in the carbon. The goal of this thesis is to detail a mass balance on the production of activated carbon and develop quick screening methods to observe and compare the effects of different precursor materials, chemical reagents, and process variables on this production process.

Activated carbon is defined as a carbonaceous material with a large internal surface area and highly developed porous structure resulting from the processing of raw materials under high temperature reactions. It is composed of 87% to 97% carbon but also contains other elements depending on the processing method used and raw material it is derived from. Activated carbon's porous structure allows it to adsorb materials from the liquid and gas phase.[1] Its pore volume typically ranges from 0.20 to 0.60 cm³/g, and has been found to be as large as 1 cm³/g. Its surface area ranges typically from 800 to 1500 m²/g [2] but has been found to be in excess of 3,000 m²/g. The surface area contains mostly micropores with pore diameters smaller than 2 nm.[3]

These favorable properties make activated carbon a popular adsorbent for many applications.

1.2: History of Activated Carbon and Present Day Applications

The useful properties of activated carbon have been known since ancient times. This traces back to 1500 BC when Egyptians used charcoal as an adsorbent for medicinal purposes and a purifying agent. Around 420 BC it was observed that Hippocrates dusted wounds with powdered charcoal to remove their odor. Ancient Hindu societies purified their water by filtration through charcoal. [2] In 1773, the Swedish chemist Karl Wilhelm Scheele was the first to observe adsorption of gases on charcoal. A few years later activated carbons began being used in the sugar industry as a decolorizing agent for syrup.

In the early 20th century the first plant to produce activated carbon industrially was built for use in sugar refining industry in Germany. Many other plants emerged in the early 1900's to make activated carbons primarily for decolorization. During World War I activated carbon was used in gas masks for protection against hazardous gases and vapors. Today, activated carbons are used to remove color from pharmaceutical and food products, as air pollution control devices for industrial and automobile exhaust, for chemical purification, and as electrodes in batteries. 500,000 tons per year of activated carbon are produced globally. [1] 80% of this is used for liquid phase applications, and 20% is used for solid phase applications. [2] This paper will focus on activated carbons

applications as a natural gas adsorbent with the intentions of using the stored natural gas as an alternative fuel to petroleum.

1.3: Activated Carbon Production Processes

The procedure for processing activated carbon typically consists of a carbonization followed by an activation of carbonaceous material from vegetable origin.

Carbonization is a heat treatment at 400-800°C which converts raw materials to carbon by minimizing the content of volatile matter and increasing the carbon content of the material. This increases the materials strength and creates an initial porous structure which is necessary if the carbon is to be activated.

Adjusting the conditions of carbonization can affect the final product significantly. An increased carbonization temperature increases reactivity, but at the same time decreases the volume of pores present. This decreased volume of pores is due to an increase in the condensation of the material at higher temperatures of carbonization which yields an increase in mechanical strength. Therefore, it becomes important to choose the correct process temperature based on the desired product of carbonization.[1]

After the initial porous structure has been created by carbonization, an oxidation, referred to as activation, is carried out in order to create micropores. [3] Typically, these micropores have a width of less than 2 nanometers and are the pores where the majority of adsorption occurs. Activation can be carried out as activation by oxidizing gases or a chemical activation.

In activation by oxidizing gases, such as steam activation, carbon reacts with the oxidizing agent producing oxides of carbon. These oxides diffuse out of the carbon resulting in a partial gasification which opens pores that were previous closed and further develops the carbons internal porous structure.

In chemical activation, the carbon is reacted at high temperatures with a dehydrating agent that eliminates the majority of hydrogen and oxygen from the carbon structure. Chemical activation often combines the carbonization and activation step, but these two steps may still occur separately depending on the process. [1] High surface areas in excess of 3,000 m²/g have been found when using KOH as a chemical activating agent. [3]

A significant amount of carbon mass loss occurs during the activation which generally correlates to an increase in porosity. Therefore, quick estimates of porosity can be made by a gravimetric measurement. These gravimetric measurements can be used to compare carbons made using different process parameters and raw materials. [1]

1.4: Activated Carbon from Different Raw Materials

In addition to being an adsorbent used for many different purposes, activated carbon can be produced from a wealth of different raw materials, making it an incredibly versatile product that can be produced in many different areas depending on what raw material is available. Some of these materials include shells of plants, the stones of fruits, woody materials, asphalt, metal carbides, carbon blacks, scrap waste deposits from sewage, and polymer scraps. Different types of coal, which already exist in a

carbonaceous form with a developed pore structure, can be further processed to create activated carbon.

Although activated carbon can be produced from almost any raw material, it is most cost effective and environmentally conscious to produce activated carbon from waste materials. Activated carbons produced from coconut shells have been shown to have high volumes of micropores, making them the most commonly used raw material for applications where high adsorption capacity is needed. Sawdust and other woody scrap materials also contain strongly developed microporous structures which are good for adsorption from the gas phase. Producing activated carbon from olive, plum, apricot, and peach stones yields highly homogenous adsorbents with significant hardness, resistance to abrasion and high micropore volume. PVC scrap can be activated if HCl is removed beforehand, and results in an activated carbon which is a good adsorbent for methylene blue. Activated carbons have even been produced from tire scrap.

In order to distinguish between the wide range of possible precursors, it becomes necessary to evaluate the resulting physical properties after activation. When choosing a precursor the following properties are of importance: specific surface area of the pores, pore volume and pore volume distribution, composition and size of granules, and chemical structure/character of the carbon surface. [1]

Choosing the correct precursor for the right application is very important because variation of precursor materials allows for controlling the carbons pore structure.

Different precursors contain varying amounts of macropores (> 50 nm,) which

determine their reactivity. These macropores are not effective for adsorption, but their presence allows more channels for creation of micropores during activation.

Additionally, the macropores provide more paths for adsorbate molecules to reach the micropores during adsorption. [3] Precursors which contain a greater amount of volatile substances yield a proportional increase in the reactivity of the activated substance. If the reactivity is too high, the degree of activation can be lowered. Achieving the correct amount of reactivity is of the utmost importance, since the extent of reaction occurring determines the carbon's internal structure. [1]

1.5: Analysis of the Petroleum Industry and its Flaws

As mentioned before, this work focuses on using activated carbon to store natural gas. This research is being conducted with the intent of making the use of natural gas more cost-effective as an alternative fuel to petroleum. Petroleum has historically been the most popular source of energy due to its high energy content and cheap price. Modern society is heavily dependent on oil and would most likely collapse if a sudden mass oil shortage occurred. [4] Gasoline accounts for about 17% of the energy consumed in the U.S., and is delivered from oil refineries through pipelines to a massive distribution chain serving 176,000 retail gas outlets, making the U.S. highly dependent on this infrastructure.

On top of the dangerous fact that the world is highly dependent on the petroleum industry, there are also several negative factors. To start, 31% of the world's oil is produced in the Middle East, which is an incredibly unstable area. This is a very large

amount compared to the U.S., which only produces 9% while consuming 25.6% of the world's oil. A diplomatic issue between the U.S. and the Middle East could cause a shortage of oil which would be catastrophic to the U.S. economy.

Oil also has many negative effects on the environment. The combustion of oil produces carbon monoxide, oxides of sulfur, and oxides of nitrogen which are harmful to humans and nature. In addition, the production of oil emits smog, carbon dioxide, ozone, methane, and nitrous oxides. Oil based carbon dioxides emissions count for slightly less than one half of the world total. Emissions from oil are roughly equivalent to those from coal and natural gas added together. 3,297 Million Metric Tons of carbon equivalent are emitted from burning oil compared to 2,507 from coal and 1,512 from natural gas.

Land based oil exploration, refining, and transportation causes damage to wildlife preserves and interferes with animal migration routes in addition to releasing a large amount of atmospheric emissions and creating extra amounts of work to rehabilitate land after mining or pipe laying. One fourth of world production of oil is from offshore fields. Large scale spills from oil tankers are a giant problem and are devastating to the environment. [5] In the year 2006 it was estimated that the present worldwide oil reserves contain about 1200 billion barrels of oil, and 900 billion barrels have been consumed to date.

It is estimated that the world is forming about 7,000 barrels of oil per year, but 30 billion barrels per year are being consumed. From these calculations, the world only has 40.6

years left of oil supply. Combining this fact with all the other negative factors, it seems obvious that alternatives to petroleum need to be pursued. [4]

1.6: The Natural Gas Industry, a Viable Alternative

One of the most readily available alternatives to petroleum is natural gas. Natural gas is composed of mostly methane (70-90 %), but also ethane (5-15%), and propane/butane (<5%). [4] Three major types of natural gas are associated gas, non-associated gas, and synthetic gas. Natural gas derived from organic matter by thermal degradation and natural degasification of coal deposited at great depths of the earth at high temperatures is referred to as non-associated gas, while natural gas occurring in association with oil reserves is deemed associated gas. Synthetic Natural gas is derived from processing of coal.

Natural gas burns cleaner and more efficiently than coal or oil and is almost free of harmful contaminants, making it an environmentally friendly alternative which contributes less to air pollution. Additionally, known reserves of natural gas are well distributed across the world, so being overly dependent on one area is not an issue. The U.S. accounts for 22.9% of the world's production of natural gas(while consuming 27.2%); the biggest producer is the former Soviet Union at 27.8%. [5]

The biggest problem with natural gas is that it has a lower energy density than oil. One liter of petroleum produces about 3.5×10^4 KJ of energy compared to 40 KJ of energy produced by natural gas upon combustion. Fortunately there are three options to enhance the energy density of natural gas: Liquefied Natural Gas (LNG), Compressed

Natural Gas (CNG) and Adsorbed Natural Gas (ANG). LNG has an energy density close to gasoline but is costly to produce. CNG must be compressed to 25 mPa or greater, which requires thick and heavy storage tanks. ANG is the most attractive option. It takes less energy to store and utilize AGN than CNG and LNG while maintaining a light weight and storage stability. [2]

1.7: Activated Carbon for the Adsorption of Natural Gas

Activated carbon's excellent gas adsorption properties make it a perfect candidate for ANG. Additionally, adsorption can occur at ambient temperatures and low pressures, so it is relatively safe. A storage vessel is filled with activated carbon and vacuumed to pressures around 6×10^{-2} Pa. Shortly after the vessel is completely evacuated, pressurized methane is introduced to the vessel causing physisorption to occur. [2] This physisorption is fully reversible and is driven by attractive dispersion forces. Most of the adsorption occurs in the micropores; the amount of adsorption in macropores is negligible. The micropores are tailored to have the correct dimensions to allow optimal methane storage while remaining large enough that adsorption is not limited. [2]

1.8: Previous Activated Carbon Research at the University of Missouri

At the University of Missouri activated carbon research is conducted under the ALL-CRAFT (Alliance for Collaborative research in Alternative Fuel Technology) project. The project is driven by a collaboration between the chemical engineering, physics, and chemistry departments, and also the MU research reactor (MURR.) After the initial

production process of activated carbon was developed, samples were pressed into monoliths and sent to Midwest Research Institute in Kansas City for testing as a natural gas adsorbent; a test tank was created and used to fuel a Ford F150 pickup.

The current focus of the ALL-CRAFT project is to increase the storage capacity of its activated carbons by doping the samples with boron and creating fission tracks on the carbons surface by neutron irradiation performed at MURR. Increased storage capacity is also being pursued by optimizing the production of activated carbon.

Chapter 2: Production of Activated Carbon from Corn Cobs; Mass Balance and Process Description

2.1: ABSTRACT

Highly nanoporous carbon with surface areas in excess of 3,000 m²/g were produced from the potassium hydroxide (KOH) activation of a high nominal surface area (700 m²/g) carbon intermediate. These materials have exhibited favorable methane and hydrogen storage capabilities with interest toward commercial production. In preparation for commercial production, detailed mass balances are needed to quantify yield, quantify the masses of waste streams, understand the propensity to recycle the KOH, and to provide a benchmark for further optimization. A mass balance on the reaction of phosphoric acid and KOH with carbon is detailed in this chapter.

2.2: INTRODUCTION

Activated carbon is a proven, high-performance material for a range of applications from water purification to catalyst supports. A key indicator of performance in many of these applications is the carbon's BET surface area as reported in m²/g. Surface areas of 300 m²/g are considered good for many materials. However, under the ALL-CRAFT (Alliance for Collaborative Research in Alternative Fuel Technology) project at the University of Missouri, BET surface areas in excess of 3,000 m²/g have been achieved (see Table 1)[6-7]. An activation temperature between 750°C and 800°C [8-9] and a

KOH:C ratio between 3 and 4 [10-11] have been shown to produce the highest surface area carbons.

Table 3: Sample BET measurements for ALL-CRAFT carbons. 3K Surface Area $\sigma=200$, 3K Porosity $\sigma=0.025$

Sample #	KOH Ratio	Process Temperature (°C)	Process Hold Time (hrs)	Specific Surface Area (m ² /g)	Porosity from Isotherm
1	0	480	1	1150	0.59
2	2	790	1	1880	0.69
3	3	790	1	2670	0.78
4	4	790	1	2600	0.81

A primary reason for the lack of commercialization of the higher surface area activated carbons is the increased complexity and costs of their synthesis. In particular, high surface areas often have low yields (kg of activated carbon divided by the kg of biomass feed stock). Also, the use of reagents like KOH can simultaneously increase reagent and waste disposal costs. Optimum methane storage occurs at activation temperatures ranging from 700°C to 800°C [12]. Storage capability also increases as BET surface area increases[13]. In addition, it has been shown that experimental methane delivery is maximized at a KOH:C ratio of 3:1 [14].

Carbon can be produced from a wide range of biomass and fossil fuels. Corncobs are the preferred feedstock for the ALL-CRAFT project because they are abundant in the Midwest, are composed mainly of woody resources, contain a low amount of minerals, and produce a carbon with high densities of 1-3 nm pores. Analysis from The

Anderson's Inc. (Maumee, OH) shows a 43.5% carbon content in corncob feedstock, which makes it a promising precursor for the production of nanoporous carbon. The corncobs also contain 48.4% oxygen, 7.9% Hydrogen, and 0.21% Nitrogen. If it is assumed that half the oxygen leaves as water and the other half as carbon dioxide, a theoretical yield of 43.5% should be obtainable from pyrolysis of the corncobs[7].

As stated in chapter 1, the properties of activated carbon can vary depending on the initial carbon source as well as the method of activation. In this study, activated carbon is produced from corncob feedstock in two chemical activation steps: a phosphoric acid carbonization, deemed charring, and KOH activation. Figure 1 summarizes this process, which will be referred to as the ALL-CRAFT synthesis process in this study.

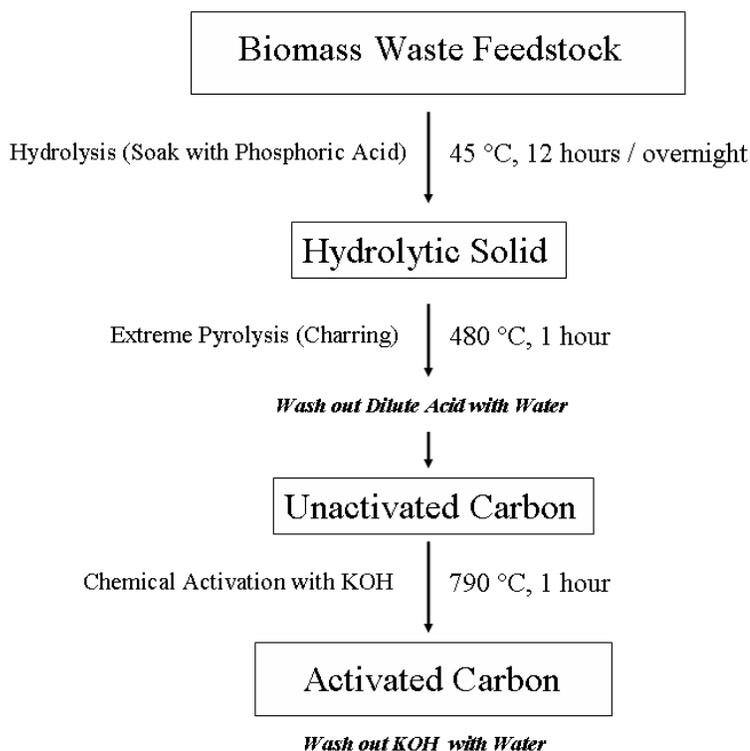


Figure 1: Summary of ALL-CRAFT Activated Carbon Production Process

During phosphoric acid carbonization, the carbon is pyrolyzed at 480°C after being soaked in phosphoric acid. The acid soak hydrolyzes carbohydrate components in the system making them water soluble and isolates the carbon containing components. Pyrolyzing the hydrolytic solid leaves only carbon and water soluble components. These products are washed to eliminate all water soluble and non-carbon constituents and isolate the carbon [15-16]. BET surface area measurements of up to 1350 m²/g have been reported for carbons which have undergone phosphoric acid carbonization [15, 17-18].

During the KOH activation at higher temperatures (700-800 °C) KOH is believed to penetrate the carbon and exfoliate the carbon matrix into groupings of graphene layers. For the mass balance in this study, an activation temperature of 790°C and a KOH:C ratio of 3:1 will be used, since carbons activated at these conditions have shown the most favorable characteristics for adsorption. [7]

The chemical activation can be described by these two reactions [19]



Similar reaction mechanisms have been proposed by Tay et al. [20] and Lillo-Rodenas et al. [21]

After the activation process, the KOH is washed from the crevices creating spaces suitable for gas adsorption. For $y = 2$ and $x = 2$ (carbon dioxide), the equations 1 and 2 reaction scheme consumes three moles of carbon (MW=12) for each six moles of KOH

(MW =56). This suggests a mass ratio of 1:9.3 for carbon dioxide formation and 1:4.7 for carbon monoxide formation

2.3: EXPERIMENTAL

2.3.1: Materials and Equipment

Corncob feedstock (14 mesh) was obtained from The Andersons' Inc. (Maumee, Ohio). This material is from the middle pith layer of the corncob. Phosphoric acid (85%) was obtained from Fisher Scientific. KOH (>90%) was obtained from Sigma Aldrich. Nitrogen (99.99%) and methane were supplied by PraxAir Inc. Samples were ball-milled using a United Nuclear Ball Mill. A 750 series model 126 Isotemp Programmable Muffle furnace obtained from Fischer Scientific was used for charring and large scale activation. A model FD1545M Furnace from ThermoScientific was used to perform the activation for small scale samples. A nitrogen purge was directed at the reactor in the oven with a purge rate of 5 L/min and adequate ventilation. 8 quart stainless steel reactors obtained from Cole Parmer were used for charring and large scale activation. 50 mL Aluminum Oxide Crucibles from Cole Parmer were used to perform activation for small scale samples. Carbon washing was carried out on in a Buchner Funnel.

2.3.2: Sample Preparation

The activated carbon was synthesized using the process of Figure 1 with details as follows: A phosphoric acid/ water mixture was prepared in the ratio 63:37 phosphoric acid: water. This mixture was mixed thoroughly in a 40/60 ratio with corncob feedstock and allowed to undergo hydrolysis overnight at 45 degrees Celsius. The hydrolytic solid

was pyrolyzed at 350°C for half an hour followed by 480 °C for one hour to produce carbon char. The resulting char was then washed with distilled water. Similar phosphoric acid processes were employed in [18] and [15] The char stock was kept in a vacuum oven at 140 °C to ensure that it did not adsorb moisture from the air. The char/chemical activating agent mixture was prepared to fill roughly 15 percent of the stainless steel reactor by volume. For large scale activation conducted to obtain the mass balance, the activating agent was added to the char in a 3:1 char: activating agent ratio (this is referred to as 3K.) The resulting mixture was mixed in the stainless steel reactor with a mass of distilled water less than or equal to the mass of the carbon char until a paste like mixture was formed. The reactor was then placed in the high temperature furnace and heated using the single setpoint mode. The samples were kept in the furnace for a process hold time of 1 hour at a process temperature of 790°C. A similar KOH activation process was used in [22]. The activated mixtures were transferred to and washed in a Buchner funnel in order to remove the potassium from the carbon. Each sample was washed with 14 L of tap water with a 0.15% concentration of formic acid followed by 14 L of tap water. The carbon was then kept in a vacuum oven overnight at 140 °C to dry. After the carbon was dried its mass was measured to determine the process yield. For the parametric study used to determine process standard deviations, one gram of char was used for each sample. The activating agent was then added to the carbon (in a ratio of 2:1, 3:1, or 4:1 by mass (2K, 3K, 4K)) and ball milled for 2.5 hours. Each individual ball milled sample was added to a 50 mL alumina crucible and placed in a small high temperature oven using the single setpoint mode.

Each small scale sample was washed in a Buchner funnel with 200 mL of tap water with a 0.15% concentration of formic acid followed by 100 mL of tap water. Parameters of investigation included the ratio of activating agent to carbon, activation temperature, and activation time. The charring step (carbonization) was the same for both large scale and small scale activation.

2.4: RESULTS

Table 4: Large Scale Mass Balance on ALL-CRAFT Activated Carbon Process: 3K Ratio, 790°C Process Temperature, 1 hour Process Hold Time

Mass Corncob Feedstock	751 g
Mass Carbon Char After Phosphoric Acid Carbonization, Washing, Drying	447 g
Yield in Phosphoric Acid Carbonization (Corncob to Char)	59.6%
Mass Carbon Char Used in KOH Activation	437 g
Mass 3K Carbon after KOH Activation, Washing, Drying	140 g
Carbon Yield in KOH Activation (Char to 3K Carbon)	31.9%
Overall Process Yield (Corncob to 3K Carbon)	18.6%

Table 2 shows a mass balance on the ALL-CRAFT process for producing activated carbon from corncobs (see figure 1 for block flow diagram.) A 40.4 % mass loss (59.6% yield) is observed in the phosphoric acid carbonization. Similar phosphoric acid carbonization yields were achieved in [17] and [15]. A 68.1 % overall carbon mass loss is observed in the KOH activation, while an 11.1% sample mass loss was observed in the activation reaction. Figures 2-5 show the results of the parametric study conducted to determine process standard deviations. Each point represents the average of four carbon samples.

The significance of these temperature and KOH: C ratio trends will be discussed further in chapter 3.

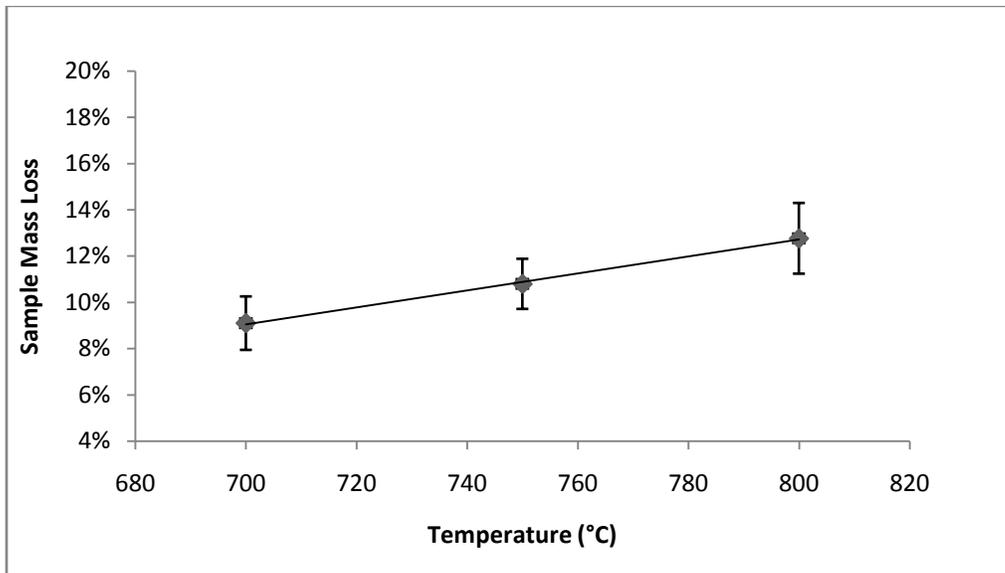


Figure 2: Percent Sample Mass Loss in 3K Carbon Activation as a function of Activation Temperature

Figure 2 shows sample mass loss increasing with increasing temperature. This indicates that more intense reactions occur at higher temperatures. At 700, 750, and 800 °C the standard deviations are ± 1.53 , 1.08 , and 1.16 % respectively.

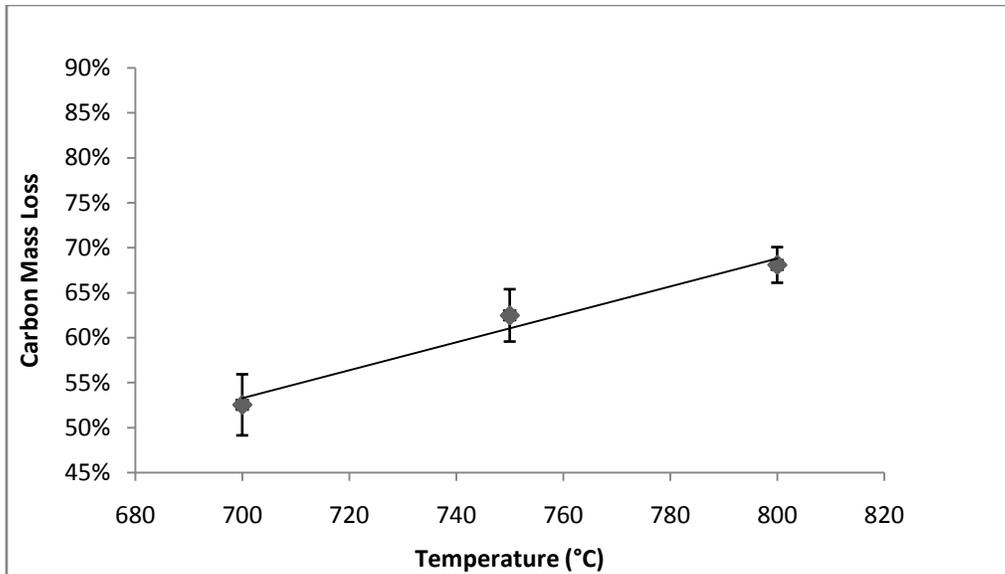


Figure 3: Percent Carbon Mass Loss in 3K Carbon Activation as a Function of Activation Temperature

At varying temperatures, the standard deviations for the percent mass loss of carbon at 700, 750, and 800 °C are as follows: ± 1.98 , 2.91, and 3.40 % respectively. Figure 4 shows the percent sample mass loss at varying KOH:C ratios. For 2K, 3K, and 4K the standard deviations are ± 1.22 , 1.38, and 2.08%.

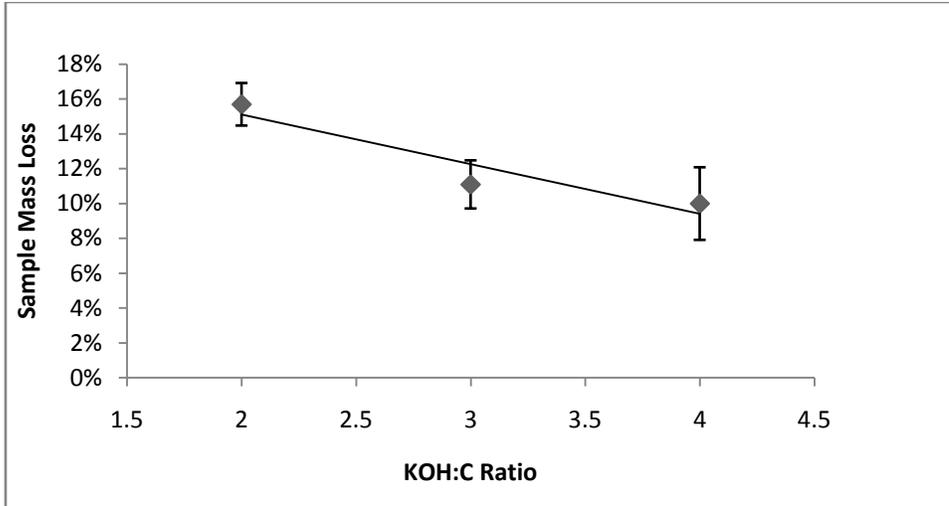


Figure 4: Percent Sample Mass Loss in KOH Activation at 790°C at Different KOH:C Ratios

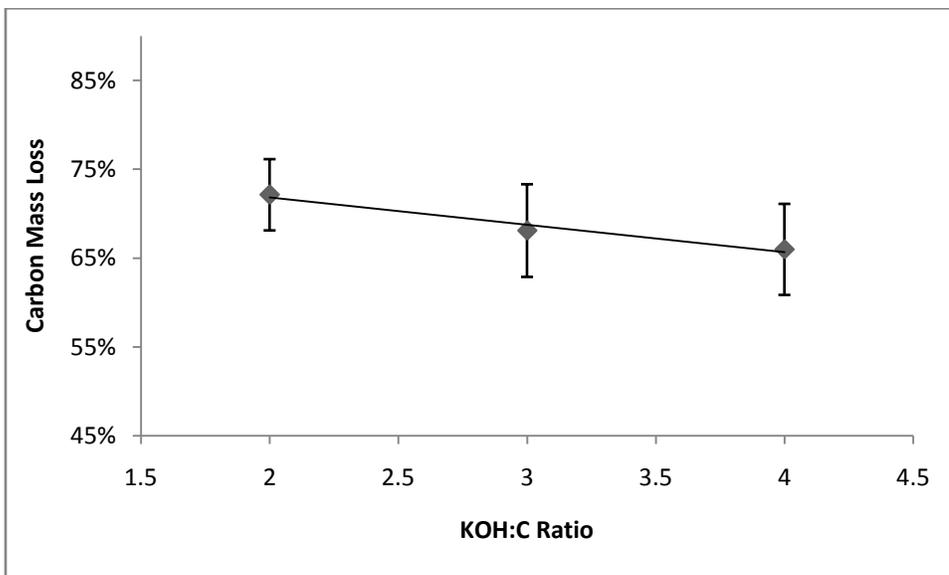


Figure 5: Percent Carbon Mass Loss in KOH Activation at 790°C at Different KOH:C Ratios

The standard deviations for the total carbon mass loss at 790°C for 2K, 3K, and 4K carbon are ± 4.01 , 5.22 , and 5.13 %. The standard deviations for different process temperatures and different KOH: C ratios can be averaged to determine a typical standard deviation for the carbon production process.

2.5: DISCUSSION

The phosphoric acid carbonization had a process yield of 59.6%, which is analogous to a 40.4% mass loss. This accounts for any volatile substances that were present in the precursor before activation. Table 3 shows an elemental analysis of the char.

Table 5: Elemental Analysis of Char

Element	Wt. % in Char
Carbon	72.2
Hydrogen	1.69
Nitrogen	1.04
Oxygen	21.5
Sodium	1.03
Potassium	0.55
Phosphorus	2.47

From the composition of corncobs given earlier, the initial 751 grams of corncob feedstock theoretically contains 326 g carbon, 363 g oxygen, 59.3 g hydrogen, and 1.60 g nitrogen. After phosphoric acid carbonization, the elemental analysis percentages show that the 447 grams of char 323 g carbon, 96.2 grams oxygen, 7.51 grams hydrogen, and 6.26 grams of nitrogen. In other words, 267 grams of oxygen were lost, 3.60 grams of carbon were lost, and 51.8 grams of hydrogen were lost. Adding these numbers together gives an estimated mass loss of around 323 grams, which is close to the 303 grams of mass loss experimentally. Table 4 provides a summary of these

results. These numbers are slightly off because the elemental analysis was conducted on a different batch of char, and every batch is slightly different. Nonetheless, these numbers support the claim that the majority of mass loss in the carbonization step is due to the loss of volatile components in the precursor such as hydrogen and oxygen. [1] The increase in mass of nitrogen is due to the nitrogen purge.

Table 6: Summary of Species Mass Loss Percentages in Phosphoric Acid Carbonization

Species	Mass Species Present Before Carbonization (g)	Mass Species Present After Carbonization (g)	Mass Loss of Species in Carbonization (%)
Carbon	327	323	1.08
Oxygen	363	96.2	73.5
Hydrogen	59.3	7.51	87.3

The 437 grams of carbon char used for activation contained 316 g carbon, 7.39 g hydrogen, and 93.9 g hydrogen. The 68.1% overall carbon mass loss is due to the KOH acting as a dehydrating agent to drive off the majority of the oxygen and hydrogen, as well as the KOH reacting corrosively with the carbon surface. As hydrogen and oxygen diffuse out of the carbon they create more paths to help develop a more porous structure with increased tortuosity. [1] Driving off the 94 grams of oxygen and 7.30 grams of hydrogen from the 437 grams of carbon leaves a mass of 336 grams. This is mostly carbon, but may also contain small amounts of sodium potassium and phosphorus. The remaining 196 grams of mass loss can be attributed to the KOH reacting with the surface to produce K_2CO_3 and CO_2 . [23] CO_2 leaves the system as a gas

and K_2CO_3 is removed in the washing step along with any unreacted KOH. Table 5 provides a summary of this data.

Table 7: Sources of Mass Loss in KOH Activation

Mass of Carbon Before Activation	Mass Loss due to Hydrogen and Oxygen Leaving System	Mass of Carbon After Oxygen and Hydrogen are Driven off	Final Mass of Carbon After Activation	Mass Loss due to Reaction with KOH	Mass Loss due to Other Species
437 g	23.2 %	336 g	140 g	41.6 %	3.33 %

From the standard deviation data in figures 4-5, it can be concluded that the activation reaction sample mass loss has an average standard deviation of $\pm 1.41\%$, while the average standard deviation for carbon mass loss is $\pm 3.78\%$. Since these standard deviations are obtained from such a large volume of samples, all carbons produced under the optimized ALL-CRAFT process and presented in chapter 3 will be assumed to possess these statistics.

2.6: CONCLUSION

Under the ALL-CRAFT project high performance activated carbon was produced from corncob feedstock through a two step phosphoric acid carbonization and KOH activation. The phosphoric acid carbonization exhibited a 59.6% yield while the 3K KOH activation had a yield of 31.9%. Combining these values gives an overall process yield of 18.6% corncobs to 3K carbon. It was determined that there is an average standard deviation of $\pm 1.41\%$ in reaction sample mass loss, and $\pm 3.78\%$ in overall carbon mass loss.

CHAPTER 3: Use of Screening Methods to Analyze Activated Carbon Produced Using Various Process Conditions, Chemical Activating Agents, and Carbon Precursor Materials

3.1: ABSTRACT

The following paper proposes several screening procedures for the production of activated carbon. Analyzing carbons can be expensive and time consuming, making it important to identify physical properties which indicate that a carbon may have favorable performance characteristics. The following paper proposes three ways of screening carbons: observing the mass loss in the chemical activation process, measuring the density of the carbon, and testing the methane uptake of the carbon in a rapid uptake fixture. Carbons made from different precursors, reacted with different activating agents, and heated at different process temperatures for different process hold times were analyzed. Previous analysis has shown that carbon activated at 790°C for one hour at a ratio of 3:1 KOH to carbon exhibits exceptional methane storage capabilities and physical properties. The goal of this paper is to propose alternatives that emulate the sample mass loss, density, and methane uptake of this carbon by using different materials, process temperatures, and process hold times.

3.2: INTRODUCTION

As stated before, activated carbon is a widely used adsorbent in many industries. For each different application of activated carbon, different pore structures, types of granules, and carbon surfaces are needed. In order to control these properties different

carbon precursors, different activating methods, and varying conditions of activation are used.

One method to identify a carbon for a certain application is to conduct a parametric study varying process conditions, precursor materials, and activating agents. Normally analysis of carbon is conducted by running adsorption isotherms, calculating the BET surface area, and measuring pore volume among other procedures. [2] However, these tests are time consuming, and a parametric study conducted with many parameters will yield a wide array of different samples which need to be tested. In order to deal with this problem, it becomes necessary to develop several different screening methods in order to eliminate certain samples which do not display performance characteristics needed for the given application of interest. In this study, screening methods are developed in order to identify desirable properties for activated carbons being used as a natural gas adsorbent.

Table 8: Summary of ALL-CRAFT Activated Carbon Synthesis Process: Parameters and Results

Carbon Precursor	Corncobs
Precursor: Phosphoric Acid +Water Ratio	40:60
Phosphoric Acid: Water Ratio	63:37
Mass Loss in Phosphoric Acid Carbonization	40.4 %
Activating Agent	KOH
Activating Agent:Char Ratio	3:1 (3K)
Process Temperature	790 °C
Process Hold Time	1hour
Mass Loss In Charring	40.4 %
Sample Mass Loss in Activation ($\sigma= \pm 1.41\%$)	11.1 %
Carbon Loss in Activation ($\sigma= \pm 3.78\%$)	68.1 %
Density	0.136 g/mL
Methane Uptake Pressure Drop	175 PSI

Table 6 shows the process parameters and properties of carbon made using the ALL-CRAFT synthesis process. The percent sample loss in carbonization, percent carbon loss in activation, carbon density, and methane uptake are target values for the present study and can be used to screen samples created with different activating agents, carbon precursors, activating agent:char ratios, process temperatures, and process hold times. The target values can be compared to experimental results in order to determine if different combinations of parameters are effective in creating a carbon which will

perform similar to 3K carbon reacted at a process temperature of 790°C and a process hold time of 1 hour.

3.3: EXPERIMENTAL

3.3.1: Materials and Equipment

Corncob feedstock (14 mesh) was obtained from The Andersons' Inc. (Maumee, Ohio). This material is from the middle pith layer of the corncob. Walnut Shells and Red Oak Sawdust were obtained from Leimkuehler farms. Phosphoric acid (85%) was obtained from Fisher Scientific. KOH (>90%), Lithium Hydroxide (>98), and Sodium Hydroxide (>97%) were obtained from Sigma Aldrich. Nitrogen (99.99%) and methane were supplied by PraxAir Inc. Samples were ball-milled using a United Nuclear Ball Mill. A model 126 750 series Isotemp Programmable Muffle Furnace obtained from Fischer Scientific was used for charring. A model FD1545M Furnace from ThermoScientific was used to perform the activation. A nitrogen purge was directed at the reactor in the oven with a purge rate of 5 L/min and adequate ventilation. 8 quart stainless steel reactors from Cole Parmer were used for charring. Aluminum oxide crucibles (100 mL) from Cole Parmer were used for activation. Carbon washing was carried out on in a Buchner Funnel. The rapid uptake fixture was constructed from Swagelock supplies.

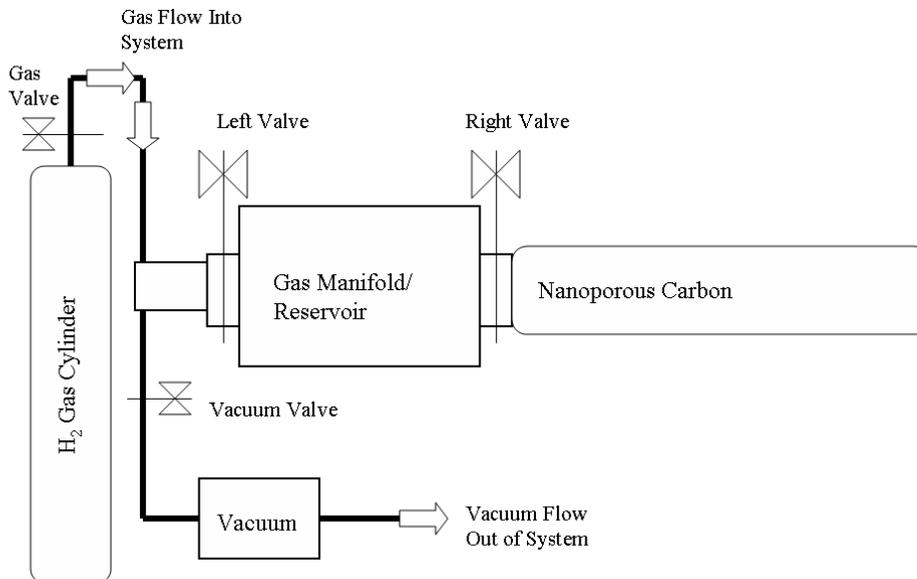


Figure 6: Diagram of Rapid Uptake System (Empty Vessel Pressure Drop = 125PSI)

3.3.2: Sample Preparation

The activated carbon was synthesized using the process described in Chapter 2 with the following variations. Phosphoric acid was reacted with three different carbon precursor feedstocks: corncobs, red oak sawdust, and walnut shells. Additionally, three different activating agents were used: KOH, NaOH, and LiOH. The activating agent was added to the char in varying char: activating agent ratios. (1:1, 2:1, 3:1, these will be referred to as 1K, 2K, 3K) The resulting mixture was ball milled for 2.5 hours.

Each individual ball milled sample was added to a 100 mL alumina crucible and placed in a high temperature oven using the single setpoint mode. The samples were kept in the high temperature oven for varying process hold times (1, 2, 3 hours) and process temperatures (750, 790°C.) When the oven temperature cooled to 100 °C the samples were removed and weighed. The activated mixtures were transferred to and washed in

a Buchner funnel in order to remove the potassium from the carbon. Each sample was washed with 200 mL of tap water with a 0.15% concentration of formic acid followed by 100 mL of tap water.

The Bulk density of the carbon was measured in a graduated cylinder. The methane uptake was measured in the rapid uptake system depicted in figure 2. 5 mL of carbon was added to a 5 mL manifold. Around 0.3 g of glass wool was used as a plug to keep the carbon from being vacuumed into the system. The manifold was vacuumed for one hour before closing the right valve to keep the sample at vacuum and isolated from the gas reservoir. The gas reservoir was charged to 750 PSI creating a pressure gradient between the gas reservoir and the vacuumed sample. The methane was then released into the sample and the system was allowed to equilibrate. The pressure drop was recorded between the equilibrium pressure and the initial manifold pressure of 750 PSI.

3.4: RESULTS

3.4.1: Effects of Process Temperature

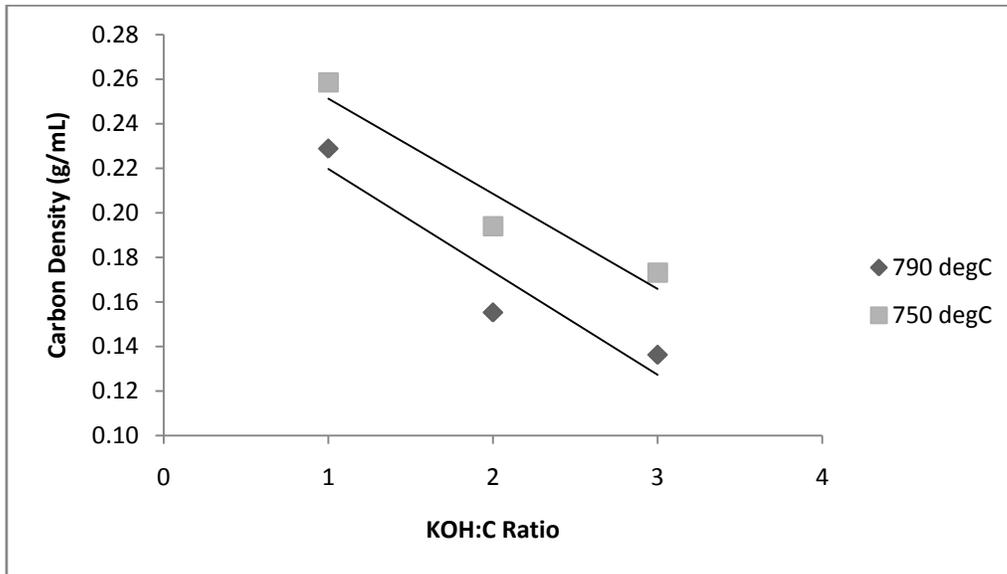


Figure 7: Effect of Process Temperature on Carbon Bulk Density ($\sigma=\pm 0.0177$ g/mL)

Figure 7 shows that a higher process temperature correlates to a lower density carbon.

Also, it shows that as the KOH:C ratio decreases, the density increases.

Kinetic reaction theories predict that as temperature increases, both the rate of reaction increases and new, more aggressive, reactions may become possible (a manifestation of increasing reaction rates with increasing temperature). These trends are consistent with the increased mass loss with increasing temperature of Figures 8 and 9. Evans et al [24] reported similar trends in yields.

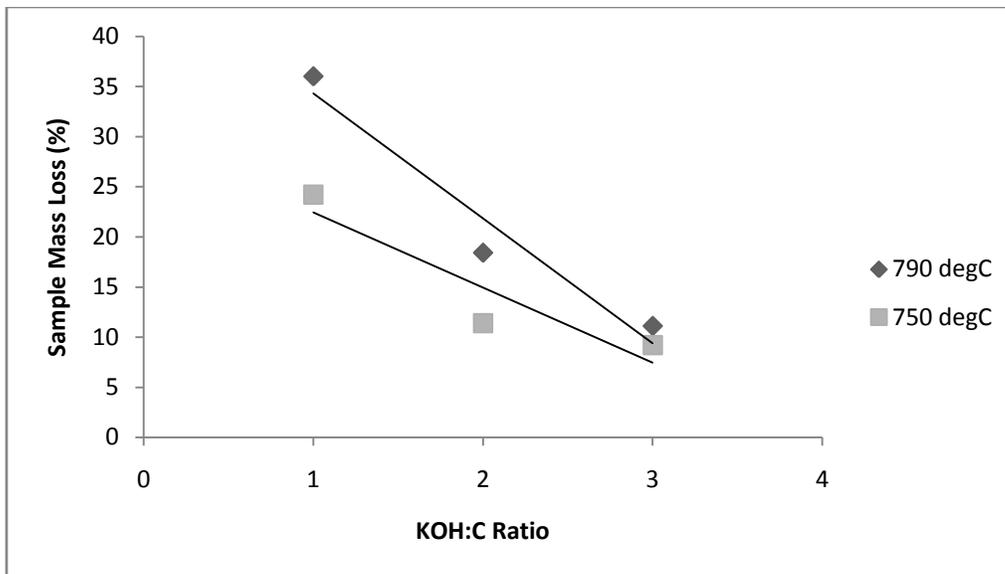


Figure 8: Effect of Process Temperature on Reaction Sample Mass Loss % ($\sigma=\pm 1.41\%$)

Figure 8 illustrates how increasing temperatures lead to increasing loss of mass during chemical activation. The mass loss is from the evolution of gases from the mixture of KOH and char. The mass loss of 3K carbon is a result of the higher loading of potassium which is not significantly volatile in any of its possible derivatives at 750 or 790°C. Figure 8 shows the reaction mass loss decreasing with temperature. 1K and 2K carbons show an increase in sample mass loss with increasing temperature, which supports the argument that a more vigorous reaction is occurring at higher temperatures.

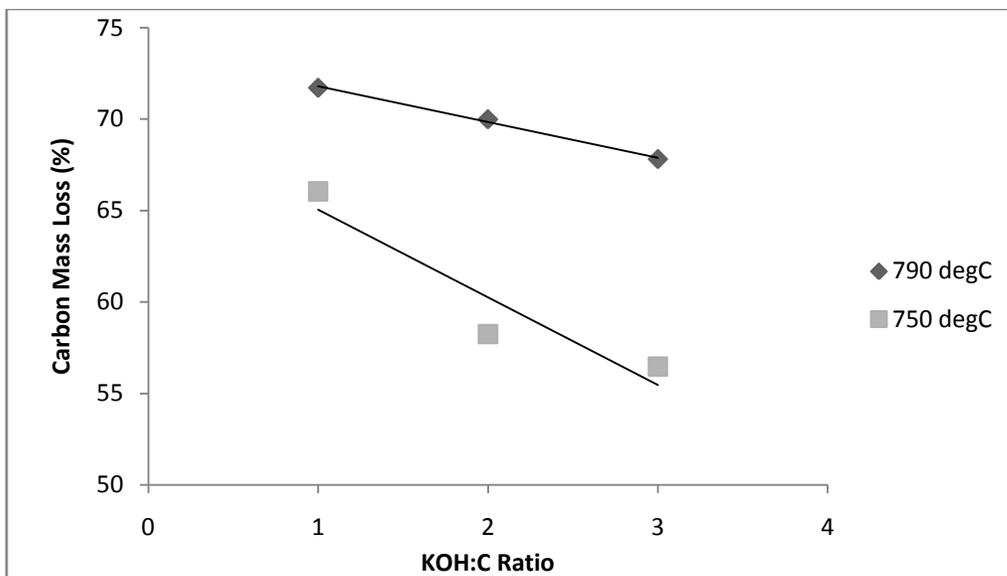


Figure 9: Effect of Process Temperature on Carbon Mass Loss % ($\sigma=\pm 3.78\%$)

Figure 9 further supports the claims of the previous figure by showing that as temperature increases, there is a higher amount of mass lost in the system, signifying that more reaction is occurring. However, a higher % mass loss is synonymous with a lower process yield, so if a higher process yield is desirable, a lower temperature reaction could be a feasible route. The yield of carbon is typically of greater interest than the loss of mass from the mixture of KOH and char during activation. However the sample mass loss during reaction can be a good screening tool to determine if the carbon will perform well if alternative activating agents, different precursors, or different process variables are being tested. Tseng reported a somewhat similar trend as that of Figure 9 where increasing loadings of KOH resulted in slightly reduced loss of carbon [13]. Others [24] [22] have observed increased carbon loss with increasing KOH loadings. Multiple competing phenomena impact the rate of carbon loss which requires a more in-depth discussion.

3.4.2: Effects of Process Hold Time

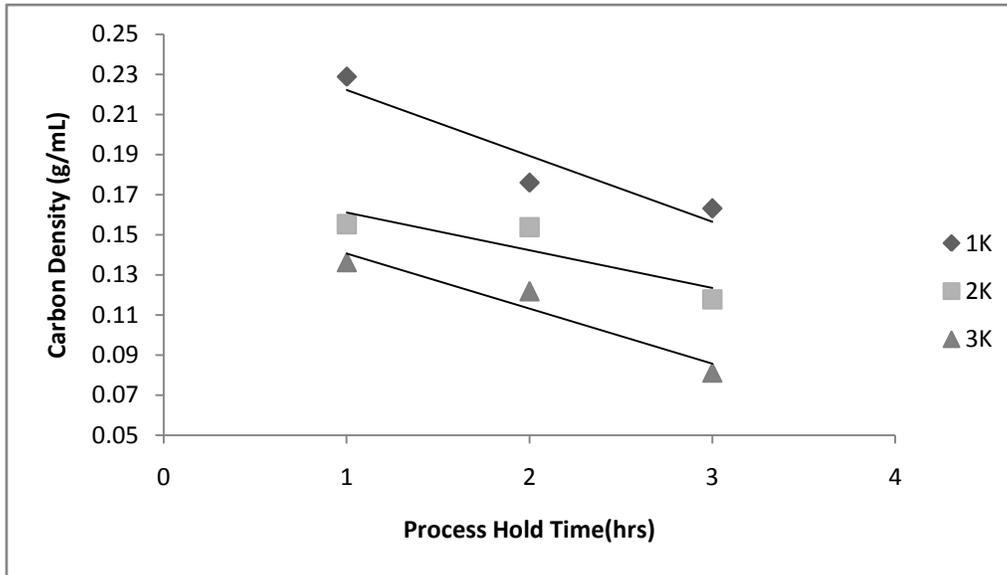


Figure 10: Effect of Process Hold time on Carbon Bulk Density at 790°C ($\sigma=\pm 0.0177$

g/mL

Figures 10 and 11 show the effect of process hold time on the density of carbons activated at 750 and 790°C. As process hold time increases, density decreases. This suggests that continuous reaction is occurring for the entire process hold time, and the surfaces of the carbon become increasingly etched as time goes on.

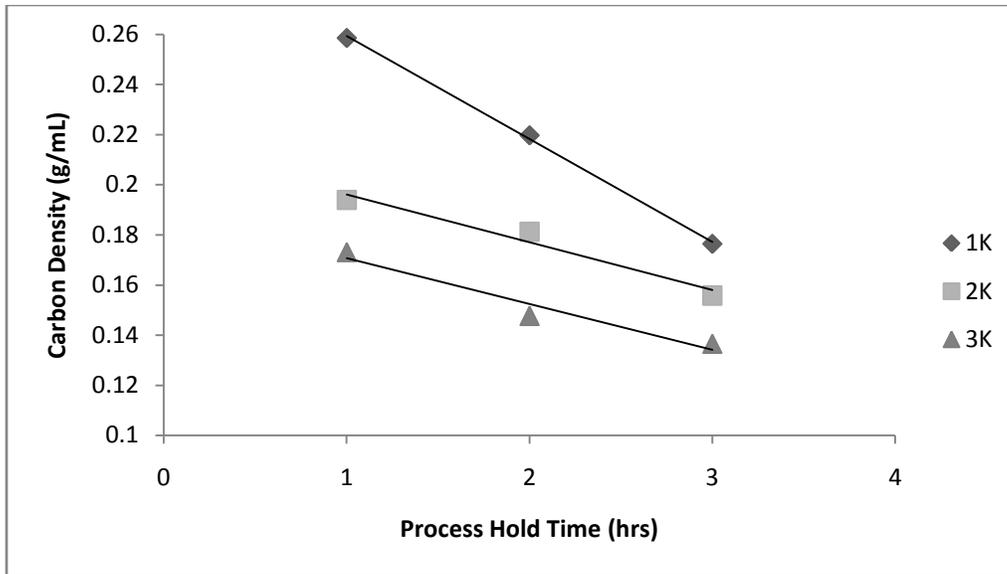


Figure 11: Effect of Process Hold Time on Carbon Bulk Density at 750 °C ($\sigma=\pm 0.0177$ g/mL)

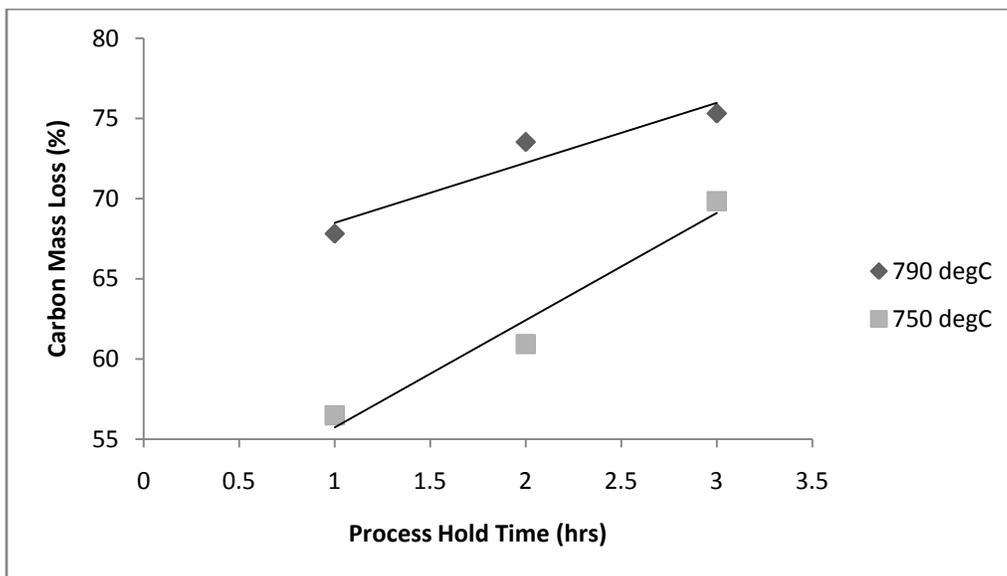


Figure 12: Effect of Process Hold Time on Carbon Mass Loss for 3K Carbon ($\sigma=\pm 3.78\%$)

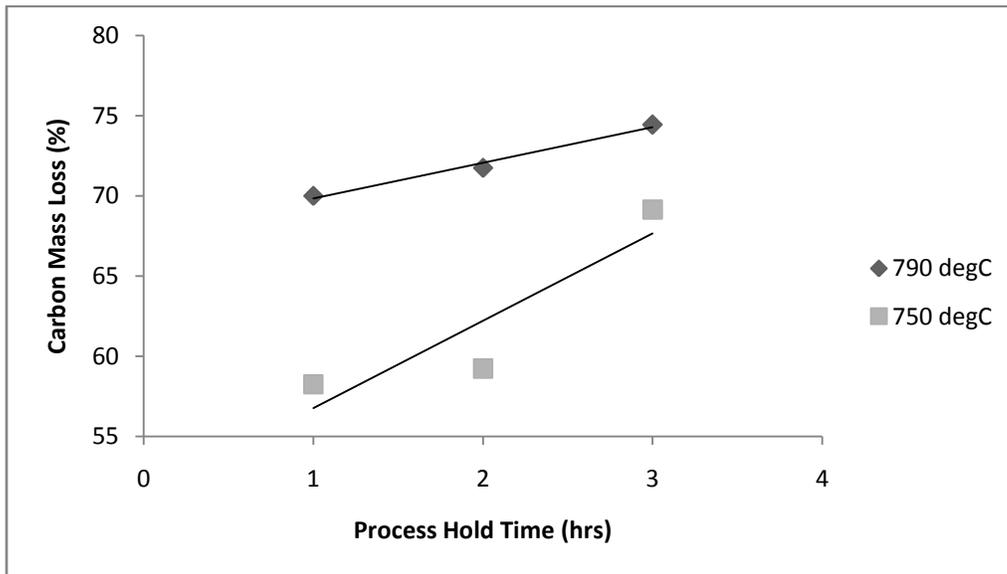


Figure 13: Effect of Process Hold Time on Carbon Mass Loss % for 2K Carbon ($\sigma=\pm 3.78\%$)

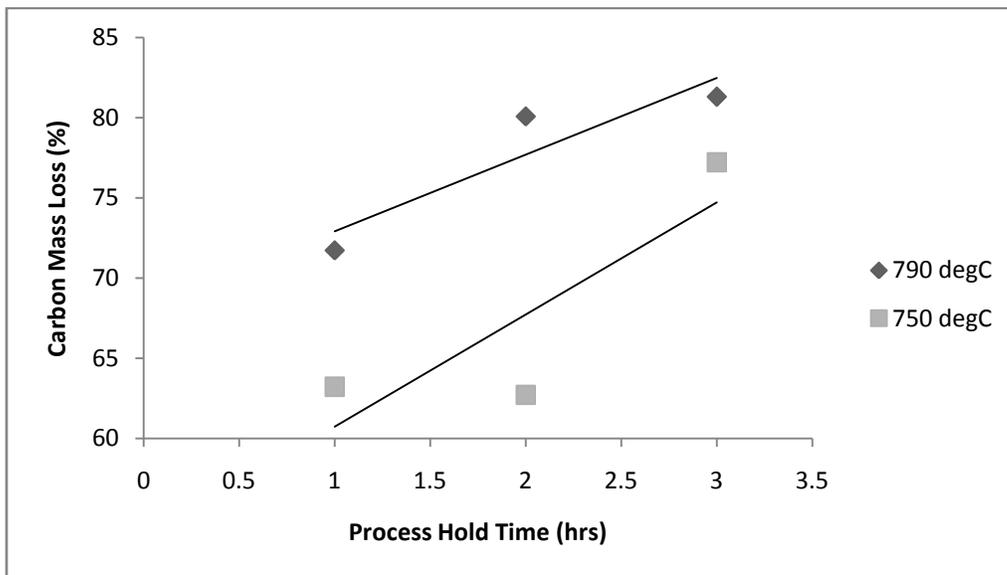


Figure 14: Effect of Process Hold Time on Carbon Mass Loss % for 1K Carbon ($\sigma=\pm 3.78\%$)

Figures 12, 13, and 14 show the effects of process hold time on Carbon Mass Loss % for 1K, 2K, and 3K carbon. All three figures show an increase in mass loss% for increasing

process hold time. Comparing the three figures shows that for 1K, 2K, and 3K carbon a 3 hour process hold time at 750°C can produce similar process yield results as a process hold time of 1 hour at 790°C

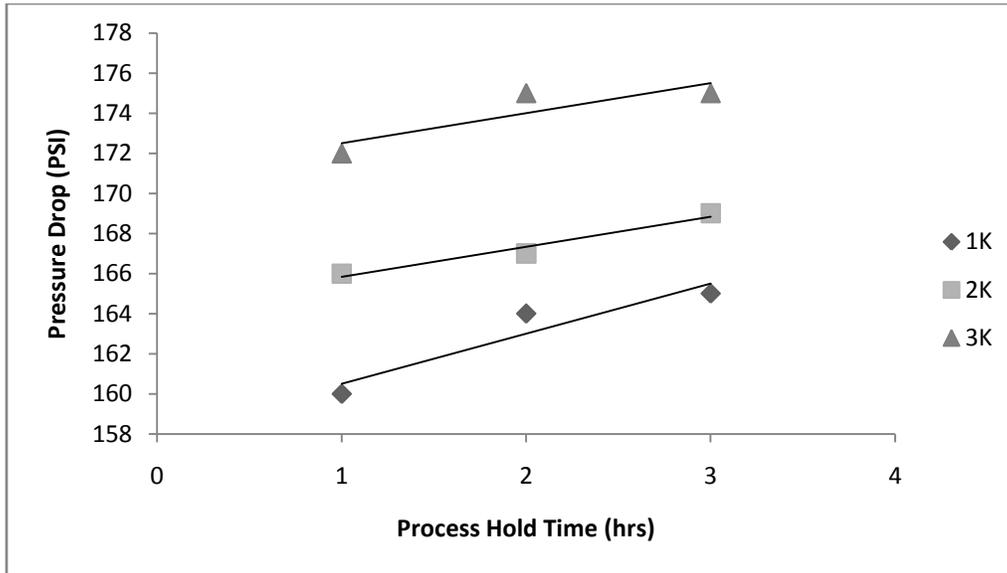


Figure 15: Effect of Process Hold Time on Methane Uptake at 790°C ($\sigma=\pm 2.5$ PSI)

Figures 15 and 16 show the effects of process hold time on methane uptake at 750 and 790°C. As process hold time increases, the methane uptake of the carbon also increases. In addition, as KOH:C ratio increases, methane uptake increases. However, there is not an appreciable difference in methane uptake from 750 to 790°C.

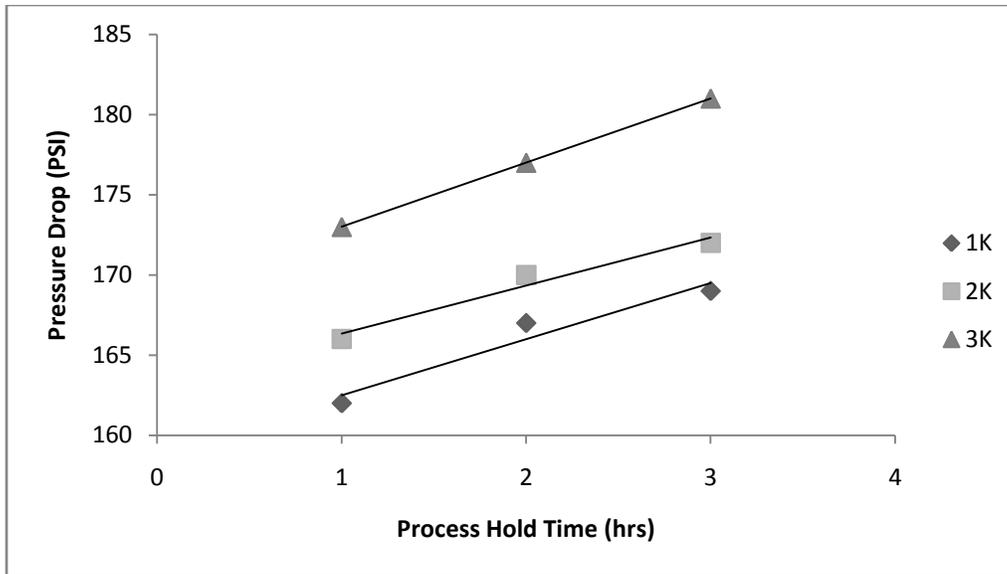


Figure 16: Effect of Process Hold Time on Methane Uptake at 750°C ($\sigma=\pm 2.5$ PSI)

3.4.3: Use of Different Activating Agents

Sodium Hydroxide in a 3:1 activating agent to carbon ratio (3N) and Lithium Hydroxide in a 2:1 activating agent to carbon ratio (2L) were compared to 3K carbon. Like KOH, LiOH and NaOH are both metal hydroxides and could react with the carbon in a similar manner.

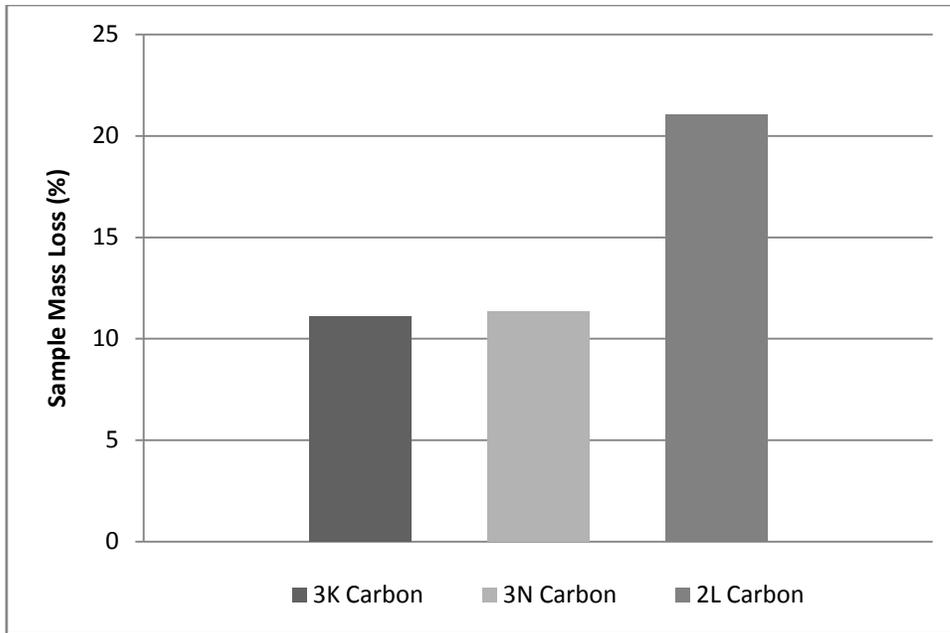


Figure 17: Effect of Activating Agent on Reaction Sample Mass Loss % at 790°C ($\sigma=\pm 1.41\%$)

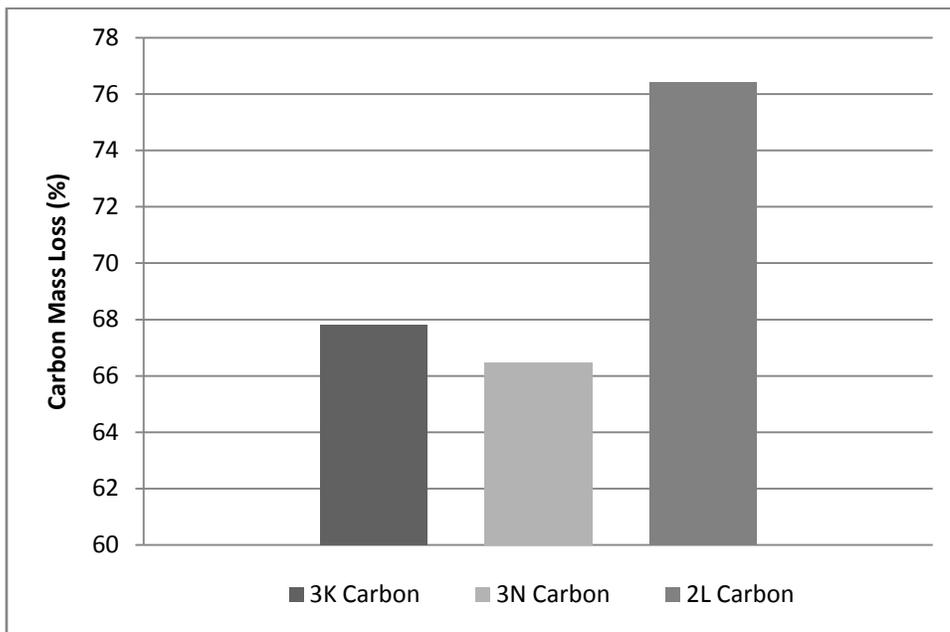


Figure 18: Effect of Activating Agent on Carbon Mass Loss % at 790°C ($\sigma=\pm 3.78\%$)

3K carbon and 3N carbon show similar sample mass loss and carbon mass loss percentages. However, 2L carbon shows a much higher percentage loss in both

categories. A higher ratio of LiOH to carbon (3L or 4L) was not used because this would result in an excessive amount of mass loss.

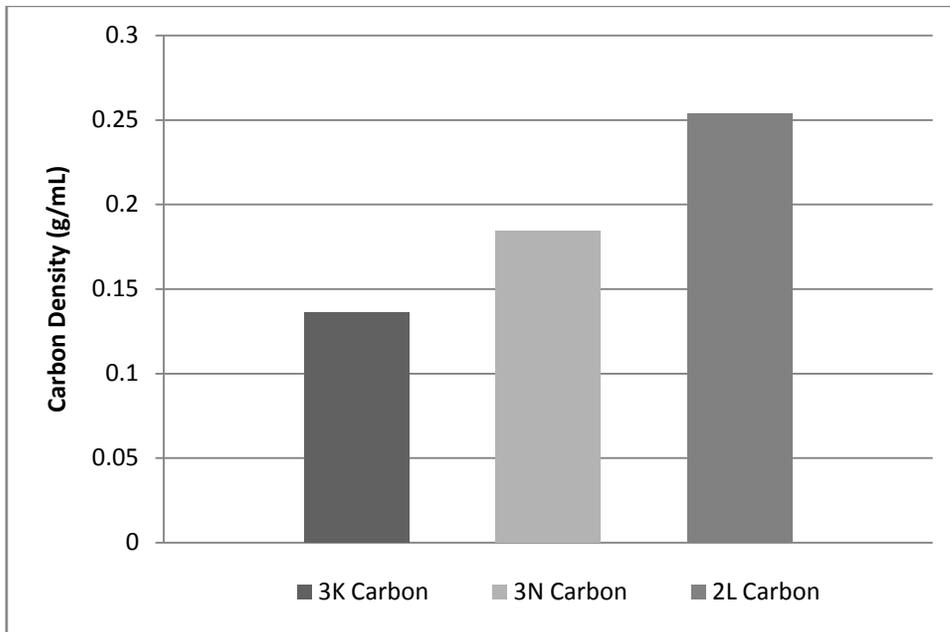


Figure 19: Effect of Activating Agent on Carbon Bulk Density at 790°C ($\sigma=\pm 0.0177$ g/mL)

Figure 19 shows a comparison of the density of the carbons prepared from different activating agents. 3N carbon's density is still in an acceptable range, however 2L carbon's density is somewhat high.

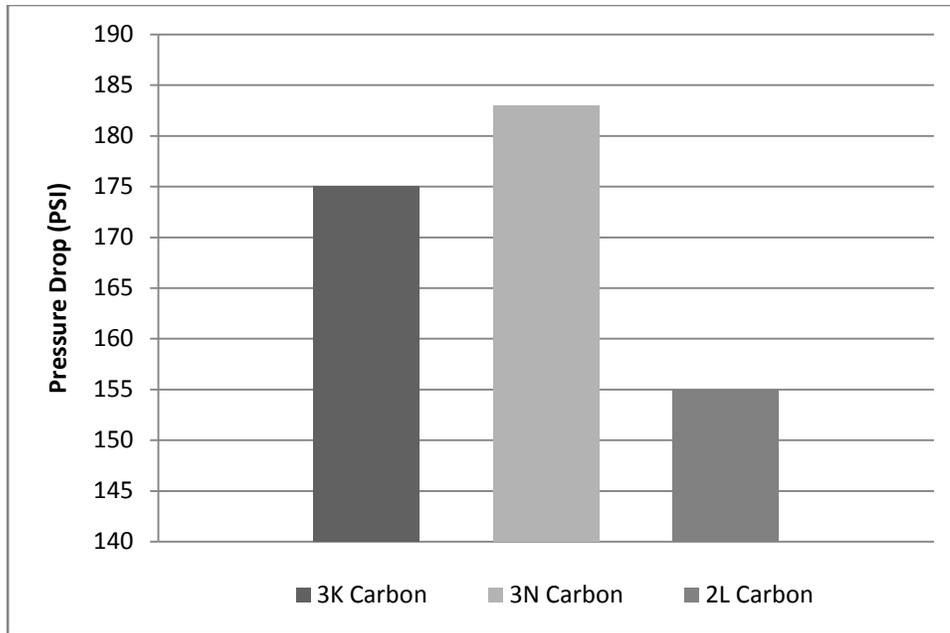


Figure 20: Effect of Activating Agent on Methane Uptake at 790°C ($\sigma=\pm 2.25$ PSI)

Figure 20 shows the effect of activating agent on samples methane uptake at 790°C.

Even though 3N carbon has a higher density than 3K carbon, it performs better on the methane uptake screening test.

3.4.4: Use of Different Carbon Precursors

Three different carbon precursors were evaluated: Corncobs, walnut shells, and red oak sawdust. Analysis was performed on the phosphoric acid carbonization reaction and the KOH activation reaction. The phosphoric acid carbonization consisted of a ½ hour process hold time at 350°C and a 1 hour process hold time at 480°C. The KOH activation reaction consisted of a 1 hour process hold time at 790°C.

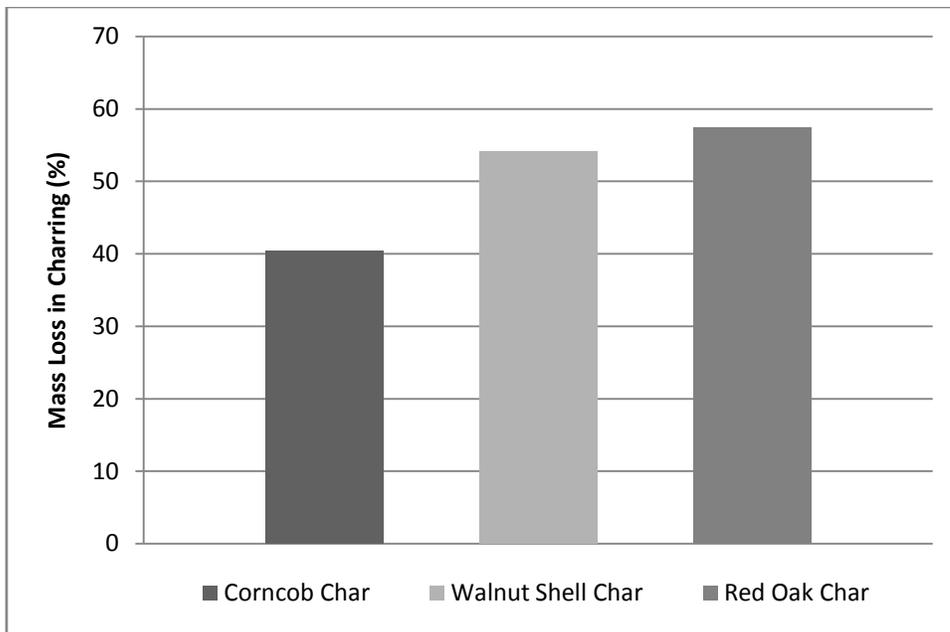


Figure 21: Mass Loss in Phosphoric Acid Carbonization for Different Carbon Precursors ($\sigma=\pm 3.78\%$)

Figure 21 shows a comparison of the amount of mass lost between the three precursors in the phosphoric acid carbonization. Red oak sawdust and walnut shells show a greater amount of mass lost than corncobs. Figure 18 shows the densities of the resulting carbon chars. Red oak sawdust and Corncobs have similar densities while walnut shell char has a slightly higher density. This may be attributed to the fact that walnut shells are denser than sawdust and corncobs.

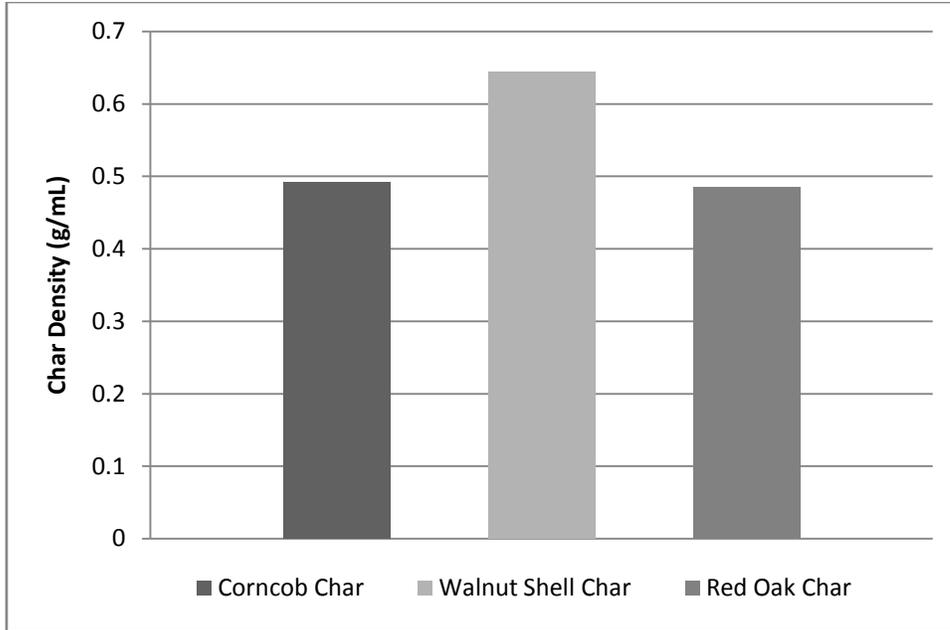


Figure 22: Bulk Density of Phosphoric Acid Activated Char for Different Carbon

Precursors ($\sigma=\pm 0.0177$ g/mL)

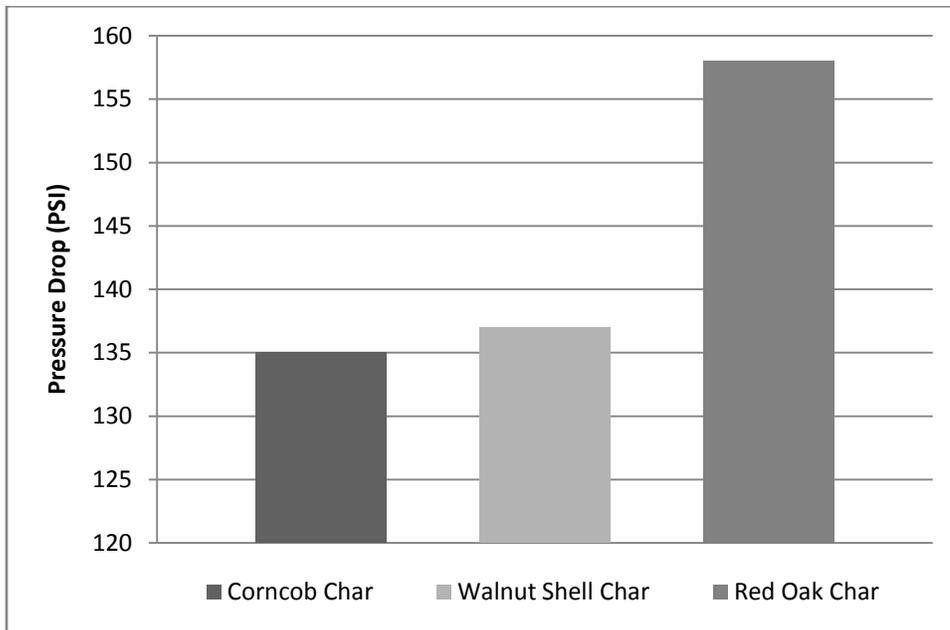


Figure 23: Methane Uptake of Phosphoric Acid Activated Char for Different Carbon

Precursors ($\sigma=\pm 2.50$ PSI)

Figure 23 shows the methane uptake of the resulting chars from phosphoric acid carbonization. Red oak char displays a much higher methane uptake than that of walnut shells and corncobs. In fact, the uptake of the red oak sawdust is almost as high as that of 1K carbon with a process temperature of 790°C and a process hold time of one hour.

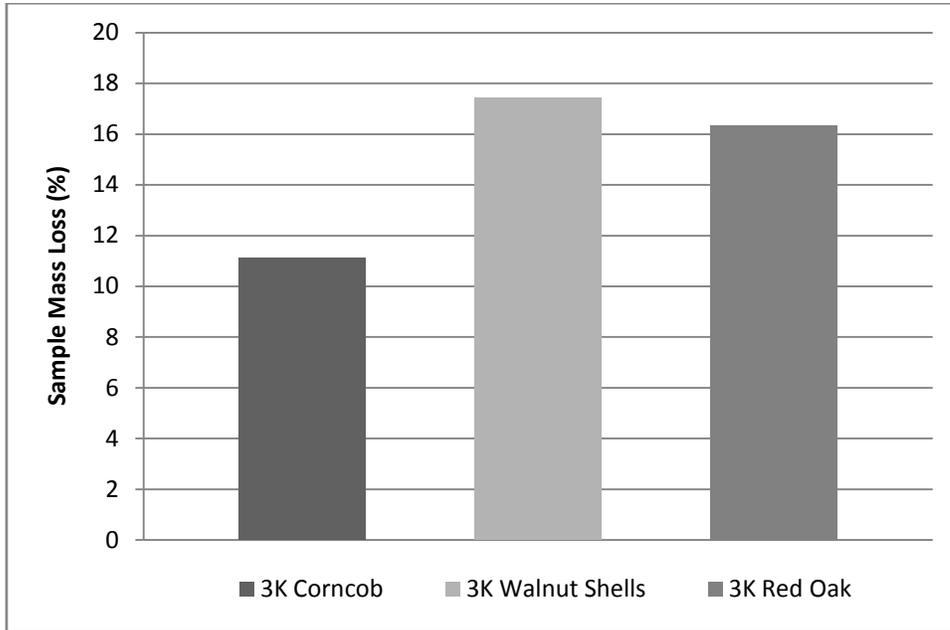


Figure 24: KOH Reaction Sample Mass Loss % at 790°C for Different Carbon Precursors ($\sigma=\pm 1.41\%$)

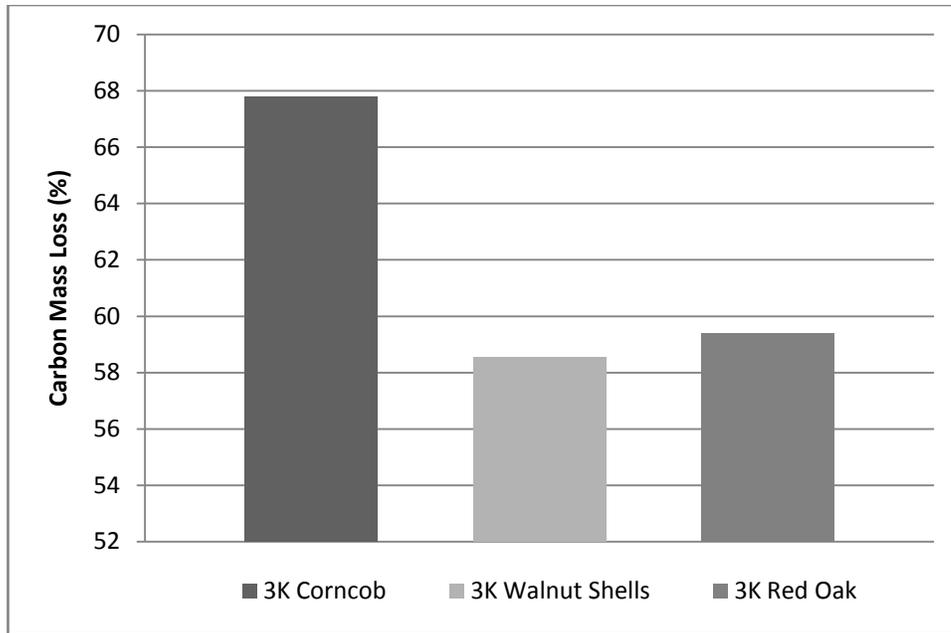


Figure 25: KOH Reaction Carbon Mass Loss % at 790°C for Different Carbon Precursors

($\sigma=\pm 3.78\%$)

Figure 24 shows that the sample mass loss of carbons derived from walnut shells and red oak sawdust is slightly higher than that of carbons from a corncob precursor.

Conversely, the overall carbon mass loss of carbons from walnut shells and red oak sawdust displayed in figure 25 is slightly lower than that of carbons from corncobs.

Figure 26 shows that the densities of carbon from the two alternate precursors are also higher than the density of carbon made from corncobs.

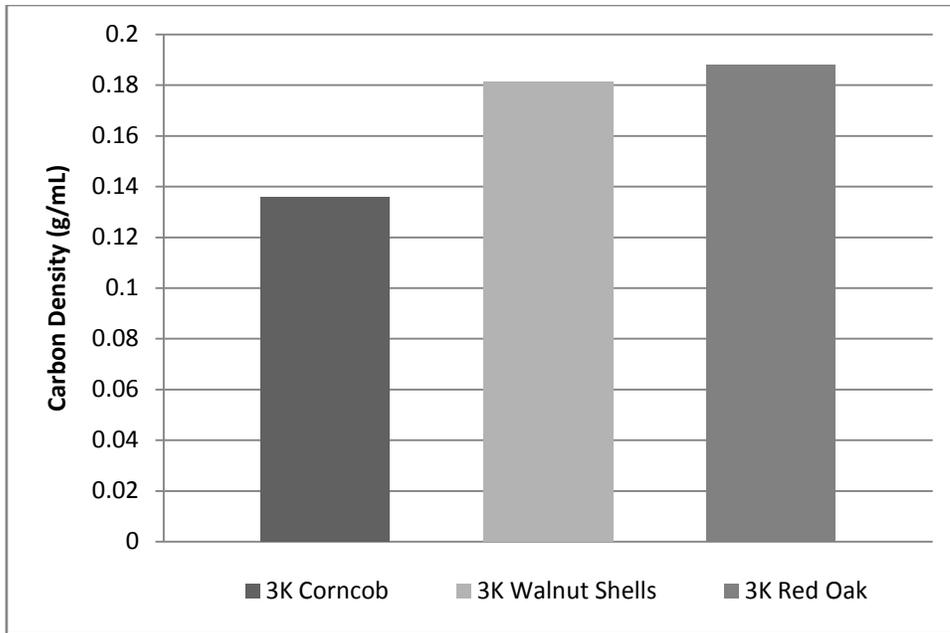


Figure 26: KOH Reaction Carbon Bulk Densities at 790°C for Different Carbon

Precursors ($\sigma=\pm 0.01774$ g/mL)

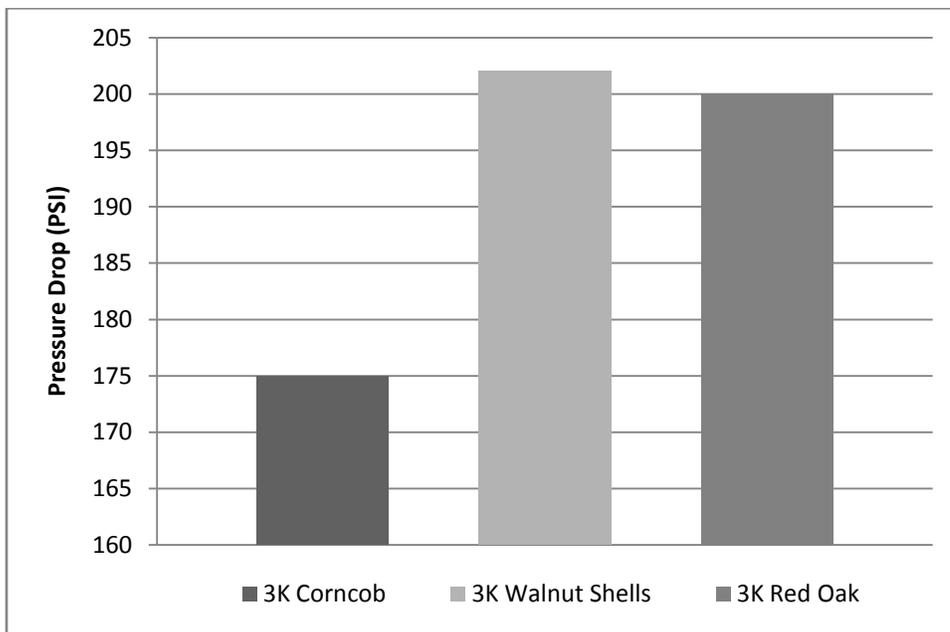


Figure 27: KOH Reaction Rapid Uptake at 790°C for Different Carbon Precursors ($\sigma=\pm$

2.5 PSI)

Figure 27 shows the methane uptake of carbons activated with KOH and derived from different precursors. Carbon from Red Oak and Walnut Shells outperform carbon made from corncobs, despite the fact that carbon from walnut shells and red oak has a higher density.

3.5: DISCUSSION

3.5.1: Effects of Process Hold Time and Process Temperature

Table 9: Comparison of Properties Generated from Varying Process Temperatures and Hold Times

KOH:C Ratio	Process Temperature (°C)	Process Hold Time (hrs)	Sample Mass Loss (%)	Carbon Mass Loss (%)	Carbon Bulk Density (g/mL)	Methane Uptake Pressure Drop (PSI)
3	790	1	11.1	67.8	0.136	175
1	790	2	38.4	80.1	0.178	164
2	790	2	18.4	71.7	0.154	167
2	750	2	11.4	55.3	0.181	170
3	750	2	14.4	60.9	0.148	177
1	790	3	40.3	81.3	0.163	165
2	790	3	20.9	74.4	0.118	169
2	750	3	14.7	69.1	0.156	172
3	750	3	12.8	74.7	0.137	181

Table 7 shows that several properties of 3K carbon at 790°C can be emulated by using lower process temperatures and longer process hold times. Densities within close

range of the target density of 0.136 g/mL can be achieved by heating 2K carbon at 790°C for 2 hours, and 2K and 3K carbon at 750°C for 3 hours. However, all of the densities in Table 7 are within reasonable distance of the target density.

1K carbon heated at 790°C for 3 hours is also of high interest because there is an appreciable decrease in density with increased process hold time, and a low amount of KOH is being used. Methane uptake readings similar to the target reading of 750 psi can be achieved by heating 2K carbon at 790°C for 2 and 3 hours, 3K carbon at 750°C for 2 hours and heating 2K and 3K carbon at 750°C for 3 hours. Heating 2K and 3K Carbon at 750°C for 3 hours produces carbon mass loss percentages similar to the target carbon mass loss of 67.8%. 2K and 3K carbon heated at 750°C for 2 and 3 hours produce similar sample mass losses to the target mass loss of 11.1%. Judging from this data, the highest samples of interest are 2K carbon heated at 790°C for 2 hours, 1K carbon heated at 790°C for 3 hours, 3K carbon heated at 750°C for 2 hours, and 2K carbon heated at 750°C for 3 hours.

A unexpected trend is noticed that samples prepared at a lower temperature have a slightly higher methane uptake. It has been cited [2] that this may be due to a higher density and smaller micropore size in carbons prepared at a slightly lower temperature. A combination of these two properties could yield a higher methane uptake.

3.5.2: Use of Different Activating Agents

At a ratio of 3:1 activating agent to carbon, KOH and NaOH have similar mass losses and densities at a process temperature of 790°C and a process hold time of one hour. NaOH

even outperforms KOH in the rapid methane uptake test. From the data collected in this paper, it appears that NaOH could be a good substitute for KOH.

However LiOH at a 2:1 activating agent to carbon ratio has a higher mass loss and lower density than KOH. Higher activating agent to carbon ratios would have unfavorable process yields, while lower temperature activations or lower activating agent:carbon ratios would yield a carbon with a higher density and lower methane uptake capability. The mass loss in LiOH activate carbon and KOH activated carbon may seem comparable, but mass loss values are calculated gravimetrically and high density LiOH activated carbon produces a very low volume of product, making it an unfavorable activating agent when compared to KOH and NaOH.

3.5.3: Use of Different Carbon Precursors

Carbon prepared from red oak sawdust and walnut shells exhibited a greater mass loss in phosphoric acid carbonization than carbon derived from corncobs. This may indicate that the phosphoric acid/ water mixture reacts more vigorously with red oak sawdust and walnut shells than with corncobs, which could be caused by a higher amount of volatile substances in the sawdust and walnut shells than in the corncobs.

This increased mass lost may suggests that the walnut shells and sawdust have a greater amount of micropores, which would yield increased adsorptivity. [1] However, only the char from red oak sawdust shows an increase in methane uptake performance over char from corncobs; walnut shell char performs nearly the same as corncob char. This may

suggest that the walnut shell carbon has the same amount of micropores as the carbon from sawdust, but a portion of the internal pore structure remains closed.

Since the red oak sawdust was more affected by the phosphoric acid carbonization, one would also expect that it would have superior methane uptake to walnut shell char and corncob char after being reacted with KOH. However, this is not the case. 3K walnut shell carbon and 3K Red Oak sawdust carbon both have a greater methane uptake than 3K corncob carbon. Methane uptake of 3K walnut shell carbon and 3K red oak sawdust carbon is nearly the same. Since the walnut shell and red oak sawdust carbons are assumed to have the same amount of micropores, this suggests that the chemical activation with KOH may have opened up pores in the walnut shell carbon that were previously closed, causing it to perform the same as the red oak sawdust carbon.

In addition, walnut shells may be a more carbonaceous material than sawdust, leading to a more intense reaction with KOH and a greater increase in adsorption capacity.[1] The sample mass loss of 3K carbon was lower than that of 3K sawdust and 3K walnut shells, but at the same time the carbon mass loss of 3K carbon was higher than that of 3K sawdust and 3K walnut shells. The lower sample mass loss of 3K corncob carbon suggests that more byproducts and salts are formed in the 3K corncob reaction than in the 3K walnut shell and 3K sawdust reactions. The overall carbon mass loss displays the mass of carbon remaining after excess salts are removed during washing. More carbon remains in 3K walnut shell carbon and 3K sawdust carbon than 3K corncob carbon,

which is supported by the higher carbon mass loss of 3K corncob carbon and lower carbon mass loss of 3K sawdust carbon and 3K walnut shell carbon.

The fact that the density of red oak and walnut shell carbons is higher than that of corncob carbons even though corncob carbons have a lower methane uptake contradicts an earlier trend observed in carbons activated exclusively from corncobs where lower densities yielded higher methane uptake. However, it was also observed that carbons from red oak sawdust and walnut shell carbon may have a larger amount of micropores, higher carbon content, and greater mechanical strength, giving them a higher density. This may suggest that density is only a valid screening device when comparing carbons created from the same precursor, since a slight increase in density could be a positive sign depending on the precursor used. The higher process yields and increased methane uptake of red oak sawdust and walnut shell carbons suggests that these two precursors are viable alternatives to corncobs, and may even generate carbons that outperform activated carbons derived from corncob biomass.

3.6: CONCLUSION

Activated carbon samples were produced varying the process hold time, process temperature, activating agent, activating agent: carbon char ratio, and carbon precursor. These samples were then analyzed using the following screening methods: observing the mass loss in chemical reaction, measuring carbon density, and measuring methane uptake.

It was observed that increasing the process hold time while decreasing the process temperature and activating agent:carbon char ratio could produce carbons with similar methane uptake, mass loss, and density as carbons reacted at lower process hold times with higher temperatures and higher activating agent: char ratios. Chemical reaction with NaOH produced carbons with similar mass loss, densities, and methane uptake to carbons reacted with KOH.

However, chemical reaction with LiOH produced carbons which were inferior to carbons produced from KOH reaction. Carbons derived from both walnut shells and red oak sawdust outperformed carbons derived from corncobs on the rapid methane uptake test, despite the fact that their final carbon density was slightly higher and their carbon mass loss was slightly lower. These observations show that carbons produced from reaction with NaOH, and carbons with walnut shells and red oak sawdust as a precursor are all practical and possibly superior alternatives to carbons derived from corncobs and reacted with KOH.

CHAPTER 4: CONCLUSION

4.1: Activated Carbon from Corncobs Using Phosphoric Acid and KOH

The production of activated carbon from waste materials for use as a natural gas adsorbent provides an environmentally friendly source of alternative energy. Activated carbon with surface areas above $2500 \text{ m}^2/\text{g}$ and 80% internal porosities can be produced from corncobs by utilizing the two step ALL-CRAFT activation process. The phosphoric acid carbonization gives a 59.6% yield of carbon char and develops the initial porous structure of the carbon while eliminating volatile substances in the corncob. The KOH activation further develops this porous structure; KOH etches the carbon surface through vigorous reaction while acting as a dehydrating agent to force all hydrogen and oxygen out of the carbon structure, increasing its tortuosity. These effects create a 68.9% mass loss in the KOH activation, which leads to an overall process yield of 18.6% (corn cob to 3K carbon.) This yield may be batch size dependent with larger batch sizes producing increased yields.

4.2: Analysis of Varying Precursors, Process Conditions, and Activating Agents Using Screening Techniques

A parametric study was conducted in order to produce a variety of samples using different process hold times and process temperatures, activating agent: carbon ratios, carbon precursors, and activating agents. The goal of this study was to find activated carbon samples which possessed similar physical characteristics to samples produced from corncobs. The samples were compared by observing the mass loss in the charring

and activation processes, density of the resulting carbon samples, and volumetric methane uptake of the resulting samples.

Optimizing process conditions can be very important in industry where spending the least amount of money is of interest. Samples heated for longer process hold times with lower process temperatures and KOH: C ratios performed similarly to samples with shorter process hold times, higher process temperatures, and higher KOH: C ratios.

It was found that using NaOH as an activating agent produced similar results as using KOH. However, when LiOH was used as an activating agent, a high density carbon was obtained with a lower process yield. This leads to a very low yield of carbon volumetrically. Carbons activated with NaOH had a slightly better methane uptake than carbons activated with KOH; carbons activated with LiOH had a significantly lower methane uptake than both of these. Two carbon precursors from waste products were investigated as alternatives to corncobs: Red oak sawdust and walnut shells. Both sawdust and walnut shells showed a greater amount of mass loss in phosphoric acid carbonization; this suggests that these carbons contain a greater amount of volatile substances and react more vigorously with phosphoric acid to produce a more defined initial internal porous structure.

Conversely, carbon produced from corncobs shows a greater mass loss in the KOH activation than carbon produced from walnut shells and sawdust, suggesting that KOH has a greater effect on corncob carbon. Despite this fact, activated carbon derived from

walnut shells and sawdust still had a slightly better methane uptake than carbon from corncobs.

4.3: Recommendations for Further Research

A positive point of this research is that a wide variety of different samples were evaluated. However, due to the high volume of samples, the only examinations performed were simple screening procedures; no surface area analyses were performed. Value would be added to the present study if adsorption isotherms, pore volume estimates, SAXS, SEM images, and other relevant analysis was conducted on each sample in this study that performed well on screening tests. Gravimetric analysis to estimate porosity and volumetric methane uptake could be a good indicator of carbon properties, but carbon's exact physical characteristics are unknown without more in-depth analysis.

More in-depth analysis of NaOH as an activating agent, walnut shells or red oak sawdust as a precursor, a longer process hold time, 750°C activation temperatures, and an activating agent : carbon ratio of 4:1 could produce an activated carbon that outperforms 3K carbon at 790°C and 1 hour.

REFERENCES

1. Jankowska, H., A. Swiatkowski, and J. Choma, *Active Carbon*. 1991: Ellis Horwood Limited.
2. Bansal, R.C. and M. Goyal, *Activated Carbon Adsorption*. 2005, Boca Raton, FL: CRC Press.
3. Beguin, F. and E. Frackowiak, *Carbons for Electrochemical Energy Storage and Conversion Systems*. 2010: CRC Press.
4. McElroy, M., *Energy Perspectives, Problems, & Prospects*. 2010, New York: Oxford University Press.
5. Shepherd, W. and D.W. Shepherd, *Energy Studies*. 2003, London: Imperial College Press.
6. Burrell, J., *Gas Adsorption in Engineered Carbon Nanospaces*, in *Physics*. 2009, University of Missouri: Columbia.
7. Shah, P., *Nanoporous Carbon from Corncobs and its Applications*, in *Chemical Engineering*. 2007, University of Missouri: Columbia.
8. Pfeifer, P., et al., *Biomass Derived High Surface Area Carbon Materials with Large Micropores*. 2008: United States.
9. Lua, A.C. and T. Yang, *Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell*. *Journal of Colloid and Interface Science*, 2004. **274**(2): p. 594-601.
10. Ubago-Pérez, R., et al., *Granular and monolithic activated carbons from KOH-activation of olive stones*. *Microporous and Mesoporous Materials*, 2006. **92**(1-3): p. 64-70.
11. Lozano-Castelló, D., et al., *Preparation of activated carbons from Spanish anthracite: I. Activation by KOH*. *Carbon*, 2001. **39**(5): p. 741-749.
12. Perrin, A., et al., *NaOH activation of anthracites: effect of temperature on pore textures and methane storage ability*. *Carbon*, 2004. **42**(14): p. 2855-2866.
13. Tseng, R.-L., *Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation*. *Journal of Hazardous Materials*, 2007. **147**(3): p. 1020-1027.
14. Lozano-Castelló, D., et al., *Influence of pore size distribution on methane storage at relatively low pressure: preparation of activated carbon with optimum pore size*. *Carbon*, 2002. **40**(7): p. 989-1002.
15. Gómez-Serrano, V., et al., *Preparation of activated carbons from chestnut wood by phosphoric acid-chemical activation. Study of microporosity and fractal dimension*. *Materials Letters*, 2005. **59**(7): p. 846-853.
16. Cheng, F., et al., *Biomass Waste-Derived Microporous Carbons with Controlled Texture and Enhanced Hydrogen Uptake*. *Chemistry of Materials*, 2008. **20**(5): p. 1889-1895.
17. Rosas, J.M., et al., *HEMP-derived activated carbon fibers by chemical activation with phosphoric acid*. *Fuel*, 2009. **88**(1): p. 19-26.

18. Vernersson, T., et al., *Arundo donax cane as a precursor for activated carbons preparation by phosphoric acid activation*. Bioresource Technology, 2002. **83**(2): p. 95-104.
19. H. Marsh, F.R.-R., *Activated Carbon*. 1 ed. 2006, Amsterdam: London: Elsevier.
20. Tay, T., S. Ucar, and S. Karagöz, *Preparation and characterization of activated carbon from waste biomass*. Journal of Hazardous Materials, 2009. **165**(1-3): p. 481-485.
21. Lillo-Ródenas, M.A., D. Cazorla-Amorós, and A. Linares-Solano, *Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism*. Carbon, 2003. **41**(2): p. 267-275.
22. Wu, F.-C., R.-L. Tseng, and R.-S. Juang, *Preparation of highly microporous carbons from fir wood by KOH activation for adsorption of dyes and phenols from water*. Separation and Purification Technology, 2005. **47**(1-2): p. 10-19.
23. Marsh, H. and F. Rodriguez-Reinoso, *Activated Carbon*. 2006: Elsevier Science and Technology Books.
24. Evans, M.J.B., E. Halliop, and J.A.F. MacDonald, *The production of chemically-activated carbon*. Carbon, 1999. **37**(2): p. 269-274.