

ABSTRACT

FITZGERALD, STERLING FRANCIS. Gasification of Swine Manure for the Production of Synthesis Gas and Bio-char. (Under the direction of Dr. Praveen Kolar and Dr. John Classen).

Traditional waste management systems for swine manure have been under increased scrutiny as meat production in the United States became consolidated over the past few decades. In response to increased environmental awareness, new innovative technologies that safe guard the water, soil, and air are becoming attractive alternatives. This has led researchers to examine thermochemical technologies, like gasification, as a theoretical alternative for manure management and renewable energy production. While previous attention has only been given to wet gasification, due to previous aqueous waste management practices, alternative waste management practices such as flocculation or belt separated solids have opened opportunities for the dry gasification of swine manure solids for the production of synthesis gas and bio-char.

The goal of this research was to examine the yield of synthesis gas produced from the gasification of swine manure under varying moisture contents and temperatures while also examining the produced bio-char as a possible value-added adsorbant. It was also the intention of this research to examine the effect a nickel plated olivine catalyst had on the process. For swine manure gasification, the yield of syngas was found to be optimized with increased reactor temperatures and decreased moisture content. In the case of this research, optimum conditions were found to be 704 °C and 40% moisture. The nickel plated olivine catalyst was shown to increase the H₂ to CO ratio and overall H₂ and CO yields. Similarly, gasified swine char (40% moisture, 704 °C) was found to be an effective adsorbant of p-

cresol. From a non-linearized Langmuir fit it was found that the theoretical maximum adsorption capacity at 25, 35, and 45 °C is 7.63, 14.99, and 14.84 mg/g respectively.

© Copyright 2012 by Sterling Fitzgerald

All Rights Reserved

Gasification of Swine Manure for the Production of Synthesis Gas and Bio-char.

by
Sterling Francis Fitzgerald

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Master of Science

Biological and Agricultural Engineering

Raleigh, North Carolina

2013

APPROVED BY:

Dr. Praveen Kolar
Co-Committee Chair

Dr. John Classen
Co-Committee Chair

Dr. Michael D. Boyette

BIOGRAPHY

Sterling Fitzgerald was born January 12, 1988 to parents Nick and Shannon Fitzgerald with siblings Lina and Hayden of which he is the oldest. He lived in Ketchikan, AK until the age of 9 when his family moved to Hillsborough, NC. After graduating from the North Carolina School of Science and Math in 2006, he enrolled at North Carolina State University. He graduated from NCSU in 2010 with a B.S. in Biological Engineering under the Environmental concentration. In 2011 he enrolled as a master's student in the BAE department.

ACKNOWLEDGMENTS

I would like to thank my advisors Dr. Praveen Kolar and Dr. John Classen for their support in my work and for giving me the opportunity to obtain an advanced degree. Also, Dr. Robert Evans, the Koniag Education Foundation, the National Pork Board and the United States Department of Agriculture for their support. I would also like to thank Dr. Mike Boyette for being part of my committee and giving me advice throughout the process.

This study was possible due to help and contributions from the following people and institutions:

David Buffalo and the BAE Research Shop

Rachel Huie and the Environmental Analysis Lab

Stephen Byrd and the Swine Education Unit

I would also like to thank my family and friends for always supporting my educational pursuits and made graduate school more enjoyable. I would especially like to thank Rebecca, Bueller, and Zoey for helping me stay positive and happy.

TABLE OF CONTENTS

LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
CHAPTER 1: Literature Review	1
1. Introduction.....	1
2. History of Gasification.....	2
3. Shift in Agricultural Waste Management Practices.....	3
4. Manure as a Sustainable Feedstock	4
5. Gasification Technologies	6
5.1 Overview.....	6
5.2 Drying	7
5.3 Pyrolysis.....	7
5. 4.1 Tar Production	10
6. Manure Gasification Technologies	11
6.1 Wet Gasification	11
6.2 Dry Gasification.....	13
6.3 Steam Gasification	13
7. Economics and Policy.....	14
8. Char Products.....	15
9. Following Research	16
Chapter 1 References	18
CHAPTER 2: Swine Manure Gasification	24
1. Introduction.....	24
2. Materials and Methods.....	27
2.1 Collection and Processing of Biomass.....	27
2.2 Fabrication of the System	27
2.3 Collection of Samples	29
2.4 Statistical Analysis & Experimental Design.....	30
2.5 Ni-olivine Catalyst	31
2.6 Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS)	31
3. Results and Discussion	32
3.1 Production of Gases	32
3.2 Effect of Moisture Content	35
3.3 Effect of Temperature.....	37
3.3 Interaction Effect of Moisture and Temperature	39
3.3 Effect of Catalysis.....	40
3.4 Time of Flight	42
4. Conclusions.....	44

Chapter 2 References	45
CHAPTER 3: Gasified swine manure char as an adsorbent for mitigation of <i>p</i> -cresol	48
1. Abstract	49
2. Introduction.....	50
2. Experimental Protocols.....	52
2.1 Materials	52
2.2 Char Synthesis:	52
3. Characterization of GMC.....	52
3.1 Brunauer-Emett-Teller (BET).....	52
3.2 Acid Value	53
3.3 Point of Zero Charge (pH_{pzc})	53
3.4 Boehm Titration	53
3.5 Adsorption Experiments	54
3.6 Adsorption Isotherms.....	54
3.7 Adsorption Kinetics	55
3.8 Adsorption Thermodynamics.....	57
3.9 Desorption Study	57
4. Results and Discussion	58
4.1 Characterization of GMC.....	58
4.2 Batch Experiment Results.....	59
4.3 Isotherms.....	60
4.4 Kinetics	62
4.5 Identification of rate-limiting steps.....	64
4.6 Adsorption Thermodynamics.....	66
5. Summary	67
Chapter 3 References	68
APPENDICES	73

LIST OF TABLES

Table 1: Heating value from different gasification agitator gases (adapted from Belgiorno et al., 2003)	9
Table 2: Energy values of animal manures and their respective ash content (adapted from Kyoung et al., 2007).....	12
Table 3: Type III ANOVA for H ₂ yield.....	36
Table 4: Type III ANOVA for CO yield	36
Table 5: Tukey's Studentized Range (HSD) Test for H ₂ yield vs moisture.....	36
Table 6: Tukey's Studentized Range (HSD) Test for CO yield vs moisture	37
Table 7: Tukey's Studentized Range (HSD) for H ₂ yield vs temperature	38
Table 8: Tukey's Studentized Range (HSD) Test for CO yield vs temperature	39
Table 9: Comparison of Hydrogen and Carbon Monoxide Yield.....	41
Table 10: Physical Characterization of GMC	58
Table 11: Chemical Characterization of GMC	58
Table 12: Adsorption parameters from non-linear Langmuir and Freunlich models	60
Table 13: Kinetic model parameters for adsorption of <i>p</i> -cresol on GMC at 25 °C (120 rpm).....	62
Table 14: External (film) and internal (pore) mass transfer constants governing adsorption of <i>p</i> -cresol on GMC at 25 °C (120 rpm).	65
Table 15: Table of Gasification Results (% of total volume)	74

LIST OF FIGURES

Figure 1: Illustration of Manure to Value Added Syngas and Bio-char (adsorbent) Products	17
Figure 2: Gasification Reactor in kiln.....	28
Figure 3: Gasification System Schematic (not drawn to scale)	29
Figure 4: Hydrogen Yield (% total) vs time (min)	33
Figure 5: Carbon Monoxide Yield (% total) vs time (min)	34
Figure 6: Yield of Hydrogen vs Temperature by moisture levels	39
Figure 7: TOF-SIM data for comparison of control, 40% M and 704 C, and catalyzed run..	43
Figure 8: Adsorption of <i>p</i> -cresol (100 mg L ⁻¹) on GMC at 25 C (120 rpm).....	59
Figure 9: Adsorption of <i>p</i> -cresol on GMC.....	60
Figure 10: Intra-particle diffusion model for adsorption of <i>p</i> -cresol on GMC (A) indicated enhanced intra-particle diffusion constants at higher concentration and temperature (B).	64
Figure 11: Rate –limiting step during adsorption of <i>p</i> -cresol on GMC at 25 °C was identified by determining film (external) (A) and pore diffusion (internal) constants (B).	65

CHAPTER 1: Literature Review

1. Introduction

Gasification is the thermochemical conversion (TCC) of biomass, under partial-oxidation conditions, into a non-condensable synthesis gas and char byproduct (Bridgwater, 2003). Due to the reaction being endothermic, energy must be supplied to start the reaction and will continue to need to be supplied either externally or internally depending on reactor design. The synthesis gas (syngas) product is mainly composed of H₂, CO, CO₂, CH₄, and N₂ (Ptasinski, 2008). Depending on the biomass or gases used during gasification, the ratios of these products may vary, but the maximization of combustible gas products is desired. Biomass gasification is considered a renewable energy source as the feedstock is considered carbon neutral and created daily (Bridgwater,2003; Ptasinkski, 2005); whereas the gasification of fossil fuels, like coal, raises the atmospheric carbon dioxide levels.

Traditional animal waste management systems have grown considerably in response to meat production being consolidated onto confined animal feeding operations (CAFO). Using traditional methods of waste management, with the increased waste production on CAFOs, has led to potentially environmentally damaging scenarios (McNab et al.,2007; Szogi et al., 2006; Mallin, 2000). Due to heightened environmental awareness, current waste management practices for swine producers in North Carolina are under increased scrutiny (Tajik and Minkler, 2007) and innovative technology is becoming an attractive alternative means for waste management. Using a TCC technology such as gasification has the potential to turn a

waste management problem into a value-added, renewable energy solution. This literature review takes an in depth look at the history of gasification, current manure management, manure as an energy feedstock, the gasification process, current technologies, the economics and policy surrounding syngas use, and the produced bio-char.

2. History of Gasification

Gasification is a well established technology, which has been in and out of mainstream research and development corresponding to the availability of cheap fossil fuels. The earliest known investigation of gasification was Thomas Shiley, who in 1659 experimented with what he called carbureted hydrogen, or what is better known today as methane (Basu, 2010).

Gasification continued to be researched and in 1788, Robert Gardner solidified its importance by obtaining the first patent with regard to gasification (Turare, 1997).

Gasification gained popularity and by the mid 1800's resulted in towns throughout Britain and the United States illuminated by coal-gas (Basu, 2010). This technology eventually waned in the turn of the 20th Century with the electric light bulb replacing gas as a light source (Highman, 2008). Throughout the 20th century, gasification was largely overlooked due to cheap fossil fuels.

However, instances in which fossil fuels became scarce gave gasification an opportunity to progress and fill the energy needs as an alternative energy technology. During WWII, many countries had a large percentage of vehicles powered by onboard coal and wood gasifiers, which were favorable because wood and coal were abundant (Basu 2010). However, at the

end of the war, gasoline and diesel became cheap and widely available in Europe and the US, up until the 1970's Oil Crisis. At that time, the US put gasification back on the forefront of energy research. Large investments were made in developing new energy technologies to improve on energy stability (Highman, 2008). Once the embargo was lifted, the US turned back to inexpensive petroleum and largely forgot about the gasification of biomass. Recently, the United States and countries abroad are looking into thermochemical conversion technologies as an alternative to fossil fuels due to climate change and increasing concerns of energy security.

3. Shift in Agricultural Waste Management Practices

The conventional practice for managing manure on a farm has been to apply it to vegetated land, whether crop or ground cover, and recycle the nutrients back to the crop and soil. However, within the last few decades, the common trend of consolidating smaller farms into larger confined feeding operations across the United States and abroad has created a unique agricultural waste management problem. This trend of consolidating has caused environmental concerns in regards to the proper disposing and recycling nutrients (Ro et al., 2007; Israel et al., 2005; Sloan et al., 1999). Biomass waste, such as manure, can create a serious public health risk due to supporting the growth of pathogens (Vanotti et al., 2006; Sneeringer, 2008). Likewise, it can cause environmental damage, such as unintended fish kills due to increased nutrient loading promoting the growth of organisms that rapidly lower the oxygen content in receiving waters (Buckley and Schwarz, 2003). With environmental concerns and public complaints rising, state legislatures across the country have been led to

pass new restrictions and more stringent manure management regulation on the swine industry (He et al., 2000).

Currently, a common means of manure storage and treatment in the swine industry is the use of open lagoons. These lagoons have the detrimental consequence of allowing produced biogas to escape into the atmosphere, resulting in a source of environmental air pollution and respiratory irritant. While federal legislation, such as the Clean Air Act (CAA), regulates large-scale US farms there is a wide range of enforcement between these and other small farms from state to state (Brouwer, 2012). In contrast, anaerobic digesters contain all produced gases allowing them to be properly disposed of; however, the nutrient rich byproduct still requires disposal and this technology requires long processing time and larger storage facilities (Ro et al., 2007). These problems have created a unique niche for thermochemical conversion (TCC) within the renewable energy research field. Considering that livestock manure can be considered both renewable and sustainable, an efficient TCC could potentially produce a renewable energy source from an environmental problem (Zhang et al., 2010; He et al., 2000).

4. Manure as a Sustainable Feedstock

One of the main criticisms of renewable energy is the selection of food crops for ethanol production. This competition of food crops as an energy feedstock is largely centered on corn grain and other human and animal staples. This is due to necessary characteristics, such as high starch content, for the feedstock of that process. Thermochemical conversion processes,

like gasification, do not require the use of food crops due to its versatility. Gasification technology has the potential to accept various carbonaceous organic waste products, including manure, which could eliminate a liability or burden for the farmer while creating value-added products (Cantrell, 2008).

Similarly, gasification has the advantage over some renewable energy processes, because of the ability to tailor the process for a wider range of feedstocks. Due to gasification systems allowing a range of moisture contents, there is potential for little to no pretreatment which makes it less burdensome than other conversion technologies. Whether wet or dry, animal manure contains high organic content compared to ash, making it an attractive feedstock.

Pairing its physical properties with its over-abundance, manure is potentially a no-cost feedstock for energy production (Cantrell et al., 2008). Perlack et al. (2005) concluded that manure comprises 18% of the total sustainable biomass feedstock from agricultural land.

Another consideration for any biomass feedstock is logistics. With crops or crop residues, the biomass will have to be harvested and transported to a pretreatment or storage facility before being loaded into the gasifier. With confined animal feeding operations, manure is produced daily and is already conveniently collected for storage or processing. This facilitates the addition of a new processing system by replacing outdated technology.

5. Gasification Technologies

5.1 Overview

Poultry litter, feedlot manure, composted manure, and manure-residue mixtures are all excellent manure candidates for dry gasification systems while swine manure and dairy manure traditionally have high moisture contents which could require time-consuming or high energy drying pretreatment. Feedstocks that have moisture contents in the 85-95% range, like combined swine and dairy waste, can be appropriate biomasses for wet gasification without the use of dewatering or drying (Ro et al., 2007).

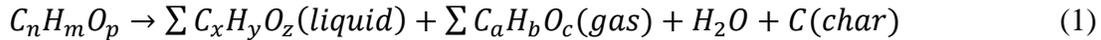
Using gasification for renewable energy production, carbonaceous manures could be converted to synthesis gas and used for heat, electricity, or fuel. While research scale experiments can easily supply heat externally to the reactor, many larger systems are designed to use partial combustion to keep the conversion process running. Gasification requires an oxidizer and air, pure oxygen, or steam can all be used. The procedure is commonly divided into four processes which each occur in a distinct zone. Although the design may change the location of these processes, gasifiers typically have a zone for the drying, pyrolysis, oxidation, and reduction processes. Gasifiers are typically paired with other instrumentation, depending on the end-use of the gas, in order to clean it through hot-gas cleaning or cool-gas cleaning. More energy can be gained through hot-gas cleaning than cool-gas cleaning although it is technically more challenging (McKendry, 2002).

5.2 Drying

For dry gasification, bringing the biomass to a low moisture content can easily be accomplished while the reactor comes up to treatment temperature. For every kilogram of moisture within the biomass, 2260 kJ of energy is used to vaporize the water. All loosely bound moisture in the biomass is irreversibly removed above 100 ° C (Basu, 2010). Heat from internal combustion or external sources drives out moisture until the reaction temperature reaches approximately 200 ° C. Before this process concludes, extractives with a low molecular weight may start to volatilize.

5.3 Pyrolysis

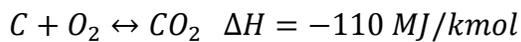
Pyrolysis is the thermal breakdown of larger hydrocarbon molecules within the biomass into smaller molecules without reacting chemically with oxygen. The temperature at which pyrolysis occurs can vary from one biomass to another and can be decreased with the addition of a catalyst. The main products of pyrolysis are char, which comes from the fixed carbon in the biomass, bio-oil, and gases from the volatiles. According to He et al. (2000), bio-oil production from swine manure requires a temperature of 285 ° C or higher to ensure formation, while higher than 335 ° C leads to bio-char formation. The bio-oil is the result of cooled volatiles leaving the pyrolysis zone while the gases make up the other fraction. The yields of these three byproducts vary depending on conditions within the reactor and the biomass (Jameel et al., 2010). The gases which are not condensed into bio-oil typically include CO, CO₂, H₂, and CH₄ (Basu, 2010). Water, typically in the form of steam, is also commonly produced and can be seen in the following equation for the pyrolysis process:



5.4 Oxidation

Oxidation, commonly referred to as the combustion zone of gasification, is the process which typically supplies heat to the reaction moving it towards complete gasification. The position of this process is located at the area which oxygen is introduced to the system. Jameel et al. (2010) recommends that 25% of the stoichiometric oxygen necessary for complete combustion should be added to create partial oxidation and combustion in a gasifier. Once released during pyrolysis, the volatiles are able to combust in the gas phase with the oxidant surrounding them. These reactions are exothermic and will raise the temperature of the produced gases significantly (Liu et al., 2009). Combustion of carbon in the presence of oxygen yields primarily CO₂ which can be characterized by the following reaction:

Carbon-Oxygen reaction



Maintaining partial oxidation conditions is crucial for gasification. With oxygen levels that allow for excess oxygen, combustion of the synthesis gas will occur. However, without enough oxygen the production of gases will not be reached or maintained. This illustrates the

importance of knowing how a system will react to a new feedstock with various oxygen/moisture contents and accounting for it during procedure. Non-reactive gases such as nitrogen are considered dilutants and although important for agitation can affect the heating value of produced synthesis gas. Belgiorno et al. (2003) found that the absence of nitrogen in the gasification agent reportedly increased efficiency and overall heating value as seen in Table 1.

Table 1: Heating value from different gasification agitator gases (adapted from Belgiorno et al., 2003)

Process	Gasification Agent	Producer Gas heating value (MJ/m ³)
Direct Gasification	Air	4-7
Pure Oxygen Gasification	Oxygen	10-12

Although nitrogen gas is usually non-reactive, in cases of high temperatures from the combustion zone there is a potential for NO_x to be produced. During thermochemical processes, it is important to regulate all inputs in order to optimize efficiency and the economics of the system. A tradeoff between gas heating value and overall gas purity may need to be considered when designing and maintaining a system.

5. 4.1 Tar Production

Oxidation is also the zone which accounts for tar synthesis within the reactor. Tars, complex condensable hydrocarbons, are produced during gasification as a result of incomplete conversion of the carbonaceous material to gases. Commonly defined, tars are any organic contaminant with a molecular weight larger than benzene (Devi et al., 2002). Thermally degrading tar, or tar cracking, is essential to the overall quality of the produced synthesis gas.

Currently there are methods to remove tar after it has left the reactor, but primary treatment within the reactor is gaining attention to eliminate the need for downstream cleanup. There are three approaches to primary treatment; they are gasifier modifications, catalysis, and proper selection of operating parameters (Devi et al., 2002). For tar cracking nickel catalysts are widely used due to their high activity and are commonly supported on dolomite, olivine, or alumina (Yang et al., 2010).

5.5 Reduction

The reduction zone in a gasifier is where the majority of CO is produced. It is also where endothermic reactions are taking place which creates gases with lower temperatures than the combustion zone. Once gasification has finished, the biomass byproducts are ash and unused char. A system which exhibits complete gasification will only exhibit leftover ash. Ash particles are light weight and can become a gas contaminate if flow rates of the agitator gas are strong enough to force it from the chamber along with produced gases. Particle traps can be used downstream but operation of the gasifier should be optimized to lower the cost and

necessity of cleanup. Reduction is characterized by the following four reactions according to Jameel et al. (2010):

Boudouard reaction



Carbon-water reaction



Water-gas shift (WGS) reaction



Methanation reaction



6. Manure Gasification Technologies

6.1 Wet Gasification

Wet gasification is an appropriate energy technology for current wash-water manure collection systems due to swine and dairy operations producing a dilute waste stream containing wash water, urine, manure, and spilled feed. This excess water used to wash out barns or underground pits can be used as a carrier fluid during thermochemical conversion. Water-based TCC technologies also have the added benefit of not requiring costly or timely drying as a pretreatment. The consequences of using a homogenized fluid biomass is the high energy required to raise the temperature and the possibility of pretreatment mixing. The

development of a catalyst becomes critical to enable gasification at lower temperatures. Kyoung et al. (2007) evaluated the energetic potential of various animal manures based on elemental compositions. They took the resulting gas proportions of CH₄, CO₂, NH₃, H₂, and H₂O from previous experiments and evaluated the adequacy of the chemical empirical formulas. These were used to estimate reaction energies and subsequent high heat value (HHV) of the produced gas. The following table is adapted from Kyoung et al. (2007).

Table 2: Energy values of animal manures and their respective ash content (adapted from Kyoung et al., 2007)

	Swine Manure	Dairy Manure	Poultry Manure	Unpaved Feedlot Manure	Paved Feedlot Manure
Ash Content (%)	12.7	17	20	58.7	20.2
Energy Value of Product Gases (kJ/mol)	501	466	450	474	499

Swine manure produced the highest energy value synthesis gas from wet gasification. This can be explained in part due to its lower ash content compared to other manures. All calculations were based on moisture contents of 85% or higher (i.e. solid contents less than 15%) due to current wet gasification systems only handling pumpable liquid feedstocks. This is advantageous to swine and dairy manure which typically exhibits moisture contents of 85-

95% but a disadvantage to feedlot and poultry manure.

6.2 Dry Gasification

There are various gasification technologies that are each tailored to different feedstocks, parameters, and optimization goals. For instance, current testing of poultry litter and feedlot manure, which each have low moisture content, have been limited to dry gasification systems (Cantrell et al., 2007; Priyadarsan et al., 2004). Dry gasification systems, use heated oxidizers such as air or oxygen typically at atmospheric conditions. Priyadarsan et al. (2004) used a fixed-bed gasification system with air as the oxidant and found that poultry litter and feedlot manure produce a low-Btu gas with an average high heating value (HHV) of 4.2 (MJ/m³). However, this gas only had 27.6% CO on average due to nitrogen dilution. This dilution was estimated to lower the potential HHV by approximately 60%. Dry gasification typically produces low-Btu gas primarily composed of H₂, CO, and CO₂ (Cantrell et al., 2007). Due to producing low-Btu gas, dry gasification of poultry litter is typically used as a low cost heating alternative.

6.3 Steam Gasification

In order to increase the production of H₂, steam can be used as the oxidant and will cause the water-gas shift (WGS) reaction of CO and H₂O to CO₂ and H₂. Hydrogen production may be improved by increasing the operational and input steam temperatures. The use of a heterogeneous catalyst, like nickel impregnated olivine, is typical for increasing the reaction

rate of the WGS reaction and the carbon-steam reaction to produce a higher quality synthesis gas (Yang et al., 2010). Garcia et al. (1999) found that using a Ni-Al catalyst, during steam gasification of pine sawdust, increased the H₂ to CO ratio by 400% and doubled the gas yield. Similarly, Zhang et al. (2011) found that using a Ni-Al catalyst and steam gasification increased tar cracking into H₂, CO, and CO₂ which increased overall yields of H₂ and CO at low temperatures due to catalysis. Wang et al. (2013) found decreased tar yields due to tar cracking and increased carbon conversion efficiency from NiO/Modified Dolomite catalytic steam gasification of swine compost.

While adding a catalyst can improve gas yields and increase tar cracking, it is important to consider the cost associated with using a catalyst in order for larger systems to be economically feasible. Sheth and Turner (2002) investigated steam gasification of poultry litter using potassium carbonate and langbeinite, common agricultural fertilizers, as a cheaper source of catalysts. They found that catalyst loading showed a significant effect on carbon conversion and overall gas yield. Including the 10% by weight catalyst loading, Sheth and Turner (2002) concluded that poultry litter to fuel gas via steam gasification is economically viable. This demonstrates how low cost catalysts could potentially facilitate an economically feasible gasification system.

7. Economics and Policy

In order for pilot-scale applications of swine gasification to gain favor in North Carolina animal operations, owners need to have an economic incentive for investing in new

technologies. In 2007, North Carolina became the first state in the Southeast to adopt a Renewable Energy and Efficiency Portfolio Standards which provides credits to electric companies which may be used or traded to attain the required amount of renewable generation. This portfolio requires NC to meet an overall target of 10% renewable energy by 2018. Unfortunately, only 0.2% is required to be from swine waste and will likely be provided by anaerobic digesters. Buckley and Schwarz (2003) pose the possibility for serious repercussions on the economy if NC does not modify its energy portfolio to encourage renewable energy from manure. They believe that North Carolina, and other states with heavy swine and poultry production, will lose producers to other pro-sustainable states as sustainability becomes the performance standard and where producers can make additional revenue from renewable energy.

8. Char Products

Char produced from thermochemical processes such as pyrolysis or gasification can potentially be a value-added product rather than a waste byproduct. Due to high costs associated with raw materials, researchers have begun to focus on the ability to produce activated carbon from waste materials. The synthesis of activated carbon has been looked into for tobacco residues (Kilic et al., 2011), corn cob (Chang et al., 2000; Tsai et al., 1997), and activated sludge (Li et al., 2012) among others. Recognizing that the majority of activated carbon is used for liquid-phase applications (Moreno-Castilla and Rivera-Utrilla, 2001), it is important to determine whether char from swine manure gasification has potential as an adsorbant. Broiler litter and cake were synthesized via pyrolysis to produce activated

carbon and have been found to contain excellent physical properties for adsorption (Lima and Marshall, 2005; Koutcheiko et al., 2007). Klasson et al. (2010) reported that activated char produced from chicken cake and litter removed mercury from simulated flue gas as well as commercially available activated carbon. An estimated cost for this activated carbon was only \$0.95/kg. Similar results have been presented by Cao and Harris (2010) who found that dairy manure char, produced from low temperature heating, can produce an effective adsorbent for the removal of lead and atrazine, models for heavy metal and organic contaminants, from aqueous solution. These results show that manure can produce a viable adsorbent as long as advantageous physical characteristics are produced during the synthesis process. Gasification of swine manure, as a thermochemical conversion process, has the ability to produce a char product but an investigation into the resulting physical characteristics, kinetics, isotherms, and mechanisms should be performed for its adsorption potential.

9. Following Research

The application of gasification as a means for high energy gas production has been focused primarily on wet gasification for swine manure due to aqueous waste management strategies. With the recent increase in alternative waste management practices, such as flocculation or belt separated solids, there is a possibility that dry gasification could be utilized for the production of syngas and an adsorbent bio-char from swine manure. A schematic of the proposed manure utilization can be found below in Figure 1. The objective of this study is to

determine if swine manure solids, are a suitable biomass for dry gasification at high temperatures with or without a Ni-olivine catalyst. By examining the temperature of the reactor and the moisture levels of the biomass, recommendations can be made as to which factors are statistically significant for synthesis gas production and bio-char production.

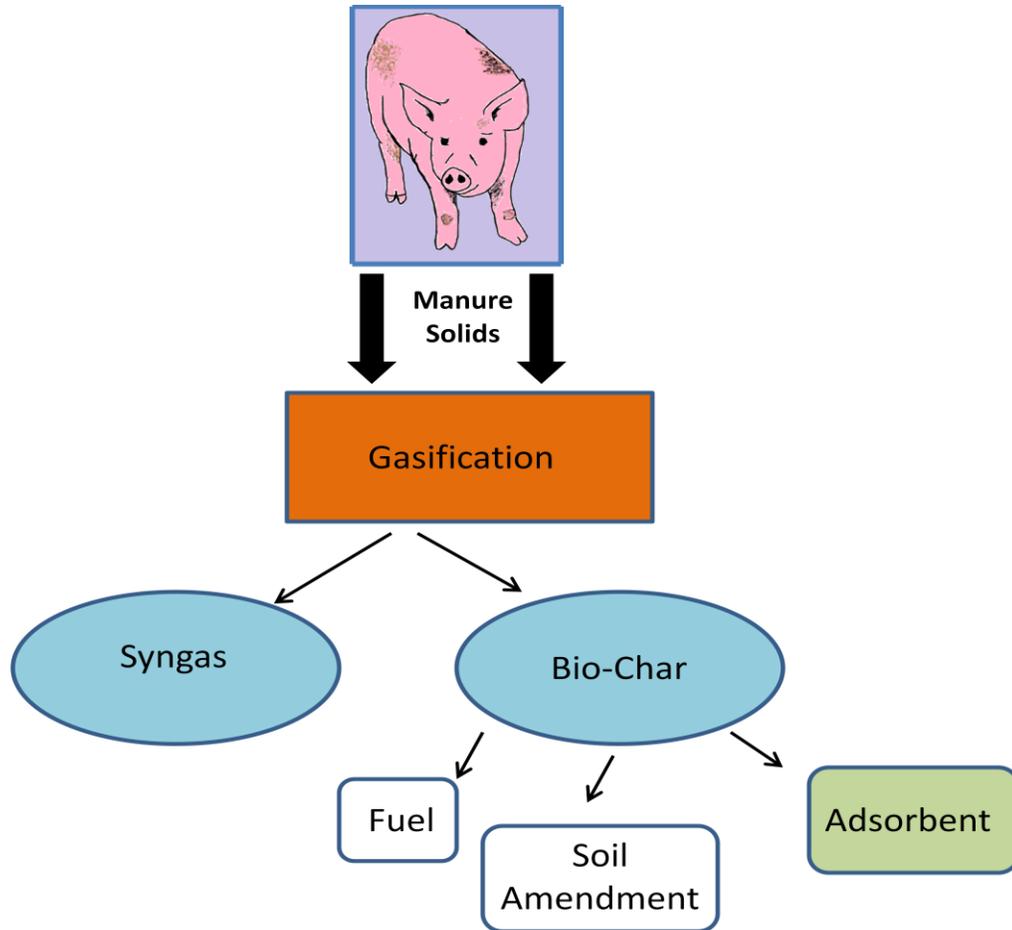


Figure 1: Illustration of Manure to Value Added Syngas and Bio-char (adsorbent) Products

Chapter 1 References

- Allen, S.J., McKay, G., Khader, K.Y.H. 1989. Intraparticle Diffusion of a Basic Dye During Adsorption onto Sphagnum Peat. *Environmental Pollution*, 56: 39-50
- Basu, P. 2010. Biomass Gasification and Pyrolysis: Practical Design and Theory, 1st ed., Elsevier Science & Technology.
- Belgiorno, V., De Feo, G., Della Rocca, C., & Napoli, R. M. A. 2003. Energy from gasification of solid wastes. *Waste Management*, 23(1), 1-15. doi:10.1016/S0956-053X(02)00149-6
- Brouwer, F. 2012. Economics of Regulation in Agriculture: Compliance with Public and Private Standards. CABI.
- Buckley, J.C.; Schwarz, P.M. 2003. Renewable Energy from Gasification of Manure: An Innovative Technology in Search of Fertile Policy. *Environmental Monitoring and Assessment*, 84, 111-127.
- Bridgwater, A.V. Renewable fuels and chemicals by thermal processing of biomass, *Chemical Engineering Journal*, Volume 91, Issues 2–3, 15 March 2003, Pages 87-102, ISSN 1385-8947, 10.1016/S1385-8947(02)00142-0
- Cantrell, K.B.; Ducey, K.; Ro, K.S.; Hunt, P.G. 2008. Livestock waste-to-bioenergy generation opportunities. *Bioresource Technology*, 99(17), 7941-7953.
- Cao, X., Harris, W. 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology* 101: 5222-5228.

- Chang, C.F., Chang, C.Y., Tsai, W. 2000. Effects of Burn-off and Activation Temperature on Preparation of Activated Carbon from Corn Cob Agrowaste by CO₂ and Steam. *Journal of Colloid and Interface Science*. 232(1): 45-49.
- Devi, L., Ptasiniski, K. J., & Janssen, F. J. J. G. 2003. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy*, 24(2), 125-140. doi:10.1016/S0961-9534(02)00102-2
- Garcia, L. Salvador, M.L., Arauzo, J., Bilbao, R. 1999. Catalytic steam gasification of pine sawdust. Effect of catalyst weight/biomass flow rate and steam/biomass ratios on gas production and composition. *Energy Fuels*. 13: 851-859.
- He, B.J. (2000). "Operating temperature and retention time effects on the thermochemical conversion process of swine manure". *Transactions of the ASAE* (0001-2351), 43 (6), p. 1821.
- Highman, Christopher; van der Burgt, Maarten. 2008. *Gasification*, 2nd ed., Elsevier.
- Israel, D.W. Showers, W.J. Fountain, M. 2005. Nitrate Movement in Shallow Ground Water from Swine-Lagoon-Effluent Spray Fields Managed under Current Application Regulations. *Journal of Environmental Quality*, 34(5): 1828-1842.
- Jameel, H. D. R. Keshwani, S. F. Carter, & T. H. Treasure. 2010. Chapter 10: Thermochemical Conversion of Biomass to Power and Fuels. *Biomass to Renewable Energy Processes*, 436-489. J. Cheng, Boca Raton, F.L.: CRC Press/Taylor & Francis.

- Khraisheh, M.A., Al-Degs, Y.S., Allen, S.J., Ahmad, M.N. 2002. Elucidation of Controlling Steps of Reactive Dye Adsorption on Activated Carbon. *Ind. Eng. Chem. Res.*, 41: 1651-1657
- Kilic, M., Apaydin-Varol, E., Putun, A.E., 2011. Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics. *J. Hazard. Materials.* 189: 397-403
- Klasson, K.T., Lima, I.M., Boihem, L.L., Wartelle, L.H. 2010. Feasibility of mercury removal from simulated flue gas by activated chars made from poultry manures. *Journal of Environmental Management* 91(12):2466-2470.
- Koutcheiko, S., Monreal, C.M., Kodama, H., McCracken, T., Kotlyar, L. 2007. Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Bioresource Technology* 98(13): 2459-2464.
- Li, D., Wu, Y., Feng, L., Zhang., L., 2012. Surface properties of SAC and its adsorption mechanisms for phenol and nitrobenzene. *Bioresources Technology.* 113:121-126
- Lima, I.M., Marshall, W.E. 2005. Granular activated carbons from broiler manure: physical, chemical and adsorptive properties. *Bioresource Technology* 96(6): 699-706.
- Liu, Ke; Song, Chunshan;Subramani, Velu. 2009. *Hydrogen and Syngas Production and Purification Technologies*, Wiley.

- Mallin, M.A. Cahoon, L.B. 2003. Industrialized Animal Production- A Major Source of Nutrient and Microbial Pollution to Aquatic Ecosystems. *Population and Environment*, 24(5): 369-385.
- McKendry, Peter. 2002. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology*. 83(1): 55-63.
- McNab, W.W. Singleton, M.J., Moran, J.E. Esser, B.K. 2007. Assessing the Impact of Animal Waste Lagoon Seepage on the Geochemistry of an Underlying Shallow Aquifer. *Environ. Sci. Technol.* 41(3): 753-758.
- Perlack, R.D., Wright, L.L., Turhollow, A.F., Graham, R.L., Stokes, B.J. Erbach, D.C. 2005. Biomass as a feedstock for a bioenergy and bioproducts industry: technical feasibility of a billion-ton annual supply. DOE/GO- 102995-2135. Washington, D.C.:U.S. Department of Energy
- Priyadarsan, S. Annamalai, K., Sweeten, J.M., Mukhtar, S., Holtzapple, M.T. 2004. Fixed-bed gasification of feedlot manure and poultry litter biomass. *Trans. ASAE*. 47(5): 1689-1696.
- Ptasinski, K.J. Thermodynamic efficiency of biomass gasification and biofuels conversion. 2008. *Biofuels, Bioproducts and Biorefining*. 2(7): 239-253.
- Ptasinski, K.J. Prins, M. Pierik, A. Exergetic evaluation of biomass gasification. 2007. *Energy*. 32(4): 568-574.
- Ro, K.S.; Cantrell, Keri; Elliott, Douglas; Hunt, P.G. 2007. Catalytic Wet Gasification of Municipal and Animal Wastes. *Industrial and Engineering Chemistry Research*, 46: 8839-8845.

- Sheth, A.C.; Turner, A.D. 2002. Kinetics and economics of catalytic steam gasification of broiler litter. *Transactions of the ASAE* 45 (4): 1111-1121.
- Sloan, A.J. Gilliam, J.W. Parsons, J.E. Mikkelsen, R.L. Riley, R.C. 1999. Groundwater nitrate depletion in a swine lagoon effluent-irrigated pasture and adjacent riparian zone. *Journal of Soil and Water Conservation*, 54(4): 651-656.
- Sneeringer, Stacy. 2008. Does Animal Feeding Operation Pollution Hurt Public Health? A National Longitudinal Study of Health Externalities Identified by Geographic Shifts in Livestock Production. *American Journal of Agricultural Economics*, 91(1): 124-137.
- Szogi, A.A. Vanotti, M.B. Stansbery, A.E. 2006. Reduction of Ammonia Emissions From Treated Anaerobic Swine Lagoons. *Transactions of the ASABE* 49(1): 217-225.
- Tajik, M. Minkler, M. 2007. Environmental Justice Research and Action: A Case Study in Political Economy and Community-Academic Collaboration. *International Quarterly of Community Health Education* 26(3): 213-231.
- Tsai, W.T., Chang, C.Y., Lee, S.L. 1997. Preparation and characterization of activated carbons from corn cob. *Carbon*, 35(8): 1198-1200.
- Turare, C. 1997. *Biomass Gasification: Technology and Utilization*. Human Development Library.
- Vanotti, M.B. Szogi, A.A. Hunt, P.G. Millner, P.D. Humenik, F.J. 2007. Development of environmentally superior treatment system to replace anaerobic swine lagoons in the USA. *Bioresource Technology*, 98(17): 3184-3194.

Wang, J., Xiao, B., Liu, S., Hu, Z., He, P., Guo, D., Hu, M., Qi, F., Luo, S. 2013. Catalytic steam gasification of pig compost for hydrogen-rich gas production in a fixed bed reactor. *Bioresource Technology*, 133: 127-133.

Yang, X., Xu, S., Xu, H., Liu, X., Lui, C. 2010. Nickel supported on modified olivine catalysts for steam reforming of biomass gasification tar. *Catalysis Communications*, 11(5): 383-386.

Zhang, S., Wang, X., Cao, J., & Takarada, T. (2011). Low temperature catalytic gasification of pig compost to produce H₂ rich gas. *Bioresource Technology*, 102(2), 2033-2039.
doi:10.1016/j.biortech.2010.09.070

CHAPTER 2: Swine Manure Gasification

Sterling Fitzgerald^a, John Classen^{a*}, Praveen Kolar^a, and Mike Boyette^a

^aBiological and Agricultural Engineering, Campus Box 7625, North Carolina State University, Raleigh, NC, 27695-7625, USA.

E-mail addresses: sffitzge@ncsu.edu, classen@ncsu.edu, pkolar@ncsu.edu, and boyette@eos.ncsu.edu

^{**}Corresponding author. Phone: +1 919 515 6800; Fax: +1 919 515 7760

E-mail address: classen@ncsu.edu

1. Introduction

With increasing population levels and urban sprawl, animal production operations are being further scrutinized by neighboring citizens due to possible health and environmental quality problems (McNab et al., 2007; Szogi et al., 2006; Vanotti et al., 2006; Sneeringer, 2008). In the past couple of decades, confined animal feeding operations (CAFOs) have undergone significant consolidations and expansion resulting in fewer operations with larger stock (Key et al., 2011). Odor associated with swine operations, anaerobic storage lagoons, and spray fields are a growing concern as agriculture continues to intensify. This odor is generated from the microbial degradation of the swine waste and continues during the anaerobic

processing in lagoons (Schiffman et al., 2001). This trend has caused environmental and health concerns in continuing the conventional practice of recycling and disposing of manure nutrients (Stone et al., 1995). An over-application of manure can lead to air, water, and soil contamination which has created a need for alternative forms of disposal (Buckley and Schwarz, 2006; Sneeringer, 2008; Sloan et al., 1999).

Concurrently, climate change and energy security is of growing importance in the United States in response to declining oil reserves and the political instability of those sources (Bang, 2010; Hoekman, 2009). This has spurred interest in alternative forms of energy as well as increasing efficiency whenever possible. Researchers have heightened interest on how to produce energy cheaply and efficiently from appropriate agricultural residues and waste products (Cantrell, 2008). A convenient means of manure conversion to energy would encompass both on-site treatment and manageable byproducts with low energy expenditure. Currently available methods such as anaerobic digestion have been used for swine manure management and energy production; however, a long retention period creates a need for large storage spaces. Open air methods such as composting can potentially lead to emission problems (Fukumoto et al., 2003). Hence newer technologies are needed. A properly scaled thermochemical disposal system would both alleviate the need for storage and produce safe, manageable byproducts.

Of the various methods for producing energy from biomass, gasification is considered the most technologically suited for medium to large scale applications (Franco et al., 2003). This

makes it an attractive option for agricultural waste management. Gasification is the thermochemical conversion (TCC) of biomass, under partial-oxidation conditions, into a synthesis gas and ash/char products. Swine manure is also high in oxygen which would allow thermochemical conversion to take place with less supplied oxygen. The process produces synthesis gas (syngas) with the intent of maximizing combustibles (H_2 , CO , and CH_4) but also may include CO_2 , N_2 , NO_x and SO_x . The reaction is endothermic, with energy supplied as heat to start the reaction, and will continue to be supplied either internally through the combustion of produced syngas or externally in the form of heat depending on the reactor design. Biomass gasification is considered a renewable energy source as the feedstock is considered carbon neutral and produced daily; whereas the gasification of fossil fuels, like coal, raises the atmospheric carbon dioxide levels (Zhang et al., 2010)

In order to determine the usefulness of swine manure, as a gasification feedstock, factors need to be studied for their statistical significance. Moisture content is the factor which most researchers use to determine if a biomass is suitable for their system. Until recently, swine manure has largely been collected with the aid of wash water making it an unsuitable biomass for dry gasification. However, due to innovative manure management technologies, such as polymer flocculation and belt separators, swine manure can be collected under lower moisture conditions than traditional wash water methods. The purpose of this study is to examine the utility of swine manure as a feedstock for the gasification process and the resulting synthesis gas by examining certain objectives. These objectives are: 1) Determine the effect of moisture content on the yield and quality of gases. 2) Examine the effect the

reactor's temperature has on the overall gasification reaction and products. 3) There have been reports of an increase in H₂, CO, and CO₂ due to the presence of a catalyst (Zhang et al., 2011) which will be investigated using a nickel plated olivine catalyst to determine its effect on syngas quality.

2. Materials and Methods

2.1 Collection and Processing of Biomass

Manure solids were collected from the North Carolina State University's Swine Education Unit, gestation building, in Raleigh, NC. The Swine Education Unit employs a flush under slatted-floor waste management system which allowed manure solids, having not passed through the slats, to be collected. All gestating sows at the Swine Education Unit were fed the same diet throughout the duration of this study. The solids were then dried at 70 ° C for 48 hours and subsequently crushed and homogenized. Dried manure was stored in a sealed container, in a 5 °C walk in refrigerator, between experiments. Samples were brought up to the correct percent moisture by adding water.

2.2 Fabrication of the System

A stainless-steel, single chambered, batch reactor with a 12.7 cm by 12.7 cm base and measuring 7.6 cm tall (external dimensions), with an internal volume of roughly 1.2 liters, was constructed to be used in conjunction with a Paragon Industries (Sapulpa, OK) 1800 W electric kiln (model TNFE10) for gasifying the biomass. The reactor's inlet and outlet ports consist of stainless-steel tube fittings manufactured by Swagelok (Cleveland, OH) which

were welded to the chamber's lid. The lid is secured to the reactor utilizing 8 bolts welded to the lip of the base unit using nuts and washers. Between the lid and base was placed a disposable, single-use gasket made of ceramic fibers, .25" thick S Durablanket with 8 lb/cu ft density, sold by Thermal Products Company Incorporated (Norcross, GA). This gasket material is specifically designed for high temperature applications and is graded to 1260 ° C. A picture of the chamber can be found below in Figure 1.



Figure 2: Gasification Reactor in kiln

The agitator gas was a 25:1 mixture of N_2 and O_2 at 2.6 L/min controlled by 2 Omega Engineering Inc. (Stamford, CT) mass flow controllers. The system uses $\frac{3}{4}$ inch stainless-steel tubing and stainless-steel fitting throughout except for the $\frac{1}{4}$ inch plastic tubing between the mass flow controllers and a $\frac{3}{4}$ inch to $\frac{1}{4}$ inch reducer. The entire system is air-tight resulting in all produced gas, and agitator gas, exiting the sampling port after flowing through a U-shaped heat exchanger submerged in a water-bath. The sampling port is left open to the atmosphere to avoid pressure build up and to keep the system at atmospheric pressure. A diagram of the system can be found below in Figure 2.

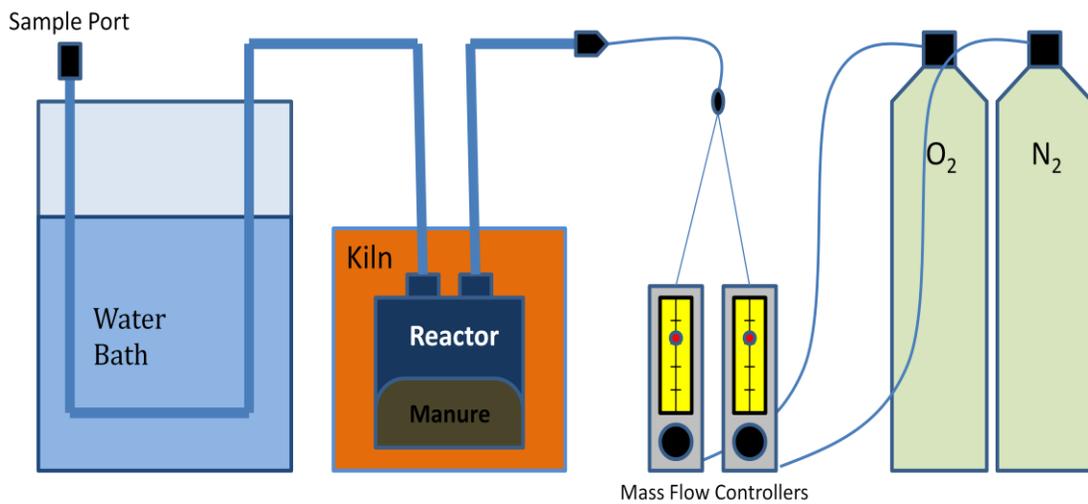


Figure 3: Gasification System Schematic (not drawn to scale)

2.3 Collection of Samples

All samples were taken using 250mL Gas Collecting Bulbs manufactured by Ace Glass Incorporated (Vineland, NJ). The biomass was brought to the treatment temperature (482,

593, and 704 °C) at 982° C/hour then gas samples were taken at time 0, 5, 10, and 15 minutes while the temperature was held constant. For the purpose of this study, time zero is considered the moment the kiln reaches the treatment temperature. After 15 minutes, the kiln was subsequently turned off and O₂ flow ceased. The gas samples were then immediately taken to the lab for analysis. Samples were analyzed using an Agilent 7890A GC system (model # G3172A/G3440A) using a Supelco 100/120 Carbosieve SII column and a thermal conductivity detector (TCD). The percent by volume (% vol.) of H₂, CO, CO₂, and CH₄ were quantified. The resulting char byproduct was cooled following the collection of gas samples with 2.5 L/min N₂ flow, in the absence of O₂, in order to minimize any further reactions. The char was then analyzed for porosity and pore volume.

2.4 Statistical Analysis & Experimental Design

All experiments performed in this study were conducted in duplicates in completely randomized order. A 3x3 factorial experimental design was utilized with treatments being % Moisture Content (40, 60, 80) and Temperature (482, 593, 704 °C). The null hypothesis is that the production of H₂, CO, CO₂, and CH₄ is the same for all treatment levels of moisture content and temperature. The statistical analysis was performed using SAS 9.2 Software (Cary, NC). The analysis was carried out using type III analysis of variance (ANOVA) test and Tukey's Studentized Range Test. Both statistical tests were performed using a 95% confidence interval ($\alpha=0.05$ level). These tests identify treatments which are statistically different and any interaction effect between them. Due to a difference in residence time for

each pairing of treatments, the raw data taken at time 0 (the time at which the kiln reached treatment temperature) was used for analysis as a % of the overall gas sample. These gas samples reflect a dilution due to the agitator gas.

2.5 Ni-olivine Catalyst

A nickel plated olivine catalyst was used in order to study the effect of catalysis on gas production. The catalyst was prepared via thermal impregnation using a modified technique similar to Kuhn et al. (2008). Olivine provided by Unimin Corporation (Green Mountain, NC) was crushed and sieved to obtain 500 micron particles then calcined at 1200 °C for 12 hours. These particles were soaked in NiSO₄ 6H₂O solution for 1 hour then heated at 1400 °C under oxygen-limited conditions. The catalyst had a nickel loading rate of 5% (w/v). Olivine was chosen as a support due to it being inexpensive and having previously shown to have promising tar cracking attributes (Yang et al., 2010). Catalyzed runs were performed at the optimum conditions with 30 g of catalyst mixed with the manure.

2.6 Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS)

Char was also analyzed using a surface analytical technique known as time-of-flight secondary ion mass spectroscopy (TOF-SIMS) which gives elemental and molecular images of the surface. This analysis was done at the NCSU Analytical Instrumentation Facility (AIF) using an ion TOF-SIMS 5 (ION TOF, Inc. Chestnut Ridge, NY, USA) equipped with a Bi_n^{m+} (n=1-5, m=1,2) liquid metal ion gun and operated below 5.0 x 10⁻⁹ mbar. For the analysis, char and the control were ground to a sample size no larger than 16.5 mm x 38 mm x 5mm

thick then an area of 500 μm x 500 μm was selected for mass spectral images using the Bi⁺ primary ion beam.

3. Results and Discussion

3.1 Production of Gases

Gas samples for all experiments were analyzed for the quantity of H₂, CO, CH₄, and CO₂ at time 0, 5, 10 and 15 minutes and results can be found in the Appendix. H₂ and CO are the primary combustible gas produced during dry gasification and their optimization is sought after. Figures 3 and 4 show the gas production over time for both H₂ and CO respectively which also show a rough representation of retention time. Due to retention time being dependent on temperature and/or moisture contents the yield at time zero was considered a strong representation of the maximum yield for all conditions. Hence, all statistical analyses were performed for yield at time zero.

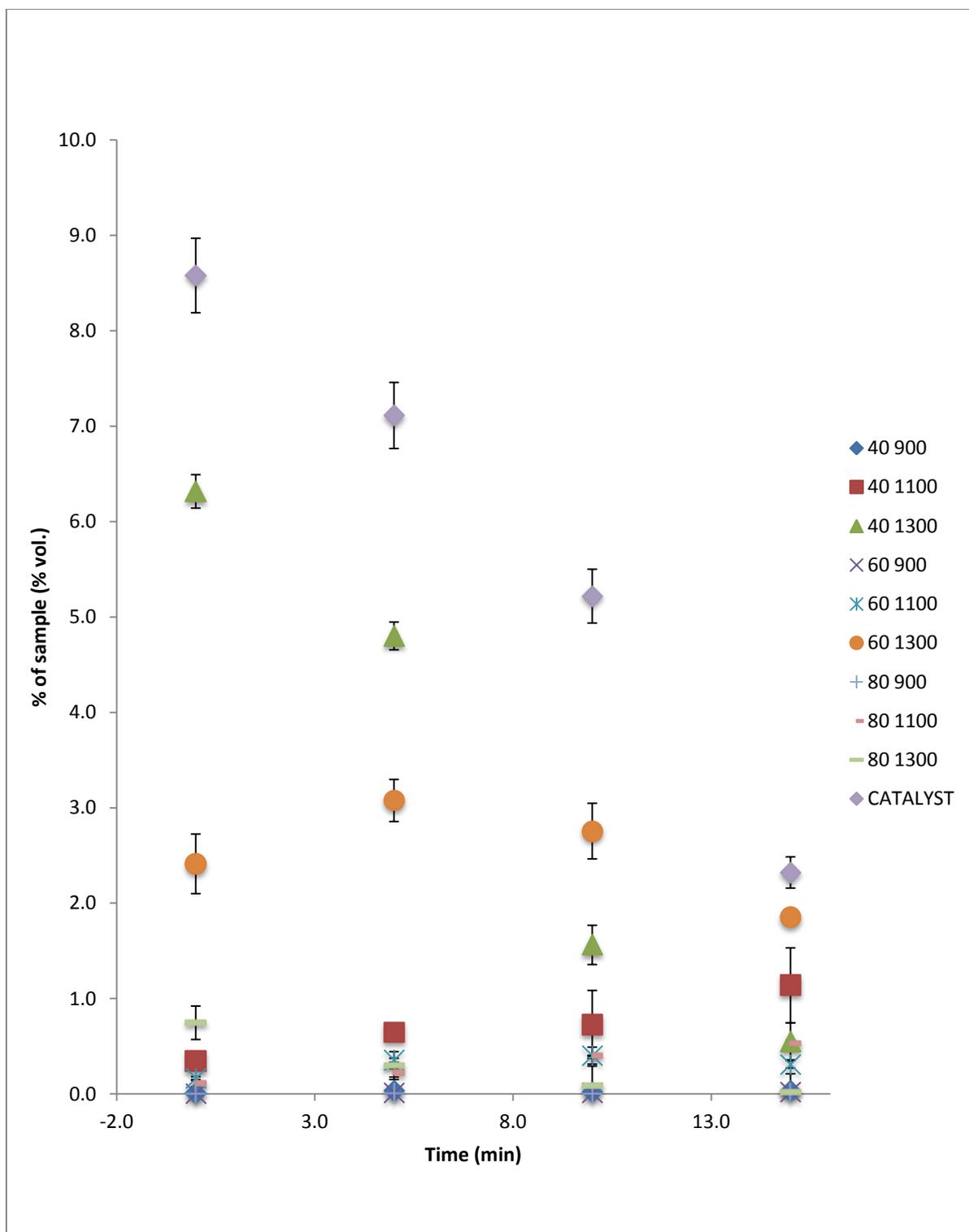


Figure 4: Hydrogen Yield (% total) vs time (min)

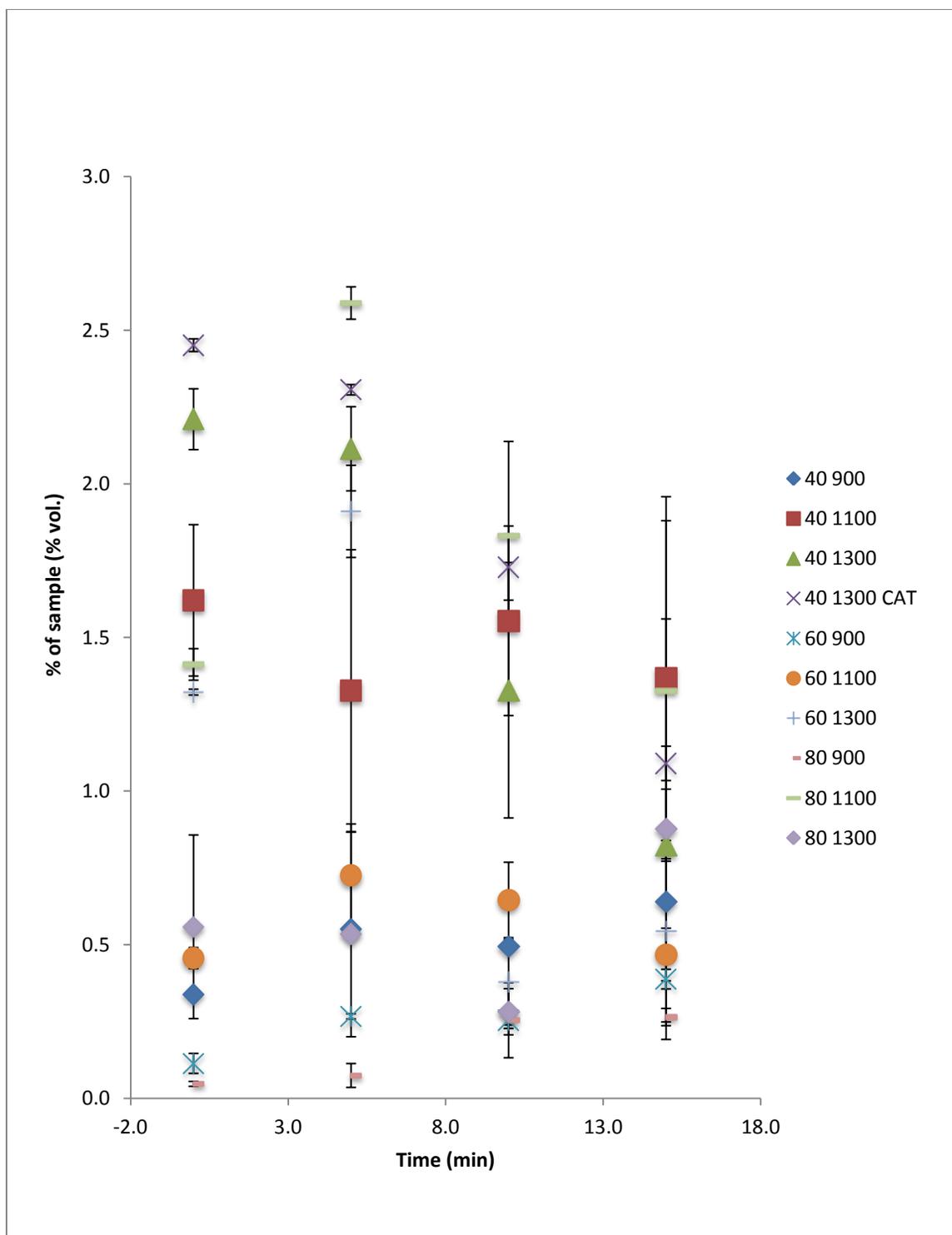


Figure 5: Carbon Monoxide Yield (% total) vs time (min)

3.2 Effect of Moisture Content

The effect of moisture content (%M) was determined through statistical analysis using type III Analysis of Variance (ANOVA) and Tukey's Studentized Range (HSD) Test for yield of H₂ and CO with respect to moisture. From the Type III SS ANOVA table for both H₂ and CO (Table 3 and 4), it is evident that moisture content is significant at the $\alpha=0.05$ level with values <0.0001 . For the statistical analysis, we disproved the null hypothesis $H_0: \mu_{40}=\mu_{60}=\mu_{80}$ in favor of the alternative hypothesis $H_a: \mu_{40}\neq\mu_{60}\neq\mu_{80}$. This means that we can reject that all average yields are the same, in favor of the alternative. Tukey's Studentized Range Test was performed in order to determine which levels are statistically different from each other and which produces the highest yield. From table 5, we are shown that hydrogen production was significantly different at all levels of moisture. For carbon monoxide production, table 6 shows that yield was significantly higher at the 40% level than the 60% and 80% which were not statistically different from each other. From this correlation it appears that all moisture had left the system as steam by the time gasification occurred. This means gas yield was directly correlated to dry matter. Unfortunately, due to high variability in the CO₂ data, it is hard to determine if there was moisture remaining in the reactor for the 80% moisture samples at time 0. However, CO₂ does not appear to increase with increasing moisture which likely means that the water-gas shift reaction, which favors CO₂ with increasing moisture, did not have a significant impact on the overall gas composition. This is consistent with the understanding that the main products of steam gasification are methane and carbon dioxide while air gasification commonly produced hydrogen and carbon monoxide (Ptasinski, 2008).

Hence, it is hard to compare the effect of moisture to other literature due to its inconsistencies with steam gasification.

Table 3: Type III ANOVA for H₂ yield

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Moisture	2	11.866	5.933	59.16	<.0001
Temp	2	37.414	18.707	186.52	<.0001
Moisture*Temp	4	20.897	5.224	52.09	<.0001

Table 4: Type III ANOVA for CO yield

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temp	2	4.325	2.163	229.11	<.0001
Moisture	2	2.007	1.003	106.31	<.0001
Moisture*Temp	4	2.565	0.641	67.93	<.0001

Table 5: Tukey's Studentized Range (HSD) Test for H₂ yield vs moisture

Tukey Grouping	Mean	N	Moisture
A	2.2221	6	40
B	0.8593	6	60
C	0.2863	6	80

Means with the same letter are not significantly different

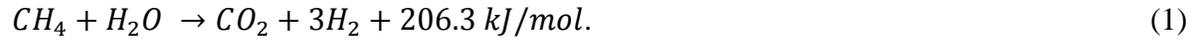
Table 6: Tukey's Studentized Range (HSD) Test for CO yield vs moisture

Tukey Grouping	Mean	N	Moisture
A	1.3383	6	40
B	0.6316	6	60
B	0.6283	6	80

Means with the same letter are not significantly different

3.3 Effect of Temperature

From this study we also observed the role that the reactor temperature had on the gas yield. The null hypothesis $H_0: \mu_{482} = \mu_{593} = \mu_{704}$ was rejected in favor of the alternative hypothesis $H_a: \mu_{482} \neq \mu_{593} \neq \mu_{704}$ where μ represents the average yield (% vol.) of H_2 and CO. From the Type III SS ANOVA table for both H_2 and CO (Table 3 and 4), it is evident that temperature ($^{\circ}C$), and the interaction effect between temperature and moisture are significant at $\alpha=0.05$ level with probability values <0.0001 . In order to determine the most advantageous temperature, and whether these levels are statistically different from each other, a Tukey's Studentized Range Test was performed. Tables 7 shows that hydrogen yield (% vol.) at 704 $^{\circ}C$ is statistically different than 482 and 593 $^{\circ}C$ which are not significantly different from each other. A similar trend is seen for carbon monoxide in which 704 $^{\circ}C$ produces the highest yield although all three levels are shown to be significantly different. This data is in agreement with Chatelier's principle which proposes that higher temperatures will favor the products of endothermic reactions. The mechanism of gasification can be explained through multiple reactions, one of which is the steam reforming methane reaction (Wang et al., 2013) as shown below:



This is an endothermic reaction with H₂ as a product which is in agreement with the statistical analysis. However, CH₄ does not appear to decrease substantially with increased temperatures which may be due to its already low quantity and high standard error.

Unfortunately, the dry gasification of swine manure has not been researched heavily and due to differences in system design other published literature does not offer much in regards to comparison. Wang et al. (2013) gasified swine compost at a constant temperature of 800 °C across all experiments although varied the catalytic temperature and found increased yield with increased temperatures. However, Zhang et al. (2011) did observe the effect of temperature on gas yield. They found that optimum yield occurred between 300-400 °C and increased temperatures actually decreased yield. This difference may possibly be explained by the differences in system and process design (non-steam vs steam) although the overall trend is still contradictory

Table 7: Tukey's Studentized Range (HSD) for H₂ yield vs temperature

Tukey Grouping	Mean	N	Temp
A	3.1581	6	704
B	0.2060	6	593
B	0.0036	6	482

Means with the same letter are not significantly different

Table 8: Tukey's Studentized Range (HSD) Test for CO yield vs temperature

Tukey Grouping	Mean	N	Temp
A	1.2950	6	704
B	1.1233	6	593
C	0.1800	6	482

Means with the same letter are not significantly different

3.3 Interaction Effect of Moisture and Temperature

According to tables 4 and 5 there is a significant interaction effect for moisture and temperature on H₂ and CO gas yield. This can be further illustrated by Figure 6 which shows the yield of H₂ gas (% total) versus temperature (°C) and the difference between the three moisture levels (40, 60, 80%). This shows that the effect of temperature on yield changes depending on the level of moisture which is evident as the lines are not parallel. From this plot and previous sections we can conclude that while temperature is significant the moisture content, or overall amount of dry matter, changes the effect substantially.

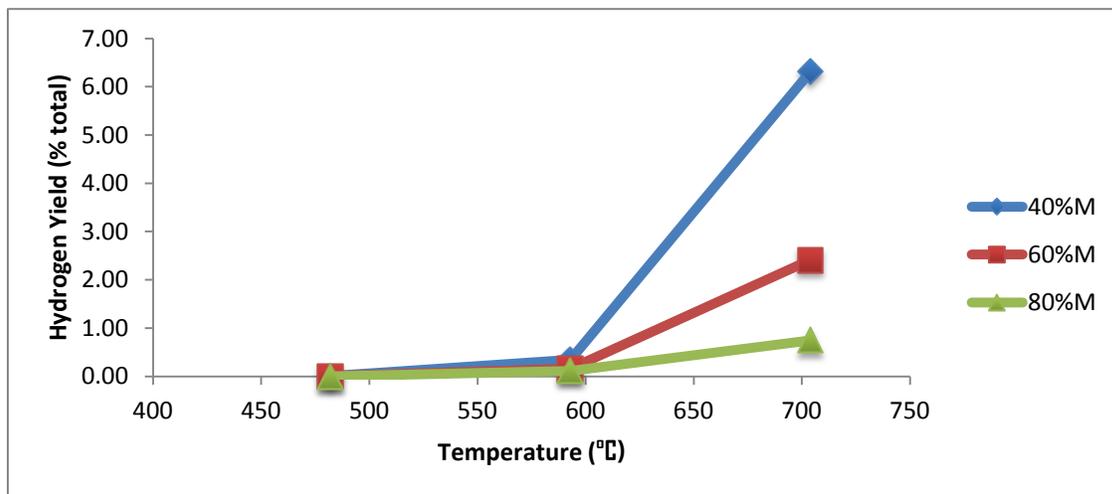


Figure 6: Yield of Hydrogen vs Temperature by moisture levels

3.3 Effect of Catalysis

The Ni-olivine catalyst was used in the main reactor, mixed with the manure, for the potential improvement of gas quality through tar cracking and gas reforming. In order to determine its importance, a run was performed at the statistically best conditions (704 °C and 40% moisture). For comparison purposes, Table 1 shows the ratio of H₂ to CO for each experiment. After ruling out 60% moisture at 704 °C for an unreasonably high ratio, due to an uncharacteristically low CO measurement, it is evident that the ratio is consistently highest for those experiments with 40% moisture at 704 °C. Between the Ni-olivine catalyzed experiment and the non-catalyzed experiment. The H₂ to CO ratio increased from 2.86 to 3.50 at time zero as seen in Table 7. This difference could possibly be explained in two ways. First, tar cracking can improve the gas quality by producing H₂ and CO from tar waste products. Secondly, increased carbon conversion may take place in the presence of the catalyst by increasing the overall amount of feedstock that is being converted. Wang et al. (2013) reported increases in H₂ content from the catalytic steam gasification of swine compost with decreased tar yields, indicating tar cracking, but also increased carbon conversion efficiency. This relationship was evident under both catalytic conditions, calcined modified dolomite (MD) and NiO/MD, with the greatest increase seen for the NiO/MD catalyst run. Similarly, Zhang et al. (2011) reports an increase in yield and H₂:CO ratio for the gasification of swine compost with use of a Ni/Al₂O₃ catalyst with steam reforming for tar cracking. This research has shown comparable results to both Zhang et al. (2011) and Wang et al. (2013) in which the addition of a catalyst improved gas yields with similar resulting H₂ to CO ratios.

Table 9: Comparison of Hydrogen and Carbon Monoxide Yield

Biomass	Process	Catalyst	H₂	CO	Ratio	Source
Pig	Air	none	35.84	57.08	0.63	Zhang et
Compost (Acid Washed)	Gasification		(mL/g)	(mL/g)		al., 2011
Pig	Air	Ni/Al ₂ O ₃	564.55	265.21	2.11	Zhang et
Compost (Acid Washed)	Gasification		(mL/g)	(mL/g)		al., 2011
Pig	Steam	Ni/Al ₂ O ₃	660.67	313.82	2.11	Zhang et
Compost (Acid Washed)	Gasification		(mL/g)	(mL/g)		al., 2011
Pig	Steam	none	36.60	20.75	1.76	Wang et
Compost	Gasification		(vol.%)	(vol.%)		al., 2013
Pig	Steam	Calcined	43.32	13.97	3.10	Wang et
Compost	Gasification	MD	(vol.%)	(vol.%)		al., 2013
Pig	Steam	NiO/MD	54.49	15.22	3.58	Wang et
Compost	Gasification		(vol.%)	(vol.%)		al., 2013
Swine	Dry	none	6.32	2.21	2.86	This study
Solids	Gasification		(vol.%)	(vol.%)		
Swine	Dry	Ni-Olivine	8.58	2.45	3.50	This study
Solids	Gasification		(vol.%)	(vol.%)		

3.4 Time of Flight

Time-of-flight analysis was able to produce a high sensitivity mapping of elements and chemicals located on the bio-char surface. From this profiling, a comparison of the control surface (dried manure) versus the gasified sample surface (40% moisture, 704 °C) and the catalyzed sample surface (40% moisture, 704 °C, with Ni-Olivine catalyst) was done as seen in Figure 5. From Figure 5 the abundance and color correspond to the quantity of the element or chemical on the surface of the bio-char.

From this comparison it is evident that long-chain fatty acids (stearic acid) were almost completely volatilized during gasification. Proteins (CNO-) were shown to decrease substantially, likely providing oxygen and carbon to the overall reaction and volatilizing into nitrogen gas, although some endured through gasification. Phosphite (PO_3^-) was shown to be only slightly more prevalent on the surface post gasification which implies that either the phosphorus was reformed or exposed due to the process. Metals were shown to substantially increase from gasification which, like phosphite, could be explained by increased exposure from loss of proteins and fatty acids. This shows that the manure underwent partial gasification, leaving trace amounts of carbon (proteins), and that the resulting char will likely contain all metals and phosphorus compounds. The elements and chemicals left after gasification can indicate to researchers whether this byproduct would be worth researching as an adsorbant, fuel, or soil amendment.

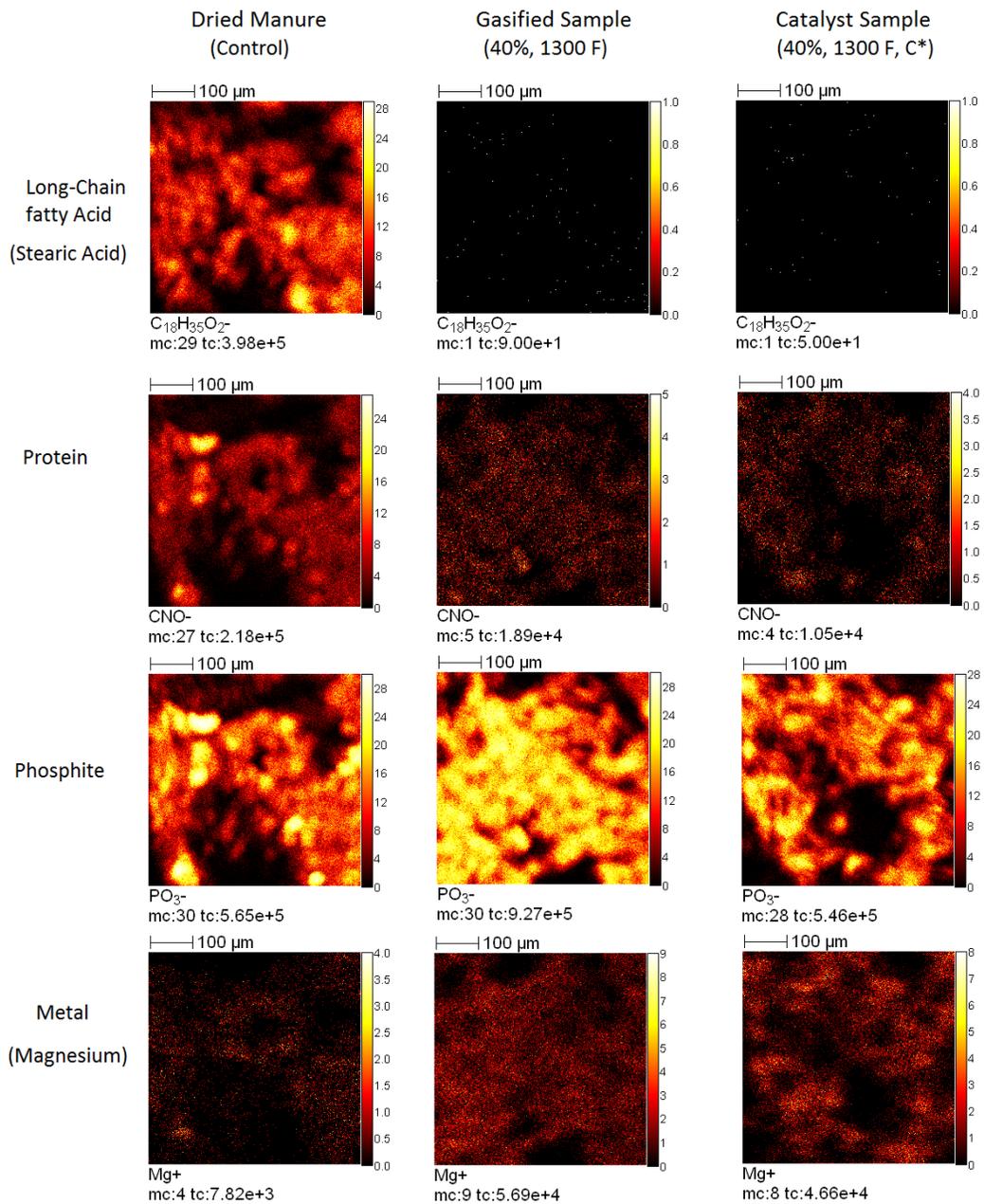


Figure 7: TOF-SIM data for comparison of control, 40% M and 704 C, and catalyzed run.

4. Conclusions

For swine manure gasification, the yield of syngas was increased with increased reactor temperatures and decreased moisture content. In the case of this research, the best conditions were found to be 704 °C and 40% moisture. Increasing the reaction temperature favors H₂ possibly due to the methane reaction. The decreased moisture content allows for higher gas yields, seemingly from the increased solids available, with moisture being lost as steam from the system before the water-gas reaction occurs. The nickel plated olivine catalyst was shown to increase the H₂ to CO ratio and overall H₂ and CO yields. This was likely due to increased carbon conversion but could also potentially be due to tar cracking.

Chapter 2 References

- Bang, G. 2010. Energy security and climate change concerns: Triggers for energy policy change in the United States? *Energy Policy*. 38(4): 1645-1653.
- Buckley, J.C.; Schwarz, P.M. 2003. Renewable Energy from Gasification of Manure: An Innovative Technology in Search of Fertile Policy. *Environmental Monitoring and Assessment*, 84, 111-127.
- Cantrell, K.B.; Ducey, K.; Ro, K.S.; Hunt, P.G. 2008. Livestock waste-to-bioenergy generation opportunities. *Bioresource Technology*, 99(17), 7941-7953.
- Fukumoto, Y.; Osada, T.; Hanajima, D.; Haga, K. 2003. Patterns and quantities of NH₃, N₂O and CH₄ emissions during swine manure composting without forced aeration – effect of compost pile scale. *Bioresources Technology*. 89(1): 109-114
- Hoekman, S.K. 2009. Biofuels in the U.S. – Challenges and Opportunities. *Renewable Energy*. 34(1): 14-22
- Key, N.; McBride, W.D.; Ribaldo, M.; Sneeringer, S. 2011. Trends and Developments in Hog Manure Management: 1998-2009. USDA-ERS Economic Information Bulletin Number 81
- Kuhn, J.N., Z. Zhao, A. Senefeld-Naber and L. G. Felix. 2008. Ni-Olivine Catalysts Prepared by Thermal Impregnation: Structure, Steam Reforming Activity, and Stability. *Applied Catalysts A: General* 341:43 – 49.

- McNab, W.W. Singleton, M.J., Moran, J.E. Esser, B.K. 2007. Assessing the Impact of Animal Waste Lagoon Seepage on the Geochemistry of an Underlying Shallow Aquifer. *Environ. Sci. Technol.* 41(3): 753-758.
- Ptasinski, K.J. 2008. Thermodynamic efficiency of biomass gasification and biofuels conversion. *Biofuels, Bioproducts & Biorefining.* 2:239-253.
- Schiffman, S.S.; Bennett, J.L.; Raymer, J.H. Quantification of odors and odorants from swine operations in North Carolina, *Agricultural and Forest Meteorology*, Volume 108, Issue 3, 25 June 2001, Pages 213-240.
- Sloan, A.J. Gilliam, J.W. Parsons, J.E. Mikkelsen, R.L. Riley, R.C. 1999. Groundwater nitrate depletion in a swine lagoon effluent-irrigated pasture and adjacent riparian zone. *Journal of Soil and Water Conservation*, 54(4): 651-656.
- Sneeringer, Stacy. 2008. Does Animal Feeding Operation Pollution Hurt Public Health? A National Longitudinal Study of Health Externalities Identified by Geographic Shifts in Livestock Production. *American Journal of Agricultural Economics*, 91(1): 124-137.
- Stone, K. C.; Hunt, P. G.; Coffey, S. W.; Matheny, T. A. Water quality status of a USDA water quality demonstration project in the eastern coastal plain. *J. Soil Water ConserV.* 1995, 50 (5), 567-571.
- Szogi, A.A. Vanotti, M.B. Stansbery, A.E. 2006. Reduction of Ammonia Emissions From Treated Anaerobic Swine Lagoons. *Transactions of the ASABE* 49(1): 217-225.

Vanotti, M.B. Szogi, A.A. Hunt, P.G. Millner, P.D. Humenik, F.J. 2007. Development of environmentally superior treatment system to replace anaerobic swine lagoons in the USA. *Bioresource Technology*, 98(17): 3184-3194.

Yang, X., Xu, S., Xu, H., Liu, X., Lui, C. 2010. Nickel supported on modified olivine catalysts for steam reforming of biomass gasification tar. *Catalysis Communications*, 11(5): 383-386.

Zhang, S., Wang, X., Cao, J., & Takarada, T. (2011). Low temperature catalytic gasification of pig compost to produce H₂ rich gas. *Bioresource Technology*, 102(2), 2033-2039. doi:10.1016/j.biortech.2010.09.070

CHAPTER 3: Gasified swine manure char as an adsorbent for mitigation of *p*-cresol

Sterling Fitzgerald^a, Praveen Kolar^{a*}, John Classen^a, and Mike Boyette^a

^aBiological and Agricultural Engineering, Campus Box 7625, North Carolina State University, Raleigh, NC, 27695-7625, USA.

E-mail addresses: sffitzge@ncsu.edu, pkolar@ncsu.edu, classen@ncsu.edu, and boyette@eos.ncsu.edu

**Corresponding author. Phone: +1 919 513 9797; Fax: +1 919 515 7760

E-mail address: pkolar@ncsu.edu

1. Abstract

There is significant interest in using agricultural waste as precursors for synthesis of value-added products. The purpose of this research is to investigate the char obtained from gasification of swine manure as an adsorbent for removal of *p*-cresol from an aqueous system. Swine manure was gasified for 15 min at 704 °C using 25:1 of nitrogen and oxygen to obtain gasified manure char. The surface of the char was characterized using physical and chemical techniques. Batch experiments were performed at 25, 35, and 45 °C in 120-mL reactors to determine the adsorption isotherms and kinetics. Results indicated that gasified manure char was basic in nature and therefore promoted chemisorption of *p*-cresol on char surface with maximum adsorption capacities of 7.6 – 14.9 mg g⁻¹. Both Langmuir and Freundlich models suggested that adsorption of *p*-cresol on char was favorable. Kinetic analysis of the data also confirmed chemisorption of *p*-cresol while the analysis of transport processes suggested that internal diffusion of *p*-cresol within the pores was the rate limiting step. Results from this research can potentially add value to gasification byproducts and simultaneously reduce water and air pollution associated with swine farming operations.

Keywords: Swine manure, gasification, char, adsorption, *p*-cresol, mass transfer

2. Introduction

Confined animal feeding operations, such as swine farming, generate several malodorous volatile organic compounds (VOC) such as *p*-cresol, volatile fatty acids, indoles, and skatoles (Bicudo et al., 2002). These VOCs are hazardous to the health of personnel involved in swine farming and can induce clinical health symptoms to neighboring residents (Zahn et al., 1997; Schiffman et al., 2005). With an increase in animal production worldwide, the effective treatment of wastewater is very critical for the sustainability of swine husbandry. In response, many methods of removal have been proposed including both chemical and physical processes.

Adsorption of pollutants on activated carbons is considered to be effective due to surface chemistry (Dabrowski et al., 2005; Moreno-Castilla and Rivera-Utrilla, 2001). However, the economic feasibility of adsorption highly depends on the cost of raw materials, which prompted many researchers to examine low-cost, carbon byproducts as possible replacement candidates.

Researchers have investigated several agricultural wastes such as tobacco stalk, maize cob, and parthenium for synthesis of low-cost adsorbents for removal of *p*-cresol (Killic et al., 2011, Sathishkumar et al., 2009; Singh et al., 2008). Recently researchers have focused their attention towards animal waste such as manure. For instance, sewage sludge and broiler litter and cake have been pyrolyzed to produce activated carbon with excellent physico-chemical properties some of which were capable of removing mercury and copper ions from

water (Ros et al., 2006; Lima and Marshall, 2005; Koutcheiko et al., 2007; Klasson et al., 2010). These chars and granulated activated carbons have been characterized as having excellent physical properties for adsorption and have been tested for the adsorption of copper ions and mercury. Dairy manure has also been shown to produce biochar, through low temperature heating, with effective adsorbent potential for environmental remediation as tested with aqueous adsorption of Pb and atrazine with high efficiency (Cao and Harris, 2010).

With the advancement of swine waste management, technologies are being put in place to separate manure solids from the waste stream. These solids, paired with a thermochemical process like gasification, are possibly a new viable alternative for the production of bio-char or activated carbon that could also be used as adsorbents. In order to determine the viability of bio-char derived from swine manure gasification as an adsorbent, information on the adsorption capacity and mechanisms is needed. However, at the present time, there is limited information on the efficiency of swine manure derived-biochar as an adsorbent. Based on our preliminary research, we hypothesize that gasification of ammonia-rich manure results in a basic char that may enhance adsorption on volatile organic compounds. Hence in this research, we investigated gasified manure (swine) char (GMC) as an adsorbent for mitigation of *p*-cresol, a commonly found VOC in swine barns. Our objectives were to (1) characterize the GMC, (2) determine the adsorption kinetics and isotherms, and (3) provide a rational mechanism for adsorption of *p*-cresol on GMC.

2. Experimental Protocols

2.1 Materials

Swine manure was collected from the gestation building of the North Carolina State University's (Raleigh, NC) Swine Education Unit. The manure solids were separated from liquids due to not having passed through the slatted-floor waste management system in place. All collected manure was dried at 70 ° C for 48 hours, crushed, homogenized, and then stored in an air-tight container in a 5 ° C walk-in refrigerator. The *p*-cresol solution was prepared for this study using *Acros Organics* (99% pure) *p*-cresol .

2.2 Char Synthesis:

Swine manure char was synthesized by gasifying swine manure (40% moisture content) in a custom built chamber maintained at 704 °C for 15 min using a mixture (2.6 L min⁻¹) of nitrogen and oxygen (25:1) for 15 min. Subsequently, the char was cooled by continuously flowing nitrogen (2.5 L min⁻¹) through the system for 2 hours. The char was dried at 70°C for 24 h and stored until use. The experimental conditions and moisture content were selected based on preliminary experiment performed separately.

3. Characterization of GMC

3.1 Brunauer-Emett-Teller (BET)

The specific surface area of GMC was determined using a Brunauer-Emett-Teller (BET) analyzer (Micrometrics Gemini VII 2390). Samples were degassed at 150 ° C for 2 hours prior to BET analysis which was performed at 77 K.

3.2 Acid Value

The acid value was also determined for three chars and control using a method comparable to that described in El-Sayed and Bandosz (2004). An equilibrated solution (24 h) was prepared with 0.5 g of char and 50 mL of deionized water then filtered. The measured pH provides information on the acidity or basicity of the char surface.

3.3 Point of Zero Charge (pH_{pzc})

The char from gasification of, 40% moisture and 1300 ° Fahrenheit, the point of zero charge pH (pH_{pzc}) was determined using a method described by Nethaji et al. (2010). To determine this value, 100 ml serum bottles containing 50 ml of KNO_3 , at seven different pH values (with duplicates) using 0.1 M H_2SO_4 and diluted NaOH, and 0.15 g of char were shook at 25 ° C and 150 rpms for 24 hours. After 24 hours, the solutions were filtered and the pH was measured. To determine the pH_{pzc} , a plot of final pH= initial pH was performed and the point of intersection with the line $y=x$ gives the pH_{pzc} of the char.

3.4 Boehm Titration

The surface functional groups were determined using Boehm titration (Boehm, 1966). This procedure consisted of shaking 1 g of char in 100 ml serum bottles with 50 ml of 0.05 M solution of either HCl, NaOH, Na_2CO_3 , or NaHCO_3 for 24 hr. After which the solution was filtered and NaOH, Na_2CO_3 , and NaHCO_3 were titrated with HCl (0.05 M) while the filtered HCl was titrated with NaOH (0.05 M) using phenolphthalein and methyl orange as indicators. The number of basic sites was determined from the amount of NaOH used to

titrate the char reacted HCl while the total number of acidic sites was determined from the amount of HCl used to titrate the reacted NaOH. NaOH is known to neutralize carbolylic, lactonic, and phenolic groups while Na₂CO₃ neutralizes carboxylic and lactonic groups and NaHCO₃ only neutralizes carboxylic groups.

3.5 Adsorption Experiments

One gram of GMC was mixed (120 rpm) with 100 ml *p*-cresol solution (50-500 ppm) in duplicates on hot plates similar to the procedure as described in Das et al. (2013). While adsorption was progressing 0.5 mL samples were taken periodically and analyzed using a UV Spectrometer (UV-1700 Pharma Spec, Shimadzu) that was set to 275 nm wavelength. The adsorption capacity of the GMC was calculated using a simple mass balance.

3.6 Adsorption Isotherms

The experimental data obtained from batch experiments were modeled using non-linear forms of Langmuir and Freundlich, (equations 1-2) by minimizing the error sums of squares using Microsoft SOLVER package.

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

For equations 1-2 q_e (mg g^{-1}) and C_e (mg L^{-1}) are adsorption capacity and *p*-cresol concentration (liquid) at equilibrium, q_{max} (mg g^{-1}) and b are Langmuir's adsorption constants associated with theoretical maximum adsorption capacity and rate of adsorption, and K_F ($\text{mg}^{(n-1)/n} \text{g}^{-1} \text{L}^{1/n}$) and n are Freundlich's adsorption constants associated with distribution and favorability of adsorption respectively.

3.7 Adsorption Kinetics

Both reaction and diffusion kinetic models were employed to analyze the kinetic data.

Linearized reaction models such as pseudo-first order (Lagergren, 1898), pseudo-second order, and Elovich (equations 3-5) as described by Tan et al. (2008) and Wang and Li (2013) were used.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are adsorption at equilibrium and at any time, t (min), k_1 (min^{-1}), k_2 ($\text{mg g}^{-1} \text{min}^{-1}$), α ($\text{mg g}^{-1} \text{min}^{-1}$), and β (g mg^{-1}) are first order, second-order, initial adsorption, and desorption rate constants, respectively.

In addition, an intra-particle diffusion kinetic model proposed by Allen et al (1989) and Cooney (1998) was used to model the data (equation 6). Further to separate out the effects of film and pore diffusion mass transfer on adsorption of *p*-cresol on GMC, the data was

analyzed using models proposed by mathematical by Mohd Din (2009), Eckhard (2012), and Cooney (1998) (equations 7-8)

$$q_t = k_p \sqrt{t} + C \quad (6)$$

$$\ln\left(\frac{C}{C_0}\right) = -\frac{m a k_f}{V} t \quad (7)$$

$$\frac{q}{q_e} = \frac{6}{R} \sqrt{\frac{D_p t}{\pi}} + C \quad (8)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are adsorption at equilibrium and at any time, t (min) respectively; C_0 (mg L^{-1}) and C (mg L^{-1}) are concentrations of *p*-cresol (initial and after time t) respectively; m (g), a (m^2g^{-1}), R (m) are the mass of GMC, specific surface area, and radius of the particle respectively; and k_p ($\text{mg g}^{-1} \text{min}^{-0.5}$), C , k_f (m min^{-1}), D_p ($\text{m}^2 \text{min}^{-1}$) are the intra-particle diffusion rate constant, intra-particle diffusion constant, film mass transfer coefficient, and pore diffusion coefficient, respectively.

The slope of the linear portion of the curve between $\ln(C_t/C_0)$ and time (equation 7) was used to estimate the film mass transfer coefficient (k_f) while the slope of the liner portion of q_t/q_e vs \sqrt{t} (equation 8) was used to predict the internal (pore) diffusivity (D_p).

3.8 Adsorption Thermodynamics

Adsorption data were analyzed using van't Hoff relationship to obtain Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes as described by Kilic et al (2011) and Khraisheh et al. (2002).

$$\ln(k_e) = \frac{q_e}{C_e} = \frac{-\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

where k_e , q_e , C_e , ΔG° , R , T , ΔH° , ΔS° represent adsorption distribution constant, equilibrium adsorption capacity (mg g^{-1}), equilibrium concentration of *p*-cresol in solution (mg L^{-1}), Gibbs free energy change (kJ mol^{-1}), universal gas constant ($8.3 \text{ J mol}^{-1} \text{ K}^{-1}$), absolute temperature (K) enthalpy change (kJ mol^{-1}), and entropy change (kJ mol^{-1}) respectively.

3.9 Desorption Study

An additional experiment was performed to obtain further insight into the nature of adsorption of *p*-cresol on GMC. Using spent char from experimentation (100 mg L^{-1} *p*-cresol, $25 \text{ }^\circ\text{C}$) char was mixed (120 rpm) with DI water at $25 \text{ }^\circ\text{C}$ for 60 min to monitor the desorption of *p*-cresol into DI water.

4. Results and Discussion

4.1 Characterization of GMC

As expected, gasification of manure resulted in a significant increase (Table 10) in specific surface area (330%) and pore volume (305%). In addition, an increase in acid value was observed suggesting that the surface basicity of the char also increased due to gasification.

Table 10: Physical Characterization of GMC

Sample	Surface Area m ² /g	Pore Volume cm ³ /g	Acid Value
Control (dried manure)	11.42 ±0.20	0.0077±0.0002	7.81±0.05
GMC	49.12±0.79	0.0312±0.0008	8.57±0.01

The GMC was further analyzed to determine the distribution of surface acidic and basic functional groups as presented in Table 11.

Table 11: Chemical Characterization of GMC

Sample	Acidic groups (mmol g ⁻¹)				Basic Groups (mmol g ⁻¹)	Point of zero charge (PZC)
	Carboxylic	Lactonic	Phenolic	Total		
40%, 704 °C	0±0	5.75±0.75	3±0.50	8.75±1.25	12.5±0.50	9.39

Boehm analysis (Boehm, 1966) indicated that GMC was relatively rich in basic functional groups. Presence of limited amount of oxygen in the gasifying medium (nitrogen:oxygen =25:1) perhaps prevented the formation of highly acidic carboxylic functional groups, while the presence of ammonia in the manure may have contributed to higher basic functional groups.

4.2 Batch Experiment Results

Results from batch experiments suggested that adsorption capacity of GMC was significantly higher than control (dried manure) (Figure 8). As theorized from the data obtained from characterization experiments, absence of carboxylic groups and presence of basic functional groups on the surface enhanced adsorption of *p*-cresol on GMC. Several researchers including Dabrowski et al. (2005), Moreno-Castilla (2004), and others have reported that basic surface functional groups promote adsorption of phenols such as *p*-cresol due to oxidative coupling mechanism, which was also observed in our previous research (Das et al. 2013).

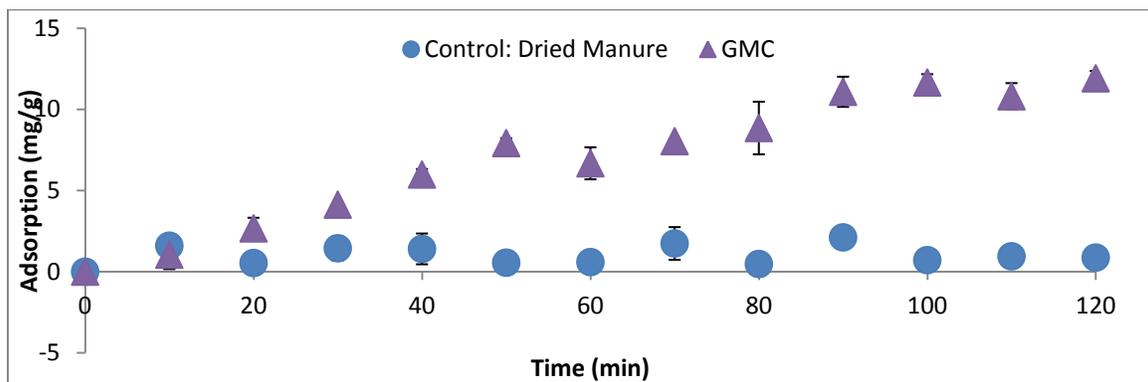


Figure 8: Adsorption of *p*-cresol (100 mg L^{-1}) on GMC at 25 C (120 rpm).

4.3 Isotherms

Adsorption isotherms for *p*-cresol at 25, 35, and 45 °C are plotted in Figure 9 and Langmuir and Freundlich isotherm parameters obtained from non-linear models are presented in Table 12.

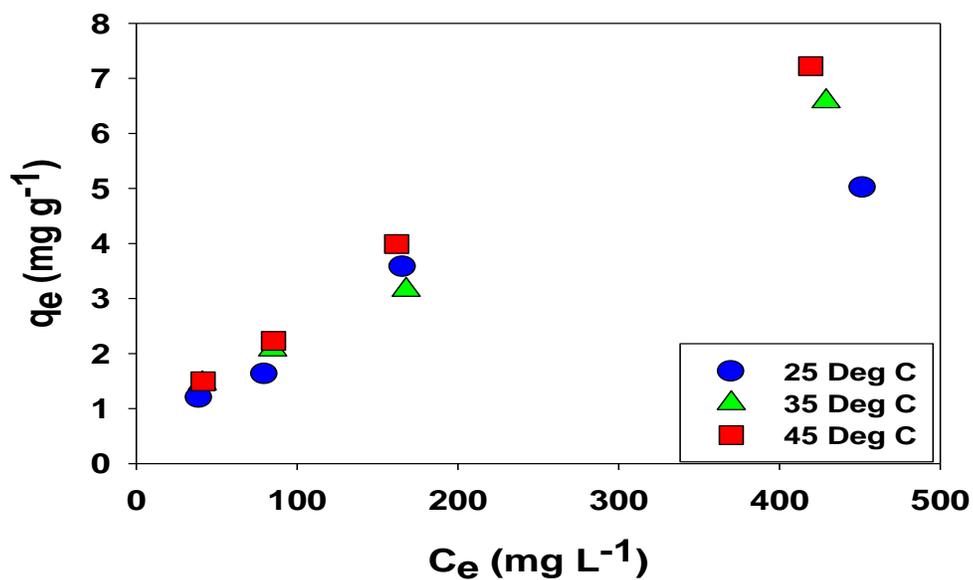


Figure 9: Adsorption of *p*-cresol on GMC

Table 12: Adsorption parameters from non-linear Langmuir and Freundlich models

Temperature	Freundlich			Langmuir		
	K_F	n	R^2	Q_{max}	b	R^2
25	0.18	1.82	0.98	7.63	0.0045	0.94
35	0.09	1.41	0.99	14.99	0.0018	0.98
45	0.11	1.46	0.99	14.84	0.0023	0.98

The maximum adsorption capacities (7.63-14.99 mg g⁻¹) obtained in this research were somewhat similar to that of adsorbents synthesized from maize cob, parthenium, tobacco and pinewood-activated char for mitigation of *p*-cresol (Singh et al., 2008; Killic et al., 2011; Das et al., 2013; Sathishkumar et al., 2009). It is encouraging to note that the adsorption capacity obtained in our research is more than adequate to treat *p*-cresol in swine lagoon water as the typical concentrations are in the range of 0.10-1 mg L⁻¹. Further, the Langmuir adsorption parameters were used to estimate the dimensionless separation factors to ascertain the favorability of adsorption as described by Tan et al. (2008). For temperature range tested (25-45 °C), the separation factors were between 0.33 and 0.56 suggesting that adsorption of *p*-cresol on GMC was favorable. Using the adsorption parameters, the Langmuir isotherms for *p*-cresol on GMC may be expressed as under:

$$q_e(25\text{ }^{\circ}\text{C}) = \frac{0.0343 C_e}{(1 + 0.0045C_e)}$$

$$q_e(35\text{ }^{\circ}\text{C}) = \frac{0.0269 C_e}{(1 + 0.0018C_e)}$$

$$q_e(45\text{ }^{\circ}\text{C}) = \frac{0.0341 C_e}{(1 + 0.0023C_e)}$$

The data analyzed using Freundlich isotherms are also summarized in Table 12. By examining the value of $1/n$, it can be determined if it indicates a normal Langmuir isotherm ($1/n < 1$) or if it is cooperative adsorption ($1/n > 1$) (Tan et al., 2008). Values of greater than 1.0 for $1/n$ suggests co-operative adsorption where as values of less than 1.0 suggested a normal Langmuir's adsorption. In our research, the vales of $1/n$ were found to be between 0.55 and 0.71 suggesting that adsorption of *p*-cresol on GMC was favorable and conforms to

normal Langmuir's adsorption process. Using the adsorption parameters obtained in our research, Freundlich's equations may be represented as below:

$$q_e (25 \text{ } ^\circ\text{C}) = 0.18C_e^{0.549}$$

$$q_e (35 \text{ } ^\circ\text{C}) = 0.09C_e^{0.709}$$

$$q_e (45 \text{ } ^\circ\text{C}) = 0.11C_e^{0.684}$$

4.4 Kinetics

The kinetic parameters for pseudo-first order, pseudo-second order, and Elovich models are presented in Table 13.

Table 13: Kinetic model parameters for adsorption of *p*-cresol on GMC at 25 °C (120 rpm)

Conc. (mg L ⁻¹)	Pseudo 1 st Order		Pseudo 2 nd Order			Elovich		
	R ²	k ₁ (min ⁻¹)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	h ₂ x 10 ² (g mg ⁻¹ min ⁻¹)	R ²	α	β
50	0.85	0.105	0.97	0.0503	7.1	0.97	0.33	3.66
100	0.90	0.041	0.66	0.0072	1.9	0.79	0.93	2.7
200	0.94	0.056	0.98	0.0212	27.0	0.98	0.86	1.32
500	0.87	0.068	0.97	0.0141	35.4	0.94	1.22	0.90

Examining the average fit for these models, the data shows that Elovich model fit the data best when compared to pseudo-first order and pseudo-second order models suggesting that adsorption of *p*-cresol on GMC was dominated by chemisorption. As *p*-cresol molecules reach the surface of GMC, they are expected to react with dissolved oxygen, promoted by GMC resulting in irreversible adsorption of *p*-cresol (Vidic et al., 1997; Terzyk, 2003).

Several researchers including Coughlin and Ezra (1968) and Grant and King (1990) have proposed that presence of carboxylic acid inhibits chemisorption of phenols. The GMC used in our study did not have any carboxylic groups on the surface. Hence, it is feasible to theorize that the absence of carboxylic groups and high presence of basic functional groups was the driving force for chemisorption of *p*-cresol. This observation was also consistent with the data obtained from desorption study, where it was observed that most of the *p*-cresol was held back on to the surface of the GMC indicating irreversible adsorption of *p*-cresol.

The plot for intra-particle diffusion model, as shown in Figure 10A, illustrates that the data was a combination of two linear portions. Adsorption from the bulk solution to the GMC surface appeared to be rapid as illustrated by the first portion which has a steeper slope than the subsequent portion. The second portion characterizes the slow movement of the *p*-cresol from the surface of GMC into the pore matrix and may be considered rate limiting.

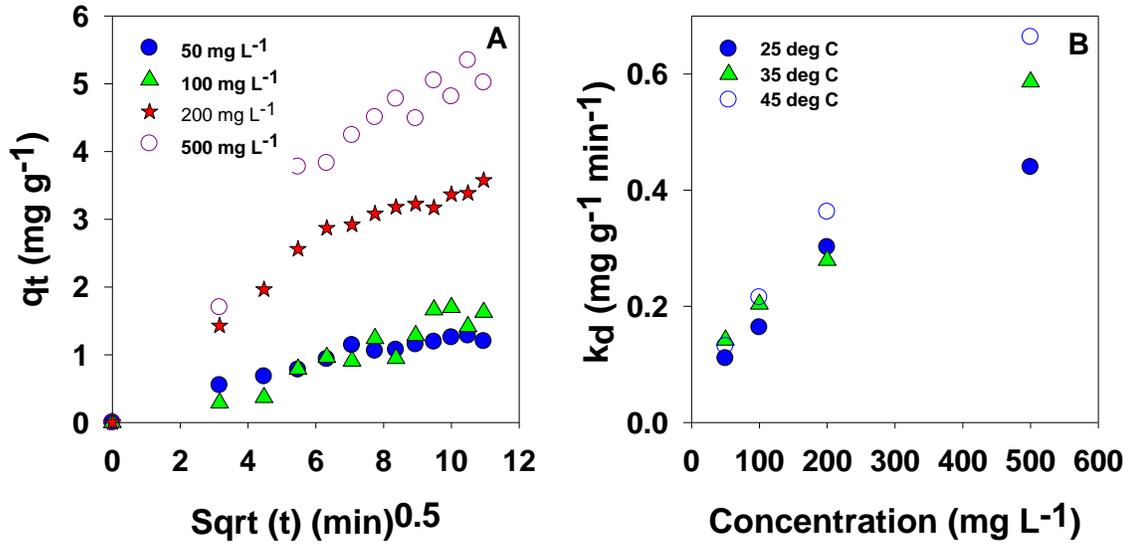


Figure 10: Intra-particle diffusion model for adsorption of p-cresol on GMC (A) indicated enhanced intra-particle diffusion constants at higher concentration and temperature (B).

Further, the intra-particle diffusion constant (k_p) is considered to be an indicator of adsorption rate (Khraisheh et al., 2002). Hence, the intra-particle diffusion constants for all experimental conditions were calculated and presented in figure 10B. It is clear that intra-particle diffusion constant increased significantly with an increase in initial concentration of p-cresol because k_p is linearly related to q_e . Similarly, as temperature increased, the slope between k_p and concentration increased due to enhanced diffusion at higher temperatures.

4.5 Identification of rate-limiting steps

To verify our preposition that movement of p-cresol from the GMC surface to the pores was the slowest step, the film mass transfer (Figure 11A) and internal diffusion coefficients

(Figure 11B) for various concentrations were estimated using equations 7 and 8 and presented in Table 14.

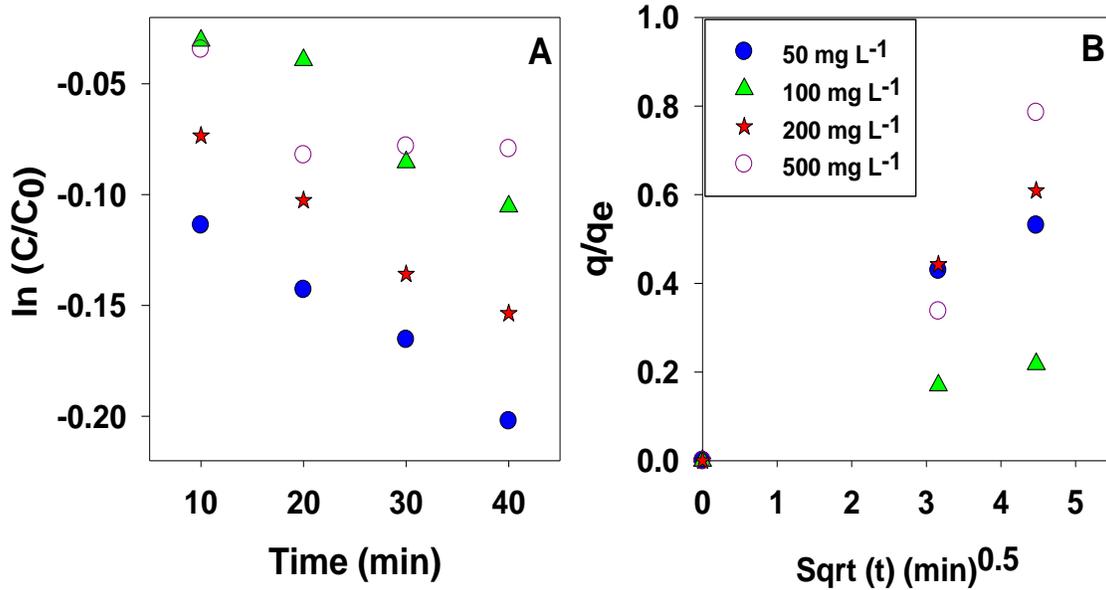


Figure 11: Rate –limiting step during adsorption of p-cresol on GMC at 25 °C was identified by determining film (external) (A) and pore diffusion (internal) constants (B).

Table 14: External (film) and internal (pore) mass transfer constants governing adsorption of p-cresol on GMC at 25 °C (120 rpm).

Conc (mg L ⁻¹)	Film mass transfer coefficient (k _f) (x 10 ³ m min ⁻¹)	Pore diffusion constant (D _p) (x 10 ⁹ m ² min ⁻¹)	N _{Bi}
50	9.57	20.7	>> 900
100	8.91	3.43	>>900
200	8.91	26.1	>>900
500	4.29	37.02	>900

Khraisheh et al. (2002) proposed that when Biot number ($d k_f/D_p$) exceeds 100, the system may be considered as pore-diffusion limiting. In our research, the Biot numbers for all concentrations were over 900 suggesting that adsorption of *p*-cresol on GMC was limited by pore-diffusion. In addition, the values of constant C (equation 6) were found to be small (0.16-0.83) suggesting that intra-particle diffusion was the major rate-limiting step. In their recent research, Rodriguez et al. (2011) reported similar results for adsorption of phenol onto activated carbon (avocado kernel seeds) where they found intra-particle diffusion to be the rate limiting step.

4.6 Adsorption Thermodynamics

Analysis of data using van't Hoff relation indicated that the enthalpy change (ΔH°) was 6.3 kJ mol⁻¹ suggesting that adsorption of *p*-cresol on GMC was an endothermic process. Costa et al. (1989) proposed that phenol adsorption increased with temperature due to a percentage of micropores becoming accessible only under high temperatures, which allowed the phenol molecule to penetrate and diffuse. Ravi et al. (1998) reported that endothermic nature of adsorption of phenol, cresols, and benzyl alcohol might be due to chemisorption or the polymerization, which increased with an increase in temperature. As we also observed via Elovich model that adsorption of *p*-cresol was perhaps dominated by chemisorption. The negative entropy change (ΔS°) of -7.52 kJ mol⁻¹ is a characteristic of reduced randomness at the *p*-cresol solution-GMC interface as suggested by Killic et al (2011). Further the Gibbs

free energy associated with adsorption was found to be between 8.5 and 8.7 kJ mol⁻¹ which indicates that the interaction between *p*-cresol and GMC surface was non-spontaneous.

5. Summary

Gasified swine char (40% moisture, 704 °C) was found to be an effective adsorbent of *p*-cresol with theoretical maximum adsorption capacities of 7.63-14.84 mg g⁻¹ (25-45 °C). The data also suggested that adsorption was endothermic and dominated by chemisorption due to basic surface of the GMC. Kinetic analysis of the data indicated that adsorption was limited by internal diffusion of *p*-cresol into the pore structure of GMC. Our research is expected to add value to swine manure gasification products while decreasing odors in swine husbandry operations.

Acknowledgments

We thank the National Pork Board and the United States Department of Agriculture for funding. In addition, we thank Ms. Rachel Huie and Mr. David Buffaloe for help with analysis and fabrication of reactor.

Disclosure

We declare no conflict of interests while performing this research.

Chapter 3 References

- Allen, S.J., McKay, G., Khader, K.Y.H. 1989. Intraparticle Diffusion of a Basic Dye During Adsorption onto Sphagnum Peat. *Environmental Pollution*, 56: 39-50
- Bicudo, J.R., Schmidt, D.R., Powers, W., Zahn, J. 2002. Odor and VOC Emissions From Swine Manure Storages. *Proceedings of the Water Environment Federation, Odors and Toxic Air Emissions*, 13(1): 123-135.
- Boehm, H.P., 1966. Chemical identification of surface groups. In: Eley, D.D., Pines, H., Weisz, P.B. (Eds.), *Advances in Catalysis*, vol. 16. Academic Press, New York, p.179.
- Cao, X., Harris, W. 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology* 101: 5222-5228.
- Cooney, D.O. (1998). *Adsorption Design for Wastewater Treatment*. New York: Lewis Publishers.
- Costa, E., Calleja, G., Marijuan, L., 1989. Comparative Adsorption of Phenol, p-Nitrophenol and p-Hydroxybenzoic Acid on Activated Carbon. *Adsorpt. Sci. Technol.*, 5: 213-228.
- Coughlin, R.W., Ezra, F.S. 1968. Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. *Environmental Science & Technology*. 2(4): 291-297.
- Dabrowski, A., Podkoscielny, P., Hubicki, Z., Barczak, M. 2005. Adsorption of phenolic compounds by activated carbon – a critical review. *Chemosphere*. 58 (8) 1049-1070.
- Das, L., Kolar, P., Classen, J.J., Osborne, J.A., 2012. Adsorbents from pine wood via K₂CO₃

- assisted low temperature carbonization for adsorption of *p*-cresol . *Industrial Crops and Products*. 45: 215-222.
- Ekhard, W. (2012). *Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling*. Berlin: Walter de Gruyter GmbH & Co.
- El-Sayed, E.Y., Bandosz, T.J., 2004. Adsorption of valeric acid from aqueous solution onto activated carbons: role of surface basic sites. *Journal of Colloid Interface Sci.* 273: 64-72.
- Grant, T.M., and King, C.J. (1990). Mechanism of irreversible adsorption of phenolic compounds by activated carbons. *Ind. Eng. Chem. Res.* 29, 264.
- Khraisheh, M.A., Al-Degs, Y.S., Allen, S.J., Ahmad, M.N., 2002. Elucidation of Controlling Steps of Reactive Dye Adsorption on Activated Carbon. *Ind. Eng. Chem. Res.* 42:1651-1657
- Kilic, M., Apaydin-Varol, E., Putun, A.E., 2011. Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics. *J. Hazard. Materials*. 189: 397-403
- Klasson, K.T., Lima, I.M., Boihem, L.L., Wartelle, L.H. 2010. Feasibility of mercury removal from simulated flue gas by activated chars made from poultry manures. *Journal of Environmental Management* 91(12):2466-2470.
- Koutcheiko, S., Monreal, C.M., Kodama, H., McCracken, T., Kotlyar, L. 2007. Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Bioresource Technology* 98(13): 2459-2464.

- Lagergren, S. (1898), Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens. Handlingar, 24 (4): 1-39.
- Lima, I.M., Marshall, W.E. 2005. Granular activated carbons from broiler manure: physical, chemical and adsorptive properties. *Bioresource Technology* 96(6): 699-706.
- Mohd Din, A.T., Hameed, B.H., and Ahmad, A.L. (2009). Batch adsorption of phenol onto physiochemical-activated coconut shell. *J. Hazard. Mater.* 161, 1522.
- Moreno-Castilla, C. 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*. 42(1): 83-94.
- Moreno-Castilla, C., Rivera-Utrilla, J. 2001. Carbon Materials as Adsorbents for the Removal of Pollutants from the Aqueous Phase. *MRS Bulletin*. 26(11): 890-894.
- Nethaji, S., Sivasamy, A., Thennarasu, G., Saravabab, S., 2010. Adsorption of malachite green dye onto activated carbon derived from *Borassus aethiopum* flower biomass. *J. Hazard. Mater.* 181: 271-280.
- Ravi, V.P., Jasra, R.V., Bhat, T.S.G., 1998. Adsorption of Phenol, Cresol Isomers and Benzyl Alcohol from Aqueous Solution on Activated Carbon at 278, 298 and 323 K. *J. Chem. Technol. Biotechnol.* 71: 173-179.
- Rodrigues, L.A., Pinto da Silva, M.L.C., Mendes, M.O.A., Coutinho, A.D.R., Thim, G.P., 2011. Phenol removal from aqueous solution by activated carbon produced from Avocado kernel seeds. *Chemical Engineering Journal*. 174: 49-57.
- Ros, A., Lillo-Rodenas, M.A., Fuente, E., Montes-Moran, M.A., Martin, M.J., Linares Solano, A. 2006. High surface area materials prepared from sewage sludge-based precursors. *Chemosphere* 65: 132-140.

- Sathishkumar, M., Binupriya, A.R., Kavitha, D., Selvakumar, R., Jayabalan, R., Choi, J.G., Yun, S.E. 2009. Adsorption potential of maize cob carbon for 2,4-dichlorophenol removal from aqueous solutions: Equilibrium, kinetics and thermodynamics modeling. *Chemical Engineering Journal*. 147: 265-271
- Schiffman, S.S., Studwell, C.E., Landerman, L.R., Berman, K., Sundry, J.S. 2005. Symptomatic Effects of Exposure to Diluted Air Sampled from a Swine Confinement Atmosphere on Healthy Human Subjects. *Environmental Health Perspectives*. 113(5): 567-576.
- Singh, R.K., Kumar, S., Kumar, S., and Kumar, A. (2008). Development of parthenium based activated carbon and its utilization for adsorptive removal of *p*-cresol from aqueous solution. *J. Hazard. Mater.* 155, 523.
- Tan, I.A., Ahmad, A.L, Hameed, B.H. 2008, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *J. Hazard. Material*. 154: 337-346.
- Terzyk, A.P. (2003). Further insights into the role of carbon surface functionalities in the mechanism of phenol adsorption. *J Colloid Interf Sci*. 268, 301.
- Vidic, R.D., Ressler, C.H., and Uranowski, L.J. (1997). Impact of surface properties of activated carbons on oxidative coupling of phenolic compounds. *Carbon* 35, 1349.
- Wang, L., Li, J., 2013. Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: kinetics, equilibrium, and thermodynamics. *Ind. Crop Prod*. 42: 153-158.
- Zahn, J.A., Hatfield, J.L., Do, Y.S., DiSpirito, A.A., Laird, D.A., Pfeiffer, R.L. 1997.

Characterization of Volatile Organic Emissions and Wastes from a Swine Production Facility. *Journal of Environmental Quality*. 26(6): 1687-1696.

APPENDICES

Appendix A

Table 15: Table of Gasification Results (% of total volume)

Condition	Time	%H ₂		%CO		%CH ₄		%CO ₂		H ₂ :CO ratio
		avg	std. error	avg	std. error	avg	std. error	avg	std. error	
40 900	0	0.006	0.006	0.338	0.044	0.010	0.004	1.971	0.334	0.02
	5	0.034	0.016	0.551	0.055	0.014	0.003	2.806	0.569	0.06
	10	0.021	0.006	0.494	0.141	0.016	0.005	2.873	1.277	0.04
	15	0.030	0.010	0.639	0.265	0.036	0.023	3.408	1.681	0.05
40 1100	0	0.344	0.087	1.621	0.246	0.437	0.269	5.130	2.646	0.21
	5	0.645	0.086	1.326	0.460	0.488	0.212	5.636	2.372	0.49
	10	0.728	0.357	1.554	0.309	0.671	0.463	5.357	2.793	0.47
	15	1.139	0.392	1.369	0.589	0.913	0.543	5.330	2.553	0.83
40 1300	0	6.317	0.175	2.210	0.099	0.027	0.025	3.653	1.059	2.86
	5	4.801	0.146	2.114	0.137	0.747	0.414	2.176	1.245	2.27
	10	1.562	0.205	1.328	0.416	0.120	0.023	3.072	2.141	1.18
	15	0.551	0.193	0.823	0.183	0.053	0.022	2.190	1.212	0.67
40 1300 C*	0	8.579	0.390	2.451	0.021	8.220	2.543	6.470	0.319	3.50
	5	7.112	0.346	2.306	0.017	3.339	0.017	5.134	0.149	3.08
	10	5.218	0.282	1.729	0.108	1.451	0.836	6.049	2.374	3.02
	15	2.321	0.164	1.090	0.056	0.340	0.102	3.281	0.302	2.13
60 900	0	0.005	0.002	0.113	0.033	0.002	0.000	0.498	0.119	0.04
	5	0.009	0.001	0.267	0.008	0.004	0.000	1.216	0.021	0.03
	10	0.012	0.003	0.254	0.026	0.006	0.002	1.181	0.170	0.05
	15	0.020	0.001	0.388	0.032	0.009	0.002	1.797	0.068	0.05
60 1100	0	0.161	0.020	0.456	0.034	0.103	0.017	2.056	0.462	0.35
	5	0.353	0.022	0.726	0.167	0.168	0.022	2.774	0.698	0.49
	10	0.399	0.006	0.646	0.123	0.202	0.016	2.371	0.492	0.62
	15	0.309	0.037	0.468	0.086	0.174	0.009	1.617	0.239	0.66
60 1300	0	2.412	0.312	1.322	0.009	0.615	0.191	2.146	0.922	1.82
	5	3.076	0.221	1.910	0.150	0.015	0.015	0.635	0.635	1.61
	10	2.755	0.291	0.378	0.139	0.009	0.009	0.601	0.601	7.28
	15	1.852	0.055	0.544	0.295	0.483	0.479	1.863	0.152	3.41

Table 15 Continued: Table of Gasification Results (% of total volume)

Condition	Time	%H ₂		%CO		% CH ₄		%CO ₂		H ₂ :CO
%M, Temp	min	avg	std. error	avg	std. error	avg	std. error	avg	std. error	ratio
80 900	0	0.000	0.000	0.047	0.008	0.000	0.000	0.173	0.173	0.00
	5	0.005	0.000	0.074	0.039	0.001	0.001	0.252	0.252	0.07
	10	0.002	0.000	0.254	0.122	0.001	0.001	0.232	0.232	0.01
	15	0.011	0.001	0.264	0.028	0.002	0.002	0.674	0.674	0.04
80 1100	0	0.113	0.037	1.412	0.051	0.012	0.001	0.946	0.225	0.08
	5	0.222	0.046	2.589	0.053	0.295	0.295	0.000	0.000	0.09
	10	0.402	0.089	1.831	0.307	0.609	0.574	1.818	1.818	0.22
	15	0.531	0.033	1.326	0.554	0.223	0.216	2.830	1.051	0.40
80 1300	0	0.746	0.560	0.558	0.299	0.084	0.080	2.334	1.273	1.34
	5	0.297	0.243	0.534	0.334	0.006	0.003	2.052	1.986	0.56
	10	0.087	0.065	0.282	0.075	0.009	0.009	1.877	1.823	0.31
	15	0.018	0.010	0.876	0.684	0.016	0.013	1.866	1.821	0.02