THE EFFECT OF BIOMASS, OPERATING CONDITIONS, AND GASIFIER DESIGN ON THE PERFORMANCE OF AN UPDRAFT BIOMASS GASIFIER

by

ARTHUR MC CARTY JAMES RIVAS

B.A., Universidad Tecnológica de Panamá, 2008

A THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Biological and Agricultural Engineering
College of Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2012

Approved by:

Major Professor
Dr. Wenqiao Yuan

Copyright

Abstract

Gasification is an efficient way to produce energy from biomass, which has significant positive impacts on the environment, domestic economy, national energy security, and the society in general. In this study, a lab-scale updraft biomass gasifier was designed, built, and instrumented for stable gasification using low-bulk density biomass. Related accessories, such as a biomass feeder, inlet air temperature controller, air injection nozzle, and tar cracking system, were also developed to enhance gasifier performance.

The effect of operation parameters on gasifier performance was studied. Two operational parameters, including air flow rate and feed-air temperature, were studied on three sources of biomass: prairie hay, sorghum biomass, and wood chips. Results showed that higher air flow rate increased tar contents in syngas for all three types. It was also found that different biomasses gave significantly different tar contents, in the order of wood chips>sorghum biomass>prairie hay. Feed-air temperature did not have a significant effect on tar content in syngas except for prairie hay, where higher feed air temperature reduced tar. A statistical model was implemented to study differences on syngas composition. Results showed that different biomasses produced syngas with different high heating value, e.g., wood chips > prairie hay > sorghum biomass. CO composition also showed differences by feed air temperature and biomass, e.g. prairie hay>wood chips>sorghum biomass, but H_2 did not show significant differences by either biomass type or operating conditions.

Moreover, because of the downstream problems caused by tars in syngas such as tar condensation in pipelines, blockage and machinery collapse, an in-situ tar cracking system was developed to remove tars in syngas. The tar cracking device was built in the middle of the gasifier's combustion using gasification heat to drive the reactions. The in-situ system was found to be very effective in tar removal and syngas enhancement. The highest tar removal of 95% was achieved at 0.3s residence time and 10% nickel loading. This condition also gave the highest syngas HHV increment of 36% (7.33 MJ/m^3). The effect of gas residence time and Ni loading on tar removal and syngas composition was also studied. Gas residence of 0.2-0.3s and Ni loading of 10% were found appropriate in this study.

Table of Contents

List of Figures

List of Tables

Acknowledgements

First of all, I would like to thank Dr. Wenqiao Yuan for his patience and dedication as my major professor. His advice in challenging moments has helped me to find solutions and succeed in both my research project and academic field.

Second, I would like to express my gratitude to IFARHU-SENACYT, Panamanian government Scholarships, for their financial support in my graduate studies.

I also want to thank my committee members, Dr. Nathan Nelson and Richard Nelson, for taking part of their valuable time to read my thesis. I also thank Dr. Nathan Nelson for providing biomass raw materials for experiments and his student, Arthur Fink, for helping me grind biomass samples.

I want to thank many other people who helped to make this work possible:

Dr. Keith Hohn from Chemical Engineering for sharing his Gas Chromatograph to analyze syngas samples,

Barb Moore, for her dedication and devotion to orientate since the first day,

Darrell Oard, for his enthusiasm and patience to build and develop equipment for experiments,

Dr. Donghai Wang for analysis experiments' raw materials and sharing his lab,

Jack Plummer from Kansas State University's engineering robotics team for his help in auto-feeder electronic controls.

Xue Bai, graduate student from the statistics department for her help on statistical analysis.

Finally, I would like to thanks the Technological University of Panama where I work in my country.

Dedication

I would like to dedicate this thesis to my fiancée, my mom, and my family that have always supported me spiritually and emotionally. I also want to dedicate this work to my friends in Manhattan, a small town that now I can call home.

“And whatever you do, whether in word or deed, do it all in the name of the Lord Jesus, giving thanks to God the Father through him.” Colossians 3.17 (NIV)

Chapter 1 - Introduction

1.1 Biomass Gasification – history and current status

Gasification is an efficient way to convert biomass into useful biofuels. This thermochemical process has been used in the last three centuries for energy and chemical generation applications. The first reported use of gasification was in 1792 when W. Murdoch, a Scottish engineer, used syngas from coal for domestic lightning purposes. In the 19th century, coal gasification became commercialized, illuminating several cities including New York City. A significant number of gasifiers were used during this time (J. Rezaiyan, 2005). The use of the biomass gasification process to produce energy began in 1930 (Knoef, 2005), in the course of the WWII, when approximately one million gasifiers were used to generate syngas from wood to power automobiles and to produce electricity. After the war period, the use of syngas to power vehicles was discontinued due to the wide availability of oils. The interest in gasification came up again in the 1970's when arguments about the limitations of the oil reserve availability compared with the demand were discussed (J. Rezaiyan, 2005).

Several gasification applications have been developed worldwide. Utilization of the gasifiers for heating purposes has achieved commercial application. Per example, The Bioneer heat gasifier in Finland is an updraft gasifier that supplies fuel to a boiler originally designed to work with oil. This system can produce 5-10 MW. Gasification units have been tested for power generation in internal combustion engines. A small-scale power plant with a downdraft gasifier was developed in Martezo, France, which can generate from 70 to 450 kW and is mainly used for electricity production. Likewise, a number of power plants with different designs and capacities are operating in Germany, USA, Switzerland, and Denmark.

The implementation of biomass gasification promotes the use of wastes, residues, improved forest land use, and agricultural and green industry development. It is important to understand that gasification is not combustion. Gasification produces more valuable products that can be used to produce chemicals, power fuel cells, and clean energy with lower emissions of sulfur, NO_x and particulates (Hasan, et al., 2010).

1.2 Feedstock – potential and sustainability

Biomass includes all living matter on earth such as algae, trees, crops and animal manure. Solar energy is stored within the chemical bonds of organic materials. Their common elemental composition can include hydrogen, oxygen, and nitrogen (Saxena, et al., 2009). In biomass gasification, several feedstocks can be used to produce energy. They include natural crops, municipal bio-based wastes, agricultural residues, and carbon based materials. Natural crops, such as prairie hay, have a number of advantages because they don't need to be fertilized or irrigated. This fact makes it cheaper to produce syngas from natural crops. However, they have the advantage to grow on their own during warmer seasons. Municipal bio-based wastes, such as wood residues, are processed for other purposes including firewood and soil compost applications. Riley County, Kansas produced an average of 8,586 tons/year of bio-solid residues from 2005-2007 (Riley County, 2009). This waste can be effectively used to generate clean energy from biomass gasification. The production of corn, sorghum, wheat, and other crops produces agricultural residues that can be used for direct combustion and gasification. An estimation of the total crop residues generated in the United States was reported in 2009 by the National Renewable Laboratory, (Knoef, 2005). In the state of Kansas, estimated county-wide production is up to 200 thousand-dry tons/year of agricultural residues in many counties. The utilization of biomasses from raw materials that are byproducts of different processes and wastes increases the feasibility of the gasification process. Clean energy can be produced at a lower energy cost (Knoef, 2005).

1.3 Gasifier design and gasification process

Biomass gasification is the thermochemical conversion of natural matters into a useful biofuel named syngas. This biofuel is the result of a partial oxidation of the biomass which produces a mixture of hydrogen, oxygen, methane, carbon monoxide, carbon dioxide and light hydrocarbons, which also contains undesirable byproducts such as aerosols, inorganic particles, and condensable organic vapors (Colomba Di Blasi, 1999). Biomass gasification in the starting point was used to produce heat and power though a variety of pathways; syngas can be used in combined gas, steam cycles, gas turbines, fuel cells, Fischer-Tropsch Diesel process, and chemical production applications. Gasification systems are divided by fixed bed, fluidized bed and heating mode gasifiers (Hasan, et al., 2010) and can be classified according to the gasification agent and the type of reactor. Air, oxygen, and steam are usually used (Cheng, 2010). A fixed-bed gasifier is a reactor that uses a bed of solid biomass particles wherein a gasification agent, flowing through from up, down or a side (Reed & Das, 1988). The most common and simple designs of fixed-bed reactors are updraft, downdraft and crossdraft gasifiers (Rajvanshi, 1986). Fixed bed reactors have a simple configuration and can operate with high carbon conversion, long solid residence time, and low gas velocity (Reed & Das, 1988). Fluidized bed gasifiers are composed of a moving bed where an inert material, such as sand, is mixed with the biomass and placed in the reactor. The heat for endothermic reactions is provided by the combustion zone's heat. Some examples of a fluidized bed reactor include a bubbling fluidized bed and a circulating fluidized bed reactor (Hasan Jameel, 2010). Heating mode gasifiers utilize external heat to conduct gasification reactions; biomass is placed in a vessel, and then simultaneous pyrolysis and gasification reactions are conducted. This study is focused on fixed bed gasifiers because they are the most thermally efficient due to their auto-thermal characteristic, simplicity (Knoef, 2005); solid residence time, low gas velocity, high carbon conversion, and low ash carry over (Reed & Das, 1988).

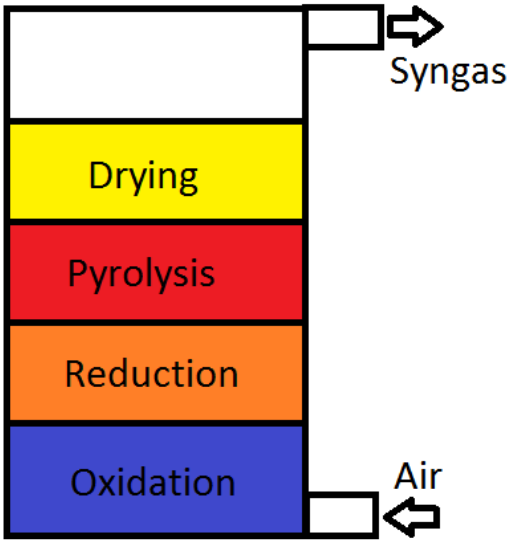


Figure 1.1 Updraft gasifier, source: (Knoef, 2005)

The updraft gasifier is the simplest of the fixed bed gasifiers and low capital cost is required (Figure 1.1). This gasifier can handle high moisture and inorganic content biomass

(Hasan, et al., 2010). The biomass in this reactor is fed from the top and moves countercurrent to the air that flows from bottom to top. The heat transfer between the syngas and the biomass helps to cool the syngas before it exits (Knoef, 2005). The product gas from this process contains 10-20% tar; this side effect is due to the fact that syngas emanating from the combustion zone carries aromatic vapors from the biomass, produced in the pyrolysis zone. These gases exit the gasifier without being decomposed (Sabgeeta Chopra, 2007). Tar removal methods are required in order to use syngas from updraft gasification for industrial and power generation applications (Lopamudra, et al., 2003), such as internal combustion engines, turbines, and fuel synthesis (Hasan, et al., 2010).

The downdraft gasifier is also known as “Imbert” gasifier in honor of its inventor Jacques Imbert, Figure 1.2. It was mass-produced during World War II (Reed & Das, 1988). In this reactor, biomass is fed from the top as in the updraft gasifier. In the same way, the gasification agent flows down. The gasification zones in a downdraft gasifier are arranged as shown in Figure 1.2. The gasification agent nozzles are located one-third from the bottom. The injection of air or air-steam mixtures keeps the combustion zone below the nozzles. The biomass and pyrolysis products react in the combustion zone to produce syngas (Reed & Das, 1988). Thus, downdraft gasifiers have a low tar generation, making it closer to be applicable on industrial applications without a downstream tar cracking system (Knoef, 2005). In contrast, the high dust and ash particle in the product gas requires an ash/tar cleanup. Others disadvantages of downdraft are that biomass requires a low moisture content and syngas exits the reactor at high temperature (700^{o}C) (Hasan, et al., 2010) decreasing the reactor efficiency.

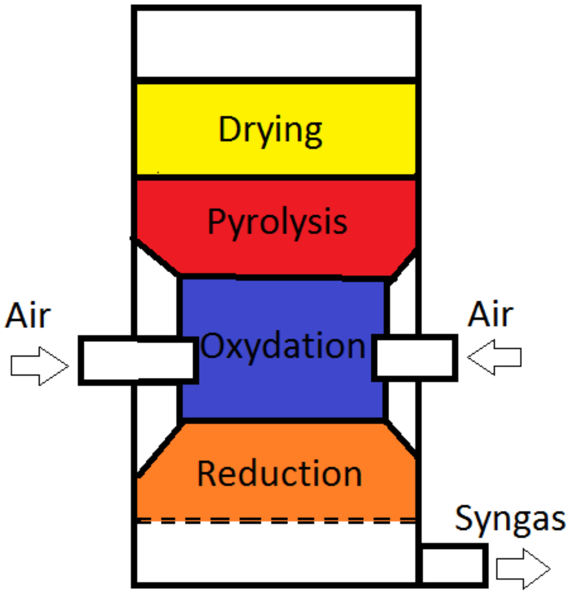


Figure 1.2 Downdraft gasifier, source: (Knoef, 2005)

Crossdraft gasifiers are simple; air flows at high velocity through a nozzle located on a side of the gasifier Figure 1.3. Crossdraft gasifiers have very fast response times. High temperature is reached in a small volume, thus low tar content can be achieved (Reed & Das, 1988). Temperatures close to 1500° C lead to a problem related to reactor materials (Knoef, 2005). It is shown in Figure 1.3 that in a crossdraft gasifier the gasification agent flows from one side to the other. The product gas exits at high temperatures.

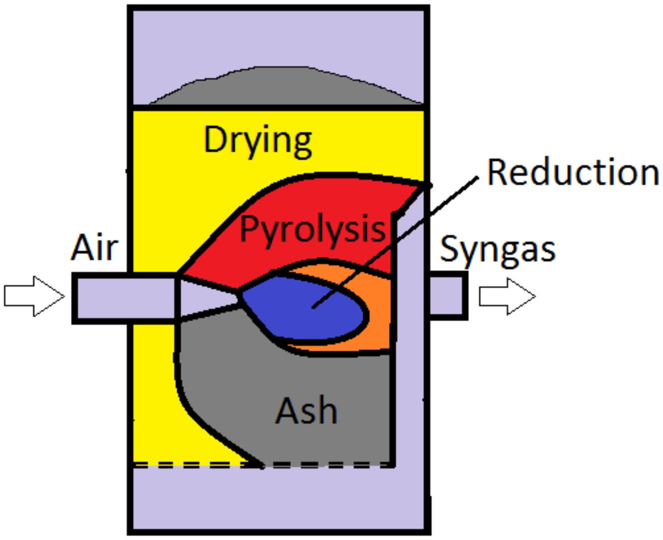


Figure 1.3 Crossdraft gasifier, source: (Knoef, 2005)

1.3.2 Thermochemical reaction and Gasification Zones

The thermo-chemical conversion of biomass includes pyrolysis, gasification, and combustion processes. In the implementation of thermal processes, all the biomass components, such as cellulose and lignin, can react to produce useful biofuels. (Reed & Das, 1988). Biomass gasification is the thermo-chemical decomposition of biomass with limited oxygen in order to produce syngas. Four zones are identified in a biomass gasifier: Combustion zone, Reduction zone, Pyrolysis zone, and Drying zone. These zones' locations in the gasifier can vary depending on the gasifier design. In each zone of the gasifier several reactions can take place; for instance, the reduction zone is where gas-solid reactions and gas phase reactions occur (Hasan, et al., 2010).

Gasifier Combustion zone

The biomass is partially combusted producing heat. This heterogeneous chemical reaction requires no more than 25% of the oxygen needed for complete combustion (Hasan, et al., 2010). Equations (1.1) and (1.2) present exothermic carbon-oxygen reactions happening in the combustion zone. A partial oxidation produces CO_2 and CO instead of CO_2 and H_2O, which are byproducts of complete combustion. The heat released in this zone is used for the endothermic reactions in the reduction and pyrolysis zones (Knoef, 2005).

$$C + O_2 \leftrightarrow CO_2 + 393.8\frac{kJ}{mol} \quad (1.1)$$

$$C + \frac{1}{2}O_2 \rightarrow CO + 123.1\frac{kJ}{mol} \quad (1.2)$$

$$C + H_2O + 118.5\frac{kJ}{mol} \leftrightarrow H_2 + CO \quad (1.3)$$

Equation (1.3) shows the water-carbon reaction; where moisture in the air reacts with carbon in the combustion zone in an endothermic reaction. This reaction produces H_2 and CO. In order to increase H_2 the use of steam as gasification agent can be implemented. Gil, et al. (1999) reported 38-56% H_2 produced using steam at reaction temperatures of 750-780°C. See Table 2.2

Gasifier Reduction zone

Several reduction reactions take place in the reduction zone of a gasifier; the most common equations are water shift reaction (1.4), Boudouard reaction (1.5) and methanation reaction (1.6) (Knoef, 2005).

$$CO_2 + H_2 + 40.9\frac{kJ}{mol} \leftrightarrow CO + H_2O \quad (1.4)$$

$$C + CO_2 + 159.9\frac{k}{mol} \leftrightarrow 2\,CO \quad (1.5)$$

$$C + 2H_2 \leftrightarrow CH_4 + 87.5\frac{kJ}{mol} \quad (1.6)$$

The final Syngas composition depends on the amount of oxygen flow in the gasifier, moisture of the feed biomass, the size of the feedstock, and reduction zone volume (Zainal, et al., 2002). Residence time and reactor temperature can also affect the producer gas composition (Hasan, et al., 2010). The heterogeneous endothermic reaction presented in Equations (1.4) and (1.5) can increase CO and H_2 volume at high temperatures and low pressure (Knoef, 2005). In contrast, the methanation reaction showed in Equation (1.6) is promoted by low temperatures and high pressures (Hasan, et al., 2010).

Pyrolysis Zone

Pyrolysis is the use of heat (pyro) to break down carbon based materials (lysis) without oxygen (Reed & Das, 1988). In the pyrolysis zone, biomass temperature rises and pyrolysis reactions take place. Thermochemical decomposition of the biomass without oxygen occurs. Hemicellulose, Cellulose and lignin are the components present in biomass; their decomposition temperatures varies. For example, Hemicellulose decomposes from 225^{o}C to 325^{o}C, Cellulose decomposition temperature varies from 300^{o}C to 400^{o}C; while lignin does at temperatures higher than 500^{o}C. Small particles in pyrolysis can react in less than a second; however, for bigger particle sizes, it can take a longer time. Pyrolysis produces hydrogen, carbon monoxide, carbon dioxide, methane, light hydrocarbons and high molecular weight hydrocarbons. Formation of tar is promoted by high molecular hydrocarbons. Pyrolysis is a process that has not been totally understood in biomass gasification because of the formation of complex products. (Hasan, et al., 2010).

Drying zone

In the drying zone, no reaction occurs. In updraft gasifiers, the air/syngas flow is from bottom to top; after syngas is produced, it flows from the pyrolysis zone at 160°C to the drying zone where biomass placed (Hasan, et al., 2010). The high temperature syngas removes moisture from the biomass solid particles. This drying process allows updraft gasifiers handle high moisture content (Knoef, 2005). The drying process in a downdraft gasifier is quite different; in this gasifier, the air/syngas flow is from top to bottom the same as the biomass. Radiation from the combustion zone heats the drying zone removing moisture from the biomass (Hasan, et al., 2010).

1.4 Challenges in biomass gasification

Gasification processes are known for their high efficiencies converting biomass into biofuels (Mathieu & Dubuisson, 2002). However, biomass gasification is not a commercial process for industrial applications because of heavy hydrocarbon formation (tars) that cause condensation problems downstream and the use of different gasification operational parameters and reactor requirements for different feedstocks (Di Blasi, et al., 1999). The gasification parameters can affect syngas composition and tar generation.

Syngas from gasification processes must be cleaned in order to reduce impurities. Table 1.1 shows the most common syngas contaminants produced from biomass gasification. Tars are a significant problem when syngas is used in gasification in industrial applications because most of industrial applications require tar content lower than 0.6 g/Nm^3 (Milne, et al., 1998). Tars are condensable aromatics, heavier than Benzene. They can condense downstream, causing problems such as clogging of equipment and deposits in pipe lines (Hasan, et al., 2010). Generation of tar in a gasifier depends on different parameters, such as type of reactor temperature, gasification agent, type of biomass, equivalent ratio, residence time, etc. (Lopamudra, et al., 2003). The optimum gasifier operational parameter can increase gasification efficiency. Yang (2006) studied the effects of using high temperature air in a fixed bed gasifier. Results showed a positive effect on hydrogen and carbon monoxide molar fractions. In the same way, Garcia (1999) studied the effect of gasification agent on biomass gasification. The study of the operational parameters for several biomass types is needed in order to identify the effect of operational parameters on gasification performance. Optimum operational parameters can increase the product's gas composition and/or decrease the amount of tar generated in this process. In order to decrease tar in syngas for industrial applications requirements, a downstream tar cracking system is required.

Table 1.1 Common syngas contaminants in biomass gasification, Summarized (Hasan, et al., 2010)

Contaminant	**Example**	**Problems**
Tar	Oxygenated aromatics	Deposits on pipes, clogging of equipment, hinders removal of particulates
Nitrogen compounds	Ammonia, hydrogen cyanide, NO_x	Environmental emissions
Chlorine compounds	Hydrogen chloride	Environmental emissions, corrosion, catalyst deactivation

1.5 Project Objectives

The objectives of this project are listed in this section as follows:

- To design, instrument and build a lab-scale updraft biomass gasifier and related accessories for stable gasification.
- To understand the effect of biomass type (wood chips, prairie grass and sorghum straw) and operating conditions (inlet air temperature and air flow rate) on the performance of an updraft biomass gasifier.
- To design and test an in-chamber tar cracking system for in-situ tar cracking and syngas reforming.

1.6 Bibliography

Cheng, J., 2010. Introduction. In: J. Cheng, ed. Biomass to Renewable Energy Processes. United States of America: CRC Press, pp. 1-6.

Di Blasi, C., Signorelli, G. & Portoricco, G., 1999. Countercurrent Fixed-Bed Gasification of Biomass at Laboratory Scale. Ind. Eng. Chem. Res., pp. 38, 2571-2581.

Gil, J., Corella, J., Aznar, M. P. & Caballero, M., 1999. Biomass gasification in a atmospheric and bubbling fluidized bed; Effect of the type of gasifying agent on the product distribution. Biomass and Bioenergy, Volume 17, pp. 389-403.

Hasan, J., Keshwani, D. R., Carter, S. F. & Treasure, T. H., 2010. Themochemical Conversion of Biomass to Power and Fuels.. In: Biomass to Renewable Energy Processes. United States of America: CRC Press, Taylor & Francis Group, pp. 437-489.

J. Rezaiyan, N. C., 2005. Gasification Technologies: a primer for engineers and scientists. United States: Taylor & Francis Group, LLC.

Knoef, H., 2005. Practical aspects of biomass gasification. In: H. Knoef, ed. Handbookd Biomass Gasification. Netherlands: BTG biomass technology group, pp. 13-37.

Lopamudra, D., Ptasinski, K. J. & Jansen, F. J., 2003. A Review of the primary measures for tar elimination in biomass gasification processes. Biomass and Energy 24, pp. 125-140.

Mathieu, P. & Dubuisson, R., 2002. Performance Analysis of a Biomass Gasifier. Energy Conversion and Management , Volume 43, pp. 1291-1299.

Milne, T., Evans, R. & Abatzoglou, N., 1998. Biomass Gasifier "Tars": Their Nature, Formation, and Conversion. National Renewable Energy Laboratory, pp. NREL/TP-570-25357.

Rajvanshi, A. K., 1986. Biomass Gasification. In: Alternative Energy in Agriculture . Maharashtra, India: CRC Press, pp. 83-102.

Reed, T. & Das, A., 1988. Handbook of Biomass Downdraft Gasifier Engine Systems. Golden, Colorado: U.S. Department of Energy.

Riley County, 2009. Solid Waste Management Plan, Kansas: Riley County, Solid waste management commitee.

Roberts, B., 2009. National Renewable Energy Laboratory for the U.S. Department of Energy. [Online] Available at: www.nrel.gov/gis [Accessed March 2011].

Sabgeeta Chopra, A. K. J., 2007. A review of Fixed Bed Gasification Systems for Biomass. Agricultural Engineering International: the CIGR Ejournal, pp. 1-23.

Saxena, R., Adhikari, D. & Goyal, H., 2009. Biomass-based energy fuel through biochemical routes: A review. Renewable and Sustainable Energy Reviews , Volume 13, pp. 167-178.

Yang, X. et al., 2010. Nickel supported on modified olivine catalyst for steam reforming of gasification tar. Catalyst Communications 11, pp. 383-386.

Zainal, Z., Rifau, A., Quadir, G. & Seetharamu, K., 2002. Experimental investigation of a downdraft gasifier. Biomass and Bioenrgy , Volume 23, pp. 283-289.

Chapter 2 - Literature Review - biomass gasification optimization.

The fact that the gasification process has been studied extensively does not mean it is very well understood. Biomass gasification is an efficient way to convert biomass into clean energy (Mathieu & Dubuisson, 2002). However, the optimization of gasification processes is needed in order to obtain a suitable gas product for industrial and power generation applications. Biomass characteristics, gasifier operational parameters, and a downstream tar cracking system are variables that need to be studied to increase gasification performance and efficiency.

Gasification performance depends on biomass characteristics because different biomasses can produce different syngas high heating values, reaction temperatures, tar content, etc. (Di Blasi, 1999). In the same way, gasification operational parameters can affect gasification performance. Gasification agent flow rate, gasification agent type, temperature of the feed air, reaction temperatures, and gasifier design are some examples of gasification parameters that can be adjusted to improve gasification performance.

Tar formation is one of the most studied phenomena in gasification. Corella (2002) modeled a tar elimination kinetic model of various tar species using a Nickel catalyst to explain how tars are formed. Tars are organic components generated under thermal or partial oxidation that have a molecular weight larger than benzene (Neef, et al., 1999). Ethylene, cyclopentadiene, and naphthalene are some examples of condensable tar components. Tars present in the gas product can cause condensation problems in downstream pipes and equipment. The average tar content for industrial applications ranges from 60 to 600 mg/Nm^3 (Milne 1998). According to Lopamudra (2003), tar removal methods can be classified into two types: primary methods and secondary methods. Primary methods remove tar without a reforming reaction, tar disposal is required. On the other hand, secondary methods are able to crack tars, increasing the heating value of the gas product. Tar removal methods must be effective, inexpensive, and should maintain or increase the product gas composition. Better tar removal results can be achieved by implementing primary and secondary methods in the same process (Basu, 2010).

This chapter reviews previous work done on gasification operational parameters, tar removal methods, and tar cracking-reforming methods for biomass gasification. A complete description of operational parameter effects on biomass gasification, tar removal methods, and several non-metallic and metallic based catalytic processes are addressed and presented.

2.1 Biomass and gasification operational parameters

2.1.1 Biomass Characteristics

A parameter not well known in gasification is the feedstock type. A gasifier should be able to use different feedstocks available in the surroundings areas (Herguido, et al., 1992).

Biomass feedstocks can exist in a multitude of types, but each species can be expected to have particular issues. The ability to identify specific biomasses for a particular gasifier is very important. The biomass chemical composition is similar for different biomass species. In contrast, coal, which can be used in gasification as well, does not have a constant composition for different species (Reed & Das, 1988).

Moisture content, ash content, heating value, bulk density, particle size and shape are some parameters of the biomass that need to be identified in order to select the best feedstock. **Moisture content** is the measure of water in the biomass, a value determine based on the weight loss when a known weight of biomass is dried at temperatures higher than $100^{o}C$. The biomass moisture content has a significant effect on biomass thermochemical conversion. Moisture content can be presented on a wet basis (MC_{w}), dry basis (MC_{d}), or dry ash-free basis (MC_{daf}). The basis should be included when the moisture content is reported. The increment of the moisture content, from 0 to 40%, can decrease the biomass heating value to 66%. Thermochemical processes need low moisture content in the biomass in order to get an overall positive energy balance (Hasan, et al., 2010). A secondary treatment is needed to reduce the moisture content. Desirable moisture content for gasification application is lower than 20% (Rajvanshi, 1986). **Ash** is the mineral or inorganic content of the biomass left after complete combustion. Ash content ranges from 0.1 to 15%, depending on the feedstock, and can cause variation in the reactor design (Knoef, 2005). The thermochemical conversion of biomass with high ash content can be difficult to apply (Hasan, et al., 2010) because it can promote ash slagging in reactors (Reed & Das, 1988). **Biomass elemental composition** identifies the amount of the biomass's main components: carbon, hydrogen, oxygen, nitrogen and sulfur. Hemicellulose, cellulose, lignin and extractive content can be used to determine biomass elemental composition. $CH_{1.4}O_{0.66}$ is the generic formula to describe biomass. It is important to mention that biomass contains 30 to 40% oxygen, which decreases its heating value (Hasan, et al., 2010). The generation of nitrogen and sulfur based emission in biomass gasification is small because of its low nitrogen and sulfur content (Knoef, 2005). Table 2.1 shows the C, H, O and heating value of typical biomasses.

Table 2.1 Thermal Properties of Typical Biomass, source: (Reed & Das, 1988)

	C	H	O
Composition (weight %)	52.3	4.3	41.7
Composition (mole %)	33.3	46.7	20.0
High Heating Value	20.9 kJ/g	(8990 Btu/lb)	
Low Heating Value	20.4 kJ/g	(8770 Btu/lb)	

The biomass heating value is the chemical available energy in a fuel per unit mass. This energy represents the net enthalpy that emanates from the biomass after it reacts with oxygen under exothermal conditions. If the water produced after the combustion of the biomass is in its liquid form, the measure of the energy is called High Heating Value (HHV). On the other hand, if the water is vapor, the energy is called Low Heating Value (LHV) (Hasan, et al., 2010). Average values of 20.9 kJ/g (HHV) and 20.4 kJ/g (LHV) were reported in Table 2.1. **Bulk density** is the weight of biomass per unit of volume. It depends on the biomass. Low bulk density biomass can be expensive to transport, handle, and store (Knoef, 2005). Biomass should be transported with the highest bulk density possible in order to decrease transportation costs (Hasan, et al., 2010). Other important parameters of the biomass are the **particle size and shape**; these parameters can help to determine whether or not an auto feeding system is needed instead of gravity feeding. They also have a considerable effect on product distribution. Small biomass particle size or shapes like straw can generate a higher syngas yield and less char than bigger particle sizes (Herguido, et al., 1992).

2.1.2 Gasification Agent

The selection of the gasification agent is important because it will depend on the reactor type. Different gasification agents can be used in the gasification processes; the most commonly used are air, oxygen, carbon dioxide, and steam. The gasification agent has a direct effect on the process economy, for instance the use of air as a gasification agent is cheap because of the low cost to supply air. On the other hand, the use of steam can lead an increment on cost because of the heat needed for the gasification reaction, the cost to produce steam, and special pipe protection to prevent condensation on the line. The gasification agent has an impact on product distribution and product quality as well. There are four common gasification agents: air, steam, CO_2, and air/steam mixtures. The gasification agent can affect the generation of tar. Gil (1999) carried out experiments to investigate the effect of the gasification agent on syngas composition; air and steam/oxygen mixtures were evaluated under several operating conditions. Table 2.2 represents tar composition for different gasification agents and shows tar is more likely to be formed when steam is used as the gasification agent. This table also shows the gasification agent could increase or decrease syngas low heating value.

Table 2.2 Tar content and Syngas characteristics at different temperatures, Summarized from, (Gil, et al., 1999)

Gasification Agent	T(^oC)	Gas Composition (dry basis)		Yields		
		H_2(%)	CO(%)	Tar (g/kg)	Gas (Nm^3/kg)	LHV (MJ/Nm^3)
Air	780-830	5.0-16.3	9.9-22.4	3.7-61.9	1.25-2.45	3.7-8.4
O2 – Steam	785-830	13.8-31.7	42.5-52.0	2.2-46	0.86-1.14	10.3-13.5
Steam	750-780	38-56	17-32	60-95	1.3-1.6	12.2-13.8

Air

Air is the most common gasification agent today (Herguido, et al., 1992). The amount of air supplied to a system is measured by the equivalent ratio (ER), which is a comparison with the air needed for complete combustion. The use of air or oxygen in gasification oxidizes the biomass partially in an exothermic process that helps to drive the endothermic reaction in the gasification process. However, the use of air can dilute the final syngas thus decreasing its heating value (Mahishi & Goswami, 2007). Sugiyama (2005) reported that air at 1000^{o}C can achieve gasification results similar to those using low air stoichiometric ratio.

Oxygen

Biomass gasification using oxygen as a gasification agent is similar to air gasification. However, the production of syngas using oxygen as a gasification agent is a way to generate nitrogen free syngas.

Air-steam mixtures

The addition of oxygen/air to the gasification medium composed of steam can generate the heat necessary for gasification reactions. Therefore, the gasifier can work in an auto-thermal condition (Lopamudra, et al., 2003). The use of air-steam gasification can produce a higher H_2 yield compared with air gasification alone (Mahishi & Goswami, 2007).

Steam

Gasification using steam is an endothermic process thus special heating supply design is needed in this process (Lopamudra, et al., 2003). Steam-gasification, which is an endothermic process, can produce syngas with a low heating value of 12-13MJ/Nm^3 (Herguido, et al., 1992). It is known that the use of steam as a gasification agent can increase H_2 content and the heating value of the producer gas. Steam gasification produces 30-80 g/m^3 tar, steam/oxygen mixtures 4-30 g/m^3, and air gasification 2-20 g/m^3, making steam gasification the highest tar producer. However, catalytic tar reforming can be used to destroy tar and increase the syngas heating value (Gil, et al., 1999).

CO_2

Carbon dioxide can be utilized as a gasification agent in biomass gasification. The reaction of CO_2 and char is not completely understood (Ollero, et al., 2003). The thermochemical reaction of CO_2 and carbon is a superficial heterogeneous reaction (Ergun, 1956). Carbon reactions play an important role in several gasification reactions. See equations 1.4 and 1.5. The use of CO_2 in gasification is promising because it is one of the gasification products. CO_2 enhances tar reduction reaction in the presence of catalysts (e.g., Ni/Al) as well as increases H_2 and CO composition (Lopamudra, et al., 2003).

2.1.3 Feed Air temperature

The increment of the feed air temperature can reduce tars produced in a gasifier as well as soot and char residues. It can also increase the high heating value of the dry producer gas (Lucas, et al., 2004). Mathieu (2002) modelled the effect of several gasification parameters in a gasifier; the results showed that by increasing the feed air temperature from 25 to 300^{o}C, the gasification efficiency can increase from 76.6 to 79.5%. The data showed that the syngas high heating value is improved. At 25^{o}C, HHV of 5129 kJ/kg was reported increasing to 5402 kJ/kg when the feed air temperature was 800^{o}C. Lucas, et al. (2004) studied the effect of high-temperature air/steam gasification, concluding that high temperatures maximize the syngas production and can reduce syngas tar content. However, there is a critical point from where preheating has a negative effect on gasification performance because it can cause decrement on gasification efficiency.

Sugiyama (2005) and Mathieu & Dubuisson (2002) analyzed gasification efficiencies using high feed air temperature. Ponzio (2006) reported that the use of a high feed air temperature promotes phenolic compounds, paraffines, olefins and alkylated aromatics to be cracked in the gasification of paper fiber mixed with fabric fiber, wood chips, and plastics when the feed air was heated up to 1200^{o}C. The increment in the outgoing syngas temperature indicated the cracking effect of the high feed air temperature. No tar was detected when the syngas outgoing temperature was 800^{o}C.

2.1.4 Reaction Temperature

Gasification temperature needs to be controlled in order to accomplish high biomass-carbon conversion as well as a low tar content. Gasification temperatures must reach up to 800^{o} C. Inappropriate reaction temperatures can increase the quantity of tar generated, but this can also impact the composition of tar. Phenol, cresol, and benzofuran are tar components formed at temperatures below 800^{o}C, however, benzene and naphthalene composition increase with the temperature (Basu, 2010). The study of pyrolysis of birch wood, carried out by Yu (1997), analyzed the impact of the temperature on tar formation in a free-fall reactor. Three temperatures were selected, 700, 800 and 900^{o}C with a residence time of 1.5s. Results showed that the formation of syngas components increased as the tar content decreased. Kinoshita (1994) studied the tar formation by applying different parameters in an indirectly-heated, fluidized bed gasifier. He found that at low temperatures the formation of tar species, such as phenol, xylene and toulene, increased similar to (Basu, 2010). In the same way, high reactor temperatures promoted the formation of benzen, naphthelene, and phenanthrene.

The reaction temperature affects syngas yield and also controls gasification energy input. Syngas rich in H_2 and CO is produced at high reaction temperatures (800-850^oC) that are the typical temperatures for most of the real life gasifiers. Mashishi & Goswami (2007) and Hanping (2008) reported that at reaction temperatures of up to 800^oC, optimum gasification conditions are reached and have a high syngas yield. This phenomenon can be due to the water shift reaction at high temperatures and tar cracking reactions at this temperature.

2.1.5 Equivalent ratio (ER)

Equivalent ratio (ER) is the amount of air or oxygen used compared with the needed amount for complete combustion (Knoef, 2005). According to Narvaez.(1996), the equivalent ratio is one of the most important factors in air biomass gasification; the tar yield, bed temperature, and syngas composition are defined by the ER. An equivalent ratio of zero represents pyrolysis. An ER of one represents complete combustion. When ER increases (more oxygen), H_2 and CO concentration decrease and CO_2 increases. This fact is due to H_2 and CO oxidation reactions to H_2O and CO_2. An increment of the equivalent ratio higher than 0.15 does not show a positive effect on the gasification biomass (Hanping, et al., 2008).

Narvaez (1996) reported that tar yield can decrease 50 wt% when the ER is adjusted from 0.2 to 0.45. However, other reserchers have reported the opposite statement (Houben, 2004). Optimal ER needs to be selected in order to supply air for the gasifier’s exothermical reactions without affecting syngas production (Mashishi & Goswami, 2007).

2.2 Tar formation

Biomass gasification is a multiple reaction process that combines pyrolysis and oxidation reactions in liquid and gas phases. Biomass gasification produces tars that are condensable components mainly aromatic hydrocarbons (Milne, et al., 1998). In the gasifier’s pyrolysis zone, when the temperature varied from 200^oC to 500 ^oC, which is a low temperature range, hemicellulose, cellulose and lignin reacted producing primary tars (Basu, 2010). Elliot (1998) presented a review of tar composition at different temperatures. In Figure 2.1 a schematic based on GC/MS analysis of aromatic hydrocarbons temperature dependency is shown.

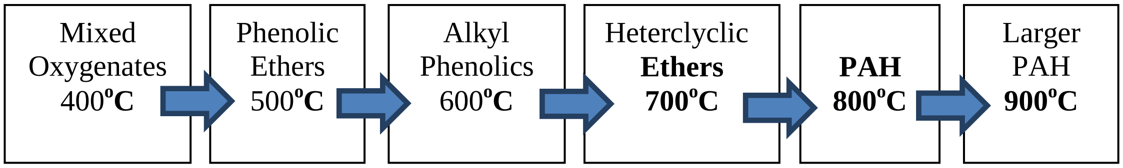


Figure 2.1 Tar formation, temperature dependency scheme. Elliot (1988)

2.3 Primary methods

Lopamudra (2003) classified tar cracking methods in two stages, primary methods and secondary methods. The primary methods are focused on preventing tar formation before syngas is produced. The gasification's operational parameters are controlled to reduce the amount of tar generated during the gasification process as well as in a bed catalyst procedure. These methods also consider the gasifier design. Corella (1999) tested the use of in-bed dolomite in a fluidized bed to compare the effect of downstream catalyst utilization, concluding that the use of in-bed dolomite produces similar results to that of dolomite downstream. The primary methods try to simplify the entire gasification process by eliminating the downstream-tar cracking stage. Gasification operational conditions, such as gasification temperature, gasification agent, air/fuel ratio, and gasifier type, are factors that depend on the feedstock. The optimal operational parameters can result in a decrement of tar content. The utilization of primary methods has not been completely studied, therefore, it is not commercially used (Lopamudra, et al., 2003). A complete description of operational parameters was presented in section 2.1.

2.3.1 In-bed catalyst

In-bed additives have a pronounced potential for tar removal application. Elimination of the downstream tar removal can reduce the complexity of the gasification process. Catalytic chemical reactions promote by in-bed catalyst can improve syngas composition, heating value and reduce tar production. This catalyst utilization can decrease feedstock agglomeration. Limestone was reported as one of the first in-bed catalysts. However, dolomite is the most commonly investigated (Lopamudra, et al., 2003). The utilization of dolomite as a catalyst was studied by Corella (1999); an experimental analysis of where to locate dolomite was presented downstream and in-bed catalysts were investigated. Conclusions showed that there was no significant difference between in-bed dolomite and downstream dolomite for tar content and syngas composition. Olivares (1997) concluded that 10 wt% of in-bed dolomite could improve the gasification product's gas composition. H_2/CO ratio was reported from 0.6 to 1.5 and tar content decreased from 12 to 2-3 g/m^3

2.4 Secondary methods

Secondary tar removal methods can be described as methods that remove tar from the producer gas (syngas) after gasification reactions. These methods can be listed as follows:

- Physical processes such as filtration, wet scrubbing, dry scrubbing, and hot gas conditioning (Milne, et al., 1998).
- Thermic tar cracking and catalytic tar cracking methods.

The main disadvantage of physical methods is that they separate tars from syngas, no additional reforming reaction occurs. The fact that tar products are generated and collected during the process adds several disadvantages, such as the production of solid hazardous wastes materials that need to be disposed of and the addition of a water treatment system (Milne, et al., 1998). However, thermic and catalytic tar cracking reforming reactions produce H_2 and CO from tar components. Equations (1) and (2) are examples of reforming reactions; C_nH_m represents tar components (Hasan, et al., 2010).

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \quad (1)$$

$$C_nH_m + nCO_2 \rightarrow (2n)CO + \left(\frac{m}{2}\right)H_2 \quad (2)$$

Catalytic tar removal and reforming is a method widely used, it can be performed by different catalyst at different temperatures. Catalysts are evaluated using different loadings, residence times, and supported materials. The use of alkali metal catalyst has been studied in order to improve the gasification reactions; however, no improvement of biomass conversion has been presented. Likewise, several other materials have been tested in downstream catalyst; dolomite, olivine, supported metal catalyst and carbon supported catalyst. (Xu, et al., 2010)

Dolomite ($CaMg(CO_3)_2$) was used by Corella (1999); the effect of dolomite was evaluated in-bed and downstream. The results of downstream treatment presented that dolomite can increase H_2 and CO_2 composition in the product gas as well as decrease tar content. Olivine (magnesium aluminosilicate), Michel (2011) reported the use of this catalyst in a fluidized bed gasifier;

experiments were carried out to investigate catalyst activity on syngas and tar content. It was found that the reforming activity of olivine can increase the yield of producer gas, up to 40% H_2 and 24% CO; effective removal of tar was achieved. However, formation of poly-molecular aromatic hydrocarbons increased at high temperatures. Huang (2011) performed tar hydrocracking experiments in an updraft gasifier using palladium catalyst supported by stainless steel turning wastes. Different catalytic reaction temperatures and flows were studied. It was seen that tar concentration decreased as the temperature increased. Conversion efficiency of 98.6% and 99.3% were accomplished at 700^{o} C. Tar content of 29 mg/Nm^3 was reported. Table 2.2 presents conversion of different tar components at different temperatures as well as H_2/CO composition of the final gas product.

Table 2.3 Catalytic tar conversion using different catalyst and tar model components.

	T (^{o}C)	Tar model Component	Conversion (%)	H_2/CO Composition	Reference
Thermal cracking	1290	Heavy tar	n/a	26.3/22.3	(Brandt & Henriksen, 2000)
Ni/dolomite	700	Naphthalene	94.8	50.1/32.5	(Wang, et al., 2005)
Ni/dolomite	730	Toluene	99.3	69.1/9.6	(Srinakruang, et al., 2005)
Ni/olivine	800	Benzene	99.5-98.7	n/a	(Yang, et al., 2010)
Ni/olivine	830	Benzene	71	61.61/28.54	(Zhang, et al., 2007)
Ni/AL_2O_3	900	Benzene	95	n/a	(Engelen, et al., 2003)
Ni/γ-Al_2O_3	800	Benzene	99.5	51.78/21.10	(Wang, et al., 2010 (1))
Ni/CeO_2 (0.75) ZrO_2 (0.25)	700	Benzene	87.2	69/4.5	(Park, et al., 2010)
Ni/char	800	n/a	99	34.33/32	(Wang, et al., 2011)
Ni/HTC-char	800	benzene	99	51.90/18.36	(Wang, et al., 2010)

n/a – Not available

2.4.1 Physical methods

Physical methods to remove tar from syngas have been found to be effective. The use of scrubbing towers can condense heavy tars; the fact that a portion of tar remained in syngas adds the use of venturi scrubbers. It was reported that tar concentration after a water scrubber can be as low as 10 ppm (Milne, et al., 1998).

Filtration, it is a physical method that removed tar from syngas in gasification. Granular filters are used in cold and hot tar removal. The downstream bed is composed by silica or alumina sand. The bed is preheated to 500°C. Static bed can be used; however the use of moving the bed can increase tar removal. The use of hot tar filtration was developed for coal gasification. In cold granular filtration, organic compounds similar than in the hot tar filtration are used. On the other hand, organic compounds such as sawdust can be mixed with silica sand or other inorganic compounds presenting effective syngas cleanup (Milne, et al., 1998). Values up to 80% and 90% removal were reported by Hasler (1997).

2.4.2Thermal cracking of tar

The use of high temperatures can reduce poly-molecular aromatics to light gases such as CO_2, H_2 and CO. These gases are some of the products of tar destruction, tar cracking reactions are driven by gasification stoichiometry (Milne, et al., 1998). It was reported in Han & Kim (2008) that effective tar decomposition can be achieved with tar thermal cracking; however, appropiated residence time and direct interaction between the hot surface and the product gas has to be accomplished. In Brandt & Henriksen (2000), thermal tar cracking procedures were analyzed. A pure Al_2O_3 reactor was built to perform the experiments. Three temperatures were studied, 1200°C, 1250°C and 1290°C and residence time of 0.5 s. It was reported that tar remal was succesfully achieved at 1290°C; tar content of 12 mg/Nm^3 was reported. H_2 and CO composition of 26.3% and 22.3% were reported after cracking process. This data shows that the use of high temperature to crack tar can be effectively implemented. The production of low-tar gas applicable for industrial applicatioms can be performed.

2.4.3 Catalytic cracking of tar

Nickel based catalyst

Ni-based catalysts are one of the most studied catalysts for tar cracking and reforming applications. Several types of Ni-based catalyst have been developed and the results have shown that Ni-based catalyst can be effectively used to crack tars and reform syngas in biomass gasification. Updraft gasifiers, downdraft gasifiers, fluidized bed reactors, entrained flow reactors are some examples of gasification units that have been used to produce syngas in order to improve its quality. In this section, several catalysts are presented

Dolomite and Olivine Ni-based Catalyst

A novel **Nickel/dolomite** catalyst was tested by Wang (2005) for steam reforming of biomass. This natural catalyst promises to be a cheap way to clean producer gas from biomass gasification. Natural dolomite from a Chinese mine was used; commercial catalyst was analyzed to compare the effect of the natural dolomite. This novel catalyst was characterized by elemental analysis in a Thermo ISIR. A quartz (8.0 mm i.d) bench reactor, and a tar sampler composed by five impinge flasks were used. Temperatures from 650C to 850°C were studied. Ni/dolomite tar conversion was compared with other commercial catalyst; the results presented conversion values of 87 and 98%, respectively. It is important to say that conversion of tar usually adjusts gas composition because some of the products' gases from tar conversion are H_2 and CO; therefore, a higher syngas quality was produced.

Wang (2005) also studied the performance of a Ni/dolomite catalyst using naphthalene as tar model component in a quartz reactor. The results presented 94.8% naphthalne conversion after a hour at 700°C and $0.81h^{-1}$ space velocity. After 20 hr tar cracking activity decreased to 57.4% under the same conditions. Srinakruang (2005) used Ni/dolomite catlyst to test gasification efficiency with steam. The use of toulene as model component was evaluated. The results reported Ni/dolomite catalyst calicnated at 500°C exhibeted the best performnace when at 730°C conversion of 99.3% was achieved.

Yang (2010) evaluated the activity of modified olivine (MO) as a support for nickel in steam reforming of biomass gasification tar. Benzene was used as tar model component in this study. Modified olivine was treated with calcium cement to increase its porosity and surface area. Nickel was impregnated and calcined at 800°C, 900°C and 1000° C. The experiments were carried out in a quartz reactor at 800^{o}C. The catalytic effect of the Ni/Mo catalyst was evaluated based on the final carbon molar fraction of benzene. Ni/MO treated at 800^{o} C and 900^{o} C showed benzene conversion levels of 66.3% and 64.4% after 2 hr; however, Ni/Mo calcined at 1000^{o}C presented lower benzene conversion. Furthemore, Ni/Mo was compared with Ni/catalyst; after 5 hr. carbon conversion 99.5% and 98.7%. Zhang (2007) evaluated the use of the Ni/olivine catalyst in a bench scale reactor at 700^{o}C and 830^{o} C using benzene as a tar model component. Tar conversion of 71% was achieved. H_2 and CO concentration of 61.61% and 28.54% were reported when 6 wt% Ni/olivine was used.

Alumina and Metal oxide Ni-based Catalyst

The use of the Al_2O_3 supported catalyst has been studied by several reserachers. The catalytic effect of Nickel catalyst in a Al_2O_3 candle filter was evaluated by Engelen (2003). The system was capable to remove 95% tars when H_2S was 200 ppm at 900^{o}C. In a commercial full size alumina candle filter of 1 m long and 0.3 m diameter and 0.1 m thick, the catalytic effect of nickel on benzene and naphthalene in syngas was studied, presenting similar tar conversion results. Benzene in Syngas was totally converted into a mixture of CO, CO_2, and H_2 when the H_2S concentration was 0 ppm. Tars such as Naphthalene are gasification by-products that need to be removed before syngas is used in industrial applications.

Wang (2010,(1)) also studied the use of the Ni alunima catlayst; the selection of the adequate parameters to perform tar cracking in the biomass gasification process was performed. Catalytic temperature, gas residence time, and nickel loading were evaluated. Syngas production from a downdraft gasifier and an updraft gasifier with air as a gasification agent was analyzed. Nickel based catalysts presented effective tar cracking activity. Benzene was used as a tar model component to determine the effect of Ni/γ-Al_2O_3 on tar cracking in a quartz reactor with temperatures from 700 to 900^{o}C. Two stages were evaluated to determine the optimum operational parameters. In the first stage, a known flow of benzene was used to evaluate the tar cracking activity of Ni/γ-Al_2O_3. In the second, syngas from a downdraft and an updraft gasifier was provided to test the cracking effect of the catalyst. Results showed that 15% Ni loading and 0.3s residence time performed the highest conversion rate with benzene. The two gasification systems were evaluated using these conditions. The results showed that the use of a Ni/γ-Al_2O_3 catalyst can increment H_2 content up to 56% in syngas from the updraft gasifier and 159% in the downdraft gasifier. Furthermore, tar content decreased 99.5% in the downdraft gasifier and 98% in the updraft (Wang, et al., 2010 (1)).

Park, et al.(2010) evaluated the effect of several Nickel metal supported catalysts. A comparison of various Nickel based catalysts and Ni/γ-Al_2O_3 catalyst was carried out. The reaction times of Ni-precursor and Ni loading were evaluated. Benzene was used as tar model component. The best benzene conversion was performed by Ni/CeO_2(75%)–ZrO_2(25%) catalyst, 87.2%. Analysis results also showed that this catalyst has the highest activity in steam reforming benzene. Catalytic activity is compared with Ni/ γ-Al_2O_3 that also performed high benzene conversion of 82.5%. The nickel loading effect in benzene conversion was also studied; when CeO_2 and ZrO_2 have a Nickel impregnation from 5 to 15%, data reported that conversion rate changes from 42% to 87%, respectively.

Kimura (2006) and Zhang (2007) investigated metal oxide tar cracking activity. Different catalyst preparations were tested under different parameters. In Kimuras' (2006), the effectiveness of Ni based catalysts (Ni/CeO_2/Al_2O_3) was performed; catalyst preparation was performed by two methods: co-impregnation and progressive impregnation. First, the co-impregnation of Al_2O_3 was performed by an aqueous solution of $Ni(NO_3)_2$ $6(H_2O)$ and $Ce(NH_4)_2(NO_3)_6$. Second, the progressive impregnation was driven by a similar impregnation from the stage explained before, however, the impregnation was done at different temperature ranges in sequential steps. Nickel loading varied from 4 to 10 wt% and CeO_2 from 10 to 50wt%. Tar and solid materials in syngas were condensed in a cold water condenser. Experiments were carried out on a lab-scale dual-bed reactor. Dependency on the catalyst type (Ni/CeO_2/Al_2O_3) was found at 873^oK. The product gas from experiments without a catalyst showed lower CO and H_2 concentration, and a high tar content. This contrasts with the 4 wt% Ni catalyst that decreased tar content and increased CO and H_2 concentrations. The use of CeO_2 has a catalytic effect on syngas. Results showed that the CeO_2 co-impregnated catalyst had a better performance than the progressive impregnated catalyst. Coke formation and tar content decreased significantly after CeO_2 was added. In the comparison between Ni/CeO_2 and Ni/$Al_2O_{3,}$ loading demonstrated that CeO_2 species can perform better reducibility than Al_2O_3. The interaction of Ni and CeO2 presented on the co-impregnated catalyst can be an effective method for tar cracking and reforming on biomass steam gasification (Kimura, et al., 2006). Similar experiments were performed by Zhang (2007) in which Ni/olivine doped with CeO_2 was tested. Two impregnation techniques were used to prepare the catalyst, NiO (3.0%) and CeO_2 (1%) in olivine were the catalyst proportions selected. Parallel, other Ni/olivine catalyst were studied. In this work, a mixture of N_2 and H_2 was injected in the reactor after equilibrium was reached (830^oC). Bezene (or toulene) and steam were injected in the rector. The steam reforming of benzene and toulene reported a conversion of benzene with Ni/olivine of 70.4% with values of 62.5% H_2 and 26.54% CO; at 830^oC. The benzene conversion of Ni/olivine doped with CeO_2 exhibited a better response than those composed just by Ni/olivine.

Carbon supported Ni-based Catalysts

The use of carbon as support for a Nickel based catalyst was implemented by Wang (2010). The hydrothermal conversion of char (HTC) to support Nickel catalytic was studied. Residence time, reaction temperatures, nickel loading and tar removal were evaluated. Benzene was used as a tar model component. A mechanical mixing was used to prepare the Ni-char catalyst. Nickel and char ratios from 5% to 20 % were investigated. Char particle sizes ranged from 1.4 to 2.0 mm. Ni loading of 3% and 6% were performed with a single step process; a two-step process was used to impregnate the catalyst with Ni loading higher than 6%. The experiment was completed by a four step process: Benzene unit supplier (tar generator), gasifier (downdraft gasifier), tar cracking unit (quartz reactor), and a tar sampler. The results showed that Ni-char catalyst and Ni/γ-Al_2O_3 have similar results when they are used in tar removal and catalytic reforming applications. Nickel loadings presented optimum performance at 15%; the same value was reported from previous experiments with Ni/γ-Al_2O_3 (Wang, et al., 2010 (1)). At this point it could be observed that Ni/γ-Al_2O_3 presented a small difference compared with Ni-char catalyst. The effect of the residence time was also evaluated. The data reported that for a residence time higher than 0.3s, 28% of tar was removed. However, the catalytic reforming was estimated in order to investigate the catalyst effect on syngas. Up to 99% of tar was converted by using Ni/γ-Al_2O_3 and Ni-char catalyst. Syngas composition without catalyst ranged between 19-20% H_2 and 14-16%. Moreover, after reaction, syngas composition increased to 51.90% H_2, 18.36% CO (Ni-char) and 51.78% H_2, 21.10% CO (Ni/γ-Al_2O_3). Furthermore, tar decreased down to 0.01 g/m^3 in both cases.

In a recent publication, Wang (2011) investigated the use of char as support material. The use of char and wood as catalysts was tested. Four catalysts were considered: wood char, coal char, Ni/wood char and Ni/char. Ni oxide was used as nickel provider. The char particle size was ranged from 0.3 to 0.45 mm. Mechanical mixing was used to prepare Ni/woodchar and Ni/char catalyst. Syngas from an updraft biomass gasifier was used to test the Ni/char catalyst. System setup was the same as presented in (Wang, et al., 2010 (1)). The reforming temperature was evaluated from 650^{o}C to 850^{o}C. In this stage, the other parameters were set as follows: 0.3s residence time, 15% nickel loading. The results presented tar removal improvement as the temperature rises. Similar results were reported for Ni/char and Ni/woodchar catalysts. However, Ni/char catalyst tar removal ranged 91% -99% and Ni/woodchar from 86%-96%. The use of char as a catalyst decreased tar content from 75% to 90%. Syngas char and coal alone didn't show reforming activity. In contrast, the use of a Ni based catalyst presented effective syngas reforming. Nickel loading was also studied at 0.3s residence time and 800^o C. Ni/char catalysts had better results than Ni/woodchar catalysts. H_2 reforming concentrations of 32.53% (Ni/woodchar) and 34.33% (Ni/char) were reported when nickel loadings varied from 0 to 20%. The residence time was also evaluated from 0.1 to 1.2s; 15%. Higher residence time and higher nickel loading is needed in order to present similar results. No Catalytic deactivation was found after 8 hr. of continuous operation for both Ni based catalysts. (Wang, et al., 2011)

2.4 Summary

In this review, the operational condition effect on biomass gasification and tar removal methods was discussed. The physical and chemical characteristics of the biomass can affect gasification performance and a previous study of the feedstock selected has to be done. Gasification operational parameters can also affect gasification performance; optimal conditions and gasifier type selection needs to be performed in order to increase syngas quality and tar minimization. Several operational parameters were presented, such as reaction temperature, feed-air temperature variation, and equivalent ratio (air flow).

Details of primary methods were listed. Primary methods prevent tar formation by modifying the reactor operational parameter or by adding in-bed catalysts in order to decrease tar formation. Several studies presented operational parameters such as reactor temperature and gasification. Effective tar removal was achieved, however, syngas reforming activity was limited. Secondary methods for tar cracking and reforming application were studied. Different support materials for Ni-based catalysts were presented as well as thermal cracking of tar and physical tar removal. Alkali metals catalyst, alumina, metal oxide, and char were presented as common materials used in biomass gasification for downstream catalytic reactions. The use of Ni/γ-Al_2O_3, Ni/char (hydrothermally treated) yielded the best results. Effective tar cracking and removal were performed. H_2 content was increased up to 156% in syngas from a downdraft gasifier. The use of secondary methods to reform syngas can increase H_2 and CO composition and convert tars efficiently when the appropriate operational parameters and catalysts are selected.

2.5 Bibliography

Basu, P., 2010. Tar Production and Destruction. Biomass gasification and pyrolysis; practical design and theory, pp. 97-116.

Brandt, P. & Henriksen, U., 2000. Decomposition of tar in gas from updraft gasifier by thermal cracking. Sevilla, Spain, London, James & James (science Publishers) Ltd.

Cheng, J., 2010. Biomass to Renewable Energy Processes. United States of America: Taylor and Francis Group, LLC.

Corella, J., Aznar, M.-P. & Javier Gil, M. C., 1999. Biomass Gasification in Fluidized Bed: Where to locate the Dolomite To Improve Gasification?. Energy & Fuels , Volume 13, pp. 1122-1127.

Di Blasi, C. G. S. G. P., 1999. Countercurrent Fixed-Bed Gasification of Biomass at Laboratory Scale. Ind. Eng. Chem. Res., pp. 38, 2571-2581.

Elliot, D., 1988. Relation of reaction time and temperature to chemical composition of pyrolisis oils.. Denver, CO, USA, ACS Symposium 376.

Engelen, K., Yuhong, Z., J., D. D. & V., B. G., 2003. A novel catalytic filter for tar removal from biomass gasification gas: Improvement of the catalytic activity in presence of H2S. Chemical Engineering, Volume 58, pp. 665-670.

Ergun, S., 1956. Kinetics of the Reaction of Carbon Dioxide with Carbon. J. Phys. Chem., 60(4), p. 480–485.

Gil, J., Corella, J., Aznar, M. P. & Caballero, M., 1999. Biomass gasification in a atmospheric and bubbling fluidized bed; Effect of the type of gasifying agent on the product distribution. Biomass and Bioenergy, Volume 17, pp. 389-403.

Han, J. & Kim, H., 2008. The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. Renewable and Sustainable Energy Reviews, Volume 12, pp. 397-416.

Hasan, J., Keshwani, D. R., Carter, S. F. & Treasure, T. H., 2010. Themochemical Conversion of Biomass to Power and Fuels.. In: Biomass to Renewable Energy Processes. United States of America: CRC Press, Taylor & Francis Group, pp. 437-489.

Hasler, P., Buhler, R. & Nussbaumer, T., 1997. Evaluation of Gas Cleaning Technologies for Smal Scale Biomass gasifiers. Zurich; Swiss Federal Office of Energy and Swiss Federal Office for Education and Science..

Herguido, J., Corella, J. & González-Saiz, J., 1992. Steam Gasification of Lignocellulosic Residues in a Fluidized Bed at a Small Pilot Scale. Effect of the Type of Feedstock. Ind. Eng. Chem. Res., Volume 31, pp. 1274-1282.

Houben, M. P., 2004. Analysis of tar removal in a partial oxidation burner, s.l.: The dissertation of Eindhoven.

Huang, J., Schmidt, K. G. & Bian, Z., 2011. Removal and Conversion of Tar in Syngas from Woody Biomass Gasification for Power Utilization Using Catalytic Hydrocracking. Energies , Volume 4, pp. 1163-1177.

Kimura, T. et al., 2006. Development of Ni catalyst for tar removal by steam gasification of biomass. Applied Catalyst B: Environmental, Volume 68, pp. 160-170.

Kinoshita, C., Y, W. & Zhou, J., 1994. Tar formation under different biomass gasification conditions. Journal of Analytical and Applied Pyrolysis , Volume 29, pp. 169-181.

Knoef, H., 2005. Practical aspects of biomass gasification. In: H. Knoef, ed. Handbookd Biomass Gasification. Netherlands: BTG biomass technology group, pp. 13-37.

Lopamudra, D., Ptasinski, K. J. & Jansen, F. J., 2003. A Review of the primary measures for tar elimination in biomass gasification processes. Biomass and Energy 24, pp. 125-140.

Lucas, C., Szewczyk, D., Blasiak, W. & Mochida, S., 2004. High-Temperature air and steam gasification of densifies biofuels. *Biomass and Bioenrgy,* Volume 27, pp. 563-575.

Mahishi, M. R. & Goswami, D. Y., 2007. Thermodynamic optimization of biomass gasifierfor hydrogen production. International Journal of Hydrogen Energy, Volume 32, pp. 3831-3840.

Mathieu, P. & Dubuisson, R., 2002. Performance analysis of a biomass gasifier. Energy Conversion and Management , Volume 43, pp. 1291-1299.

Michel, R. et al., 2011. Steam gasification of Miscanthus X Giganteus with olivine as catalyst production of syngas and analysis of tars (IR, NMR, and GC/MS). Biomass and Bioenergy, Volume 35, pp. 2650-2658.

Milne, T., Evans, R. & Abatzoglou, N., 1998. Biomass Gasifier "Tars": Their Nature, Formation, and Conversion. National Renewable Energy Laboratory, pp. NREL/TP-570-25357.

Narvaez, I., Orio, A., Aznar, M. P. & Corella, J., 1996. Biomass Gasification with Air in a Atmospheric Bubbling Fluidized Bed. Effect of Six Operational Variables on the Quantity of the Produced Raw Gas.. Ind. Eng. Chem. Res., Volume 35, pp. 2110-2120.

Neef, J., Knoef, H. & Onaji, P., 1999. Behaviour of tar in biomass gasification systems. Tar related problems and Solutions. Energy from Wastes and Biomass (EWAB), p. Novem Report No. 9919.

Olivares, A. et al., 1997. Biomass Gasification: Produced Gas Upgrading by In-Bed Use of Dolomite. Ind. Eng. Chem. Res. , Volume 36, pp. 5220-5226.

Ollero, P., Serrera, A., Arjona, R. & Alcantarilla, S., 2003. The CO2 gasification kinetics of olivine residue. Biomass and Energy, Volume 24, pp. 151-161.

Park, H. J. et al., 2010. Steam reforming of biomass gasification tar using benzene as a model compound over various Ni supported metal oxide catalsyts. Bioresourse Technology, Volume 101, pp. S101-S103.

Ponzio, A., Kalisz, S. & Blasiak, W., 2006. Effect of operating conditions on tar and gas composition in high temperature air/steam gasification (HTAG) of plastic containing waste. Fuel Processing Technology , Volume 87, pp. 223-233.

Rajvanshi, A. K., 1986. Biomass Gasification. In: Alternative Energy in Agriculture . Maharashtra, India: CRC Press, pp. 83-102.

Reed, T. & Das, A., 1988. *Handbook of Biomass Downdraft Gasifier Engine Systems.* Golden, Colorado: U.S. Department of Energy.

Riley County, 2009. Solid Waste Management Plan, Kansas: Riley County, Solid waste management commitee.

Sabgeeta Chopra, A. K. J., 2007. A review of Fixed Bed Gasification Systems for Biomass. Agricultural Engineering International: the CIGR Ejournal, pp. 1-23.

Srinakruang, J., Sato, K., Vitidsant, T. & Fujimoto, K., 2005. A highly efficient catalyst for tar gasification with steam. Catalyst Communications, Volume 6, pp. 437-440.

Sugiyama, S. et al., 2005. Gasification performance of coals using high temperature air. Energy, Volume 30, pp. 399-413.

Wang, D., Yuan, W. & Ji, W., 2010 (1). Effective syngas cleanup and reforming using Ni/ -Al2O3. Int. J. Agric.& Biol. Eng., 3(2), pp. 39-45.

Wang, D., Yuan, W. & Ji, W., 2010. Use of Biomass Hydrothermal Conversion Char as the Ni Catalyst support in Benzene and Gasification Tar Removal. Transactions of the American Society of Agricultural and Bilogical Engineers, 53(3), pp. 795-800.

Wang, D., Yuan, W. & Ji, W., 2011. Char and Char-supported Nickel Catalyst for Secondary Syngas Cleanup and Conditioning. Applied energy, Volume 88, pp. 1656-1663.

Wang, T. et al., 2005. The Steam reforming of naphthalene over a nickel-dolomite cracking catalyst. Biomass and Bioenergy, Volume 28, pp. 508-514.

Xu, C., Donald, J., Byambajav, E. & Ohtsuka, Y., 2010. Recent advances in catalyst for hot-gas removal of tar and NH3 from biomass gasification. Fuel 89, pp. 1784-1795.

Yang, W., Anna, P., Lucas, C. & Blasiak, W., 2006. Performance analysis of a fixed-bed biomass gasifier using high-temperature air. Fuel Processing Technology, Issue 87, pp. 235-245.

Yang, X. et al., 2010. Nickel supported on modified olivine catalyst for steam reforming of gasification tar. Catalyst Communications 11, pp. 383-386.

Yu, Q., Brage, C., Chen, G. & Sjostrom, K., 1997. Temperature impact on the formation of tar from biomass pyrolysis in a free-fall reactor. Journal of Analytical and Applied Pyrolysis , Volume 40-41, pp. 481-489.

Zhang, R., Wang, Y. & Brown, R. C., 2007. Steam reforming of tar compounds over Ni/olivine catalyst doped with CeO2. Energy Conversion and Management , Volume 48, pp. 67-77.

Chapter 3 - Gasification System Design

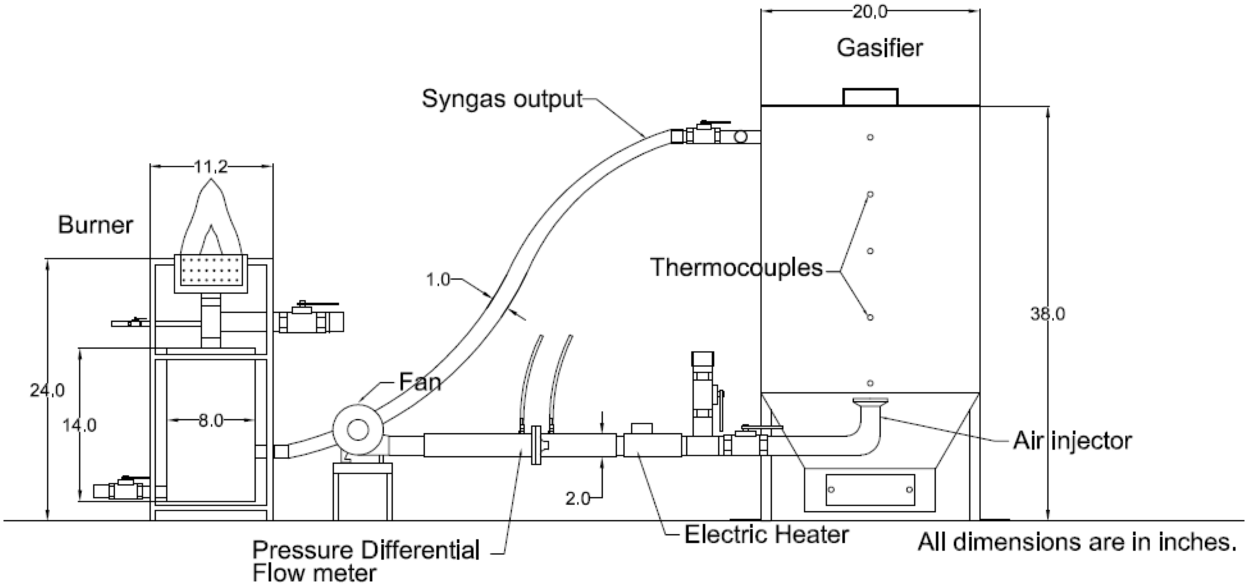
3.1 Introduction

Global warming and air pollution are some examples of environmental problems that we need to overcome in this century. The need to develop biofuels with energetic efficiency close to petroleum based fuels is a current need. Biomass gasification is a process which can generate syngas, a gas fuel with an average Low Heating Value of 5.0 -6.0 MJ/Nm^3 in updraft gasifiers (Knoef, 2005). Updraft gasifiers have a higher thermal efficiency when they are compared with downdraft gasifiers (Di Blasi, et al., 1999). A biomass updraft gasifier produces high quantities of tar and pyrolysis gases. In this gasifier, the pyrolysis products do not flow within the combustion zone. The production of aromatic components such as benzene, naphthalene, and toluene make the use of syngas for industrial application unsuitable. However, tar is not a major problem for direct heating applications. Tar removal methods are necessary for industrial and power applications (Knoef, 2005). The use of primary and secondary methods for tar removal application was presented in Chapter 2. In this section, the setup of a gasifier to test different operational parameters of an updraft biomass gasifier will be presented. In addition, the design and construction of a modified updraft biomass gasifier equipped with a tar cracking system and automatic feeder will also be presented.

3.2Gasification Unit

The gasification unit is an updraft biomass gasifier composed by an air injector, heater, reactor, condenser and burner (Figure 3.1, 3.2). A centrifugal blower is used to supply air to the gasifier. In the pipe line, an electric heater is used to preheat the air flowing into the gasifier. The reactor is a packed-bed updraft biomass gasifier. Air is injected from the bottom within a nozzle. The gasifier pressure is kept at atmospheric pressure with a water seal. Thermocouples measure the combustion, reaction, pyrolysis and drying zones' temperatures. After the gas is produced, it flows from the reactor to a room-temperature condenser, which is a steel tank that condenses water and heavy tars. A 190.5mm diameter gas burner is located on top of the water/tar condenser. It is used to burn syngas after it emanates from the gasifier.

Figure 3.1 Biomass gasification System



All dimensions are in inches.

Figure 3.2 Biomass updraft gasifier diagram

3.2.1 Air injection

The air blower is a 5.96 watt, centrifugal blower model 1C180 (Dayton electric). It generates a maximum air flow 8.5 lpm at 124.42 Pa of pressure. The blower air flow is controlled by reducing the aperture of the blower-air suction in order to keep the static pressure high.

3.2.2 Air Heating System

An electrical heater was used to preheat the feed air before injected in the gasifier. The electrical-resistive heater used was an Omega AHF-06120 (Omega Engineering, Stamford, CT) with a nominal voltage 120 V, 1000 Watts, 5663 lpm (max.) (Figure 3.3). Adjusting the heater voltage manually controlled this electrical heater. A rheostat, model SC-5M (Variac, Maumee, OH); with an output of 500VA, 0-130V AC was used to control the set-point temperature of the feed air. When manual operation was performed, no stable temperature was achieved. An automatic control was needed to keep a stable feed-air temperature. The development of an automatic air-heating system was carried out. A PID (Proportional Integral Derivative) computer controlled system was designed. The system is composed of LabVIEW control code, which includes a PID controller. A solid state relay controlled the electrical power supplied to the heater and an independent temperature measurement system was used as feedback. Section 3.3.1 presents details of this measurement system.

Figure 3.3 Electrical Heater, Omega Engineering.

In order to achieve a stable temperature, the selection of the adequate proportional, integral, and derivative values is required. PID controllers are the most used feedback controllers. They work using a closed-loop system and calculate the error based on the differences between the set point and a measured value. Equation (3.1) shows the equation of a PID algorithm.

$$u(t) = K_p e(t) + K_i \int_0^t e(t)dt + K_d \frac{d}{dt} e(t) \quad (3.1)$$

Where,
Kp: proportional gain, tuning parameter;
Ki: integral gain, tuning parameter;
Kd: Derivative gain, tuning parameter;
e: error;
t: time/instantaneous time.

This system uses the inlet-air temperature measured by the temperature-data acquisition system and compares it with the input signal (set-point temperature). The PID output is a variable duty cycle at a constant frequency. A NI-USB-6008 multifunction data acquisition which produces a 0-5 Volts digital signal is connected to the relay; the digital signal controls the heater's power. The feed air temperature changes by the amount of heat generated in the heater. The feed-air temperature control loop takes the temperature of the feed-air with a thermocouple, and then this value is fed in the LabVIEW code and compared with the set-point temperature. Therefore, the heater power can decrease or increase depending on the feed air temperature. Figure 3.4 shows how the feed-air temperature changes when the set-point temperature is changed.

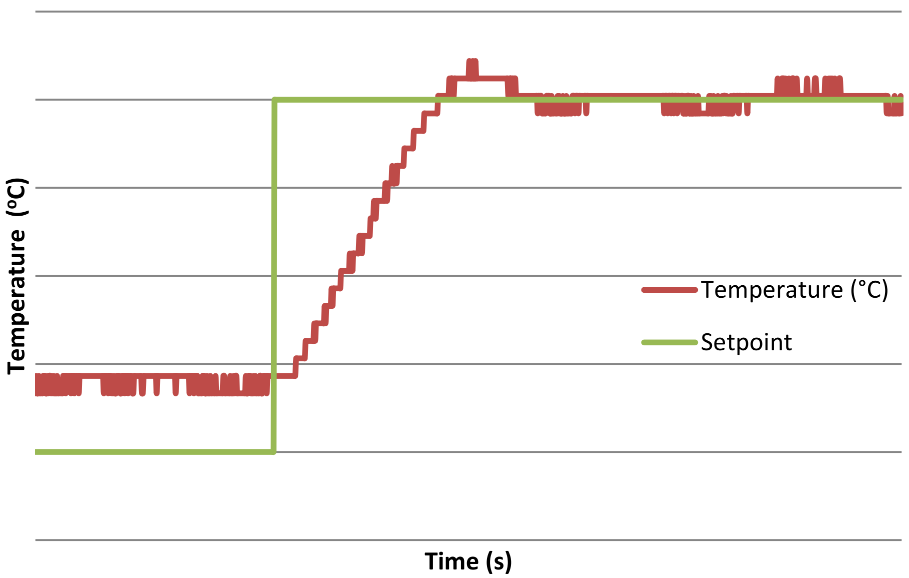


Figure 3.4 Temperature – PID controller

3.3 Data Acquisition

3.3.1 Temperature measurement system

A temperature measurement system built by Ming (2007) was used to measure the chamber's temperatures in different zones of the gasifier. This system is composed by Chromel-Alumel type K thermocouples (Omega Engineering, Stamford, CT). These thermocouples can measure temperatures from -200^{o} C to 1200^{o} C. The system was equipped of AD595 and TS921 integrated circuits that can measure temperatures from thermocouples in different zones of the gasifier. AD595 is a thermocouple conditioner integrated with an instrumentation amplifier, cold junction compensation, and TS921, which is an operational amplifier used to reduce noise and distortion. A NI-USB-6008 multifunction data acquisition unit in communication with control software (National Instruments LabVIEW 2009) was used as an interface to read and record gasification temperatures in a computer (Hu, 2007). In Figure 3.5, the temperature profiles for sorghum straw gasification are shown. The feed air, combustion zone, reduction zone, pyrolysis zone, and drying zone temperatures are presented. These temperatures in different zones of the updraft biomass gasifier were measured with the data acquisition system described in this section.

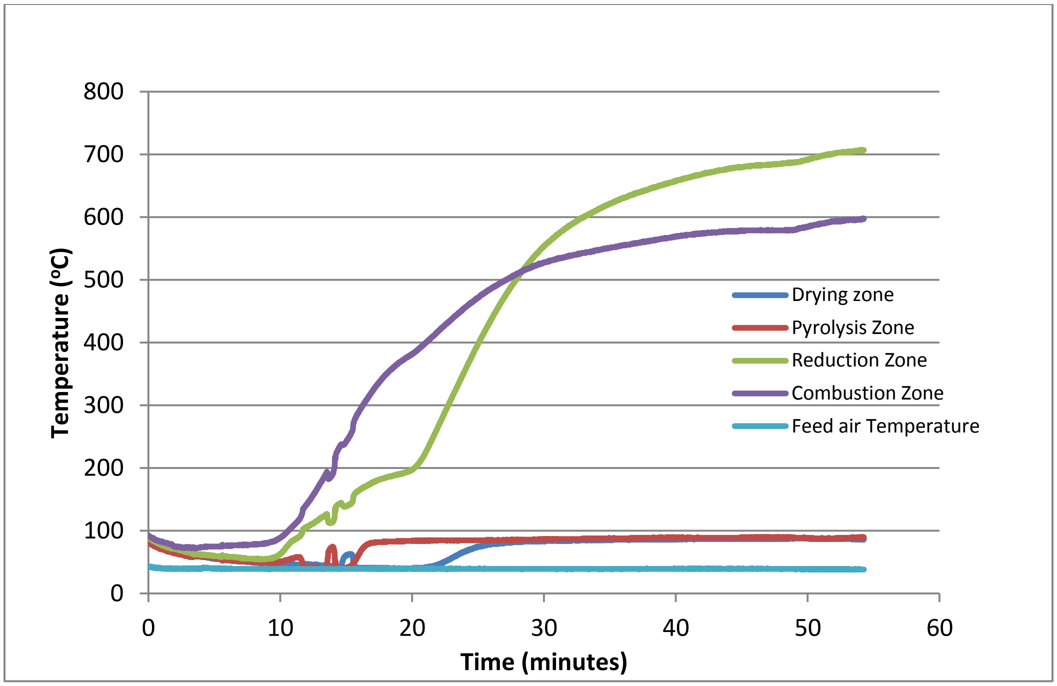


Figure 3.5 Sorghum Straw Gasification - Temperature Profiles –Updraft Gasifier

3.3.2 Pressure differential flow meter

The ASME standard of measuring gas flow with differential pressure was used. A pressure differential transducer (Omega Engineering, Stamford, CT) was used to measure the pressure variation between two points. A nozzle (1 inch i.d.) in a 2 inch PVC pipe was used. NI-USB-6008 multifunction data acquisition unit measured and recorded the differential pressure using LabVIEW software. Figure 3.6 shows the nozzle connection, pressure transducer, and the data acquisition unit. This system was similar to the system used by Hu (2007) to measure syngas and air flow in a biomass downdraft gasifier. However, a lower-range pressure trasducer was used (0-0.25 inch H_2O) considering that low differential pressure was measured. The fact that air and syngas have a similar density due to its high nitrogen content allows both flows to be measured with the same unit, however, syngas flow needs to be corrected because of temperature changes. Parameters selected in a previous study (Hu, 2007) were selected to measure syngas and air flow from the updraft gasifiers in accordance with ASME standards. The metodology used is based on the measurement of fluid flow in pipes using orifice, Nozzle & venturi, MFC-3M – 2004 standard. Calcualtion details are presented in Appendix C.

Figure 3.6 Pressure differential flow meter

3.4 Tar trapping system

A cold trapping system was used to measure tar content in syngas. A similar cold trapping was used for Wang, et al., (2010 (1)) to measure the amount of tar generated from an updraft biomass gasifier. This system was composed of four 300-mL Erlenmeyer flasks series connected with 3/16” pipes under commercial dry ice. A vacuum pump was used to flow syngas constant within the system; paper filter was used to remover tar and light particles.

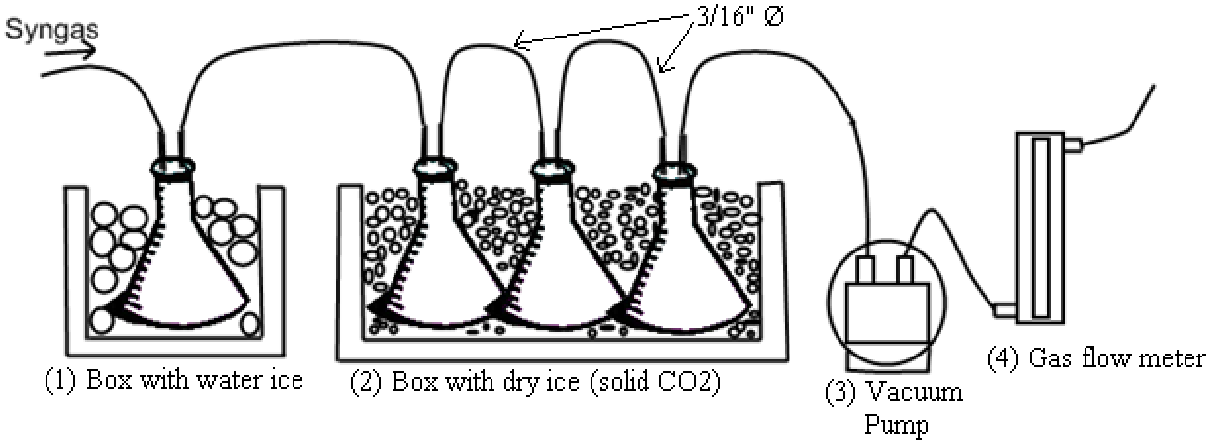


Figure 3.7 Tar trapping system, four 300-mL Erlenmeyer flasks series connected with a vacuum pump and a gas flow meter.

Direct tar sampling from the gasifier’s chamber can condense water and tar in syngas. However, the low temperature provided by dry ice froze the syngas moisture in the pipe lines. A different system was developed to effectively condense tar in syngas gas. The system consisted of a first stage where a 300 mL flask under water-ice condenses water and heavy tar components followed by three 300 mL flasks connected, and placed under dry ice, Figure 3.7. Tar content was calculated based on syngas flow and tar sampling time. This configuration allows the effective measure of condensable tar components using a modified cold trapping method. Tars in the flasks were dried for 24 hours in an oven at 105°C; after drying, samples were weighed.

3.5 Modified Updraft Gasifier equipped with a tar cracking unit

An updraft biomass gasifier was modified. It was equipped with a catalytic tar cracking system and an automatic feeder. This reactor can be used for small-scale applications. A diagram of the gasifier is presented in Figure 3.8. The gasifier is composed of an air camera located in the bottom, where an air injection plate was installed. The gas flows throughout the gasifier zone, where exothermic and endothermic reactions take place (Hasan, et al., 2010). After syngas is generated, this gas is conducted to a vertical and a horizontal steel pipeline that composed the catalytic tar cracking system. Gas excess before the cracking unit was directed to the gas burner. The air/gas flow in the gasifier is provided in two ways: by an electric blower connected in the bottom of the gasifier or by a vacuum pump connected after the cracking system. A room-temperature condenser was used to decrease syngas temperature before it flowed in the vacuum pump. Figure 3.8 shows an overview of this biomass gasifier. A sequential block diagram of this system is presented in Figure 3.9.

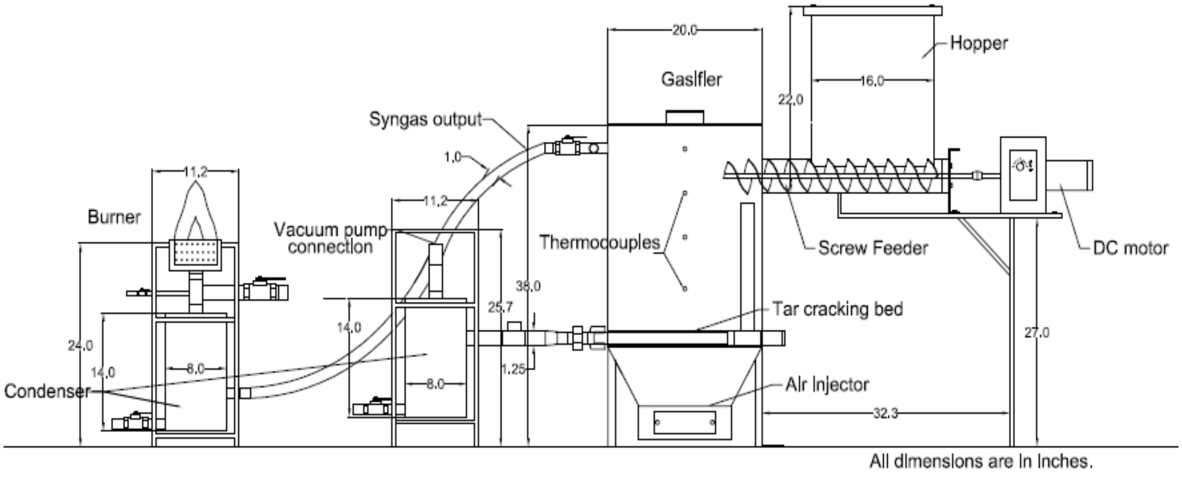


Figure 3.8 Gasifier equipped with a tar cracking system

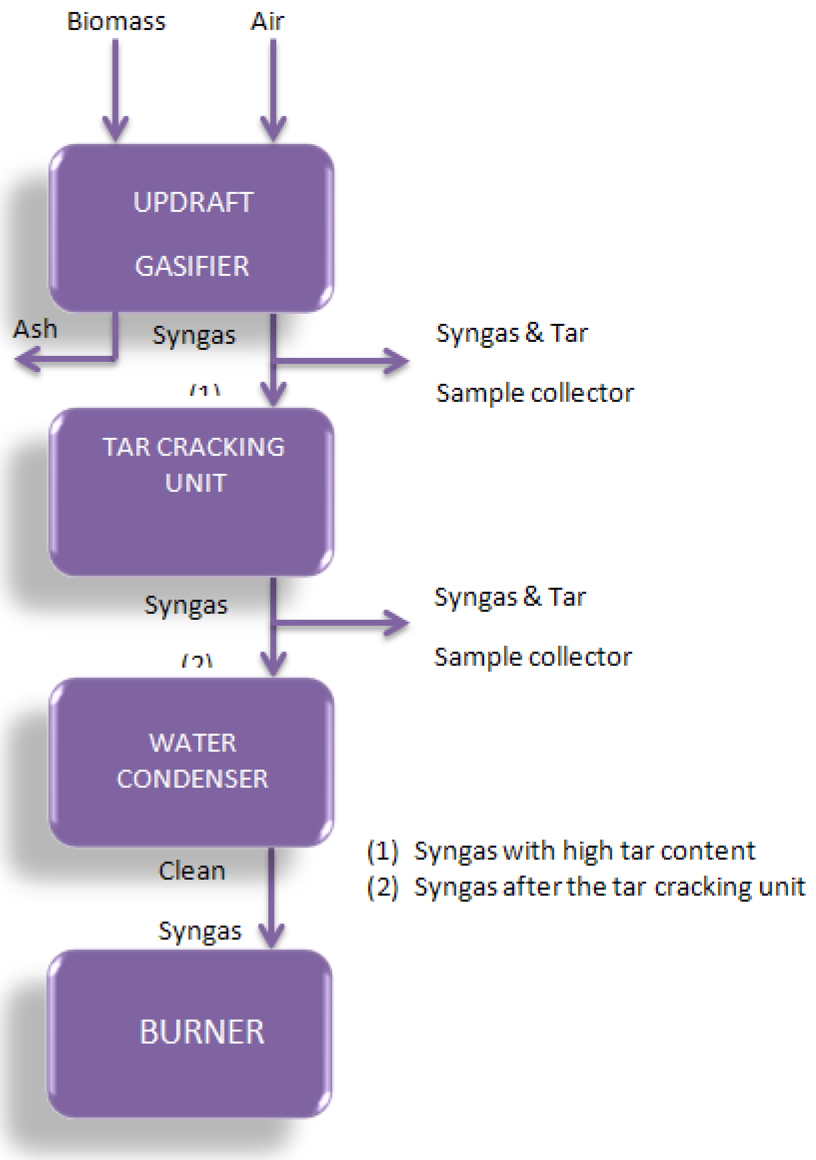


Figure 3.9 A sequential block diagram of an updraft biomass gasifier equipped with a tar cracking unit.

3.5.1 Air-injection plate

The previous air injector in the updraft gasifier consisted of a cast iron nozzle centrally located in the bottom of the gasifier. This injection system presented two main problems. First, the reaction zone's heat was located around it causing the nozzle to collapse when temperatures were close to the melting point on its surface. This occurred because once the reactor was in operation; the nozzle was placed in the middle of the combustion zone. Second, non-uniform burning when irregular particle size was used, gasification was limited due to air flow distribution in the bed. Figure 3.10, a picture of the old nozzle, is illustrating holes located around the pipe.

The new gasification injection system idea comes from the principle of a bubbling fluidized reactor. In a bubbling fluidized bed reactor, fine particles react with a medium forming bubbles where gas solid reaction occurs (Kinii & Levenspiel, 1991). In contrast, an updraft biomass gasifier runs with a particle size 5 to 100 mm (Knoef, 2005). For this reason, an updraft gasifier doesn't have the same performance of a bubbling fluidized bed reactor.

Figure 3.10 Old gasification injection design

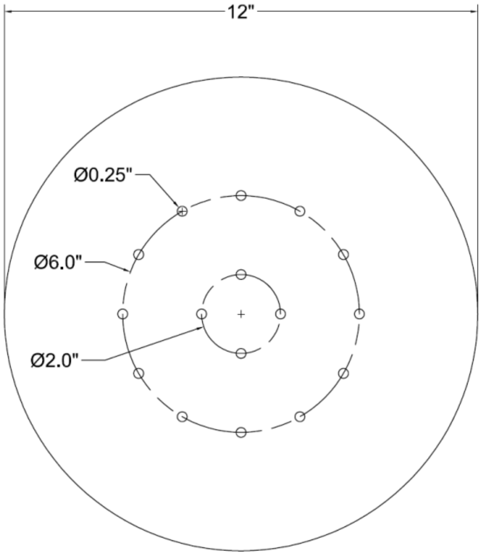


Figure 3.11 New air-injection plate design

The perforations on the air-injection plate help the air to be distributed uniformly in the gasifier. It also helps to distribute the heat on the reaction zone. The injection plate temperature is lower than the previous nozzle because the air flowing from bottom to top can help cool down the face of the injection plate facing downward. In this design, 16 perforations of 6.35 mm (¼") were made symmetrically in 304.8 mm (12-inch) diameter steel plate and 6.35 mm (¼") thick. See Figure 3.11. The gasifier airflow was measured using the pressure-differential flow meter.

3.5.2 Automatic feeding system

The use of an updraft biomass gasifier for industrial and power generation requires a continuous feeding system. An automatic feeder was designed and built. The automatic feeder is equipped with a steel hopper from where the biomass is transported to the gasifier. When the gasifier is running, the hopper is sealed to avoid gas being released. A steel auger driven by a DC gear motor model 6ML67, 0.186 Kw (1/4 HP), 21 RPM (Dayton electric) was arranged. A variable speed control was used to control the biomass rate; biomass was fed in the gasifier within a 4 inch (i.d.) steel pipe. The auto-feeder was designed to work when the temperature in the pyrolysis zone exceeded the set temperature. A PIC16F877A-I/P micro-controller in conjunction with an AD595 and TS921 integrated circuits was used to develop the automatic feeder-temperature controller system. Two set points were selected to run and stop the DC motor. For example, if the temperature in the pyrolysis zone increased more than 300^{o}C the auto-feeder ran until the temperature went back to 200^{o}C. A display Hitachi LM071L LCD was used to show the actual temperature and both low and high temperature set points. A solid state relay was used to turn the DC motor on and off based on the temperatures. The fact that the microcontroller works with a maximum voltage of 5 volts makes the analog-to-digital converter take measures of up to 5 volts, limiting the maximum range of temperatures read by the system, which is from 0 to 450^{o} C. The program used by the micro-controller is provided in the Appendix D.

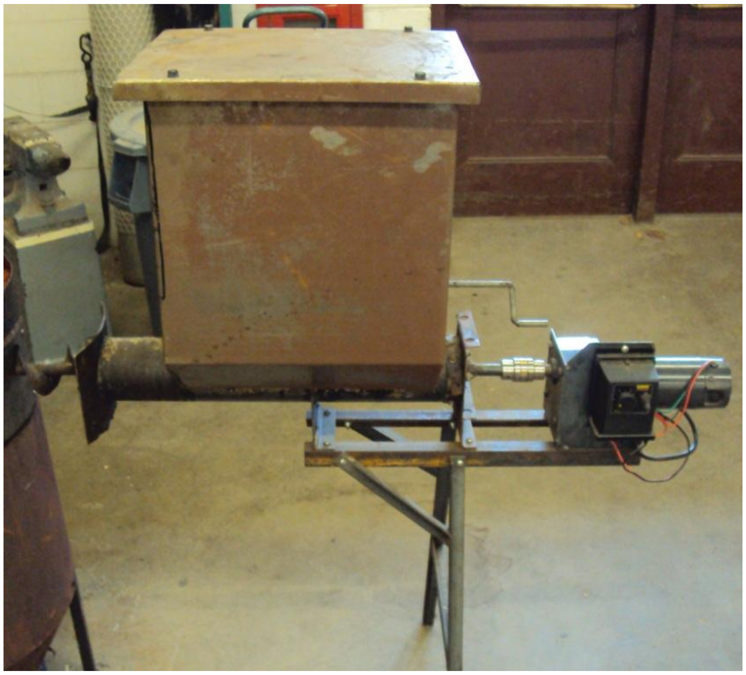


Figure 3.12 Automatic biomass feeding system

3.5.3 Tar cracking system and collector

Since the combustion zone showed an average reaction temperature from 600^{o} C to 900^{o} C for different biomasses, the gasifier itself can produce the heat needed to crack tars. The use of the reactor's heat for tar removal is evaluated in the development of a tar cracking system. This system was designed to decrease the amount of tar in the final syngas and increase the product gas composition. Two black iron pipes (31.75 mm/1.25-inch i.d.) were arranged in the gasifier as it is shown in Figure 3.13. Syngas flows from top to bottom in the vertical pipe. Char is loaded in this pipe to remove moisture and condense tar in order to prevent blockage of the catalytic bed. The vertical pipe is connected to the horizontal pipe that is placed within the combustion zone. The horizontal pipe was equipped with an additional black iron pipe (25.4 mm/1-inch i.d.) where the catalyst was placed; mesh and snap rings inside kept the catalyst in place, Figure 3.13 shows details of this system. Tar cracking experiments were carried out by Wang, et al.,(2005) and Yang, et al.,(2010) in quartz reactors to test the effect of Ni/dolomite and Ni/char catalysts on biomass gasification using external heating units. External heat decreases the efficiency of gasification processes because external power is needed. The fact that this gasifier can use its heat to crack tar is economically feasible and thermally efficient. In this gasifier several catalysts can be tested. In Chapter 5, the use of this modified updraft biomass gasifier reactor is tested. Gasification performance and the effect of using the combustion zone's heat for tar cracking are evaluated using char and nickel-char catalysts.

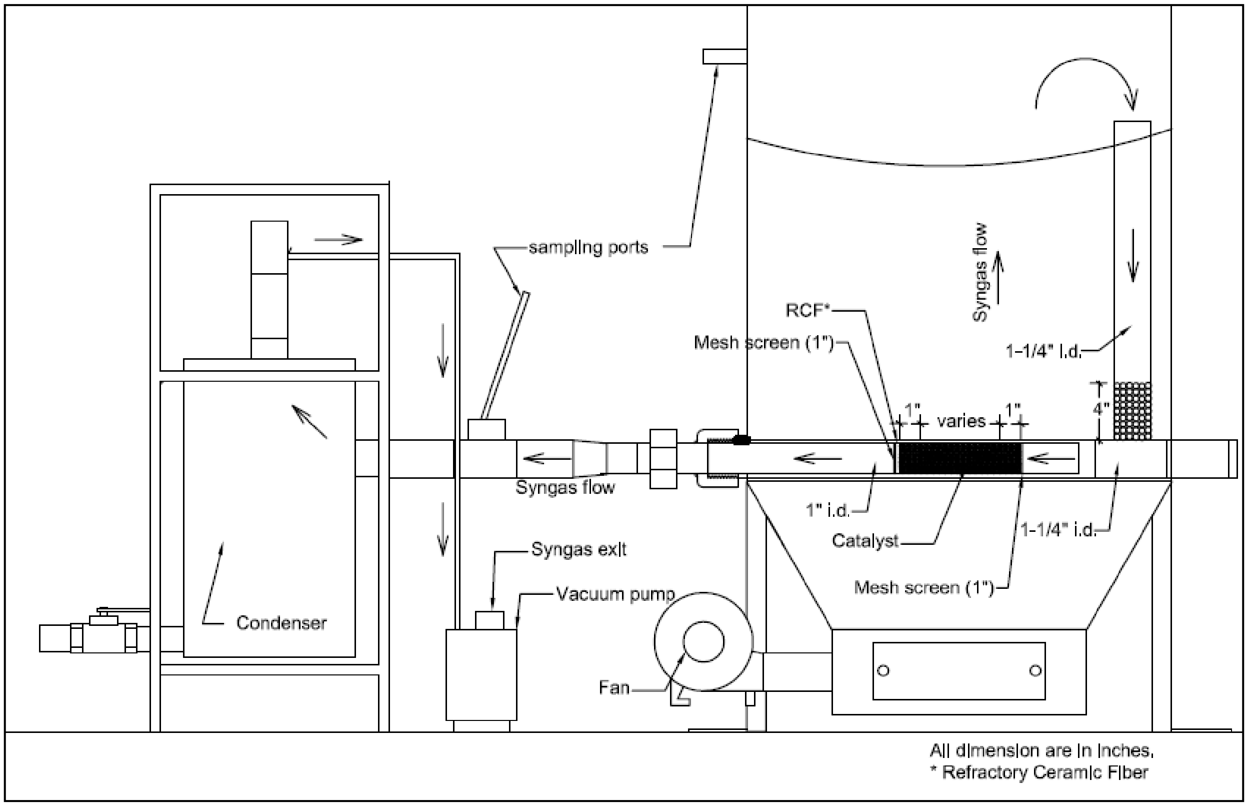


Figure 3.13 Tar cracking and syngas reforming system

3.6 Bibliography

Di Blasi, C., Signorelli, G. & Portoricco, G., 1999. Countercurrent Fixed-Bed Gasification of Biomass at Laboratory Scale. *Ind. Eng. Chem. Res.*, Volume 38, pp. 2571-2581.

Hasan, J., Keshwani, D. R., *Carter*, S. F. & Treasure, T. H., 2010. Themochemical Conversion of Biomass to Power and Fuels.. In: *Biomass to Renewable Energy Processes.* United States of America: CRC Press, Taylor & Francis Group, pp. 437-489.

Hu, M., 2007. Instrumentation *and Tar Measurement System for a Downdraft Biomass Gasifier.* Manhattan, Kansas: Kansas State University.

Kinii, D. & Levenspiel, O., 1991. *Fluidization Engineering.* Second edition ed. USA: Butterworth-Heinemenn.

Knoef, H., 2005. Practical aspects of biomass gasification. In: H. Knoef, ed. *Handbookd Biomass Gasification.* Netherlands: BTG biomass technology group, pp. 13-37.

Wang, D., Yuan, W. & Ji, W., 2010 (1). Effective syngas cleanup and reforming using Ni/ -Al2O3. *Int. J. Agric.& Biol. Eng.*, 3(2), pp. 39-45.

Wang, T. et al., 2005. The Steam reforming of naphthalene over a nickel-dolomite cracking catalyst. *Biomass and Bioenergy,* Volume 28, pp. 508-514.

Yang, X. et al., 2010. Nickel supported on modified olivine catalyst for steam reforming of gasification tar. *Catalyst Communications 11*, pp. 383-386.

Chapter 4 - Performance evaluation of an updraft biomass gasifier

Abstract

Although updraft gasifiers are one of the most efficient gasifier designs, they are reported to generate more tar than any other gasifiers. The selection of the operational parameters in an updraft gasifier can result in the increment of syngas heating values and a decrement on tar content. In this study, the operational parameters, including air flow rate and feed-air temperatures of an updraft biomass gasifier, have been studied using prairie hay, sorghum biomass, and wood chips. Results showed that different biomass types produced different tar content, e.g. wood chips>sorghum biomass>prairie hay. It was also found that the air flow rate increment promoted formation of tar species in all biomasses studied. Higher feed-air temperatures reduced tar in syngas from prairie hay; however, in sorghum biomass and wood chips, tar only slightly decreased. A statistical model was implemented to study differences on syngas composition. Results showed that different biomasses produced syngas with different high heating values, e.g., wood chips > prairie hay > sorghum biomass. CO composition also showed differences by feed air temperatures and biomass, e.g. prairie hay>wood chips>sorghum biomass, but H_2 did not show significant differences by either biomass types or operating conditions.

4.1 Introduction

Biomass is the organic matter composition in plants and animal residues. There are different ways to process biomass to produce electricity, heat, steam, and liquid fuels. The use of biomass to produce energy generates CO_2 the same way petroleum based fuels do. However, the use of biomass represents lower CO_2 emissions because of its “net gain of zero.” This means that the plant eventually uses $CO_{2,}$ which is released after consuming biomass (Onyekwelu & Akindele, 2006). Biomass gasification is an effective way to convert solid biomasses into useful biofuels. However, the conversion of biomass is affected by its characteristics. Biomass from different resources needs to be analyzed before it is utilized in a thermochemical conversion process. Syngas composition and tar content can vary for different feedstocks (Hasan, et al., 2010).

Biomass gasification for energy production has attracted tremendous attention in recent years for its low emissions, but the use of gasification is not new as it has been used and studied for more than three centuries (Reed & Das, 1988). Gasification is a theoretically complicated thermochemical process in which biomass materials experience incomplete combustion in a medium such as air, oxygen, or steam to produce a combustible gas called synthetic gas (syngas). Syngas is a mixture of hydrogen, carbon monoxide, carbon dioxide, water, nitrogen, and small amounts of methane and higher hydrocarbons (Lucas, et al., 2004). It can be burned directly in furnaces, boilers, stoves, internal combustion engines, or micro-turbines for heat and power generation (Knoef, 2005). It can also be further converted to a wide variety of useful, high-margin petrochemicals or transportation fuels, such as synthetic diesel (via the Fischer-Tropsch method), ethanol (via fermentation), dimethyl, and methanol (via catalytic reactions) (Hasan, et al., 2010).

Gasification performance depends on reactor type and operational conditions. There are several types of gasification reactors, these include: fixed-bed and fluidized bed reactors. Fixed-bed reactors are simple to build and can perform good carbon conversion using low gas velocity. However, tar formation is a major problem in fixed-bed reactors. On the other hand, fluidized bed reactors can operate with a high carbon conversion, low tar content and a uniform syngas yield (Hasan, et al., 2010), (Reed & Das, 1988). Performance operation of fixed bed gasifiers can be improved. The selection of optimal gasification parameters can have a positive effect on biomass gasification. Lucas, et al. (2004) and Mathieu (2002) studied the effect of the operational condition on gasification perfomance, and found that syngas yield can be maximized and tar content decreased.

The objective of this study was to understand the effect of biomass types and operating conditions on gasification performance in an updraft biomass gasifier. Sorghum biomass, prairie hay, and woodchips were selected because of their local availability and energy potential. Various levels of air flow rates (low, medium, and high) and feed-air temperatures (60, 120, and 200°C) were investigated. Gasification performance was evaluated based on syngas composition, high heating values, and tar content.

4.2 Materials and Methods

4.2.1 Biomass gasification system setup

The experiments were carried out in an updraft biomass gasifier described in Chapter 3. Tar and syngas samples were collected from the gasification chamber. The tar sampling unit was composed of four 250-ml Erlenmeyer flasks series connected in a two steps process. One flask was placed under water-ice in a box to condense water and heavy tars, and three other flasks were placed under dry ice (solid CO_2) where lighter tar species were collected. Tar was sampled for 15 min; after collected, the flasks were dried in an oven at $105^{o}C$ for 24 hr. and weighed on a precision balance. A similar tar collection method was used by Wang, et al., (2010 (1)). Syngas was collected using a tedlar sampling bag after the gasifier was running at a steady state; syngas composition was determined using a SRI 8610 Gas Chormatograph with a TCD detector (SRI, Torrance, CA). Helium was used as carrier gas; H_2, O_2, N_2, CH_4, CO, and CO_2 concentration were measured.

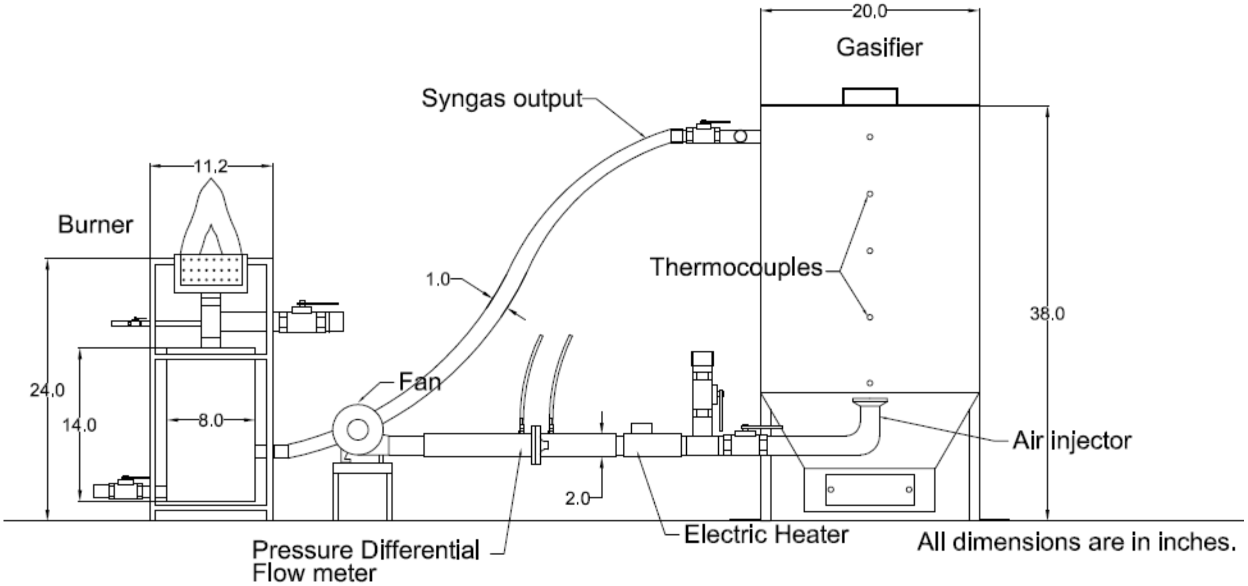


Figure 4.1 Updraft gasifier system

4.2.2 Biomass studied

The use of biomass residues from industrial processes and natural crops can increase the overall efficiency of biomass gasification. In this project, three feedstocks were utilized to test the effect of biomass type on gasification performance. Prairie hay is a natural crop that presents a number of advantages for its wild nature; it does not need to be fertilized or irrigated. In the same way, sorghum biomass, a byproduct from agricultural processes, has a wide energy potential for biofuel production. Prairie hay and sorghum biomass (PS Sorghum Partners) from a local farm were selected and ground using a Tub grinder (Model H-100 - Haybuster Big Bite, Jamestown, ND). Furthermore, wood chips from a local transfer station were utilized; wood chips selected were byproducts from construction and gardening applications. Table 4.1 shows biomass characteristics. All biomasses present similar heating values. The high heating values reported are similar to averages for wood (20.2 MJ/kg) and crops residues (18.8 MJ/kg) (F. Rosillo-Calle, 2007). Wood chips presented the highest lignin content (19.24) and the lowest ash content (2.86). Ash content in wood chips is lower than in crop residues (F. Rosillo-Calle, 2007).

Table 4.1 Biomass characteristics (weight %)

	Prairie Hay	Sorghum Biomass	Wood Chips
C	43.34	43.0	46.8
H	5.5	5.9	5.3
O	49.4	49.3	46.6
High Heating Value (MJ/kg)	18.17	18.18	18.8
Hemicellulose (%)	29.78	27.99	14.99
Cellulose (%)	30.01	41.53	34.31
Lignin (%)	2.06	4.37	19.24
Ash (%)	8.41	7.18	2.86
Moisture (% db)	10.0	8.56	10.9

4.2.3 Methodology of gasification experiments.

A three way experiment design was used to investigate gasification operational conditions on gasifier performance. Several authors have studied the effect of the air flow rate of gasification performance (Hanping, et al., 2008) (Mahishi & Goswami, 2007). In this study, low, medium, and high air flow rates were evaluated. Table 4.2 presents air flow in liters per minute and equivalence ratio calculated using the mass of air used to gasify the biomass. It was divided by the mass of air required to completely burn the biomass. Equation (4.1) was used to calculate the mass of air needed for the complete combustion of biomass. Mass of air used for gasification was calculated using the air flow and the reaction time in gasification experiments. Equation (4.2) was used to calculate ER (Basu, 2010).

$$\boldsymbol{C_xH_yO_z + A(O_2 + 3.773\, N_2) \rightarrow (B)H_2O + (D)CO_2 + N_2} \quad \textbf{(4.1)}$$

$$ER = \frac{M_g(Actual\ air)}{M_c\ (Stoichiometric\ air)}, \qquad ER < 1.0\ (gasification) \quad (4.2)$$

Table 4.2 Air flow rate levels

Biomass	Flow level	Flow (lpm)	ER
Prairie hay	Low	17.4	0.20
	Medium	36.6	0.23
	High	44.1	0.27
Sorghum biomass	Low	39.8	0.20
	Medium	44.1	0.26
	High	56.2	0.32
Wood chips	Low	47.4	0.25
	Medium	62.9	0.27
	High	73.1	0.30

Preheating the feed-air is a technique that has been used by several authors to improve biomass gasification performance. However, most of the studies were focused on high-temperature air gasification (HTAG) using feed-air temperatures up to 1400°C (Anna Ponzio, 2006). Results reported that HTAG can effectively reduce tar formation and increase the high heating values of syngas (Lucas, et al., 2004). In this study, feed-air was preheated to 80, 140, and 200°C. In each experiment, the gasifier was loaded with one type of biomass; 30 pounds of prairie hay or sorghum, or 40 pounds of wood chips. All experiments were carried out for at least 60 minutes with stable gasification.

Heating values of syngas is calculated using the following equation (Saad, 1966):

$$\Delta H^o = \sum \left(H_f^o\right)_p - \sum \left(H_f^o\right)_r \quad (4.3)$$

4.3 Results and discussion

4.3.1 Effect of air flow rate on tar content

Results of prairie hay, sorghum biomass, and wood chips gasification at low, medium, and high air flows are presented in Figure 4.2, 4.3, and 4.4. Averages of tar content at each level of temperature were calculated. Figure 4.2 shows tar content in syngas from prairie hay increasing as the air flow rate increases. High air flow rate presents the highest tar content of 3.0 g/m^3; at this level of flow, sorghum biomass also showed their highest tar content of 4.0, in contrast with wood chips which had its highest tar content at medium air flow. An increment in the air flow leads the formation of tar species. Kinoshita (1994) and Hanping (2008) reported that variation in the air flow can affect tar yield in biomass gasification, they found that tar content has a linear increment with air flow. It is important to say that prairie hay's tar content at low flow (1.62 g/m^3) is comparable to tar values in a downdraft gasifier (Milne, et al., 1998). Wood chips also presented increment on tar species when the air flow increased. However, at high air flow tar content reported was lower than at medium air flow. Excess in the addition of air can have a negative effect on gasification performance because of the production of tar (Houben, 2004).

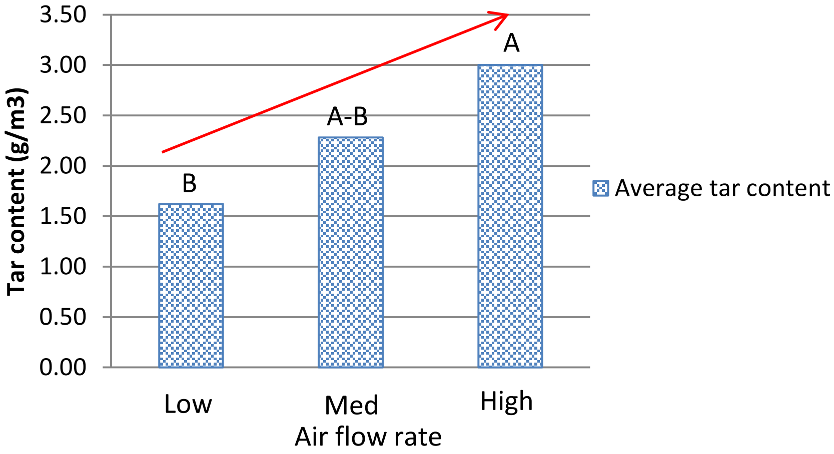


Figure 4.2 Tar content of prairie hay gasification at different air flow rates. Tar content at low air flow presented significant difference from tar content at high air flow; medium air flow can have results similar to low or high tar content. See Table 4.4 and Appendix E

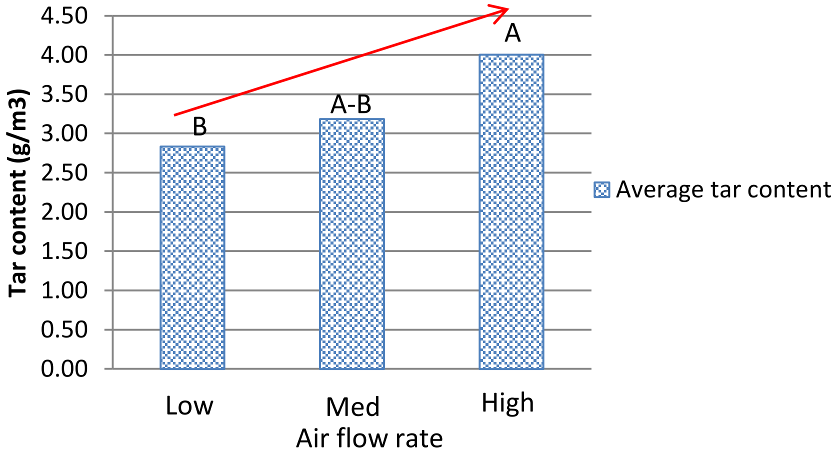


Figure 4.3 Tar content of sorghum biomass gasification at different air flow rates. Tar content at low air flow presented significant difference from tar content at high air flow; medium air flow can have results similar to low or high tar content. See Table 4.4 and Appendix E

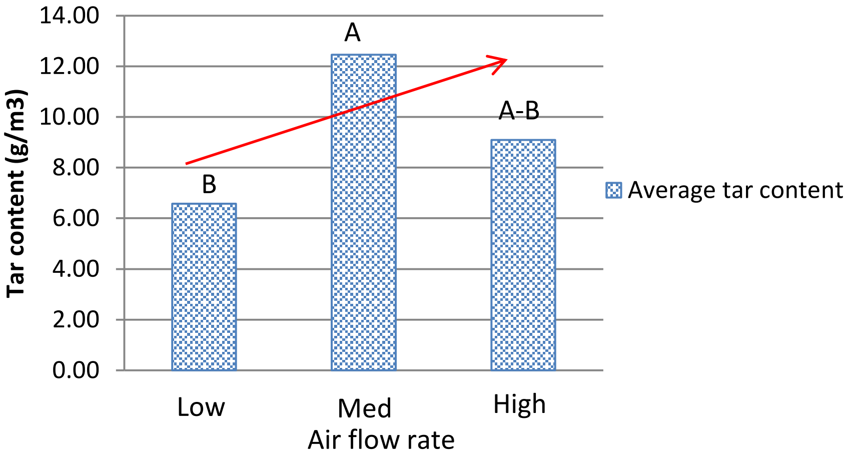


Figure 4.4 Tar content of woodchips gasification at different air flow rates. Tar content at low air flow presented significant difference from tar content at high air flow; medium air flow can have results similar to low or high tar content. See Table 4.4 and Appendix E

Figure 4.5, 4.6, and 4.7 present the average of the combustion zone's temperature for prairie hay, sorghum biomass, and wood chips. In Figure 4.5, prairie hay presents its highest temperature (712°C), the lowest tar content at low air flow was reported at this point. Hanping (2008) reported that increment in the combustion zone temperature can increase syngas yield and decresase formation of tar species. However, decrement in the combustion zone's temperature can increase the production of tar species. A comparison of Figure 4.2 and Figure 4.5 shows that the increment in the air flow reduces the combustion zone's temperature, thus more tar species are formed. Figure 4.6 presents a decrement in the combustion zone's temperature when low and high air flow are compared. In this case the highest combustion zone temperature (732°C) was presented at medium air flow; at this point slight increment on tar content (3.1 g/m^3) was reported compared with low air flow (2.8 g/m^3).

Temperature in the combustion zone for wood chips increased as the air flow increased. This could be due to the fact that wood chips are a more dense material compared with prairie hay and sorghum biomass and additional air is required to increase its combustion temperature. The effect of air flow on combustion zone temperature and tar content was also presented. Comparison of Figure 4.4 and Figure 4.7 show that the highest tar content occurred at the lowest combustion temperature (770°C). In contrast, the highest combustion zone's temperatures occured at high air flow, therefore, decrement in tempreature was shown from medium (12.5 g/m^3) to high air flow (9.0 g/m^3).

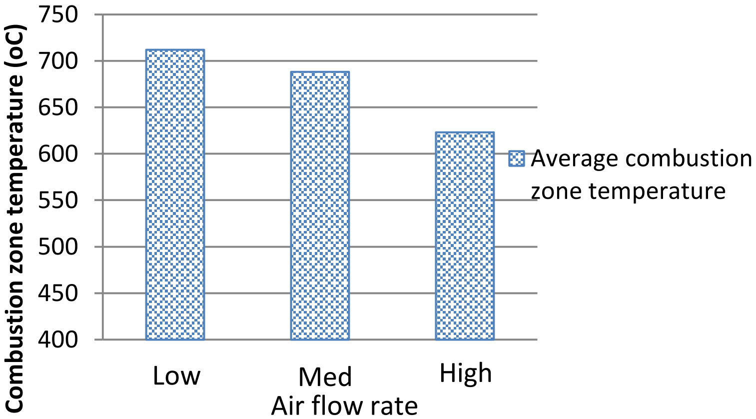


Figure 4.5 Gasification of prairie hay – average combustion zone temperatures at different air flow rates.

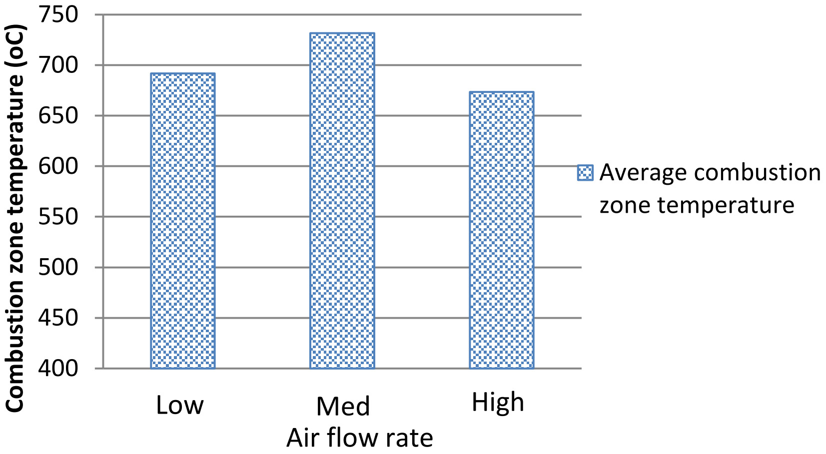


Figure 4.6 Gasification of sorghum biomass – average combustion zone temperatures at different air flow rates.

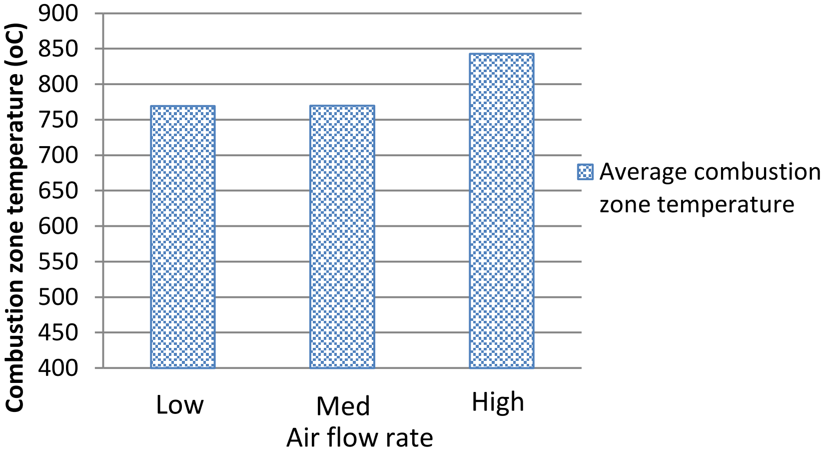


Figure 4.7 Gasification of wood chips – average combustion zone temperatures at different air flow rates.

4.3.2 Effect of the feed-air temperature on tar content

Results of the effect of feed-air temperatures on tar content and combustion zone's temperatures are presented. Figure 4.8 shows that by increasing the feed-air temperatures from 80^o C to 200^o C, tar content in syngas from prairie hay decreased from 3.3 to 1.5 g/m^3. The combustion zone temperatures at this point increased from 668^o C to 708^o C. When the feed-air temperatures varied from 80° C to 140° C, tar content decreased as the temperature increased. Increment in the feed-air temperatures of wood chips presented a similar behavior, Figure 4.10; tar content decreased from 10.3 to 8.7 g/m^3 when the feed-air temperatures increased. Figure 4.13 presents the combustion temperature of wood chip gasification; comparison of 80°C and 200°C presented increment on combustion temperature from 795° C to 822° C. Lucas (2004) evaluated the effect of using temperatures from 350° C to 900° C in the feed-air concluding that the addition of heat in the feed-air can increase the bed temperature and promote decrement in tar content.

Nevertheless, tar content presented an opposite tendency in sorghum biomass gasification. Tar content increased from 3.0 to 3.7 g/m^3 when feed-air temperatures of 80° C to 200° C were compared. When the feed-air temperatures increased from 80° C to 140° C, the combustion zone's temperatures increased from 682° C to 714° C; this increment slightly increased the tar content. Then, at 200° C feed-air temperatures, the combustion temperature dropped to 701° C and tar content increased to 3.7 g/m^3. This suggests that the effect of feed-air temperatures on syngas' tar content depends on biomass types.

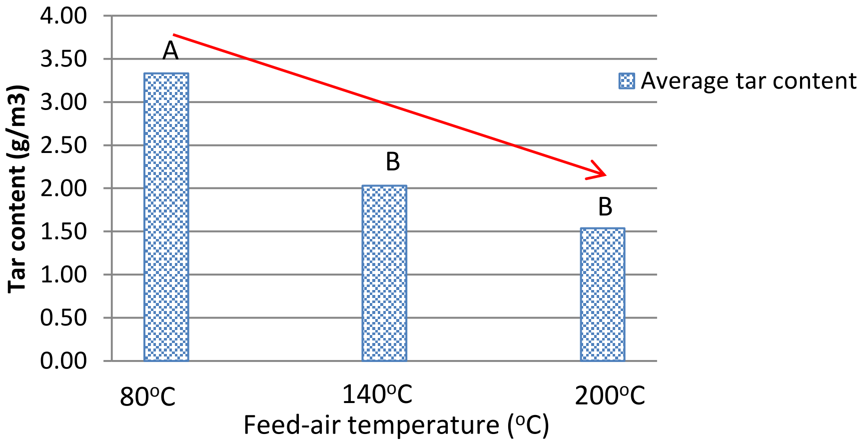


Figure 4.8 Tar content of prairie hay gasification at different feed-air temperatures. The individual analysis of prairie hay presented at 80°C feed-air temperature significant difference when temperature of 140°C and 200°C were used. See Appendix E-Tar individual analysis.

Non stable increment in the combustion temperature was found when the feed-air temperatures were increased from 80° C to 200° C in all cases. This phenomenon can be due to the fact that gasification performance of agricultural residues and wastes can present instability because of the non-uniform biomass distribution on the bed, ash agglomeration, and fast pyrolysis rates (Di Blasi, et al., 1999).

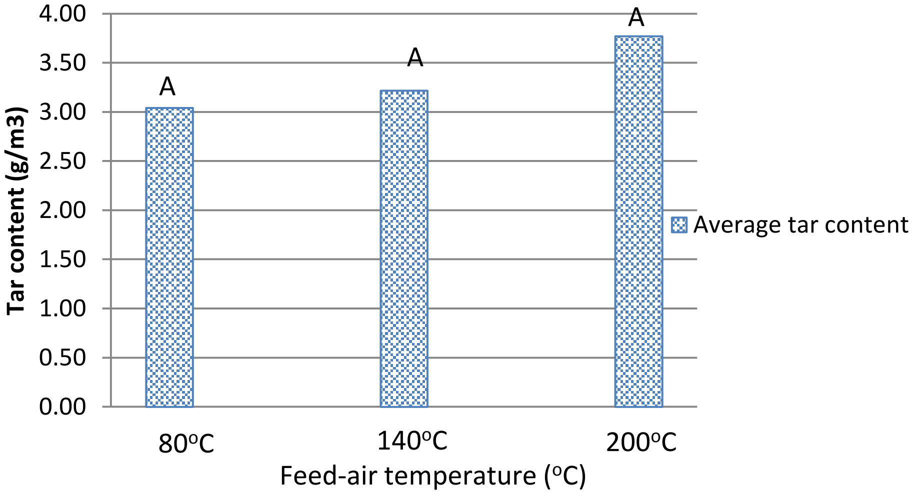


Figure 4.9 Tar content of sorghum biomass gasification at different feed-air temperatures. No significant difference was found in sorghum biomass gasification en the temperature was varied from 80°C to 200°C. See Appendix E-Tar individual analysis.

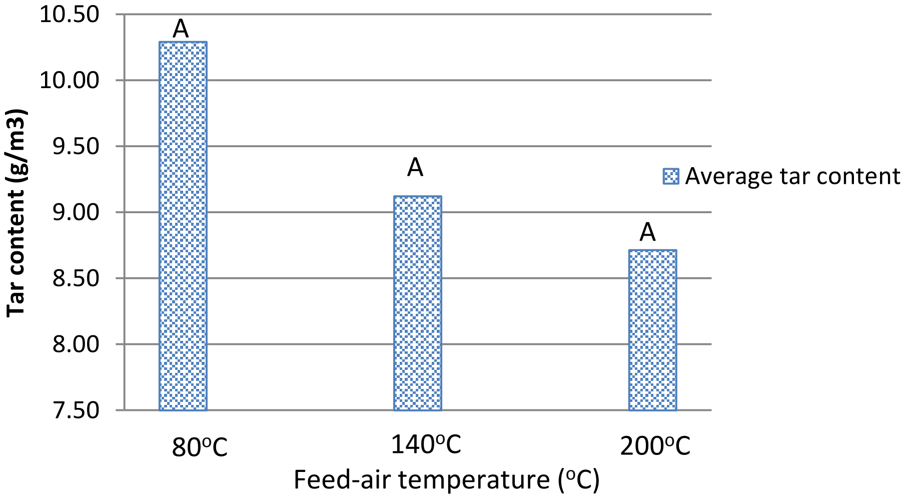


Figure 4.10 Tar content of wood chips gasification at different feed-air temperatures. No significant difference was found in wood chips gasification when the temperature was varied from 80°C to 200°C. See Appendix E-Tar individual analysis.

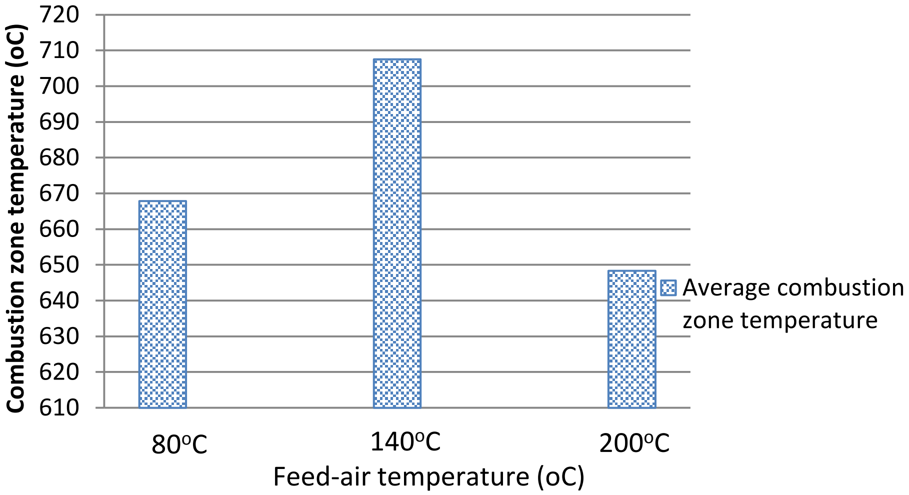


Figure 4.11 Prairie hay - Combustion zone temperatures at different feed-air temperatures

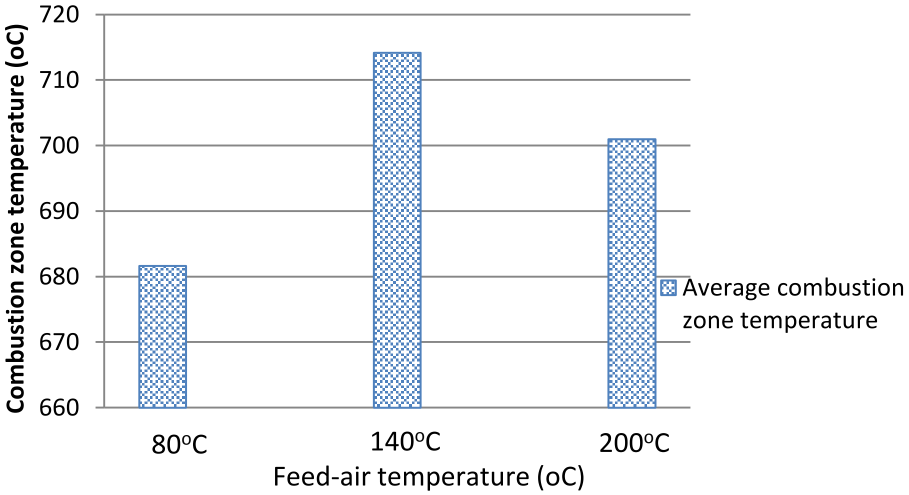


Figure 4.12 Sorghum biomass - Combustion zone temperatures at different feed-air temperatures

.

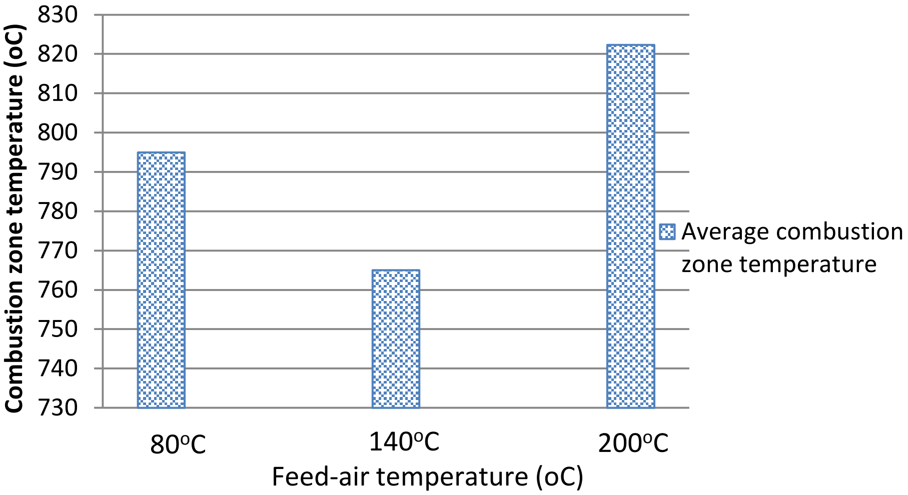


Figure 4.13 Wood chips - Combustion zone temperatures at different feed-air temperatures

4.3.3 Effect of biomass type on tar content

In this section a comparison of average syngas' tar content in different biomass types is presented. Figure 4.14 presents an average of tar content for prairie hay, sorghum biomass, and wood chips at different air flow rates. Prairie hay presented the lowest tar content of 1.6 g/m^3 and also presented the lowest overall tar content compared with sorghum biomass and wood chips. Gasification of wood chips showed the worst scenario with 12.5 g/m3 at medium air flow.

The difference of tar content is due to the biomass characteristics; in Figure 4.1 elemental analysis and biomass characteristics are presented. Wood chips present the highest tar content (16.84 g/m3) as well as the highest lignin content 19.24%. Lignin is an aromatic polymer with the funtion of joining cellulose fibers in order to keep adjacent cells together. This polymer is mainly composed of monomeric units of benzene rings (Basu, 2010). Benzene is commonly used as a tar model component in studies of tar formation in gasification systems (Wang, et al., 2010) because it is a likely intermediate in heavy hydrocarbons formation in syngas gasification (Milne, et al., 1998). Hanaoka (2005) studied the effect of biomass components on gasification, hemicellulose, xyan, and ligning were evaluated. reporting that lignin can produce the highest tar content when compared with other biomass components.

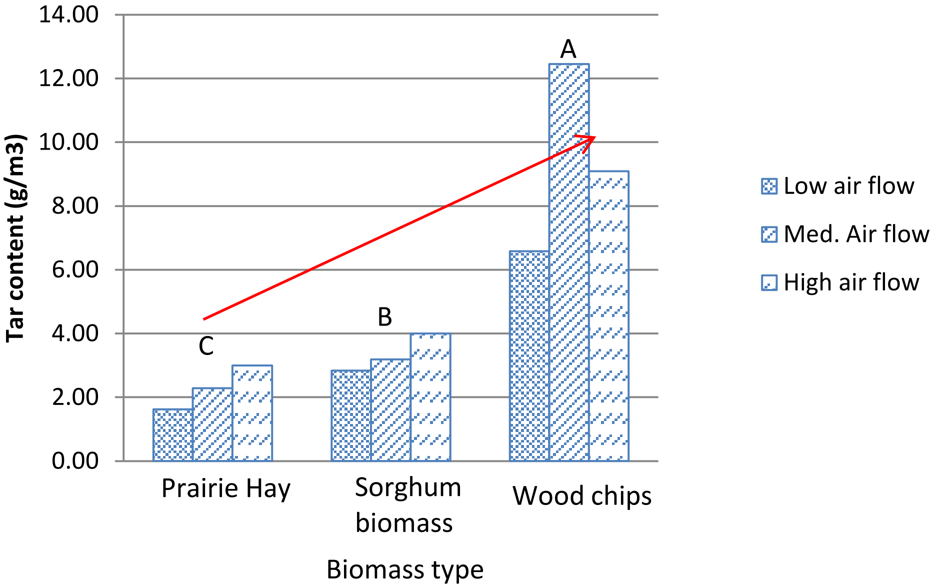


Figure 4.14 Effect of the biomass types on tar content at different air flow rates. Tar content presented significant difference for all biomass types; wood chips>sorghum biomass>prairie hay. See Table 4.4 and Appendix E

4.3.4 Effect on syngas composition and heating values

Table 4.3 presents syngas composition and high heating values (HHV) for all experiments' levels. The composition of the dry gas shows that H_2 varies from 7.15% to 11.21% and CO from 11.69% to 23.43%. High heating values from 3.28 to 6.10 MJ/m^3 are reported which are comparable to those reported by Di Blasi (1999) in a study of different woods and agricultural residues. Syngas composition and heating values did not present a clear difference when air flow rate and feed-air temperatures were varied. In section 4.3.5, a statistical analysis evaluated the differences in syngas from different biomass types, air flow rates, and feed-air temperatures.

Table 4.3 Operation conditions, dry gas composition and HHV - Biomass Gasification in an updraft biomass gasifier, mass charge 30 lbs (prairie hay and sorghum) or 40 lbs (wood chips).

Case number	Air flow	Feed-air temperatures (^{o}C)	H2 (%)	CO (%)	HHV (MJ/m^3)
PH021412 001	Low	80	8.00	16.44	4.68
PH021512 001	Low	140	7.32	15.89	4.50
PH021612 002	Low	200	8.71	17.26	4.87
PH022412 001	Med	80	9.89	16.56	4.69
PH021812 002	Med	140	8.40	14.89	4.17
PH021912 002	Med	200	7.15	17.57	4.34
PH022112 001	High	80	9.69	14.28	4.32
PH022112 002	High	140	10.25	17.90	5.15
PH022212 002	High	200	9.86	18.00	5.00
SG 031512 001	Low	80	8.53	15.73	4.63
SG 030812 001	Low	140	7.81	14.60	3.98
SG 031312 002	Low	200	8.58	14.81	4.13
SG 030812 002	Med	80	9.22	17.17	4.54
SG 031212 001	Med	140	9.10	14.13	3.88
SG 030712 002	Med	200	11.21	17.37	4.92
SG 022412 002	High	80	7.94	11.69	3.28
SG 031412 001	High	140	9.32	13.51	3.89
SG 022712 001	High	200	7.00	11.71	3.28
WC 032612 001	Low	80	8.28	20.01	5.76
WC 032512 001	Low	140	6.63	18.43	4.91
WC 032212 002	Low	200	8.79	19.54	5.47
WC 032412 002	Med	80	7.85	22.96	6.10
WC 032712 001	Med	140	8.41	20.84	5.72
WC 032112 001	Med	200	8.59	20.58	5.74
WC 032112 002	High	80	8.48	21.43	5.93
WC 032712 002	High	140	9.21	23.43	6.41
WC 032412 001	High	200	8.53	21.73	5.98

PH(prairie hay), SG (sorghum biomass), WC (wood chips)

4.3.5 Statistical Analysis

A statistical analysis was carried out to investigate the differences of tar content and syngas composition. Experiments were performed with three biomasses: prairie hay, sorghum biomass and wood chips. Air flow rate and feed-air temperatures were varied. Tukey's HSD is used to analyse the difference among groups. Since we used different biomasses, tar content did not present a linear relationship. Tar was converterd to log(tar) in order to get better results. A SAS-GLM procedure was performed and adjusted for Tukey comparisons (Appendix E). Tests were performed for each variable analyzed. Table 4.4, 4.5, 4.6 and 4.7 show results of SAS output. Values with significant differences are presented with different letters (A, B or C). Letter "A" represents the highest composition (or content) followed by "B" and "C". Significant difference means that the p-vlaue is lower than (<0.05), a p-value higher than this indicates that there is not enough evidence to probe that groups have significant difference (Kuehl, 2000).

Table 4.4 Tukey's HSD output for tar content analysis for all biomasses at all levels - air flow and feed-air temperature.

Biomass		**LSMEAN (g/m3)**
Prairie hay	C	1.95
Sorghum biomass	B	3.00
Wood chips	A	8.08
Interpretation: Tar content presented a significant difference for different biomasses.		
Air flow rate		LSMEAN (g/m3)
Low	B	2.77
Med	A-B	3.86
High	A	4.44
Interpretation: Tar content at low air flow rate presented a significant difference from high air flow. Medium air flow rate can produce tar content similar to low or high air flow rate.		
Temperature (^{o}C)		LSMEAN (g/m3)
80	A	4.22
140	A	3.46
200	A	6.11
Interpretation: No significant difference in tar content was found when the feed air temperature was varied.		
Different letters indicate a significant difference; the same letter indicates no significant difference. The letters A,B and C represent differences among groups, increasing from A>B>C.		

Table 4.4 presents results for tar content. Syngas' tar content presented significant differences for different biomass types. Prairie hay presented the lowest tar content with a

LSMEAN of 1.95 g/m^3. In contrast, wood chips, as mentioned in section 4.3.3, presented the highest tar content. However, sorghum biomass had an overall lower tar content than prairie hay in Figure 4.11 and a higher tar content than prairie hay according to the statistical analysis. These results validate data presented in Figure 4.14. Tar content produced with agricultural residues (sorghum biomass), municipal wastes (wood chips), and natural crops (prairie hay) can present different tar content when used in biomass gasification.

Analysis of air flow rate was also reported in Figure 4.4. The increment in the air flow can increase tar content in syngas. However, increment in the feed-air temperatures did not have a significant difference, which means that there is not enough evidence to probe that tar content increases when the temperature is increased from 80^{o} C to 200^{o} C.

Table 4.5 shows SAS output for high heating values' analysis. For different biomass types, different HHVs were reported. In this case, wood chips presented the highest heating values, which means that the energetic potential of syngas from wood chips was superior to those presented by sorghum biomass and prairie hay. High heating values can be affected by the amount of oxygen in the biomass. A biomass with a higher oxygen content has lower HHV compared with a biomass with low oxygen content. In Table 4.1, oxygen contents for prairie hay sorghum and wood chips are presented. The HHV's output was reported as follows: Woodchips>sorghum biomass>prairie hay; however, oxygen contents are reported the opposite Prairie hay>sorghum biomass>wood chips. This indicates that oxygen content affected the HHV of the biomasses.

No significant difference was found on HHV for air flow and feed-air temperatures. Syngas produced at a different level of air flow and feed-air temperatures presented similar values.

Studies of syngas from biomass gasification stated that the heating potential in syngas is produced by the amount of hydrogen and carbon monoxide (Weihong Yang, 2006). Table 4.6 presents analysis of hydrogen composition in syngas at different levels of gasification operational parameters. Results show that there is not a significant difference on syngas from different biomass types. It was also found that syngas at different air flow rates and feed-air temperatures has similar composition.

Table 4.7 presents results of carbon monoxide analysis. Data showed that carbon monoxide presented a significant difference. Prairie hay presented the highest carbon monoxide composition, followed by wood chips and sorghum biomass. Feed-air temperatures' data reported that, at 200^{o}C feed-air temperature, carbon monoxide has a significant difference from carbon monoxide produced at 140^{o}C. The use of feed-air temperature can improve the formation of CO because of the promotion of the Boudouard endothermic reaction presented in equation (4.4).

$$C + O_2 + 159.9\frac{kJ}{mol} \leftrightarrow 2CO \quad (4.4)$$

Table 4.5 Tukey's HSD output for High Heating values analysis for all biomasses at all levels - air flow and feed-air temperature.

Biomass		**LSMEAN (MJ/m^3)**
Prairie hay	B	4.66
Sorghum biomass	C	4.1
Wood chips	A	5.88
Interpretation: High heating values presented a significant difference for different biomasses.		
Air flow rate		**LSMEAN (MJ/m^3)**
Low	A	4.96
Med	A	4.93
High	A	4.75
Interpretation: No significant differences in high heating values were found when the feed-air temperature was varied.		
Temperature (^{o}C)		**LSMEAN (MJ/m^3)**
80	A	4.83
140	A	4.7
200	A	5.11
Interpretation: No significant differences in high heating value were found when the feed air temperature was varied.		
Different letters indicate a significant difference; the same letter indicates not a significant difference. The letters A,B and C represent differences among groups, increasing from A>B>C.		

Lucas (2004) studied the implementation high-temperature air gasification; this study found that the addition of heat in the feed-air can promote the Bounderuard reaction. Air flow rate variation did not present a significant difference on carbon monoxide composition.

Table 4.6 Tukey's HSD output for hydrogen composition analysis for all biomasses at all levels - air flow and feed-air temperature.

Biomass		**LSMEAN (%)**
Prairie hay	A	9.08
Sorghum biomass	A	8.51
Wood chips	A	8.65
Interpretation: No significant difference in hydrogen composition was found for different biomasses.		
Air flow rate		**LSMEAN (%)**
Low	A	8.68
Med	A	8.79
High	A	8.77
No significant difference in hydrogen composition was found when the air flow rate was varied.		
Temperature (^oC)		**LSMEAN (%)**
80	A	8.71
140	A	8.55
200	A	8.97
Interpretation: No significant difference in hydrogen composition was found when the feed air temperature was varied.		
Different letters indicate a significant difference; the same letter indicates not a significant difference. The letters A,B and C represent differences among groups, increasing from A>B>C.		

Table 4.7 Tukey's HSD output for carbon monoxide composition analysis for all biomasses at all levels - air flow and feed-air temperature.

Biomass		**LSMEAN (%)**
Prairie hay	A	21.37
Sorghum biomass	C	14.45
Wood chips	B	16.72
Interpretation: Carbon monoxide composition presented a significant difference for different biomasses.		
Air flow rate		**LSMEAN (%)**
Low	A	17.58
Med	A	18.11
High	A	16.86
Interpretation: No significant difference in carbon monoxide composition was found when the air flow rate was varied.		
Temperature (^{o}C)		**LSMEAN (%)**
80	A-B	17.2
140	B	16.84
200	A	18.5
Interpretation: Carbon monoxide composition at 140^{o}C feed-air temperatures presented a significant difference from feed-air temperatures at 200^{o}C. 80^{o}C feed-air temperatures can produce carbon monoxide composition similar to 80^{o}C or 200^{o}C.		
Different letters indicate a significant difference; the same letter indicates not a significant difference. The letters A,B and C represent differences among groups, increasing from A>B>C.		

In addition, Figure 4.15 presented data for syngas composition and high heating values for prairie hay, sorghum biomass and wood chips. The results presented in the comparison of the least squares' means showed that hydrogen content does not have a significant difference when different biomasses are utilized in the updraft gasifier. Carbon monoxide composition in syngas presented a significant difference while syngas produced with prairie hay is the highest and sorghum biomass presents the lowest concentration. The high heating values also presented a significant difference for biomass types as follows: Wood chips > pririe hay > sorghum biomass.

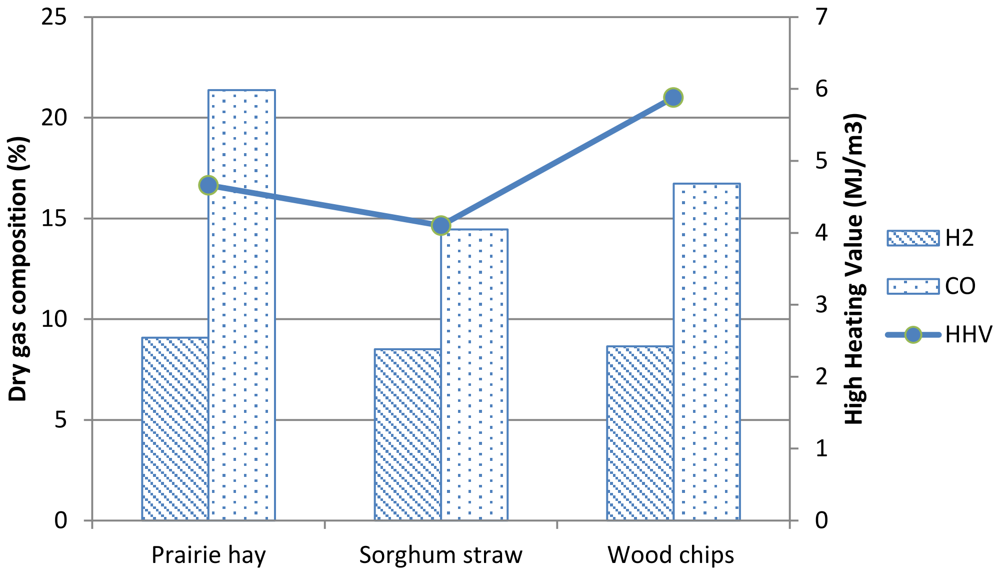


Figure 4.15 LSMEAN of SAS-GLM procedure for Analysis of hydrogen, carbon monoxide content, and high heating value in syngas from gasification of prairie hay, sorghum biomass, and wood chips.

4.4 Conclusions

Effect of gasification operational parameters was evaluated in an updraft biomass gasifier. Biomass types, feed-air temperatures, and air flow rate effect on syngas composition and tar content were investigated. A Tukey's HSD statistical analysis was performed to validate the experimental data. The results presented that different biomass types can produce different tar content and syngas high heating values. Tar content in syngas from different biomasses was presented as follows: Wood chips>sorghum biomass>prairie hay. High heating values also varied for different biomasses, e.g., wood chips>prairie hay>sorghum biomass. The effect of the air flow rate showed that the formation of tar species is increased when the air flow rate increases. In syngas composition, it was found that hydrogen presents similar values for different biomasses, air flow rates, and feed-air temperatures. This contrasts with carbon monoxide, which can have different concentrations in syngas from different biomasses. Carbon monoxide composition for different biomasses types also presented variation, e.g., prairie hay>wood chips>sorghum biomass. The appropriated selection of the biomass types and gasification operational parameters can increase syngas heating values and decrease the formation of tar species in biomass gasification process.

4.5 Bibliography

Anna Ponzio, S. K. W. B., 2006. Effect of operating conditions on tar and gas composition in high temperature air/steam gasification (HTAG) of plastic containing waste. Fuel Processing Technology , Issue 87, pp. 223-233.

Basu, P., 2010. Tar Production and Destruction. Biomass gasification and pyrolysis; practical design and theory, pp. 97-116.

Chris Hilgam, M. V. d. B., 2003. Gasification. United States of America: Elservier .

Di Blasi, C., Signorelli, G. & Portoricco, G., 1999. Countercurrent Fixed-Bed Gasification of Biomass at Laboratory Scale. Ind. Eng. Chem. Res., Volume 38, pp. 2571-2581.

F. Rosillo-Calle, P. G. S. H. J. W., 2007. The Biomass Assessment Handbook. UK and USA: Earthscan.

Hanaoka, T. et al., 2005. Effect of woody biomass components on air-steam gasification. Biomass ans Bioenergy, Issue 28, pp. 69-76.

Hanping, C. et al., 2008. Experimental Investigation of Biomass Gasification in a Fluidized Bed Reactor. Energy & Fuels, Volume 22, pp. 3493-3498.

Hasan, J., Keshwani, D. R., Carter, S. F. & Treasure, T. H., 2010. Themochemical Conversion of Biomass to Power and Fuels.. In: Biomass to Renewable Energy Processes. United States of America: CRC Press, Taylor & Francis Group, pp. 437-489.

Houben, M. P., 2004. Analysis of tar removal in a partial oxidation burner, s.l.: The dissertation of Eindhoven.

Kinoshita, C., Y, W. & Zhou, J., 1994. Tar formation under different biomass gasification conditions. Journal of Analytical and Applied Pyrolysis , Volume 29, pp. 169-181.

Knoef, H., 2005. Practical aspects of biomass gasification. In: H. Knoef, ed. Handbookd Biomass Gasification. Netherlands: BTG biomass technology group, pp. 13-37.

Kuehl, R. O., 2000. Design of experiments: statistical principles of research design and analysis. Second edition ed. Belmont, CA: Brooks/Cole.

Lucas, C., Szewczyk, D., Blasiak, W. & Mochida, S., 2004. High-Temperature air and steam gasification of densifies biofuels. Biomass and Bioenrgy, Volume 27, pp. 563-575.

Mahishi, M. R. & Goswami, D., 2007. Thermodynamic optimization of biomass for hydrogen production. International Journal of Hydrogen Energy, Volume 32, pp. 3731-3840.

Mathieu, P. & Dubuisson, R., 2002. Performance analysis of a biomass gasifier. Energy Conversion and Management , Volume 43, pp. 1291-1299.

Milbrandt, A., 2005. A Geographic Perspective on the Current Biomass Resource Availability in the United States. National Renewable Energy Laboratory Technical report. NREL/TP-560-39181, pp. 1-62.

Milne, T., Evans, R. & Abatzoglou, N., 1998. Biomass Gasifier "Tars": Their Nature, Formation, and Conversion. National Renewable Energy Laboratory, pp. NREL/TP-570-25357.

Onyekwelu, J. C. & Akindele, S. O., 2006. Biomass and Bioenergy Research in Tropical Africa: State of the Art Chellenges and Future Directions. In: M. D. Brenes, ed. Biomass and Bioenergy: New Research . New York: Nova Science Publishers, Inc, pp. 1-34.

Reed, T. & Das, A., 1988. Handbook of Biomass Downdraft Gasifier Engine Systems. Golden, Colorado: U.S. Department of Energy.

Saad, M. A., 1966. Thermodynamics for engineers. Englewood Cliffs, N.J.: Prentice-Hall Inc.

Wang, D., Yuan, W. & Ji, W., 2010. Use of Biomass Hydrothermal Conversion Char as the Ni Catalyst support in Benzene and Gasification Tar Removal. Transactions of the American Society of Agricultural and Bilogical Engineers, 53(3), pp. 795-800.

Weihong Yang, A. P. C. L. W. B., 2006. Performance analysis of a fixed-bed biomass gasifier using high-temperature air. Fuel Processing Technology , Issue 87, pp. 235-245.

Chapter 5 - In-situ thermo-catalytic tar cracking and syngas reforming in an updraft biomass gasifier

Abstract

Biomass gasification is known as one of the effective ways to convert organic matters into useful biofuels. However, the production of heavy hydrocarbons (tars) as byproducts causes downstream problems such as tar condensation in pipe lines and machinery, resulting in system collapse. A tar cracking system is needed in order to reduce tars in syngas. In this study, a tubular tar cracking reactor was built in the combustion zone of the gasifier using gasification heat to drive the reactions. Char and nickel-char catalysts were evaluated in the cracking reactor. The in-situ system was found to be very effective in tar removal and syngas enhancement. The highest tar removal of 95% was achieved at 0.3s residence time and 10% nickel loading. This condition also gave the highest syngas HHV increment of 36.01% (7.33 MJ/m^3). The effect of gas residence time and Ni loading on tar removal and syngas composition was also studied. Gas residence of 0.2-0.3s and Ni loading of 10% were found appropriate in this study.

5.1 Introduction

Biomass gasification can be used to produce clean energy from biomass (Mathieu & Dubuisson, 2002). This thermochemical process with an incomplete combustion of biomass leads the formation of a gas mixture named syngas. The heating value in syngas is mainly provided by hydrogen, carbon monoxide, and methane (Hasan, et al., 2010). The utilization of biomass to produce energy can decrease carbon dioxide emission because the carbon dioxide released during syngas burning is balanced with the carbon dioxide utilized during plant growth (Cheng, 2010). Syngas can be implemented in industrial applications such as turbines, boilers, internal combustion engines, etc. Several gasification units have been developed in the world for power and heat generation applications (Knoef, 2005). However, the formation of heavy hydrocarbons species that can be condensed downstream is a disadvantage in the implementation of biomass gasification in industrial applications. Nevertheless, updraft gasifiers that have a higher tar production also have a higher thermal efficiency compared with downdraft gasifiers (Di Blasi, et al., 1999). However, this syngas is not feasible for most industrial applications which require tar contents lower than 0.6g/Nm^3 (Milne, et al., 1998). A downstream tar cracking system is needed. Tar cracking systems need to be inexpensive, effective, and they should improve hydrogen and/or carbon monoxide content in the product gas (Basu, 2010). Tar cracking systems can drive cracking and reforming reactions with the use of a catalyst at high temperatures (Han & Kim, 2008). However, high temperatures without a catalyst can be used for tar cracking as well, but temperatures from 1200^{o}C to 1290^{o}C are required (Brandt & Henriksen, 2000) (Stevens, 2001). The Thermal cracking process is not as effective as catalytic tar cracking which can perform tar removal of 99% (Wang, et al., 2011). Several authors have studied catalytic activity on syngas tar. Yang (2010) and Zhang (2007) evaluated a nickel-olivine catalyst in which conversions of 98.7 and 71% were achieved, respectively. In the same way, alumina (Al_2O_3) catalysts have been investigated reporting tar removal rate of 99.5% (Wang, et al., 2010 (1)). Nickel-char catalysts are a cheap and simple way to crack tars due to the local availability of nickel and char and achievable conversion efficiencies of 99%. In order to be effective, catalytic tar cracking and syngas reforming require temperatures from 650 to 1290^{o}C (Wang, et al., 2005) therefore requiring a heating source.

Dayton (2002) states that the use of high temperature for tar cracking is not efficient because of the high temperatures it requires. Neverthless, the implementation of a tar cracking system in the gasifier combustion zone does not require external heat supply. As the overall efficiency of the system increases, syngas with high quality and low tar content can be produced. In-situ tar reduction is a way to reduce tar components in syngas by modifing the gasifier to reduce the amount of tar in the final gas product, thus gas reforming can be performed at the same time. The implementation of a tar cracking system introduces several thermochemical reactions such as tar cracking, reforming and carbon-steam reaction (5.1) that leads the formation of the most simple components (Baker, et al., 1987).

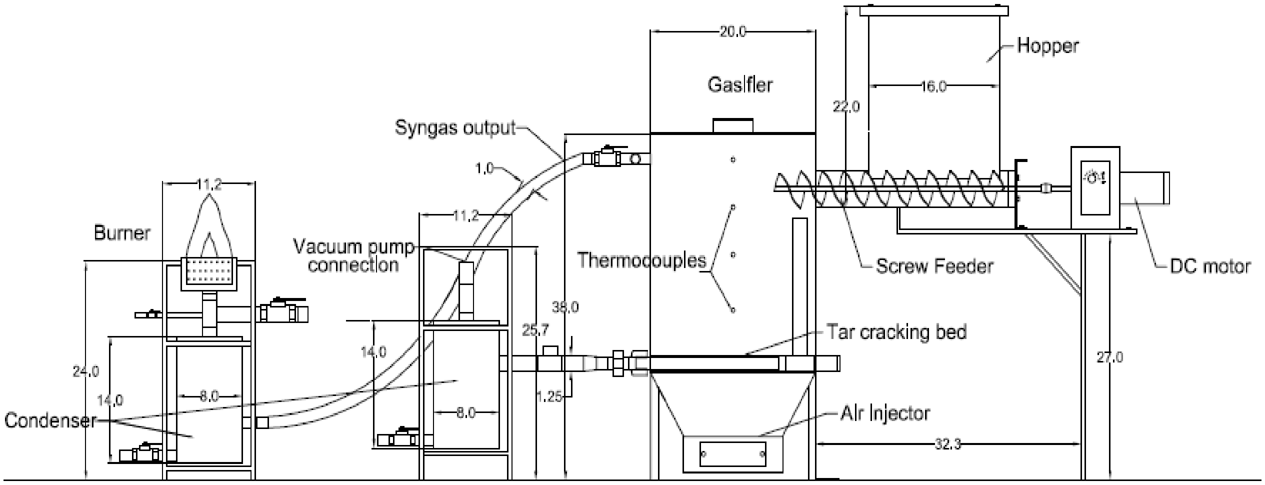
$$Tar \rightarrow \begin{bmatrix} Tar\ cracking \\ Reforming \\ Steam\ reforming \end{bmatrix} \rightarrow\ CO_2 + CO +\ H_2 + CH_4 + \cdots . + Coke \quad (5.1)$$

The objective of this study was to test an experimental catalytic tar cracking and syngas reforming system. This system is composed of a tubular reactor placed in the middle of the combustion zone of an updraft biomass gasifier. The combustion zone's heat generated in exothermic combustion reactions of biomass and air can reach temperatures of more than 950^{o} C

(Hasan, et al., 2010). This heat can drive tar cracking and reforming reactions in the tubular reactor. Char and nickel-char catalysts were evaluated in the newly designed tar cracking system.

5.2 Materials and methods

Experiments were carried out in an updraft biomass gasifier (Figure 5.1). It was equipped with a biomass auto-feeder system, a temperature measurement system and a tar cracking device. Temperatures in the chamber were measured using type K thermocouples connected to a digital data acquisition system.



All dimensions are in inches.

Figure 5.1 Updraft biomass gasification system equipped with a tar cracking reactor

The tar cracking device was a tubular reactor located in the middle of the combustion zone (Figure 5.2). This tubular reactor was divided in two stages. First, a vertical black iron pipe of 31.75 mm i.d. (1.25 inch.) was filled by char with a particle size ranging from 6.3 to 9.52 mm, at a length of 101.6 mm. This vertical pipe was used as a pre-cracking reactor and to filter excess tar, ash, and moisture in syngas in order to avoid blockage in the catalytic bed. Second, a horizontal black iron pipe (31.75 mm i.d.) held a 25.4 mm i.d. (1 inch) pipe where the catalyst was loaded.

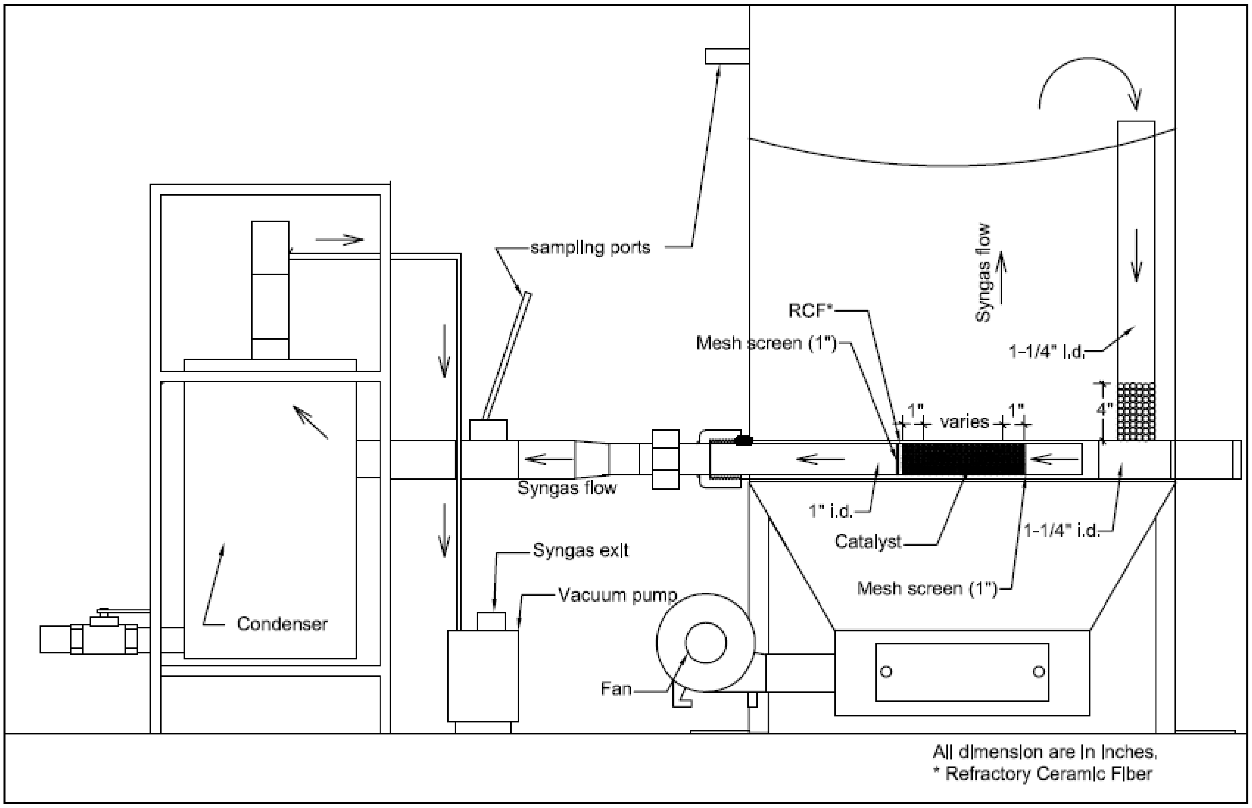


Figure 5.2 Tar cracking system

Char and Ni/char catalysts were evaluated. A nickel-char catalyst was prepared with char from a charcoal briquettes brand with particle size ranging from 1.4 to 2 mm and nickel oxide (Ni(II)O) from Acros Organic. Mechanical mixing was performed with a method used by Wang (2010). Catalyst loading was performed as follows. First, a mesh screen was set inside the reactor to keep the catalyst in position. Second, a layer of refractory ceramic fiber was placed to prevent nickel oxide from running off. Third, one inch layer of char was introduced into the catalytic bed. Then, the catalyst was loaded in the middle of the catalytic bed and another char layer was loaded. Finally, mesh and a snap ring were used to secure the catalyst in place. Various catalyst mixtures were used. Nickel oxide loadings of 5, 10, and 15% (weight) with a residence time of 0.2 s were evaluated. The char alone catalyst, without NiO, was also evaluated at 0.2 s. Evaluation of three residence times (0.1, 0.2 and 0.3 s) was carried out with nickel oxide loading of 10 %.

5.2.3. Experimental procedure

A mixture of sawdust and sawdust pellets was selected as the feedstock; 40 pounds (18.18 Kg) of sawdust were mixed with 20 pounds (9.09 Kg) sawdust pellets. The reactor was started by burning 4 pounds (1.81 Kg) of sawdust mixture for 4 minutes to create a fire-bed; 100 ml of methanol was used as lighter fluid. The remaining sawdust mixture was added on top of the fire-bed. Air was injected from the bottom of the gasifier and then flowed up within the gasifier's zones, giving place to combustion, reduction, and pyrolysis thermo-chemical reactions.

Syngas from the gasifier was guided to the burner and burned until the temperature in the reaction zone reached $800^{o}C$. Syngas then flowed within the tubular reactor at 0.5 CFM (14.2 liter per minute) and excess syngas was burned. Experiments were performed at a constant flow; a vacuum pump and air flow meter were used. Syngas inside the gasifier flowed down within the tubular reactor, giving place to tar cracking and reforming reactions. Tar samples were collected before and after the tubular reactor using the cool trapping method described in Chapter 3. This tar trapping method condenses heavy tars in syngas. The syngas flowed within a flask under water-ice and three flasks under dry ice (CO_2) for 15 min at 7.8 cubic feet per hour (3.8 lpm). After collected, tar samples were dried overnight in an oven at $105^{o}C$ and weighed. Syngas samples were collected before and after the tar cracking device in order to compare gas composition. After collected, syngas composition was measured in Gas Chromatograph (SRI 8610) equipped with a TCD detector. Hydrogen, carbon monoxide, carbon dioxide, methane, oxygen and nitrogen were analyzed. High heating value was calculated using the gas composition and enthalpy of combustion of reactants, hydrogen, carbon monoxide and methane when the products of combustion are water (liquid) and CO_2 (gas). This method is presented in Saad (1966), equation is presented below:

$$\Delta H^{o} = \sum \left(H_f^{o}\right)_p - \sum \left(H_f^{o}\right)_r \quad (5.2)$$

5.3 Results and Discussion

5.3.1 Tar cracking system effect on combustion zone' temperature

Catalytic activity experiments were performed using heat from the combustion zone. Figure 5.3 shows temperature profiles of two experiments. Other experiments showed similar behaviors. After the reactor temperature reached $800^{o}C$, the temperature continued increasing until the tar cracking system unit was turned on. The temperature then dropped and, after 5 to 10 minutes, it started to increase again. This phenomenon states that heat removal from the reactor's combustion zone for tar cracking and reforming reactions is compensated in the same way as the heat used in endothermic reactions in the reduction and pyrolysis zone is compensated. Examples of endothermic reactions in a gasifier are water gas reaction (5.3) and water shift reaction (5.4 (Hilgam & Burgt, 2003).

$$C + H_2O \leftrightarrow CO + H_2 \qquad (5.3)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad (5.4)$$

Moreover, a slight instability in the reaction's zone temperature is presented; this can also be affected by char movement in the chamber. All experiments were performed with temperatures between 800 to 930°C.

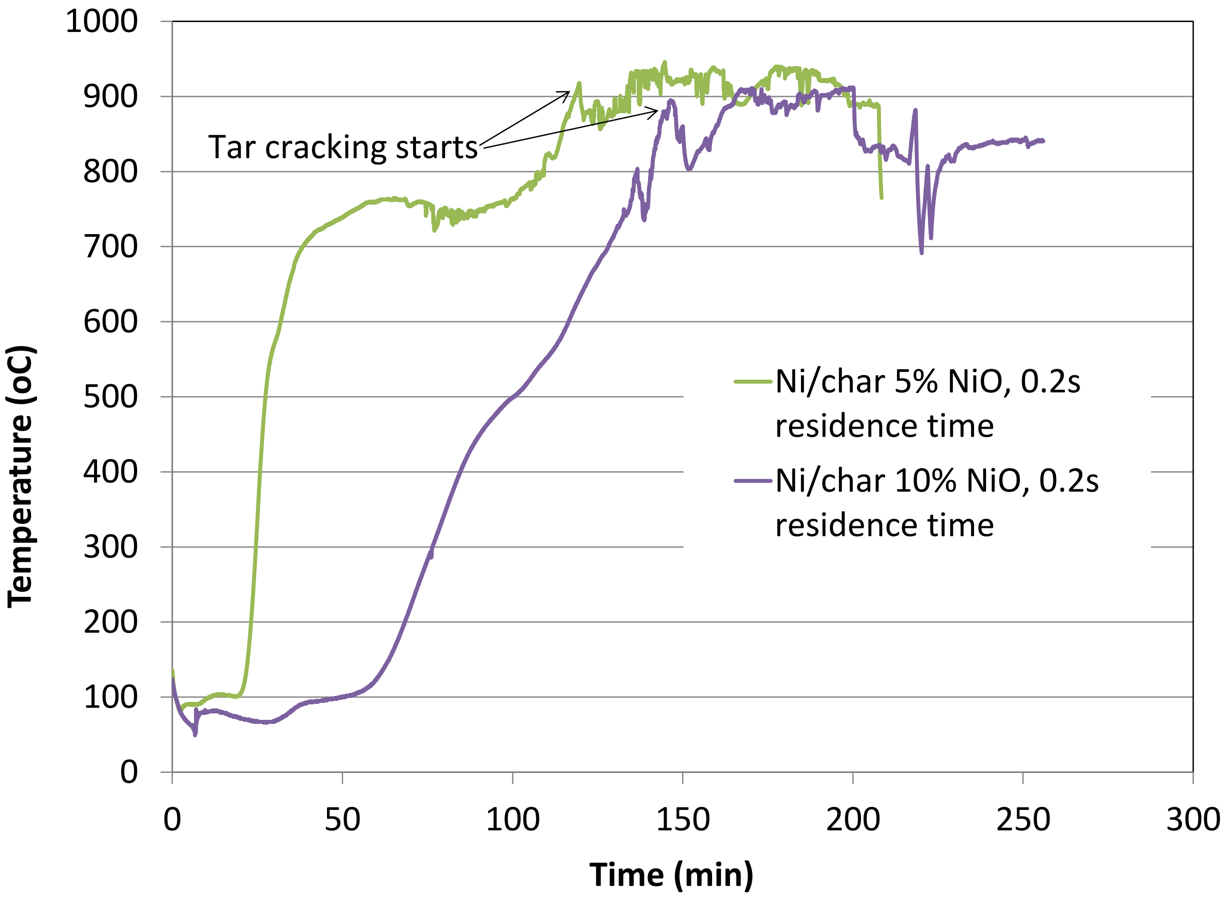


Figure 5.3 Temperature profile – Reactor's combustion zone

5.3.2 Effect of residence time on tar removal and syngas reforming

The effect of using the reaction zone's temperature on catalytic activity is presented with nickel loading of 10%. Figure 5.4 shows that a residence time of 0.1s was not long enough because it had the lowest tar removal (~65%). Residence times of 0.2 and 0.3s had no significant difference in tar removal; both were very effective at 94% and 95%, respectively. Therefore, 0.2s residence time was considered appropriate in this study. Wang (2010) evaluated the effect of residence time with Nickel-char catalysts on tar removal experiments in two gasification systems and found that 0.3s residence time presented optimal performance at 800^{o}C while 0.1s was not long enough.

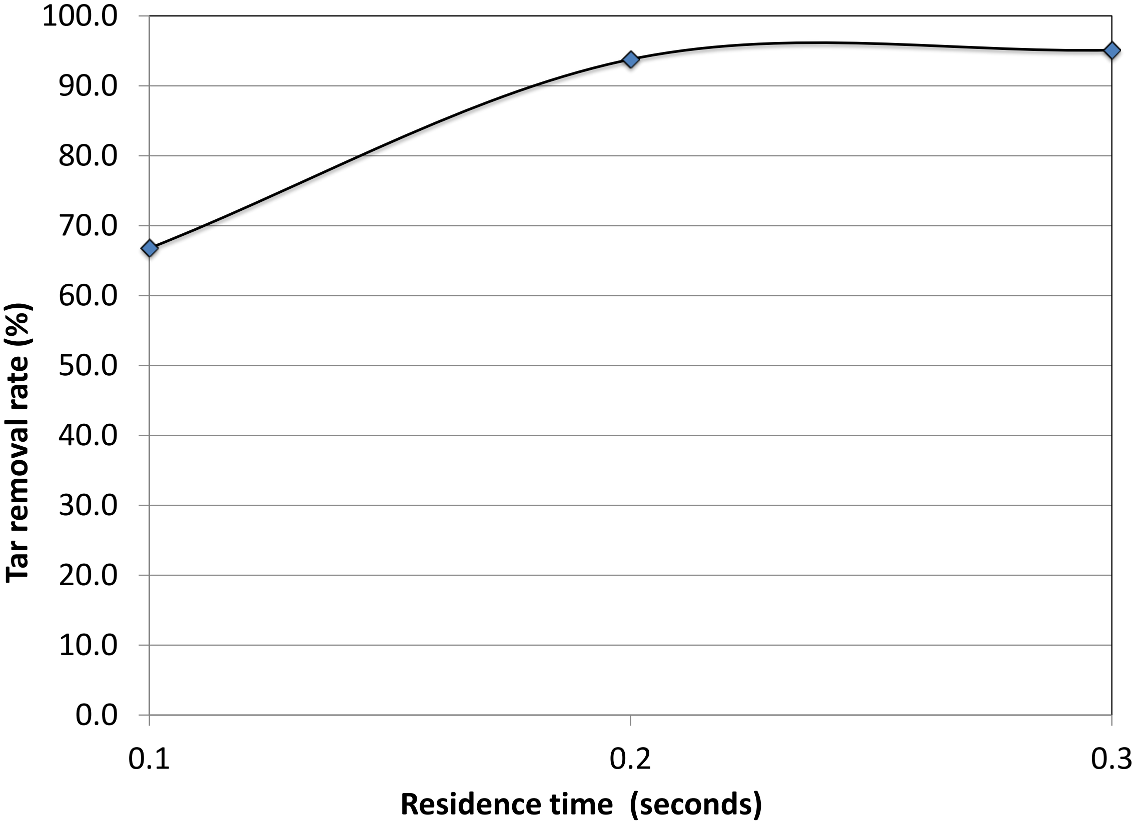


Figure 5.4 Effect of residence time on tar removal rate (10% Nickel loading)

Figure 5.5 shows product gas composition before and after reforming at all residence times. A significant increase in CO and H_2 was observed in all cases, especially at 0.2s residence time. Increment of CO was 3.9%, 31.9%, and 19.2%, and increment of H_2 was 35.1%, 66.2%, and 126.7% for 0.1, 0.2, and 0.3s residence, respectively. CH_4 concentration did not change or slightly increased in all cases.

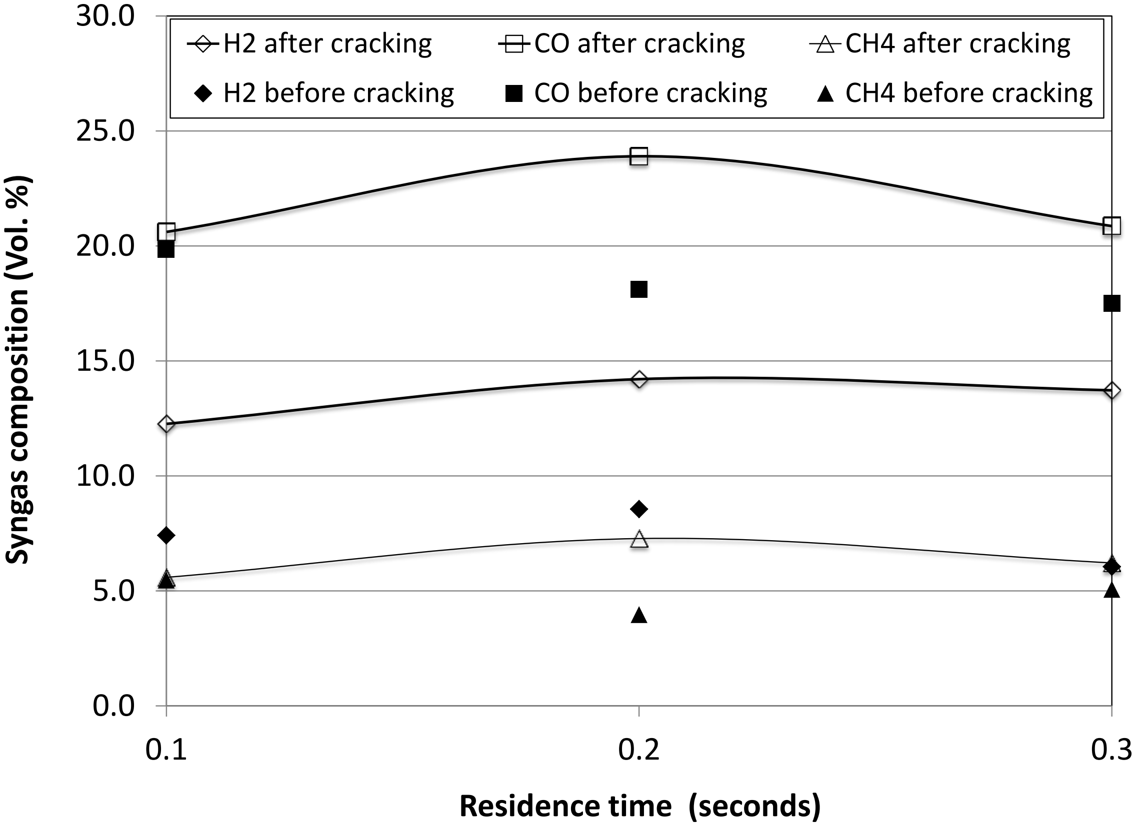


Figure 5.5 Effect of residence time on syngas composition (10% Nickel loading)

5.3.3 Effect of nickel loading on tar removal and syngas reforming

Figure 5.6 shows tar removal of Nickel-char catalysts at different nickel loadings as well as the char effect on tar removal at 0.2 s residence time. Char alone (0% Ni loading) achieved a tar removal rate of 60.86%. Tar removal rate significantly increased as Ni loading increased, suggesting that NiO played a significant role in tar removal. When Ni loading increased to 15%, the tar removal rate started to decrease. The use of char as a catalyst support has several advantages: char has local availability, low acquisition prices, and a catalyst can be prepared using mechanical mixing, saving catalyst preparation time (Wang, et al., 2010). It is important to note that tar cracking activity depends on reaction temperature and char particle size. Wang (2011) reported that tar removal has a linear relasionship with reaction temperature when char and nickel-char catalysts were used. In Figure 5.2 the combustion zone's temperature ranged from 800 to 930° C. This variation can cause decrement on tar cracking and reforming activity when temperatures are close to 800° C. As a result, performance might be affected.

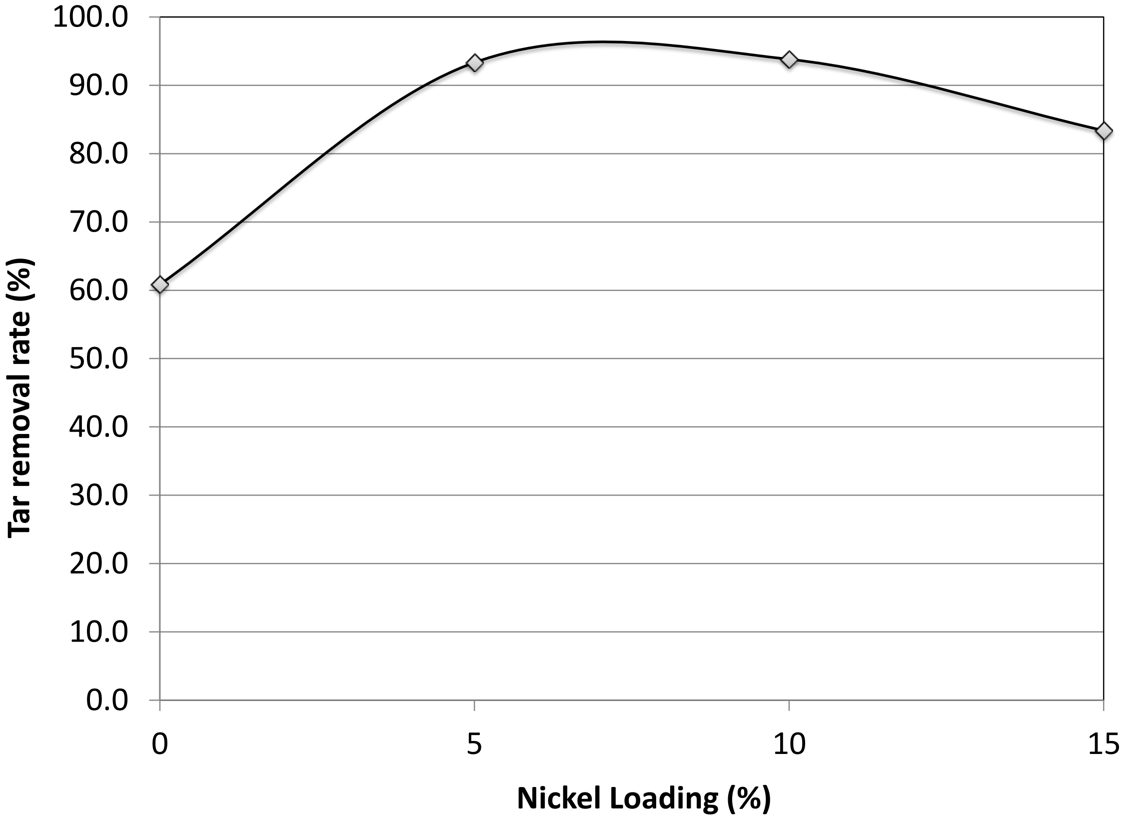


Figure 5.6 Effect of nickel loading on tar removal (0.2s residence time)

Figure 5.7 presents the nickel loading effect on syngas composition. It is seen that at 10% loading and 0.2 s, CO and CH_4 show their highest composition of 23.90% and 7.28%, respectively. Hydrogen composition at this point is 14.21%. Figure 5.7 shows syngas composition at this condition, with CO (18.12%) and CH_4 (3.97%) presenting the lowest syngas composition before reforming, and, after reforming, presenting the highest. Char reforming activity was also presented. Hydrogen was increased from 6.04% to 11.34%, however, No significant increment of CO was shown.

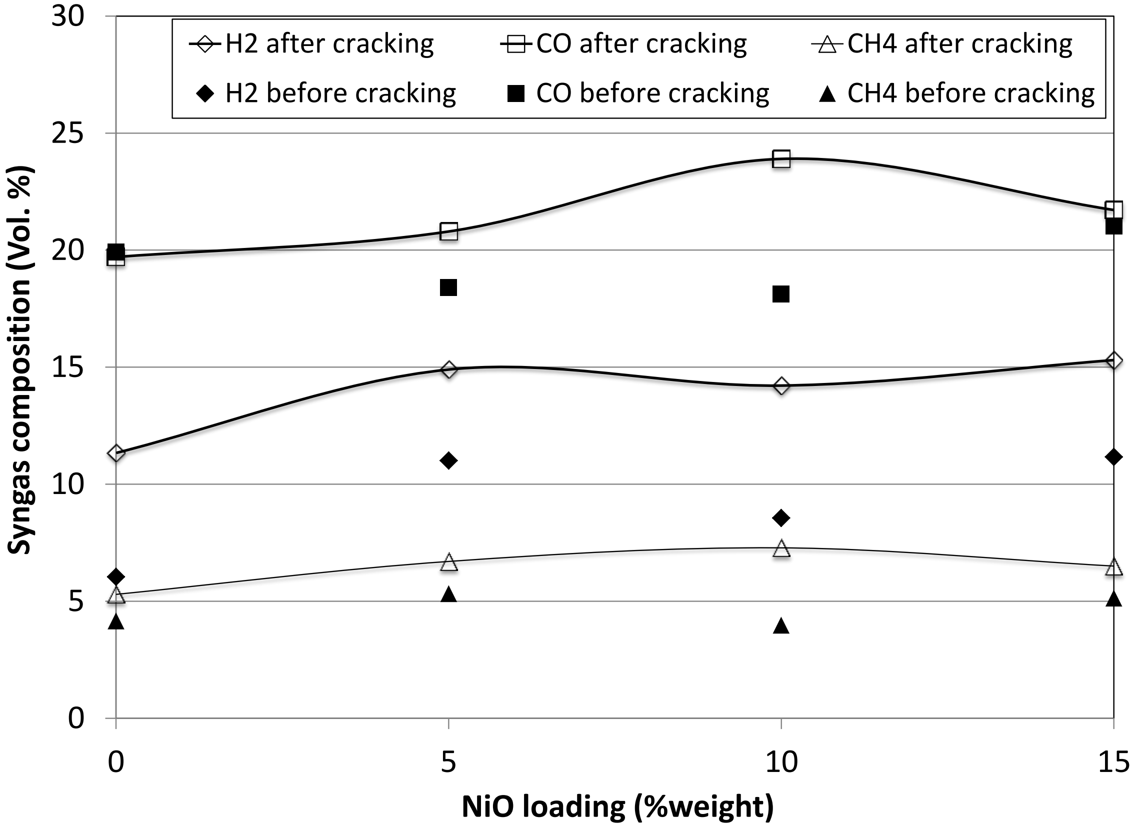


Figure 5.7 Effect of nickel loading on syngas composition (0.2 s residence time)

Table 5.1 High heating value of syngas before and after tar cracking and reforming

Catalyst	HHV (1) (MJ/m3)	HHV (2) (MJ/m3)	Increment (%)
Char	5.31	6.11	14.97
Ni 10%/Char, 0.1s	6.06	6.55	8.05
Ni 5%/Char, 0.2s	6.26	7.69	22.88
Ni 10%/Char, 0.2s	5.52	7.46	35.16
Ni 15%/Char, 0.2s	6.55	7.77	18.72
Ni 10%/Char, 0.3s	5.39	7.33	36.01

The high heating values (HHV) of syngas before and after reforming are reported in Table 5.1. It is important to note that the increment of HHV depends on the initial heating value of the gas. Nickel-char catalysts with 10% loading and a residence time of 0.3s gave the highest increase in HHV (36%). The effect of gas residence time can be clearly seen, as longer residence time (0.2 to 0.3s) gave higher HHV due to more efficient tar removal and better syngas. The effect of Ni loading is also apparent. It seemed 5% was too low and 15% was too much, while 10% was appropriate.

5.4 Conclusions

The catalytic activity of a tubular tar cracking and syngas reforming system built in the combustion zone of an updraft biomass gasifier was evaluated using char and char-supported NiO catalysts. The in-situ system was found to be very effective in tar removal and syngas enhancement. The highest tar removal of 95% was achieved at 0.3s residence time and 10% nickel loading. This condition also gave the highest syngas HHV increment of 36% (7.33 MJ/m^3). The effect of gas residence time and Ni loading on tar removal and syngas composition was also studied. Gas residence of 0.2-0.3s and Ni loading of 10% were found appropriate in this study.

5.5 Bibliography

Baker, E. G., Mudge, L. K. & Brown, M. D., 1987. Steamgasifiaction of biomass with nickel secondary catalyst. *Ind. Eng. Chem. Res.* , Issue 26, pp. 1335-1339.

Basu, P., 2010. Tar Production and Destruction. *Biomass gasification and pyrolysis; practical design and theory,* pp. 97-116.

Brandt, P. & Henriksen, U., 2000. *Decomposition of tar in gas from updraft gasifier by thermal cracking.* Sevilla, Spain, London, James & James (science Publishers) Ltd.

Chembukulam, S. K. et al., 1981. Smokeless Fuel from Carbonized Sawdust. *Ind. Eng. Chem. Prod. Res. Dev.* , Issue 20, pp. 714-719.

Cheng, J., 2010. Introduction. In: J. Cheng, ed. *Biomass to Renewable Energy Processes.* United States of America: CRC Press, pp. 1-6.

Dayton, D., 2002. A Review of the Literature on Catalytic Biomass Tar Destruction. *National Renewable Energy Laboratory,* Volume NREL/TP-510-32815, pp. 1-11.

Engelen, K., Yuhong, Z., J., D. D. & V., B. G., 2003. A novel catalytic filter for tar removal from biomass gasification gas: Improvement of the catalytic activity in presence of H2S. *Chemical Engineering,* Volume 58, pp. 665-670.

Han, J. & Kim, H., 2008. The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. *Renewable and Sustainable Energy Reviews,* Volume 12, pp. 397-416.

Hasan, J., Keshwani, D. R., Carter, S. F. & Treasure, T. H., 2010. Themochemical Conversion of Biomass to Power and Fuels.. In: *Biomass to Renewable Energy Processes.* United States of America: CRC Press, Taylor & Francis Group, pp. 437-489.

Hilgam, C. & Burgt, M. V. d., 2003. *Gasification.* United States of America: Elservier.

Knoef, H., 2005. Practical aspects of biomass gasification. In: H. Knoef, ed. *Handbookd Biomass Gasification.* Netherlands: BTG biomass technology group, pp. 13-37.

Mathieu, P. & Dubuisson, R., 2002. Performance analysis of a biomass gasifier. *Energy Conversion and Management* , Volume 43, pp. 1291-1299.

Milne, T., Evans, R. & Abatzoglou, N., 1998. Biomass Gasifier "Tars": Their Nature, Formation, and Conversion. *National Renewable Energy Laboratory,* pp. NREL/TP-570-25357.

Saad, M. A., 1966. *Thermodynamics for engineers.* Englewood Cliffs, N.J.: Prentice-Hall Inc.

Stevens, D. J., 2001. *Hot gas conditioning: Recent progress with larger-scale biomass gasification systems,* Colorado, United States of America: National Renewable Energy Laboratory.

Wang, D., Yuan, W. & Ji, W., 2010 (1). Effective syngas cleanup and reforming using Ni/ -Al2O3. *Int. J. Agric.& Biol. Eng.,* 3(2), pp. 39-45.

Wang, D., Yuan, W. & Ji, W., 2010. Use of hydrothermal conversion char as the Ni catalyst in benzene and gasification tar removal. *Transactions of the ASABE,* 53(3), pp. 795-800.

Wang, D., Yuan, W. & Ji, W., 2011. Char and Char-supported Nickel Catalyst for Secondary Syngas Cleanup and Conditioning. *Applied energy,* Volume 88, pp. 1656-1663.

Wang, T., Chang, j. & Lv, P., 2005. Novel Catalyst for Cracking of Biomass Tar. *Energy & Fuels,* Volume 19, pp. 22-27.

Yang, X. et al., 2010. Nickel supported on modified olivine catalyst for steam reforming of gasification tar. *Catalyst Communications 11,* pp. 383-386.

Zhang, R., Wang, Y. & Brown, R. C., 2007. Steam reforming of tar compounds over Ni/olivine catlyst doped with CeO2. *Energy Conversion and Management* , Volume 48, pp. 67-77.

Chapter 6 - Summary

An investigation of biomass, operating conditions, and gasifier design on the performance of an updraft biomass gasifier was performed. Prairie hay, sorghum biomass and wood chips under three different levels of air flow and feed air temperatures were studied. Modification on the updraft gasifier' design was made to improve gasification performance. The new design included a new air injection system and a tar cracking device, which was built inside the combustion zone where temperature could reach up to 950^{o} C to drive tar cracking and syngas reforming reactions.

The projects' goals were accomplished as follows:

1. A lab-scale updraft biomass gasifier was successfully designed, built, and instrumented for stable gasification using low-bulk density biomass. Related accessories such as a biomass feeder, inlet air temperature controller, air injection nozzle, and tar cracking system were also developed to enhance gasifier performance. The gasifier was successfully tested with three biomass resources (prairie hay, sorghum biomass and woodchips) at various conditions and stable syngas was produced.
2. The study of biomass and operational gasification parameters showed that different biomasses gave different tar contents in syngas at the same condition, e.g., wood chips > sorghum straw > prairie grass. The effect of air flow rate was evaluated and results showed that by increasing the air flow rate, the formation of tar in syngas also increased for all the three biomass. Feed-air temperature was also studied. In prairie grass gasification, the increment of the feed temperature decreased tar in the final gas product, but no significant correlations were found between tar and feed air temperature for the other two biomasses. Syngas composition analysis showed that different biomasses produced syngas with a different high heating value, e.g., wood chips > prairie hay > sorghum biomass. CO composition also showed differences by feed air temperature and biomass, e.g. prairie hay>wood chips>sorghum biomass, but H_2 did not show significant differences by either biomass type or operating conditions.

3. The design of a tubular tar cracking reactor built in the combustion zone of the updraft biomass gasifier was tested. Combustion zones' heat was used for tar cracking; char and nickel-char catalysts were tested on tar cracking and syngas reforming in this device. Results showed the highest tar conversion of 95% with nickel-char catalyst at 0.3 s residence time and 10% nickel loading. At the same conditions, syngas had the highest heating value increment of 36% (7.33MJ/m^3). These results confirm that heat from the combustion zone can be effectively used for tar cracking and syngas reforming purposes, and the in-situ reactor and char-supported Ni catalysts can effectively remove tars and enhance syngas compositions.

Chapter 7 - Future work

This study was focused on biomass type, operational parameters and gasification design effect on gasification performance in a biomass updraft gasifier. In order to extend this work, biomass characteristics and other operational parameters need to be investigated.

1. Evaluation of biomass physical properties’ effect on gasification performance. Per example, moisture content, particle size and bulk density.
2. Implementation of biomass gasification using steam and air-steam mixtures.
3. Comparison of the tar cracking unit and an external heating system for tar cracking and syngas reforming.
4. Modeling and comparison of the gasification kinetics in tar cracking and syngas reforming.

Appendix A - Standard procedure – Gasification experiments in an updraft biomass gasifier

A.1. Gasifier Operation

1.1. 30 lbs. of biomass were weighted.

1.2. 4.5 lbs. of biomass from point (1.1) were burned in the gasifier reactor. 200 ml of methanol was used to ignite the biomass. Burning time: 4 min.

1.3. After the fire bed was created, the reactor was filled with the remained biomass.

1.4. Air was injected to increase the temperature in the combustion zone of the reactor. Thus, smoke started to emanate from the reactor.

1.5. The measurement system was connected to measure temperature and air flow.

1.6. Air was injected in the burner to mix the smoke with air.

1.7. A propane torch was used to test the burning properties of the gas mixture. Ignition waiting time: 15 s to 1 min.

1.8. After the gasifier run steady state condition (stable combustion zone temperature, 25 to 30 min after point (1.5)) tars were collected using cooling-tar sampling system. This tar sampling system consisted in four flask series connected under dry and regular ice. Syngas was flowed within them to condense tar. While collecting tar, a gas sample was taken using a gas sampling bag. Tar collection time is from 10 to 15 min.

1.9. Syngas flow was measured. A differential pressure transducer and a nozzle were used according to the ASTM standard for measure of flow with orifice and nozzle in pipe lines. The unit was connected in an outlet pipe and syngas flows within the nozzle.

1.10 After 1 hr. run, the air supply valve was closed. Temperatures in the gasifier started to decrease; therefore, syngas flow stopped.

A.2. Tar measure

2.1. Flasks with tar collected in (1.8) are place in an oven for 24 hr.

2.2. Flasks are weighted and final tar content is determined.

A.3. Syngas – Gas composition

3.1 A gas chromatograph equipped with a TCD detector is used to determine syngas composition.

Peak Simple version 4.09 – 32 bit (for SRI product, Torrance, CA)

Channel configuration:

Initial temperature: 35°C, keep for 6 min, ramp of 20degrees/min until 200°C keep for 4 min. Figure A1 shows a picture of syngas analysis. Table A1 presents calibration factor to correct peak areas.

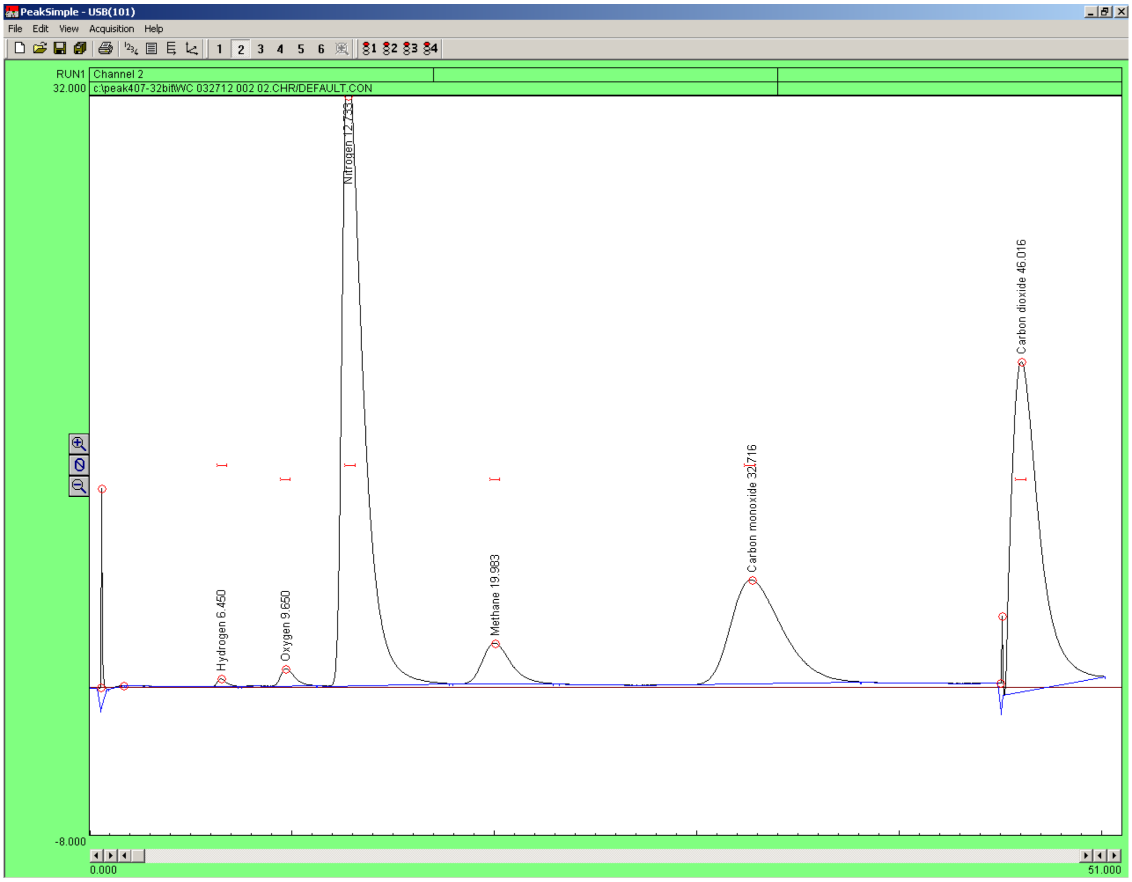


Figure A.1 Diagram of syngas measure in Peak Simple version 4.09 – 32 bit

Table A.1 Calibration factors for Syngas composition analysis.

Calibration factors	
H2	38.3483
O2	1.0016

N2	1.0000
CH4	1.1870
CO	1.2593
CO2	0.5500

Appendix B - Nickel loading – Experimental procedure

Char and Ni2O/char will be used to create tar cracking and syngas (synthetic gas) reforming in biomass gasification in an updraft gasifier. Ni2O/char catalyst will be prepared using mechanical mixing. Three Nickels loading will be tested (5%, 10%, 15%) as well as three residence times (0.05s 0.1s and 0.2s). The char particles ranged from 1.4 to 2.0 mm. The Nickel (II) oxide loadings are show in Figure B.1. At a residence time of 0.2 s, three Ni2O loadings are performed.

Materials: Charcoal, Nickel (II) Oxide.

Catalyst loading - procedure

1. Char was weighted in a 100 ml beaker, 36.14g (residence time 0.2s) and mixed with 5.42 g (15%) of Ni2O using mechanical mixing. The same procedure was used for others catalyst; others loading are presented in Table B1.

Table B.1 Nickel and char weights for nickel-char catalyst preparation

		Nickel loading (g)		
Residence time (s)	Char weight (g)	5%	10%	15%
0.1	24.09		1.95	
0.2	36.14	1.81	3.61	5.42
0.3	48.19		3.91	

2. The catalytic reactor was 1 inch diameter black iron pipe with an internal diameter of 1.071 inches (27.3 mm) and 18 inches long. In this reactor, char and nickel-char mixtures were loaded as follow:
   2.1. One inch diameter mesh screen was set in the reactor and a layer of char coal of 1 inch was placed next to the mesh to avoid NiO release. The mixture of nickel-char catalyst was loaded in the tubular reactor and covered with another layer of char (1 inch long) and secured with a mesh screen. A clamp holds the catalyst in place. The use of an inch of char in both ends can prevent NiO particles to be exposed to the environment.

2.2. Once secure, using pipe caps in both ends, the tubular reactor was transported and connected to the gasifier and experiments were carried out.

2.3. The reactor’s cleaning process was performed in the hood to avoid NiO exposure. The NiO mixture was placed in a bottle for chemical waste materials.

Appendix C - Air/gas flow – Microsoft Excel file

Table C.1 Air/gas flow calculation using differential pressure, Source (Hu, 2007)

Flow rate of Syngas.			0.25"			
				ΔP(in H2O)	0.0000	
d(m)	0.0254	D(m)	0.0508	P1 (Pa)		
ε	1	Rd	300000	P2 (Pa)		
β	0.5	Rd=(V1*D/V1)		ΔP(Pa)	0	
ρ1(Kg/m3)	1.2	V1 (m/s)	2.1771	r=(P2/P1)		
v1(m2/s)	1.33E-05			k		
ρ(Kg/m3)	1.2			ε(Y)		
π	3.14					
C	0.9758			ΔP(Pa)	qv (cfm)	
qm (kg/s)	0			32.4	9.3	
qv(m3/s)	0			69.7	13.7	
qv(cfm)	0			122	18.1	
				159.4	20.7	
0.25" H2O						
mA	4.0000	<----insert value here (Amps)				
Resistance Ω	470					
ΔP(in H2O))	0.0000					
ΔP(Pa)	0.0000					
C is the discharge coefficient;						
ε is the expansibility factor;						
Δp is the differential pressure;						
ρ1 is the density of the fluid at the upstream pressure tap;						
ρ is the fluid density at the temperature and pressure for which the volume is stated;						
β is the diameter ratio;						
RD is the Reynolds number referred to D.						
1m3/s = 2118.9cfm						
1m3/hr = 0.5886cfm						
κ is the isentropic exponent (its value depends on the nature of the gas)						

Appendix D - Automatic feeder Microcontroller code

Programming code used in the microcontroller:

```
#include <htc.h>
#include "bootloader\bootloader.h"

#include "datatypes.h"
#include "serial_port.h"
int voltagebuffer[40];
int1 gateKeeper = 0;
register16 ADRES = 0;

void wait2microsec(void)
{
        unsigned int16 count=0;
        while (count<2)
        {
                CLRWDT();
                count++;
        }
}
void wait40microsec(void)
{
        unsigned int16 count=0;
        while (count<27)
        {
                CLRWDT();
                count++;
        }
}
void wait1point64ms(void)
{
        unsigned int16 count2=0;
                while (count2<41)
                {
                        CLRWDT();
                        wait40microsec();
                        count2++;
                }
}
void sendcommand(int8 a)
{
        RC2=0;
        RC2=1;//pin6 enable line--high to low to write commands
        PORTB=a;//RB0 to RB7
        wait40microsec();
        RC2=0;//pin6 enable line--high to low to write commands
        wait1point64ms();
}
void senddata(int8 a)
{
        RC0=1;//print character
        RC2=1;//pin6 enable line--high to low to write commands
        PORTB=a;//RB0 to RB7--move to first position in first line
```

```
        wait40microsec();
        RC2=0;//pin6 enable line--high to low to write commands
        RC0=0;//change back to command
        wait1point64ms();
}

void current_temp(int16 num)
{
        char temps;
        if(num >= 100)
        {
                temps = num / 100;
                num -= temps * 100;
                temps += 0x30;
                senddata(temps);
        }
        else
                senddata('0');
        if(num >= 10)
        {
                temps = num / 10;
                num -= temps * 10;
                temps += 0x30;
                senddata(temps);
        }
        else
                senddata('0');
        if(num >= 1)
        {
                num += 0x30;
                senddata(num);
        }
        else
        {
                senddata('0');
        }
        //Transfer Data for printing character
        senddata(0x43);//C
}



 void main(void)
{
         gateKeeper = 0;
         int8 ohml = 0;
         int8 ohmh = 0;
         int16 testvalue=0;
         double temp3=0, sum=0;
         int16 temp4=0;
         int8 i=0, j=0, k=0;
         int8 counter=0;
         int ON=300;
         int OFF=200;
         //intialize array to zero
         j=0;
```

```
     while(j<=39)
     {
        voltagebuffer[j]=0;
        j++;
     }


        Reset_from_Bootloader();

        //    Bits: 76543210
        INTCON  = 0b01000000;
        //      Bit 7:  Global interrupt disabled (for now)
        //      Bit 6:  Periph interrupt enabled
        //      Bit 5:  TMR0   interrupt disabled
        //      Bit 4:  Ext.   interrupt disabled
        //      Bit 3:  PORTB  interrupt disabled
        //      Bit 2:  TMR0   interrupt clear
        //      Bit 1:  Ext.   interrupt clear
        //      Bit 0:  PORTB  interrupt clear

        //    Bits: 76543210
        T1CON   = 0b00110001;//timer 1 control
        //      Bit 7:          unused
        //      Bit 6:          unused
        //      Bits 5-4:       Prescaler = 1:8   (used as how the clock is
divided)
        //      Bit 3:          Oscillator disabled
        //      Bit 2:          don't care when Bit1 = 0
        //      Bit 1:          TMR1 use Fosc/4 (not RC0)
        //      Bit 0:          TMR1 enabled

        //    Bits: 76543210
        PIE1    = 0b00000001;
        // Periphial interrupt enable (periphial means something the computer
uses w/o watching all the time.  Such as a serial port.)
        //      Bit 7:  PSP  interrupt disabled
        //      Bit 6:  ADC  interrupt disabled
        //      Bit 5:  RX   interrupt disabled
        //      Bit 4:  TX   interrupt disabled
        //      Bit 3:  SSP  interrupt disabled
        //      Bit 2:  CCP1 interrupt disabled
        //      Bit 1:  TMR2 interrupt disabled
        //      Bit 0:  TMR1 interrupt enabled

        //    Bits: 76543210
        PIR1    = 0b00000000;
        // Where interupt flags are located(Periphial interrupt register)
        //      Bit 7:  PSP  interrupt clear
        //      Bit 6:  ADC  interrupt clear
        //      Bit 5:  RX   interrupt clear - read-only
        //      Bit 4:  TX   interrupt clear - read-only
        //      Bit 3:  SSP  interrupt clear
        //      Bit 2:  CCP1 interrupt clear
        //      Bit 1:  TMR2 interrupt clear
        //      Bit 0:  TMR1 interrupt clear
```

```
//    Bits: 76543210
OPTION  = 0b10001000;
//      Bit 7:         PORTB pullups disabled
//      Bit 6:         Interrupt on falling edge of RB0
//      Bit 5:         TMR0 use Fosc/4 (not RA4)
//      Bit 4:         TMR0 increment on rising edge
//      Bit 3:         Assign Prescaler to WDT (TMR0 fixed at 1:1)
//      Bits 2-0:      Prescaler = 1:1 (Unscaled WDT timeout = 7-33ms)

//    Bits: 76543210   1=input, 0=output
TRISA   = 0b11111111;  //Use AN0 for ADC
TRISB   = 0b00000000;  //LED counter
TRISC   = 0b11110000;  //required by UART to be 0b11xxxxxx
TRISD   = 0b11110111;  //all unused
TRISE   = 0b00000111;  //see notes below
//      Bit 7:  read-only - PSP  input buffer full flag
//      Bit 6:  read-only - PSP output buffer full flag
//      Bit 5:  PSP input buffer overflow flag
//      Bit 4:  PSP disabled (PORTD is normal I/O)
//      Bit 3:  unused
//      Bit 2:  RE2 is input
//      Bit 1:  RE1 is input
//      Bit 0:  RE0 is input

//    Bits: 76543210
RCSTA   = 0b10010000;
//      Bit 7:  Serial port enabled (takes over RC7 & RC6)
//      Bit 6:  8-bit RX
//      Bit 5:  don't care in asynch. mode
//      Bit 4:  Continuous RX enabled
//      Bit 3:  Address detection disabled
//      Bit 2:  read-only - Framing error flag
//      Bit 1:  read-only - Overrun error flag
//      Bit 0:  read-only - 9th bit of RX

//    Bits: 76543210
TXSTA   = 0b00100100;
//      Bit 7:  don't care in asynch. mode
//      Bit 6:  8-bit TX
//      Bit 5:  TX enabled
//      Bit 4:  Asynch. mode
//      Bit 3:  unused
//      Bit 2:  High speed baud generator
//      Bit 1:  read-only - TX shift register empty flag
//      Bit 0:  9th bit of TX


//Real baud rate = Fosc/(16(SPBRG+1))
SPBRG   = 129;  //9615.4 = 0.16% fast for 9600

//    Bits: 76543210
ADCON0  = 0b10000000;
//      Bit 7:  ADCS1   A/D conversion clock select bits
//      Bit 6:  ADCS0   A/D conversion clock select bits
//      Bit 5:  CHS2    Analog channel select bits
//      Bit 4:  CHS1    Analog channel select bits
```

```
        //      Bit 3:  CHS0    Analog channel select bits
        //      Bit 2:  GO/DONE A/D conversion status bit
        //      Bit 1:  Unused
        //      Bit 0:  ADON    A/D ON bit

        //    Bits: 76543210
        ADCON1  = 0b10000101;
        //      Bit 7:  ADFM    A/D result format select bit
        //      Bit 6:  ADCS2   A/D conversion clock select bits
        //      Bit 5:  Unused
        //      Bit 4:  Unused
        //      Bit 3:  PCFG3   A/D port configuration control bits
        //      Bit 2:  PCFG2   A/D port configuration control bits
        //      Bit 1:  PCFG1   A/D port configuration control bits
        //      Bit 0:  PCFG0   A/D port configuration control bits

        ei();   // Global interrupts enabled


        put_str("Ready!\r\n");
        //Intitalize the display
                    //pin1 Vss=gnd
                   //pin2 Vdd=5V
                    //pin3 contrast adjusted by Potentiometer
                RC0=0;//pin4--low means data bytes are transferred to display
are commands--high means data bytes are transferred as characters
                RC1=0;//pin5--always tied low to write

                //command for shutdown display and restart
                sendcommand(0x08);

                //command for blinking cursor
                sendcommand(0x0C);

                //command for clearing display
                sendcommand(0x01);

                //Transfer Data for printing character
                senddata(0x4F);//O

                //Transfer Data for printing character
                senddata(0x46);//F

                //Transfer Data for printing character
                senddata(0x46);//F

                //Transfer Data for printing character
                senddata(0x3A);//:

                //Transfer Data for printing character
                current_temp(OFF);//200

                //command for allowing a second line
                sendcommand(0x38);

                //command set display address to memory location 40
```

```
                sendcommand(0xC0);

                //Transfer Data for printing character
                senddata(0x4F);//O

                //Transfer Data for printing character
                senddata(0x4E);//N

                //Transfer Data for printing character
                senddata(0x3A);//:

                //Transfer Data for printing character
                senddata(0x20);//

                //Transfer Data for printing character
                current_temp(ON);//300

                //Transfer Data for printing character
                senddata(0x20);//

                //Transfer Data for printing character
                senddata(0x54);//T

                //Transfer Data for printing character
                senddata(0x3A);//:

                //Outputs default temperature
                current_temp(999);

                //intialize RC3--turns on the light
                RC3=1;

        while (1)
        {
                CLRWDT();
                //turn on A/D module
                                ADON = 1;
                //check to see if voltage on/off values are to be incremented
                while (RD2==1)//add 25 to ON Temp
                {
                        //put_str("d");
                        RD3=1;
                        CLRWDT();//clears watchdog timer
                        while (RD2==1)//waits for button to not be pressed
                        CLRWDT();
                        wait1point64ms();//get rid of bounce by debouncing
                        ON=ON+25;//increment temperature
                        if (ON>=450) ON=450;//450(5volts)is the maximum value
for the PIC'S ADC
                        //command set display address to memory location 44
                     sendcommand(0xC4);
                     current_temp(ON);
                }
                wait1point64ms();//get rid of bounce by debouncing
                RD3=0;
```

```
while (RD0==1)//subract 25 from ON Temp
{
        RD3=1;
        CLRWDT();
        while (RD0==1)
        CLRWDT();
        wait1point64ms(); //get rid of debounce
        ON=ON-25;
        if(ON<=0) ON=0;
        //command set display address to memory location 44
     sendcommand(0xC4);
     current_temp(ON);
}
wait1point64ms();//get rid of debounce
RD3=0;

while (RD5==1)//add 25 to OFF TEMP
{
        k=0;
        RD3=1;
        CLRWDT();
        while (RD5==1)
        CLRWDT();
        wait1point64ms(); //get rid of debounce
        OFF=OFF+25;
        if(OFF>=450) OFF=450;
        //command set display address to memory location 05
     sendcommand(0x84);
     current_temp(OFF);
     while (k<8)
     {
         //Transfer Data for printing character
         senddata(0xA0);//blank space
         k++;
     }
}
wait1point64ms();//get rid of debounce
RD3=0;

while (RD4==1)//Subtract 25 from OFF TEMP
{
        RD3=1;
        CLRWDT();
        while (RD4==1)
        CLRWDT();
        wait1point64ms(); //get rid of debounce
        OFF=OFF-25;
        if(OFF<=0) OFF=0;
        //command set display address to memory location 05
    sendcommand(0x84);
    current_temp(OFF);
        while (k<8)
    {
        //Transfer Data for printing character
        senddata(0xA0);//blank space
        k++;
```

```
                }
            }
            wait1point64ms();//get rid of debounce
            RD3=0;

        sum-=voltagebuffer[i];
        voltagebuffer[i]=ADRES.val;
        sum+=ADRES.val;
        temp3=sum/40;
        i++;
        if (i==40) i=0;

        //Determine current voltage
            temp4=(temp3*500)/1023;//converted to degrees Celsius
            if (counter>=250)
            {
                    //command set display address to memory location 4B
                sendcommand(0xCB);
                    current_temp(temp4);
            //Transfer Data for printing character
            senddata(0xA0);//blank space
                    if((temp3-5)>=ON) RC3=1;
                    else if((temp3+5)<=OFF)  RC3=0;

                    counter=0;
            }
            counter++;

            if(RCIF)
            {
                    char temp = RCREG;
                    if(temp == 0x14)        //new program?
                    {
                            //alert terminal if connected
                            put_str("Going to bootloader...\r\n");
                            //goto bootloader
                            Run_Bootloader();
                    }
                    //troubleshooting using serial port
                    if(temp == 'r')         //ohmmeter
                    {
                            put_num(temp4);
                            put_num(temp3);
                            put_num(ADRES.val);
                            put_str("\n");
                            }
                     //&& ADRES.val < 0b1110011101
//                  put_char(temp);//echo the received data
            }
            if(!GODONE)
            {
                    if(gateKeeper)
                    {
                            ohml = ADRESL;
                            ohmh = ADRESH & 0b00000011;
```

```
                                ADRES.bytes.lo = ohml;
                                ADRES.bytes.hi = ohmh;
                                gateKeeper = 0;
                        }
                }
        }
}
 void interrupt isr(void)
{
         /***** Timer 1 Code *****/
        if(TMR1IF)
        {

                TMR1IF=0;       // clear event flag
                //start up the conversion!!!
                GODONE = 1;
                gateKeeper = 1;
                //PORTB++;

        }
}
```

Appendix E - SAS Code and Outputs

tar

```
data gasifier;
input biomass $ day flow $ temp tar hhv H2 CO;
logtar=log(tar);
cards;
ph      21212  Low     80      2.8947 4.93429          8.472374951   18.56941516
ph      21412  Low     80      3.4211 4.68393          8.001018172   16.4398127
ph      21412  Low     140     0.7895 4.09548          8.340692962   14.26944566
ph      21512  Low     140     1.0526 4.49661          7.31947842    15.88627328
ph      21612  Low     200     1.0526 5.42631          10.45109464   20.15140611
ph      21612  Low     200     0.5263 4.87152          8.713163193   17.25703904
ph      22312  Med     80      2.9825 4.47293          8.857870751   15.93148373
ph      22412  Med     80      3.6842 4.68821          9.886245613   16.55966522
ph      21812  Med     140     1.5789 5.22937          10.19247443   19.29732768
ph      21812  Med     140     2.4561 4.16847          8.403231714   14.89084287
ph      21912  Med     200     0.7018 4.91553          10.61502269   16.95659567
ph      21912  Med     200     2.2807 4.33871          7.153983448   17.57186366
ph      22012  High    80      2.807   4.41765         9.728284743   15.41797833
ph      22112  High    80      4.2105 4.32283          9.690447459   14.27565796
ph      22112  High    140     3.5088 5.14586          10.25271182   17.89797648
ph      22212  High    140     2.807   4.211            8.172814232  15.71365489
ph      22212  High    200     2.807   4.99645         9.85952081    17.99890766
ph      22312  High    200     1.8676 4.5048           9.412058412   15.88411281
ss      30712  Low     80      5.0877 4.12917          9.800282636   13.54746971
ss      31512  Low     80      2.2807 4.62556          8.526068428   15.72964042
ss      30812  Low     140     2.807   3.98021         7.811141436   14.60062196
ss      31312  Low     140     2.6316 3.4009           8.767411674   10.93019538
ss      31212  Low     200     2.807   6.13748         9.48871383    21.62227603
```

ss	31312	Low	200	1.4035	4.13224	8.57715517	14.80526564
ss	22812	Med	80	1.5789	4.02429	7.600093417	12.76615738
ss	30812	Med	80	2.4561	4.53653	9.224920742	17.16778215
ss	30912	Med	140	4.2105	3.15749	7.530144395	11.30777722
ss	31212	Med	140	1.5789	3.88053	9.095958222	14.12901059
ss	30712	Med	200	2.2807	4.91693	11.2142098	17.36843109
ss	31012	Med	200	7.0175	4.36421	8.062532304	17.54523702
ss	22412	High	80	3.5088	3.28354	7.938136142	11.69395282
ss	22512	High	80	3.3333	4.05783	8.718602568	14.13242601
ss	31412	High	140	2.1053	3.89083	9.322592436	13.50773746
ss	22712	High	140	5.9649	4.00007	7.451351409	13.69110336
ss	22712	High	200	3.5088	3.28152	6.999142954	11.71462693
ss	22812	High	200	5.614	4.04802	7.180887979	13.99695105
wc	32012	Low	80	3.6842	5.82181	8.802723569	20.56461795
wc	32612	Low	80	6.6667	5.7581	8.281062943	20.01215775
wc	32512	Low	140	4.7368	4.90555	6.632150639	18.42839432
wc	32312	Low	140	9.1228	6.40725	9.777430934	22.79509753
wc	32212	Low	200	8.4211	5.46753	8.794287445	19.53560575
wc	32612	Low	200	6.8421	6.11134	9.832854849	21.30614043
wc	32412	Med	80	10.7018	6.09865	7.848744938	22.96220125
wc	32812	Med	80	27.3684	5.93293	8.243104677	23.924625
wc	32312	Med	140	12.2807	6.01308	8.47011971	21.9421824
wc	32712	Med	140	8.2456	5.72086	8.408208993	20.83586542
wc	32512	Med	200	12.1053	6.5522	8.945347833	24.32549904
wc	32112	Med	200	4.0351	5.74373	8.586607781	20.58008828
wc	31912	High	80	4.7368	5.37556	8.827310225	18.6004357
wc	32112	High	80	8.5965	5.93265	8.47795534	21.4314861
wc	32012	High	140	3.5088	5.49469	8.917254351	19.63042394
wc	32712	High	140	16.8421	6.41114	9.211816774	23.43153967
wc	32212	High	200	8.5965	6.25043	9.188530327	22.74553543
wc	32412	High	200	12.2807	5.98365	8.534294269	21.72525897

```
;
run;
proc print data=gasifier;
run;
proc glm data=gasifier;
class  biomass flow temp;
model tar= biomass flow temp biomass*flow biomass*temp flow*temp biomass*flow*temp;
lsmeans biomass flow temp /pdiff adjust=tukey cl;
output out=Residuals r=Resid p=Predicted stdp=stdp stdi=stdi stdr=stdr;
run;
proc gplot data=Residuals;
plot resid*Predicted  /vref=0;
plot resid*day /vref=0;
run;
proc univariate data=Residuals plot normal;
var resid;
run;
```

SAS Outputs

Tar content Analysis

```
                 The GLM Procedure

              Class Level Information

       Class         Levels    Values

       biomass            3    ph ss wc

       flow               3    High Low Med

       temp               3    80 140 200


      Number of Observations Read          54
      Number of Observations Used          54
```

```
                                The SAS System         22:11 Thursday, March 29, 2012   4

                               The GLM Procedure

Dependent Variable: logtar

                                             Sum of
         Source                      DF         Squares     Mean Square    F Value    Pr > F

         Model                       26     27.99679823      1.07679993       4.32    0.0002

         Error                       27      6.73606850      0.24948402

         Corrected Total             53     34.73286673


                         R-Square     Coeff Var      Root MSE    logtar Mean

                         0.806061      38.74141      0.499484       1.289276


         Source                      DF       Type I SS     Mean Square    F Value    Pr > F

         biomass                      2     19.02008298      9.51004149      38.12    <.0001
         flow                         2      2.11712410      1.05856205       4.24    0.0250
         temp                         2      0.68865546      0.34432773       1.38    0.2687
         biomass*flow                 4      1.19516923      0.29879231       1.20    0.3345
         biomass*temp                 4      2.10564395      0.52641099       2.11    0.1072
         flow*temp                    4      0.68748601      0.17187150       0.69    0.6060
         biomass*flow*temp            8      2.18263650      0.27282956       1.09    0.3975


         Source                      DF     Type III SS     Mean Square    F Value    Pr > F

         biomass                      2     19.02008298      9.51004149      38.12    <.0001
         flow                         2      2.11712410      1.05856205       4.24    0.0250
         temp                         2      0.68865546      0.34432773       1.38    0.2687
         biomass*flow                 4      1.19516923      0.29879231       1.20    0.3345
         biomass*temp                 4      2.10564395      0.52641099       2.11    0.1072
         flow*temp                    4      0.68748601      0.17187150       0.69    0.6060
         biomass*flow*temp            8      2.18263650      0.27282956       1.09    0.3975
                               The GLM Procedure
                              Least Squares Means
                    Adjustment for Multiple Comparisons: Tukey

                                     logtar      LSMEAN
                          biomass          LSMEAN      Number

                          ph           0.67519508           1
                          ss           1.10082328           2
                          wc           2.09181041           3


                        Least Squares Means for effect biomass
                         Pr > |t| for H0: LSMean(i)=LSMean(j)

                              Dependent Variable: logtar

                     i/j              1             2             3

                        1                      0.0423        <.0001
                        2        0.0423                      <.0001
                        3        <.0001        <.0001


                               logtar
                 biomass          LSMEAN      95% Confidence Limits
```

```
ph            0.675195        0.433634     0.916756
ss            1.100823        0.859262     1.342384
wc            2.091810        1.850250     2.333371


       Least Squares Means for Effect biomass

            Difference         Simultaneous 95%
               Between      Confidence Limits for
i    j           Means       LSMean(i)-LSMean(j)

1    2       -0.425628       -0.838438    -0.012819
1    3       -1.416615       -1.829425    -1.003806
2    3       -0.990987       -1.403797    -0.578178


   Tukey Comparison Lines for Least Squares Means of biomass

 LS-means with the same letter are not significantly different.

                 logtar               LSMEAN
                 LSMEAN    biomass    Number

       A     2.09181041    wc              3

       B     1.10082328    ss              2

       C     0.67519508    ph              1

                 The GLM Procedure
                Least Squares Means
      Adjustment for Multiple Comparisons: Tukey

                        logtar      LSMEAN
          flow          LSMEAN      Number

          High      1.49051257           1
          Low       1.02002547           2
          Med       1.35729071           3


           Least Squares Means for effect flow
           Pr > |t| for H0: LSMean(i)=LSMean(j)

                Dependent Variable: logtar

   i/j              1              2              3

      1                       0.0231         0.7061
      2        0.0231                        0.1253
      3        0.7061         0.1253


               logtar
 flow          LSMEAN      95% Confidence Limits

 High        1.490513        1.248952     1.732073
 Low         1.020025        0.778465     1.261586
 Med         1.357291        1.115730     1.598852


           Least Squares Means for Effect flow

            Difference         Simultaneous 95%
               Between      Confidence Limits for
i    j           Means       LSMean(i)-LSMean(j)
```

```
     1    2        0.470487        0.057677     0.883297
     1    3        0.133222       -0.279588     0.546031
     2    3       -0.337265       -0.750075     0.075544


    Tukey Comparison Lines for Least Squares Means of flow

LS-means with the same letter are not significantly different.

                     logtar           LSMEAN
                     LSMEAN    flow    Number

            A     1.4905126    High         1
            A
       B    A     1.3572907    Med          3
       B
       B          1.0200255    Low          2

                 The GLM Procedure
                Least Squares Means
       Adjustment for Multiple Comparisons: Tukey

                        logtar      LSMEAN
          temp          LSMEAN      Number

          80        1.44516422           1
          140       1.24139095           2
          200       1.18127359           3


             Least Squares Means for effect temp
             Pr > |t| for H0: LSMean(i)=LSMean(j)

                  Dependent Variable: logtar

        i/j             1             2             3

           1                     0.4497        0.2692
           2        0.4497                     0.9308
           3        0.2692       0.9308


                 logtar
      temp       LSMEAN      95% Confidence Limits

      80         1.445164        1.203603     1.686725
      140        1.241391        0.999830     1.482952
      200        1.181274        0.939713     1.422834


             Least Squares Means for Effect temp

                Difference        Simultaneous 95%
                   Between      Confidence Limits for
     i    j          Means       LSMean(i)-LSMean(j)

     1    2        0.203773       -0.209036     0.616583
     1    3        0.263891       -0.148919     0.676700
     2    3        0.060117       -0.352692     0.472927


    Tukey Comparison Lines for Least Squares Means of temp

LS-means with the same letter are not significantly different.

                  logtar            LSMEAN
                  LSMEAN    temp    Number
```

```
                   A     1.4451642    80          1
                   A     1.2413909    140         2
                   A     1.1812736    200         3
```

High heating value analysis

```
                                 The GLM Procedure

                              Class Level Information

                       Class         Levels    Values

                       biomass            3    ph ss wc

                       flow               3    High Low Med

                       temp               3    80 140 200


                      Number of Observations Read          54
                      Number of Observations Used          54

                                 The GLM Procedure

Dependent Variable: hhv

                                            Sum of
         Source                      DF         Squares     Mean Square    F Value    Pr > F

         Model                       26     36.29199769      1.39584607       5.12    <.0001

         Error                       27      7.35740557      0.27249650

         Corrected Total             53     43.64940327


                  R-Square     Coeff Var      Root MSE      hhv Mean

                  0.831443      10.68770      0.522012      4.884231


         Source                      DF       Type I SS     Mean Square    F Value    Pr > F

         biomass                      2     30.01359032     15.00679516      55.07    <.0001
         flow                         2      0.45480814      0.22740407       0.83    0.4450
         temp                         2      1.59078242      0.79539121       2.92    0.0712
         biomass*flow                 4      1.08350451      0.27087613       0.99    0.4277
         biomass*temp                 4      0.59733997      0.14933499       0.55    0.7020
         flow*temp                    4      1.31054628      0.32763657       1.20    0.3326
         biomass*flow*temp            8      1.24142605      0.15517826       0.57    0.7934


         Source                      DF     Type III SS     Mean Square    F Value    Pr > F

         biomass                      2     30.01359032     15.00679516      55.07    <.0001
         flow                         2      0.45480814      0.22740407       0.83    0.4450
         temp                         2      1.59078242      0.79539121       2.92    0.0712
         biomass*flow                 4      1.08350451      0.27087613       0.99    0.4277
         biomass*temp                 4      0.59733997      0.14933499       0.55    0.7020
         flow*temp                    4      1.31054628      0.32763657       1.20    0.3326
         biomass*flow*temp            8      1.24142605      0.15517826       0.57    0.7934

                                 The GLM Procedure
                                Least Squares Means
                      Adjustment for Multiple Comparisons: Tukey
```

```
                                     LSMEAN
        biomass      hhv LSMEAN      Number

        ph           4.66221937           1
        ss           4.10263160           2
        wc           5.88784193           3


       Least Squares Means for effect biomass
        Pr > |t| for H0: LSMean(i)=LSMean(j)

              Dependent Variable: hhv

   i/j            1            2            3

      1                    0.0091        <.0001
      2       0.0091                     <.0001
      3       <.0001       <.0001


biomass      hhv LSMEAN      95% Confidence Limits

ph             4.662219        4.409763     4.914675
ss             4.102632        3.850176     4.355088
wc             5.887842        5.635386     6.140298


       Least Squares Means for Effect biomass

            Difference        Simultaneous 95%
               Between      Confidence Limits for
i    j           Means       LSMean(i)-LSMean(j)

1    2        0.559588        0.128159     0.991016
1    3       -1.225623       -1.657051    -0.794194
2    3       -1.785210       -2.216639    -1.353782


   Tukey Comparison Lines for Least Squares Means of biomass

LS-means with the same letter are not significantly different.

                                      LSMEAN
          hhv LSMEAN    biomass    Number

        A     5.8878419    wc              3

        B     4.6622194    ph              1

        C     4.1026316    ss              2

               The GLM Procedure
              Least Squares Means
      Adjustment for Multiple Comparisons: Tukey

                                   LSMEAN
         flow      hhv LSMEAN      Number

         High      4.75602954           1
         Low       4.96584895           2
         Med       4.93081441           3


        Least Squares Means for effect flow
        Pr > |t| for H0: LSMean(i)=LSMean(j)

              Dependent Variable: hhv
```

```
        i/j              1             2             3

           1                      0.4600        0.5804
           2        0.4600                      0.9779
           3        0.5804        0.9779


      flow      hhv LSMEAN      95% Confidence Limits

      High        4.756030        4.503574     5.008486
      Low         4.965849        4.713393     5.218305
      Med         4.930814        4.678358     5.183270


             Least Squares Means for Effect flow

                 Difference         Simultaneous 95%
                    Between      Confidence Limits for
     i    j           Means       LSMean(i)-LSMean(j)

     1    2       -0.209819       -0.641248     0.221609
     1    3       -0.174785       -0.606213     0.256644
     2    3        0.035035       -0.396394     0.466463


    Tukey Comparison Lines for Least Squares Means of flow

LS-means with the same letter are not significantly different.

                                         LSMEAN
                   hhv LSMEAN    flow    Number

              A     4.9658490    Low          2
              A
              A     4.9308144    Med          3
              A
              A     4.7560295    High         1

                      The GLM Procedure
                     Least Squares Means
          Adjustment for Multiple Comparisons: Tukey

                                         LSMEAN
               temp      hhv LSMEAN      Number

               80        4.83869298           1
               140       4.70052208           2
               200       5.11347786           3


             Least Squares Means for effect temp
             Pr > |t| for H0: LSMean(i)=LSMean(j)

                   Dependent Variable: hhv

        i/j              1             2             3

           1                      0.7098        0.2717
           2        0.7098                      0.0626
           3        0.2717        0.0626


      temp      hhv LSMEAN      95% Confidence Limits

      80          4.838693        4.586237     5.091149
      140         4.700522        4.448066     4.952978
      200         5.113478        4.861022     5.365934
```

```
                         Least Squares Means for Effect temp

                             Difference        Simultaneous 95%
                                Between      Confidence Limits for
                 i    j           Means       LSMean(i)-LSMean(j)

                 1    2        0.138171       -0.293258     0.569599
                 1    3       -0.274785       -0.706213     0.156644
                 2    3       -0.412956       -0.844384     0.018473


                Tukey Comparison Lines for Least Squares Means of temp

            LS-means with the same letter are not significantly different.

                                                      LSMEAN
                               hhv LSMEAN    temp    Number

                          A     5.1134779    200          3
                          A
                          A     4.8386930    80           1
                          A
                          A     4.7005221    140          2
```

Hydrogen composition analysis

```
                                 The GLM Procedure

                              Class Level Information

                         Class         Levels    Values

                         biomass            3    ph ss wc

                         flow               3    High Low Med

                         temp               3    80 140 200


                        Number of Observations Read          54
                        Number of Observations Used          54

                                 The GLM Procedure

Dependent Variable: H2

                                                 Sum of
         Source                      DF         Squares     Mean Square    F Value    Pr > F

         Model                       26     20.84031869      0.80155072       0.72    0.7931

         Error                       27     29.87843941      1.10660887

         Corrected Total             53     50.71875810


                          R-Square     Coeff Var      Root MSE       H2 Mean

                          0.410900      12.01950      1.051955      8.752067


         Source                      DF       Type I SS     Mean Square    F Value    Pr > F

         biomass                      2      3.15482591      1.57741295       1.43    0.2579
         flow                         2      0.11559932      0.05779966       0.05    0.9492
         temp                         2      1.60724738      0.80362369       0.73    0.4930
```

```
biomass*flow              4      6.44654154      1.61163538       1.46    0.2429
biomass*temp              4      0.78321338      0.19580334       0.18    0.9483
flow*temp                 4      4.09139490      1.02284873       0.92    0.4644
biomass*flow*temp         8      4.64149626      0.58018703       0.52    0.8277


Source                   DF     Type III SS     Mean Square    F Value    Pr > F

biomass                   2      3.15482591      1.57741295       1.43    0.2579
flow                      2      0.11559932      0.05779966       0.05    0.9492
temp                      2      1.60724738      0.80362369       0.73    0.4930
biomass*flow              4      6.44654154      1.61163538       1.46    0.2429
biomass*temp              4      0.78321338      0.19580334       0.18    0.9483
flow*temp                 4      4.09139490      1.02284873       0.92    0.4644
biomass*flow*temp         8      4.64149626      0.58018703       0.52    0.8277

                                 The GLM Procedure
                                Least Squares Means
                      Adjustment for Multiple Comparisons: Tukey

                                          Standard                  LSMEAN
          biomass       H2 LSMEAN            Error    Pr > |t|      Number

          ph           9.08458269      0.24794812      <.0001           1
          ss           8.51718586      0.24794812      <.0001           2
          wc           8.65443364      0.24794812      <.0001           3


                        Least Squares Means for effect biomass
                         Pr > |t| for H0: LSMean(i)=LSMean(j)

                               Dependent Variable: H2

                   i/j             1             2             3

                      1                     0.2555        0.4481
                      2        0.2555                     0.9193
                      3        0.4481       0.9193


                biomass       H2 LSMEAN      95% Confidence Limits

                ph             9.084583        8.575835     9.593330
                ss             8.517186        8.008438     9.025933
                wc             8.654434        8.145686     9.163181


                        Least Squares Means for Effect biomass

                             Difference         Simultaneous 95%
                                Between      Confidence Limits for
                i    j            Means       LSMean(i)-LSMean(j)

                1    2         0.567397       -0.302015     1.436809
                1    3         0.430149       -0.439263     1.299561
                2    3        -0.137248       -1.006660     0.732164


               Tukey Comparison Lines for Least Squares Means of biomass

            LS-means with the same letter are not significantly different.

                                                    LSMEAN
                             H2 LSMEAN    biomass    Number

                        A     9.0845827    ph             1
                        A
                        A     8.6544336    wc             3
```

```
           A
           A     8.5171859    ss              2

                    The GLM Procedure
                   Least Squares Means
          Adjustment for Multiple Comparisons: Tukey

                            Standard                  LSMEAN
flow       H2 LSMEAN           Error    Pr > |t|      Number

High      8.77131735      0.24794812      <.0001           1
Low       8.68828366      0.24794812      <.0001           2
Med       8.79660119      0.24794812      <.0001           3


            Least Squares Means for effect flow
            Pr > |t| for H0: LSMean(i)=LSMean(j)

                  Dependent Variable: H2

       i/j             1             2             3

          1                     0.9696        0.9971
          2        0.9696                     0.9489
          3        0.9971        0.9489


     flow       H2 LSMEAN      95% Confidence Limits

     High        8.771317        8.262570     9.280065
     Low         8.688284        8.179536     9.197031
     Med         8.796601        8.287854     9.305349


            Least Squares Means for Effect flow

                Difference        Simultaneous 95%
                   Between      Confidence Limits for
    i    j           Means       LSMean(i)-LSMean(j)

    1    2        0.083034       -0.786378     0.952445
    1    3       -0.025284       -0.894696     0.844128
    2    3       -0.108318       -0.977729     0.761094


   Tukey Comparison Lines for Least Squares Means of flow

LS-means with the same letter are not significantly different.

                                        LSMEAN
                   H2 LSMEAN    flow    Number

            A     8.7966012    Med          3
            A
            A     8.7713173    High         1
            A
            A     8.6882837    Low          2

                    The GLM Procedure
                   Least Squares Means
          Adjustment for Multiple Comparisons: Tukey

                            Standard                  LSMEAN
temp       H2 LSMEAN           Error    Pr > |t|      Number

80        8.71806930      0.24794812      <.0001           1
140       8.55983248      0.24794812      <.0001           2
200       8.97830043      0.24794812      <.0001           3
```

```
             Least Squares Means for effect temp
             Pr > |t| for H0: LSMean(i)=LSMean(j)

                    Dependent Variable: H2

        i/j              1             2             3

           1                      0.8943        0.7409
           2        0.8943                      0.4672
           3        0.7409        0.4672


      temp       H2 LSMEAN      95% Confidence Limits

      80          8.718069        8.209322     9.226817
      140         8.559832        8.051085     9.068580
      200         8.978300        8.469553     9.487048


             Least Squares Means for Effect temp

                 Difference         Simultaneous 95%
                    Between      Confidence Limits for
     i    j           Means       LSMean(i)-LSMean(j)

     1    2        0.158237       -0.711175     1.027649
     1    3       -0.260231       -1.129643     0.609181
     2    3       -0.418468       -1.287880     0.450944


    Tukey Comparison Lines for Least Squares Means of temp

LS-means with the same letter are not significantly different.

                                         LSMEAN
                    H2 LSMEAN    temp    Number

              A     8.9783004    200          3
              A
              A     8.7180693    80           1
              A
              A     8.5598325    140          2
```

Carbon monoxide composition Analysis

```
                      The GLM Procedure

                   Class Level Information

            Class         Levels    Values

            biomass            3    ph ss wc

            flow               3    High Low Med

            temp               3    80 140 200


           Number of Observations Read          54
           Number of Observations Used          54

                      The GLM Procedure
```

```
Dependent Variable: CO

                                               Sum of
         Source                      DF         Squares     Mean Square    F Value    Pr > F

         Model                       26     562.2471901      21.6248919       5.52    <.0001

         Error                       27     105.8577037       3.9206557

         Corrected Total             53     668.1048938


                          R-Square     Coeff Var      Root MSE       CO Mean

                          0.841555      11.30266      1.980065      17.51858


         Source                      DF       Type I SS     Mean Square    F Value    Pr > F

         biomass                      2     447.9002747     223.9501373      57.12    <.0001
         flow                         2      14.2576067       7.1288034       1.82    0.1816
         temp                         2      27.4628336      13.7314168       3.50    0.0444
         biomass*flow                 4      16.4696363       4.1174091       1.05    0.4000
         biomass*temp                 4      11.5737852       2.8934463       0.74    0.5743
         flow*temp                    4      18.8029935       4.7007484       1.20    0.3340
         biomass*flow*temp            8      25.7800602       3.2225075       0.82    0.5904


         Source                      DF     Type III SS     Mean Square    F Value    Pr > F

         biomass                      2     447.9002747     223.9501373      57.12    <.0001
         flow                         2      14.2576067       7.1288034       1.82    0.1816
         temp                         2      27.4628336      13.7314168       3.50    0.0444
         biomass*flow                 4      16.4696363       4.1174091       1.05    0.4000
         biomass*temp                 4      11.5737852       2.8934463       0.74    0.5743
         flow*temp                    4      18.8029935       4.7007484       1.20    0.3340
         biomass*flow*temp            8      25.7800602       3.2225075       0.82    0.5904
                                            The GLM Procedure
                                           Least Squares Means
                                 Adjustment for Multiple Comparisons: Tukey

                                                  Standard                   LSMEAN
                   biomass       CO LSMEAN           Error    Pr > |t|      Number

                   ph           16.7205255       0.4667057      <.0001           1
                   ss           14.4587035       0.4667057      <.0001           2
                   wc           21.3765086       0.4667057      <.0001           3


                                   Least Squares Means for effect biomass
                                    Pr > |t| for H0: LSMean(i)=LSMean(j)

                                          Dependent Variable: CO

                            i/j              1              2              3

                               1                       0.0054         <.0001
                               2        0.0054                        <.0001
                               3        <.0001         <.0001


                         biomass       CO LSMEAN      95% Confidence Limits

                         ph             16.720525       15.762925    17.678126
                         ss             14.458703       13.501102    15.416304
                         wc             21.376509       20.418908    22.334110
```

```
            Least Squares Means for Effect biomass

                 Difference        Simultaneous 95%
                    Between      Confidence Limits for
     i    j           Means       LSMean(i)-LSMean(j)

     1    2        2.261822        0.625353     3.898291
     1    3       -4.655983       -6.292452    -3.019514
     2    3       -6.917805       -8.554274    -5.281336


  Tukey Comparison Lines for Least Squares Means of biomass

LS-means with the same letter are not significantly different.

                                          LSMEAN
                  CO LSMEAN    biomass    Number

             A     21.37651    wc              3

             B     16.72053    ph              1

             C     14.45870    ss              2
                      The GLM Procedure
                     Least Squares Means
          Adjustment for Multiple Comparisons: Tukey

                             Standard                    LSMEAN
 flow        CO LSMEAN          Error    Pr > |t|      Number

 High       16.8605425      0.4667057      <.0001           1
 Low        17.5806042      0.4667057      <.0001           2
 Med        18.1145909      0.4667057      <.0001           3


             Least Squares Means for effect flow
             Pr > |t| for H0: LSMean(i)=LSMean(j)

                    Dependent Variable: CO

        i/j             1             2             3

           1                     0.5277        0.1581
           2        0.5277                     0.7007
           3        0.1581       0.7007


      flow       CO LSMEAN      95% Confidence Limits

      High       16.860543       15.902942    17.818144
      Low        17.580604       16.623003    18.538205
      Med        18.114591       17.156990    19.072192


             Least Squares Means for Effect flow

                 Difference        Simultaneous 95%
                    Between      Confidence Limits for
     i    j           Means       LSMean(i)-LSMean(j)

     1    2       -0.720062       -2.356531     0.916407
     1    3       -1.254048       -2.890517     0.382421
     2    3       -0.533987       -2.170456     1.102482
```

```
    Tukey Comparison Lines for Least Squares Means of flow

LS-means with the same letter are not significantly different.

                                         LSMEAN
                    CO LSMEAN    flow    Number

               A     18.11459    Med          3
               A
               A     17.58060    Low          2
               A
               A     16.86054    High         1

                      The GLM Procedure
                     Least Squares Means
          Adjustment for Multiple Comparisons: Tukey

                             Standard                     LSMEAN
 temp       CO LSMEAN           Error    Pr > |t|      Number

 80        17.2070536       0.4667057      <.0001           1
 140       16.8436372       0.4667057      <.0001           2
 200       18.5050467       0.4667057      <.0001           3


             Least Squares Means for effect temp
             Pr > |t| for H0: LSMean(i)=LSMean(j)

                    Dependent Variable: CO

        i/j             1             2             3

           1                     0.8470        0.1400
           2       0.8470                      0.0461
           3       0.1400        0.0461


      temp       CO LSMEAN      95% Confidence Limits

      80         17.207054       16.249453    18.164655
      140        16.843637       15.886036    17.801238
      200        18.505047       17.547446    19.462648


             Least Squares Means for Effect temp

                 Difference         Simultaneous 95%
                    Between      Confidence Limits for
     i    j           Means       LSMean(i)-LSMean(j)

     1    2        0.363416       -1.273053     1.999885
     1    3       -1.297993       -2.934462     0.338476
     2    3       -1.661409       -3.297879    -0.024940


    Tukey Comparison Lines for Least Squares Means of temp

LS-means with the same letter are not significantly different.

                                           LSMEAN
                      CO LSMEAN    temp    Number

                 A     18.50505    200          3
                 A
            B    A     17.20705    80           1
            B
            B          16.84364    140          2
```

Tar Individual analysis – prairie hay, sorghum biomass and wood chips

Prairie Hay

```
         Obs     day     flow    temp     tar     hhv      H2       CO

           1    21212    Low       80    2.89    4.93     8.47    18.57
           2    21412    Low       80    3.42    4.68     8.00    16.44
           3    21412    Low      140    0.79    4.10     8.34    14.27
           4    21512    Low      140    1.05    4.50     7.32    15.89
           5    21612    Low      200    1.05    5.43    10.45    20.15
           6    21612    Low      200    0.53    4.87     8.71    17.26
           7    22312    Med       80    2.98    4.47     8.86    15.93
           8    22412    Med       80    3.68    4.69     9.89    16.56
           9    21812    Med      140    1.58    5.23    10.19    19.30
          10    21812    Med      140    2.46    4.17     8.40    14.89
          11    21912    Med      200    0.70    4.92    10.62    16.96
          12    21912    Med      200    2.28    4.34     7.15    17.57
          13    22012    High      80    2.81    4.42     9.73    15.42
          14    22112    High      80    4.21    4.32     9.69    14.28
          15    22112    High     140    3.51    5.15    10.25    17.90
          16    22212    High     140    2.81    4.21     8.17    15.71
          17    22212    High     200    2.81    5.00     9.86    18.00
          18    22312    High     200    1.87    4.50     9.41    15.88
                              The SAS System                   15:16

                             The GLM Procedure
```

```
Dependent Variable: tar

                                     Sum of
Source                      DF      Squares     Mean Square    F Value    Pr > F

Model                        8  17.83240000      2.22905000       5.20    0.0118

Error                        9   3.85665000      0.42851667

Corrected Total             17  21.68905000


              R-Square     Coeff Var      Root MSE      tar Mean

              0.822184      28.44078      0.654612      2.301667


Source                      DF    Type I SS     Mean Square    F Value    Pr > F
```

```
flow                   2      5.73123333      2.86561667       6.69    0.0166
temp                   2     10.27823333      5.13911667      11.99    0.0029
flow*temp              4      1.82293333      0.45573333       1.06    0.4282


Source                DF     Type III SS     Mean Square    F Value    Pr > F

flow                   2      5.73123333      2.86561667       6.69    0.0166
temp                   2     10.27823333      5.13911667      11.99    0.0029
flow*temp              4      1.82293333      0.45573333       1.06    0.4282



                        The GLM Procedure
                       Least Squares Means
              Adjustment for Multiple Comparisons: Tukey

                                       LSMEAN
                    flow      tar LSMEAN      Number

                    High      3.00333333          1
                    Low       1.62166667          2
                    Med       2.28000000          3


                  Least Squares Means for effect flow
                  Pr > |t| for H0: LSMean(i)=LSMean(j)

                       Dependent Variable: tar

              i/j           1           2           3

                 1                    0.0132       0.1902
                 2       0.0132                    0.2428
                 3       0.1902       0.2428


              flow     tar LSMEAN      95% Confidence Limits

              High       3.003333        2.398785     3.607882
              Low        1.621667        1.017118     2.226215
              Med        2.280000        1.675452     2.884548


                  Least Squares Means for Effect flow
```

```
              Difference       Simultaneous 95%
                Between      Confidence Limits for
      i    j     Means       LSMean(i)-LSMean(j)

      1    2    1.381667      0.326455    2.436878
      1    3    0.723333     -0.331878    1.778545
      2    3   -0.658333     -1.713545    0.396878


                    The SAS System
                  The GLM Procedure
                 Least Squares Means
        Adjustment for Multiple Comparisons: Tukey

   Tukey Comparison Lines for Least Squares Means of flow

LS-means with the same letter are not significantly different.

                              LSMEAN
                  tar LSMEAN   flow   Number

              A    3.0033333   High      1
              A
         B    A    2.2800000   Med       3
         B
         B         1.6216667   Low       2


                       The SAS System


                  The GLM Procedure
                 Least Squares Means
        Adjustment for Multiple Comparisons: Tukey

                           LSMEAN
            temp    tar LSMEAN    Number

            80      3.33166667      1
            140     2.03333333      2
            200     1.54000000      3


             Least Squares Means for effect temp
             Pr > |t| for H0: LSMean(i)=LSMean(j)
```

```
              Dependent Variable: tar

        i/j          1          2          3

          1                0.0184     0.0027
          2       0.0184              0.4272
          3       0.0027     0.4272


       temp     tar LSMEAN     95% Confidence Limits

       80        3.331667       2.727118    3.936215
       140        2.033333       1.428785    2.637882
       200        1.540000       0.935452    2.144548


            Least Squares Means for Effect temp

                Difference       Simultaneous 95%
                  Between      Confidence Limits for
       i    j        Means       LSMean(i)-LSMean(j)

       1    2       1.298333       0.243122    2.353545
       1    3       1.791667       0.736455    2.846878
       2    3       0.493333      -0.561878    1.548545


                   The GLM Procedure
                  Least Squares Means
         Adjustment for Multiple Comparisons: Tukey

      Tukey Comparison Lines for Least Squares Means of temp

   LS-means with the same letter are not significantly different.

                              LSMEAN
              tar LSMEAN    temp    Number

           A    3.3316667    80          1

           B    2.0333333    140         2
           B
           B    1.5400000    200         3
```

Sorghum Biomass

```
                   Obs     day     flow    temp     tar     hhv      H2       CO

                     1    30712    Low       80    5.09    4.13     9.80    13.55
                     2    31512    Low       80    2.28    4.63     8.53    15.73
                     3    30812    Low      140    2.81    3.98     7.81    14.60
                     4    31312    Low      140    2.63    3.40     8.77    10.93
                     5    31212    Low      200    2.81    6.14     9.49    21.62
                     6    31312    Low      200    1.40    4.13     8.58    14.81
                     7    22812    Med       80    1.58    4.02     7.60    12.77
                     8    30812    Med       80    2.46    4.54     9.22    17.17
                     9    30912    Med      140    4.21    3.16     7.53    11.31
                    10    31212    Med      140    1.58    3.88     9.10    14.13
                    11    30712    Med      200    2.28    4.92    11.21    17.37
                    12    31012    Med      200    7.02    4.36     8.06    17.55
                    13    22412    High      80    3.51    3.28     7.94    11.69
                    14    22512    High      80    3.33    4.06     8.72    14.13
                    15    31412    High     140    2.11    3.89     9.32    13.51
                    16    22712    High     140    5.96    4.00     7.45    13.69
                    17    22712    High     200    3.51    3.28     7.00    11.71
                    18    22812    High     200    5.61    4.05     7.18    14.00

                                 The SAS System                   15:16 Friday, March 30,
2012  39

                                The GLM Procedure

                             Class Level Information

                          Class         Levels    Values

                          flow               3    High Low Med

                          temp               3    80 140 200


                          Number of Observations Read          18
                          Number of Observations Used          18


                                The GLM Procedure

Dependent Variable: tar
```

```
                           Sum of
Source               DF       Squares     Mean Square    F Value    Pr > F

Model                 8     15.32580000     1.91572500      0.58    0.7719

Error                9     29.67020000     3.29668889

Corrected Total          17     44.99600000


           R-Square     Coeff Var      Root MSE      tar Mean

           0.340604      54.30744      1.815679      3.343333


Source               DF      Type I SS     Mean Square    F Value    Pr > F

flow                2      4.31123333      2.15561667       0.65    0.5431
temp                 2      1.74310000      0.87155000       0.26    0.7734
flow*temp              4      9.27146667      2.31786667       0.70    0.6093


Source               DF     Type III SS     Mean Square    F Value    Pr > F

flow                2      4.31123333      2.15561667       0.65    0.5431
temp                 2      1.74310000      0.87155000       0.26    0.7734
flow*temp              4      9.27146667      2.31786667       0.70    0.6093

                        The GLM Procedure
                       Least Squares Means
               Adjustment for Multiple Comparisons: Tukey

                                 LSMEAN
                  flow      tar LSMEAN      Number

                  High      4.00500000         1
                  Low       2.83666667         2
                  Med       3.18833333         3


                 Least Squares Means for effect flow
                 Pr > |t| for H0: LSMean(i)=LSMean(j)

                     Dependent Variable: tar

             i/j          1          2          3
```

```
         1              0.5295      0.7245
         2    0.5295                0.9403
         3    0.7245    0.9403


    flow     tar LSMEAN     95% Confidence Limits

    High      4.005000      2.328181     5.681819
    Low       2.836667      1.159848     4.513485
    Med       3.188333      1.511515     4.865152


            Least Squares Means for Effect flow

               Difference      Simultaneous 95%
                 Between     Confidence Limits for
    i    j        Means      LSMean(i)-LSMean(j)

    1    2      1.168333      -1.758477     4.095144
    1    3      0.816667      -2.110144     3.743477
    2    3     -0.351667      -3.278477     2.575144

                   The GLM Procedure
                  Least Squares Means
         Adjustment for Multiple Comparisons: Tukey

   Tukey Comparison Lines for Least Squares Means of flow

 LS-means with the same letter are not significantly different.

                           LSMEAN
              tar LSMEAN    flow    Number

         A     4.0050000    High       1
         A
         A     3.1883333    Med        3
         A
         A     2.8366667    Low        2

                   The GLM Procedure
                  Least Squares Means
         Adjustment for Multiple Comparisons: Tukey

                           LSMEAN
           temp      tar LSMEAN      Number
```

```
          80       3.04166667         1
          140       3.21666667         2
          200       3.77166667         3


         Least Squares Means for effect temp
         Pr > |t| for H0: LSMean(i)=LSMean(j)

              Dependent Variable: tar

     i/j          1          2          3

       1                  0.9848     0.7715
       2       0.9848                0.8591
       3       0.7715     0.8591


    temp      tar LSMEAN      95% Confidence Limits

    80         3.041667       1.364848     4.718485
    140         3.216667       1.539848     4.893485
    200         3.771667       2.094848     5.448485


         Least Squares Means for Effect temp

              Difference       Simultaneous 95%
                Between      Confidence Limits for
    i    j        Means      LSMean(i)-LSMean(j)

    1    2      -0.175000      -3.101811     2.751811
    1    3      -0.730000      -3.656811     2.196811
    2    3      -0.555000      -3.481811     2.371811

                  The GLM Procedure
                  Least Squares Means
        Adjustment for Multiple Comparisons: Tukey

    Tukey Comparison Lines for Least Squares Means of temp

  LS-means with the same letter are not significantly different.
```

```
                       LSMEAN
      tar LSMEAN    temp    Number

  A     3.7716667    200         3
  A
  A     3.2166667    140         2
  A
  A     3.0416667    80          1
```

Wood Chips

```
Obs    day     flow    temp    tar     hhv     H2      CO

  1   32012    Low       80    3.68    5.82    8.80   20.56
  2   32612    Low       80    6.67    5.76    8.28   20.01
  3   32512    Low      140    4.74    4.91    6.63   18.43
  4   32312    Low      140    9.12    6.41    9.78   22.80
  5   32212    Low      200    8.42    5.47    8.79   19.54
  6   32612    Low      200    6.84    6.11    9.83   21.31
  7   32412    Med       80   10.70    6.10    7.85   22.96
  8   32812    Med       80   27.37    5.93    8.24   23.92
  9   32312    Med      140   12.28    6.01    8.47   21.94
 10   32712    Med      140    8.25    5.72    8.41   20.84
 11   32512    Med      200   12.11    6.55    8.95   24.33
 12   32112    Med      200    4.04    5.74    8.59   20.58
 13   31912    High      80    4.74    5.38    8.83   18.60
 14   32112    High      80    8.60    5.93    8.48   21.43
 15   32012    High     140    3.51    5.49    8.92   19.63
 16   32712    High     140   16.84    6.41    9.21   23.43
 17   32212    High     200    8.60    6.25    9.19   22.75
 18   32412    High     200   12.28    5.98    8.53   21.73

                 The GLM Procedure

              Class Level Information

         Class       Levels    Values

         flow             3    High Low Med

         temp             3    80 140 200


         Number of Observations Read          18
```

```
                         Number of Observations Used         18

                                   The GLM Procedure

Dependent Variable: tar

                                         Sum of
        Source                  DF         Squares     Mean Square    F Value    Pr > F

        Model                    8     263.1039111      32.8879889       0.99    0.4984

        Error                    9     298.0032500      33.1114722

        Corrected Total         17     561.1071611


                     R-Square     Coeff Var      Root MSE      tar Mean

                     0.468901      61.36419      5.754257      9.377222


        Source                  DF       Type I SS     Mean Square    F Value    Pr > F

        flow                     2     104.4400444      52.2200222       1.58    0.2587
        temp                     2       8.0535444       4.0267722       0.12    0.8869
        flow*temp                4     150.6103222      37.6525806       1.14    0.3984


        Source                  DF     Type III SS     Mean Square    F Value    Pr > F

        flow                     2     104.4400444      52.2200222       1.58    0.2587
        temp                     2       8.0535444       4.0267722       0.12    0.8869
        flow*temp                4     150.6103222      37.6525806       1.14    0.3984

                                   The GLM Procedure
                                  Least Squares Means
                         Adjustment for Multiple Comparisons: Tukey

                                                 LSMEAN
                               flow     tar LSMEAN      Number

                               High      9.0950000           1
                               Low       6.5783333           2
                               Med      12.4583333           3
```

```
            Least Squares Means for effect flow
            Pr > |t| for H0: LSMean(i)=LSMean(j)

               Dependent Variable: tar

       i/j          1          2          3

        1                   0.7369     0.5879
        2        0.7369                0.2335
        3        0.5879     0.2335


      flow     tar LSMEAN     95% Confidence Limits

      High      9.095000      3.780818    14.409182
      Low       6.578333      1.264152    11.892515
      Med      12.458333      7.144152    17.772515


            Least Squares Means for Effect flow

               Difference       Simultaneous 95%
                 Between      Confidence Limits for
      i   j       Means       LSMean(i)-LSMean(j)

      1   2     2.516667      -6.758995   11.792328
      1   3    -3.363333     -12.638995    5.912328
      2   3    -5.880000     -15.155662    3.395662

                   The GLM Procedure
                  Least Squares Means
          Adjustment for Multiple Comparisons: Tukey

     Tukey Comparison Lines for Least Squares Means of flow

  LS-means with the same letter are not significantly different.

                               LSMEAN
                 tar LSMEAN    flow    Number

            A    12.458333    Med        3
            A
            A     9.095000    High       1
            A
            A     6.578333    Low        2
```

```
                  The GLM Procedure
                 Least Squares Means
        Adjustment for Multiple Comparisons: Tukey

                             LSMEAN
           temp     tar LSMEAN     Number

           80      10.2933333        1
           140      9.1233333        2
           200      8.7150000        3


           Least Squares Means for effect temp
           Pr > |t| for H0: LSMean(i)=LSMean(j)

                Dependent Variable: tar

     i/j          1          2          3

       1                  0.9344     0.8845
       2      0.9344                 0.9917
       3      0.8845      0.9917


   temp     tar LSMEAN     95% Confidence Limits

   80       10.293333       4.979152    15.607515
   140       9.123333       3.809152    14.437515
   200       8.715000       3.400818    14.029182


           Least Squares Means for Effect temp

             Difference       Simultaneous 95%
               Between      Confidence Limits for
   i    j       Means       LSMean(i)-LSMean(j)

   1    2     1.170000      -8.105662    10.445662
   1    3     1.578333      -7.697328    10.853995
   2    3     0.408333      -8.867328     9.683995

                  The GLM Procedure
                 Least Squares Means
        Adjustment for Multiple Comparisons: Tukey

  Tukey Comparison Lines for Least Squares Means of temp
```

```
LS-means with the same letter are not significantly different.

                      LSMEAN
     tar LSMEAN    temp    Number

A     10.293333    80         1
A
A      9.123333    140        2
A
A      8.715000    200        3
```