Biomass Gasification for Power and Fuel Applications using a Bench-Scale Bubbling Fluidized Bed Gasifier

by

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A dissertation submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

Auburn, Alabama
May 10, 2015

Keywords: Gasification, switchgrass, torrefied biomass, olivine, and ash content

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Abstract

Today fossil fuels are a major source of energy. Coal is used extensively around the world for power applications, while petroleum products are used to fulfill liquid fuel needs. This extensive use of fossil fuels has led to environmental pollution, including release of greenhouse gases and hazardous impact on human health. These factors combined with the possibility of the extinction of fossil fuels have led to the development of alternate and renewable sources of energy. Renewable resources like wind and solar provide an excellent option for alternative modes of electricity production. However, biomass is the only source which has a potential to fulfill not only our electric power needs but also liquid fuel demands. Lignocellulosic biomass such as agricultural and forest waste are found in abundance in the southeastern U.S. It can be processed into fuel via either a biochemical or thermochemical route. A popular thermochemical process, gasification, yields a gaseous fuel known as synthesis gas or "syngas", composed primarily of a mixture of carbon monoxide and hydrogen, which can be further converted into liquid fuel via Fischer-Tropsch synthesis or fermentation. The syngas composition depends upon several factors such as type of biomass used, type of gasifier selected, type of bed material in the gasifier, gasifying media used and the operating condition (temperature, pressure, and equivalence ratio). These factors affect the primary syngas composition and the amount of tar and contaminants released during the gasification process, which need to be controlled for downstream use of the syngas produced.

This dissertation is presented as a series of three chapters, each of which represents a manuscript that has been submitted for archival publication. The content of these chapters is

preceded by an overarching introductory commentary that includes an exhaustive survey of the literature. The dissertation ends with a segment that indicates an overall summary of key conclusions and a series of recommendations on possible extensions of this effort.

Among different types of lignocellulosic biomass, energy crops such as switchgrass are attractive because they can be grown on marginal lands with minimal maintenance and in a short period. In this dissertation, gasification of switchgrass has been studied in Chapter 3. The objective of this study is to understand the effect of temperature (790, 935 and 1000˚C), equivalence ratio (0.21, 0.24, 0.27), biomass ash content (2.71, 3.19, 4.59%), and feed rate (3.63, 6.38, 9.34 g/min) on switchgrass gasification in a bench-scale bubbling fluidized bed gasifier with sand as bed material. In this study, nitrogen was used as a fluidizing agent and oxygen was used as a gasifying agent. The effect of process variables were evaluated in terms of (i) product yield, (ii) syngas components, (iii) carbon balance, (iv) syngas energy content, and (v) contaminants. It is shown that carbon monoxide (CO) and hydrogen (H_2) yields increased with an increase in temperature resulting in an increase in energy content of the syngas. The CO and H_2 yield increased with an increase in ER. This was due to the decomposition of acetylene in the presence of excess oxygen. The gas yield was not affected by an increase in the ER in the range under study (0.21 to 0.27). The ash content in the range of 2.71 to 4.59% did not affect syngas composition and syngas yield, These results obtained from the ash content study were unique, it can be said that a bubbling fluidized bed gasifier can efficiently handle a biomass ash content (up to 4.6 wt%) material, without significantly affecting the performance or the syngas composition. The increase in biomass feed rate (g/min) helped improve the volumetric concentrations of primary components in the syngas, thereby improving the syngas heating value. However, the overall yield of components per kg of biomass, and the carbon balance were not affected; suggesting that the conversion of biomass was independent of feed rate.

The focus of Chapter 4 is on gasification of switchgrass with a bench-scale bubbling fluidized bed gasifier using naturally occurring olivine as a bed material (or in-situ catalyst). Olivine primarily contains iron and magnesium silicate and is found in abundance on earth. As in the sand study presented in Chapter 3, the study was carried out to understand the effect of temperature (790, 935 and 1000˚C) and equivalence ratio, ER, (0.20, 0.25, 0.30 ERs) with olivine as bed material on i) product yield, ii) syngas components, iii) syngas energy, iv) the carbon balance and v) the energy efficiencies. The data obtained were then compared with that of sand as a bed material. It was found that with an increase in temperature, the CO and H_2 yield increased, while the CO_2 and methane yield decreased. With an increase in ER, the CO_2 and water yield increased due to oxidation of CO and hydrogen in presence of increased oxygen. When compared with use of sand as bed material, the olivine use resulted in higher concentration of CO, H_2 and CH_4 at 790°C. However, with increase in temperature the sand performed better, resulting in gas with higher energy content and higher concentration of CO, H_2 and CH_4. Olivine did not reduce the tar yield from switchgrass. The elutriation and thermal decomposition of olivine particles accompanied by coking of the olivine in the reactor could be the possible reason for the unexpectedly ordinary performance of olivine.

Lastly in Chapter 5, gasification of thermally pretreated biomass has been studied. Torrefied biomass has higher C:O ratio, resulting in improved heating value and reduced hygroscopic nature of the biomass, thus enabling longer storage times. In the southeastern United States, pine is abundant and has been identified as a potential feedstock for energy production. Thus, torrefaction of pine has been proposed to improve the properties of pine. The objective of

this component of the study was to understand the performance of the torrefied biomass as a gasification fuel in a bench-scale bubbling fluidized bed gasifier. As expected the CO and H_2 concentrations increased and CH_4 concentration decreased significantly with an increase in temperature; while with an increase in ER, only the CO_2 concentrations increased in the syngas. The performance of torrefied pine was comparable with pine and switchgrass under similar experimental conditions. Torrefied pine gasification led to much higher char yield (more than twice) than pine i.e. lower carbon conversion; however, it produced less than half as much tar and ammonia.

Acknowledgements

I would like to thank my advisors, Dr. Sushil Adhikari and Dr. Sushil Bhavnani for their guidance, support and encouragement. This journey would have been very difficult without their support. During toughest times, the tremendous help and encouragement they provided will always be appreciated. I aspire to be a researcher like you both and I would like to emulate your teaching and research style in future. I would like to sincerely thank my committee members, Dr. Oladiran Fasina, Dr. Roy Knight, and Dr. Amnon Meir for their valuable comments and suggestions. I would also like to thank Dr. Maobin Tu for graciously accepting to be my external reader.

I am extremely grateful to Electric Power Research Institute (EPRI) and Integrated Biomass Supply System (IBSS) for providing funding for this research project.

Additionally, I would like to thank Dr. Steve Taylor and the Department of Biosystems Engineering for providing world class facilities and resources for my research. I would like to thank Ms. Joy Brown, Ms. Linda Newton, Ms. Kelley Terry and Ms. Genta Stanfield for being extremely helpful. Also, I would like to thank Christian Broadbeck, Jonathan Griffith, James Johnson, Dawayne 'Doc' Flynn and Bobby Epling for all the help with the gasifier. Special thanks to Ryan Baker for his help with gasification work. I would like to acknowledge Dr. Nourredine Abdoulmoumine and Vaishnavi Srinivasan for being extremely helpful and supportive.

My deepest gratitude to my research group colleagues and Dr. Fasina's research group for all their support and help. Special thanks to my friends Hiral and Bhavin Vadgama for being my Auburn family, and being there for me through all difficult times. Thanks to my grandparents, Late

Mrs. Nirmala and Mr. Dattatraya Kulkarni, and Late Mrs. Sumati and Mr. Anant Sirsikar, for making my childhood memorable, for being there for me when I knew nothing. To my cousin Ashin Kekre for helping ever since I came to US, thank you very much. My sister-in-law Swapnali and her husband Ashish Dalvi, thank you for being there for me from oceans away. To my brother Atul Kulkarni and sister-in-law Vidula Patgaonkar, thank you very much for your love, endless encouragement and support, sorry for the late night calls for help with homework, I really appreciate all your help. Most importantly, my Mom and Dad, Mrs. Sucheta & Mr. Shashank Kulkarni, for loving me unconditionally, believing in me and my abilities, for being my constant source of inspiration, always standing strong with me and letting me achieve my dreams without any restrictions. My father-in-law, Mr. Pravin Tamhane, who has been a tremendous help and inspiration, who has always supported my interest in work and education, I cannot thank you enough. My loving daughter Anika Tamhane, who has let me work late night, early morning, on weekends without ever complaining and made me laugh with her silly jokes. My dear husband, Nikhil Tamhane, I do not have words to express my gratitude, for letting me follow my dreams, for encouraging me and standing with me through all. You are the source of my professional aspirations; I would like to emulate you in my professional life, thank you for everything. Lastly, I whole heartedly dedicate this work to my late mother-in-law, Mrs. Mohini Tamhane, whom I love and miss a lot, who was a strong woman, wonderful teacher, and a strong advocate of women's equality and independence.

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Chapter 1

Introduction

1.1 Background

Currently, fossil fuels are being used extensively as a primary source of fuel and power all over the world. With the growing economic development worldwide, energy demand has increased leading to an increase in fossil fuel consumption. Specifically, the economic development in China, India and other southeastern Asian countries has caused a steady increase in the demand as well as cost of fossil fuels.(Wolfram et al., 2012) According to the world energy outlook of 2013, coal is the cheapest source of electricity in many countries around the world with the global coal demand projected to increase by 17% by 2035.(Agency, 2013) In the United States, 68% of electricity is derived from fossil fuel sources with coal, natural gas and petroleum accounting for 39, 27 and 19% of the total electricity produced in 2013, respectively as illustrated in Figure 1.1.

In addition to electricity production, fossil fuels, particularly petroleum-derived fuels, are the major source of transportation fuels in the United States. In 2012, it was estimated that 18.6 million barrels per day of crude petroleum was consumed. Out of this, around 40% was imported and half of the crude oil imported came from the western hemisphere with Canada and Mexico as leading suppliers.(Administration, 2011) Crude oil imports from the western hemisphere supply chain are stable as these countries are politically and economically stable.

While this stability and other geopolitical ties makes western hemisphere oil markets (Canada and Mexico) reliable for U.S. future demand, a different and less reliable partnership characterizes the relationship with other crude oil suppliers in the Middle East, Venezuela and other regions.

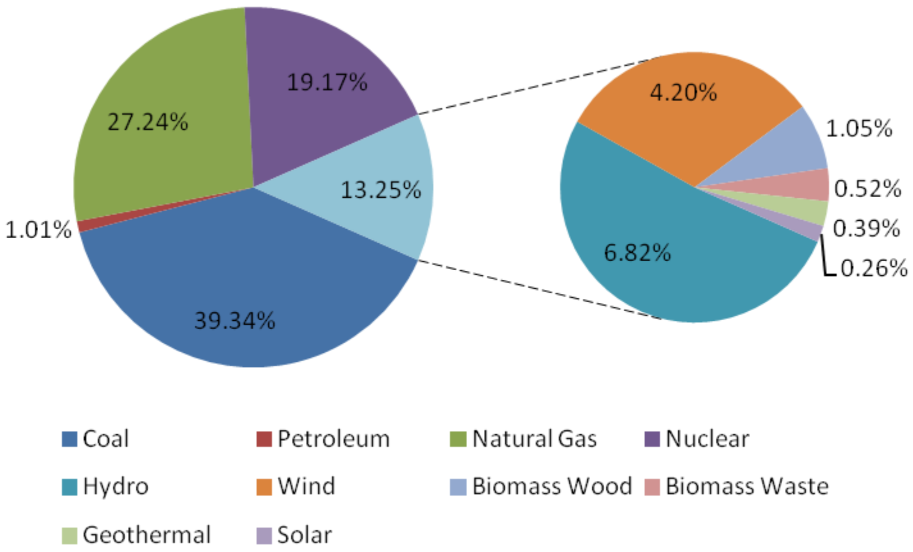


Figure 1.1: Sources of electricity generation in the U.S. in 2013(Administration, 2014)

These tumultuous relationships are regarded as potential national security problems due to the heavy dependence on fossil fuels. Efforts have been made to decrease this dependence with foreign oil imports declining since 2005.(Administration, 2012) However, due to the U.S. crude oil needs, dependence on foreign oil imports will likely continue for years to come especially since the largest oil reserves known are in the Middle East. Therefore, in the long-term, continued reliance on foreign oil is problematic since it might jeopardize U.S. national security. To counter the dependence on foreign oil, an increase in offshore drilling and fracking of shale (natural) gas has been initiated. Even though natural gas is a fossil fuel, it burns cleaner than coal and other petroleum fuel and release lower amount of greenhouse gases. However, in recent months, the decline in oil prices from $100 to $43 a barrel, has drastically affected the natural gas production due to availability of cheap petroleum crude from Middle East.

In the United States and elsewhere in the world, fossil fuels continue to be the major source of energy (heat and electricity) and transportation fuel. As the world population and economic development increase, fossil fuel reverses will be heavily tapped into to guarantee energy requirements. The increasing use of these major fossil fuels constitutes a great risk to their depletion. As an example, the coal reserves are projected to last up to 2112 and could possibly be the only fossil fuel left after the year 2042.(Agency, 2013; Shafiee and Topal, 2009) Consequently, the heavy dependence on fossil fuels, as primary energy source, is problematic in light of their forecasted depletion.

Environmentally, the use of fossil fuels raises challenges as well. Fossil fuels are the major contributors to the rising levels of carbon dioxide (CO_2), a greenhouse gas, in the atmosphere. At the current rate of emissions and taking into account the regulations undertaken by countries like U.S. and China, the CO_2 emissions are still expected to increase by 20% by 2035. This implies a rise of 3.6°C in the average global temperature, 1.6°C above the internationally agreed upon 2°C threshold.(Agency, 2013)

Environmental concerns due to increasing CO_2 emissions from fossil fuels, long term supply and national security issues are the major problems related to using fossil fuels. The United States, as well as many national and regional organizations worldwide, are aware of this problem and have taken steps to address these issues. One important method to address problems of related to fossil fuel usage is to promote the development of sustainable and renewable means to produce energy and fuel. In 2013, as illustrated in Figure 1.1, the contribution of renewable energy (including wind and hydrothermal) sources towards electricity production was around 13%. The largest share of the latter comes from hydroelectric and wind turbines which making up 84% of the total renewable energy sources. Biomass wood and biomass waste contributed only 1.2% of the total energy sources. Yet biomass is an abundant source of renewable feedstock for energy and fuel product. According to the U.S. Department of Energy (DOE), the U.S. can produce enough biomass to displace 30% of petroleum consumption in 2012. This highlights the present gap in biomass utilization for energy and fuel and the potential for future bio-based industries(Perlack et al., 2005).

1.2 Research motivation

Biomass is the only renewable resource for the production of liquid fuels and chemicals. When energy is obtained from biomass, CO_2 consumed during photosynthesis is recycled into the atmosphere, thus resulting in net zero carbon emissions. This is called a carbon neutral cycle. If biomass is supplied sustainably, the carbon neutral cycle resolves the environmental challenges of CO_2 emissions derived from fossil fuel and their nefarious effects on the global climate. Biomass can be converted to energy and fuel by various methods that general fit within two main approaches: (i) biochemical and (ii) thermochemical approaches. Figure 1.2 groups various biomass conversion technologies into these two main approaches.

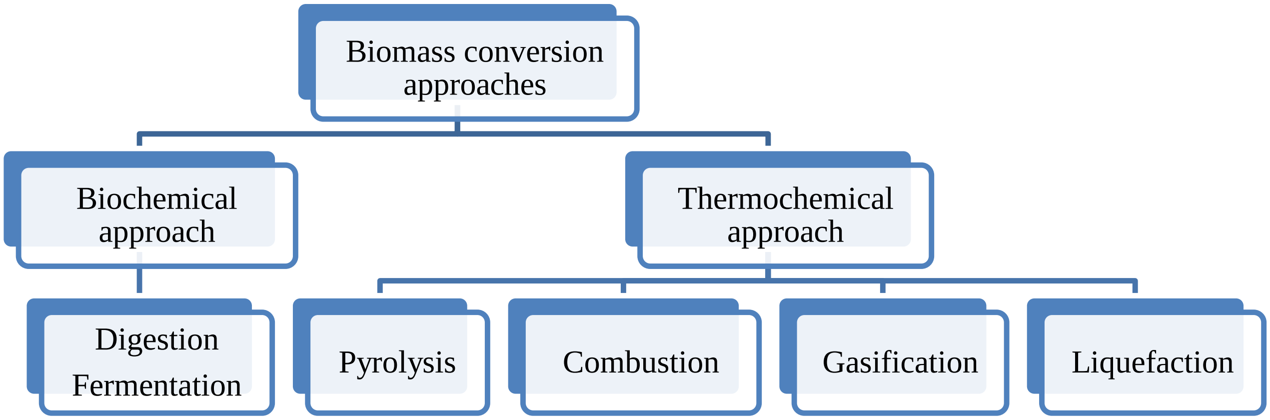


Figure 1.2: Classification of biomass conversion methods. Classification adapted from Regalbuto*(Regalbuto, 2009)*

The biochemical approach includes digestion (aerobic and anaerobic) and fermentation processes that take place with the help of microorganisms. While this approach has many merits, one major disadvantage is that some of these methods presently use sugar/grain based feedstocks that are also food sources thus leading to a food versus fuel dilemma.(Pimentel, 2003) To overcome the food vs. fuel debate, biochemical conversion of lignocellulosic biomass has been proposed. However, extensive labor and capital cost make it an expensive process.(Limayem and Ricke, 2012) The thermochemical conversion platform, which relies on thermal energy for conversion includes combustion, pyrolysis, liquefaction and gasification processes. The economic feasibility of producing fuel from biomass has been previously analyzed(Bridgwater, 1995), these studies have included the cost of equipment, cost of new technology, logistics(Caputo et al., 2005), biomass availability and supply(Perlack et al., 2005), along with primary and secondary products(Bridgwater, 2003), as well as potential to produce electricity and various other chemicals. All thermochemical processes are characterized by thermal decomposition of biomass into intermediate energy carriers that could be in the form of liquid, solid and gas products. Relative to the biochemical platform, thermochemical conversion technologies have the benefit of being feedstock independent as they are well suited for lignocellulosic biomass as well as other forms of biomass feedstocks.

1.3 Research rationale

This research project is centered on the investigation of an energy crop (switchgrass), and a pretreated woody biomass (torrefied pine) for conversion through the gasification process. The rationale for the selection of these feedstocks will be discussed in the next subsections, along with comparison between sand and olivine when used as bed material. As for gasification, it was selected because the main product of this process, syngas, a mixture of carbon monoxide and hydrogen, can be used in an array of applications from fuel synthesis via the Fischer-Tropsch process or methanol synthesis to produce power via combustion.

1.3.1 Rationale for selecting switchgrass as an energy crop

Ambitious targets for displacing fossil fuels with biomass resources to energy and fuel will require adapting the current biomass production scheme with increasing importance given to energy crops.(Sims et al., 2006a),(Downing et al., 2011) While agricultural residues and forest products will remain significant contributors, the largest share is expected to come from energy crops.(Sims et al., 2006a) Energy crops are important since growing them requires lower cost and maintenance relative to other biomass feedstocks. Additionally, they serve multiple purposes: they can be used for biochemical or thermochemical conversion, can be grown in shorter rotation than woody biomass and can improve soil health by incorporating carbon and nitrogen in the soil.(Sanderson et al., 1996a) Among potential energy crops in the United States, switchgrass (*Panicum viragatum*) is the most promising for several reasons. It is native to the prairie grass lands and its different varieties grow naturally all over the United States. It is a warm-season perennial grass that can be cultivated with high yields, low pesticide and fertilizer use, and on marginal lands. (Sanderson et al., 1996a), (Khanna et al., 2008) It has natural resistance to heat, cold, and drought, which has enabled its spread in North America.(Casler et al., 2007) A switchgrass variety, Alamo, was found to have natural resistance to the pests in the southeastern United States, thus reducing the cost of production. The warmer winters in southeast allow for switchgrass cultivation during the winter months providing a winter crop for the farmers which needs very little care and helps improve the quality of soil for the summer crop and extra income during winter months. Due to the expected pivotal role switchgrass will likely play in the future bio based economy, it was selected for this project.

1.3.2 **Rationale for selecting torrefied pine as a pretreated wood biomass**

Pine is the most abundant woody biomass in southern states and as such is a key feedstock for any gasification project in Alabama.(Perlack and Stokes, 2011) Torrefied pine is obtained through mild pyrolysis, a pretreatment process that occurs at 230-300°C in the absence of oxygen. This process, named torrefaction, improves properties such as energy content, grindability, hygroscopic nature and volatile matter.(Basu, 2010) The improvements in these properties are significant in the overall process. Increased energy content in torrefied pine makes it more suitable for blending with coal for co-feeding in existing infrastructures. Furthermore, its improved grindability and reduced hygroscopic nature could potentially reduce grinding energy and thus cost, and extend storage time due to reduced moisture absorption.(Bergman et al., 2005b) Finally, a decrease in volatile matter might impact tar formation, the highest impurity in syngas. Owing to the reasons above, and due to the limited availability of comprehensive data on torrefied pine air gasification, this feedstock was selected for this project.

1.3.3 **Rationale for selecting olivine as a bed material**

Olivine is primarily a silicate of iron and magnesium, which is widely available on earth. Before the use of olivine, some studies have referred to the role of iron in reducing the tar formed during gasification, which led to the testing of olivine as a bed material in fluidized bed gasification. Olivine has good attrition resistance, that means it is resistant to breakage, which is an important characteristic for a material to be used in the gasifier bed.(Rapagna et al., 2000) The iron present in the olivine forms iron oxides when heated in presence of air and during the gasification run the these iron oxide molecules react with heavy hydrocarbons which to reduce them into water and carbon dioxide.(Corella et al., 2004a),(Devi et al., 2005) This results in reduction in tar present in syngas, thus reducing the cost of syngas clean-up downstream. This gives olivine an advantage over sand. Therefore, olivine was chosen as an alternative bed material to sand.

1.4 Research objectives

The objective of this dissertation was to investigate the effect of biomass feedstocks (energy crop and pretreated biomass) on syngas and contaminants production as well as to study the effect of olivine as an alternative to sand as a bed material with switchgrass as a feedstock in the process.

1.4.1 Research goal 1

The first research goal was to understand the performance of switchgrass as a gasification fuel at different temperatures and equivalence ratios, to study the effect of higher amount of ash content in switchgrass on gasification products, and to study effect of feeding rate on concentration of syngas components in syngas.

1.4.2 Research goal 2

The second objective was to understand the performance of olivine as a bed material compared with sand, with high ash content material like switchgrass as gasification fuel. Effect of temperature and equivalence ratio on performance of olivine was also studied.

1.4.3 Research goal 3

The third objective was to understand the performance of pretreated feedstock (torrefied pine) as a gasification fuel. The performance of torrefied pine was studied at different temperature and equivalence ratio. A comparison was made between torrefied pine and performance of pine and switchgrass at similar experimental conditions.

1.5 Organization of dissertation

This dissertation has been presented as a series of three chapters, which are preceded by a detailed summary of literature review. Chapter 2 discusses the background for bio-energy production is provided. A detailed description of various thermochemical processes are provided in this chapter. Different types of gasifiers are compared with each other. A review of effect of various gasification parameters on syngas composition and contaminant yield has been included. These parameters include: type of gasifier under study, type of biomass, gasifying media, operating conditions (temperature and equivalence ratio), and type of bed material.

The third chapter presents the results obtained when switchgrass was gasified. The effect of temperature, equivalence ratio, ash content, and switchgrass feed rate on syngas profile, composition, energy content, mass and energy balance and contaminants were studied. In the fourth chapter, the effect of using olivine as the bed material and the corresponding impact on syngas composition, energy content, mass and energy balance and the contaminants at three temperatures and equivalence ratios have been discussed. The fifth chapter details the effect of biomass torrefaction (a pretreatment process) on syngas profile, composition, energy content, mass and energy balance, and contaminants at three different temperature and equivalence ratios. The performance of torrefied pine was compared with that of pine and switchgrass. Last chapter summarizes the conclusions of this study and further lists some recommendations for further research based on the conclusions from this research projects.

Chapter 2

Literature Review

2.1 Introduction

The heavy dependence of human society on fossil fuels has led to severe global warming signs and fossil fuel depletion. This has prompted various nations to research and develop alternatives to the fossil fuels via renewable energy sources. In the United States, the Energy Independence and Security Act (Independence, 2007) has laid out criteria for research and development of biofuels as one of the measures to tackle the growing concerns over consumption of fossil fuels.

The utilization of biomass to obtain energy is an ancient practice. The use of biomass for cooking and space-heating is still used in various developing nations. However, after the industrial revolution and discovery of coal, the heavy dependence on the forest in industrialized nations reduced. Further, with the introduction of crude petroleum and various chemicals which could be derived from it, the dependence shifted to fossil fuels.

Fossil fuels are formed by fossilization of biomass and other living organism under the layers of earth for millions of years. These reserves are finite and pose a definite threat of depletion in the future. A formula used to predict fossil fuel reserves predicted that the coal, oil, and gas would last 35, 37, and 107 years respectively(Shafiee and Topal, 2009). This gives a window of around 35 years for development of petroleum and oil alternative and around 100 years to find an alternative to coal. Along with depletion, the use of fossil fuel has led to global warming and climate change. The warming and melting of ice in Arctic and Antarctic regions has led to serious concerns of rise in water level and has threatened several major cities and ports across the world. The degrading air quality in several of the developing and densely populated economies around the world is due to heavy use of fossil fuels for energy and transport. Air pollution has led to serious health concerns in many Asian countries.

In the United States, there is a debate regarding production of bio-based fuel and food production, or, in other words, the food vs. fuel debate. However, due to the Green Revolution and increase in high yielding crops, several countries are becoming self-sufficient and in turn exporting the produce grown. Along with the higher production volumes, the large-scale transformation of land in order to facilitate row crop agriculture has led to a net reduction of carbon in the soil, and contributed to carbon in atmosphere through oxidation of soil organics (Haas et al., 1957)To tackle this issue the United States carried out a Conservation Reserve Protection (CRP) so that the producers could grow trees or grasses and harvest them. This could help fix soil erosion and depletion of nutrients from soil and provide grasses for use as biomass energy sources. Along with this, agricultural waste could also be used as an energy fuel.

The renewable energy to be developed depends on the natural availability of local resources. The southeastern United States is rich in forest resources, and the warmer winter provides an option of cultivating an energy crop during winter months. Energy production through various biomass species have been researched extensively around the world. This chapter presents a review of different types of biomass and corresponding thermal conversions using fluidized bed gasifiers to obtain a renewable form of energy.

2.2 Bioenergy

Biomass availability varies widely according to the geographic location and corresponding weather patterns. The development of a technology to convert several types of biomass into a uniform biofuel is extremely challenging. It requires an extensive study of various biomass types for the purpose of energy production.

Biomass was defined by the United Nations Framework Convention on Climate Change (UNFCCC, 2005) as follows:

> *a "non fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and bio-degradable organic fractions of industrial and municipal wastes."*

The formation of biomass is a result of photosynthesis of CO_2 and H_2O by sunlight in the presence of chlorophyll. The CO_2 formed by combustion of biomass derived fuel is reabsorbed by the biomass during photosynthesis and thus makes biomass a carbon neutral feedstock for energy production, this is can be seen in Figure 2.1.

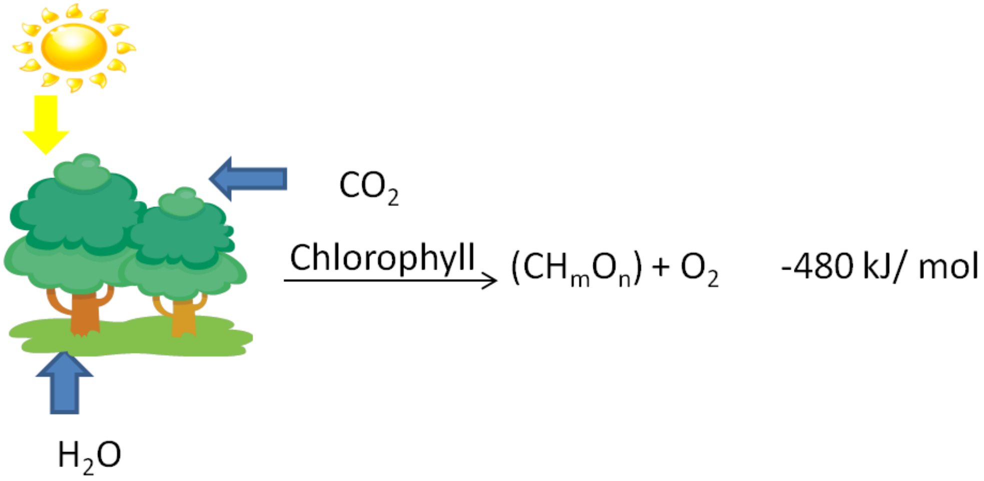


Figure 2.1: Pictorial depiction of photosynthesis

The biomass available has been classified mainly into two main categories; virgin and waste. Virgin biomass includes terrestrial and aquatic biomass, where some examples include forest biomass, grasses, and algae, while waste biomass includes municipal, agricultural, forestry, and industrial (biomass related) waste.

There are several advantages of using biomass as fuel, the most important one being the ability of biomass to recycle the CO_2 as shown in Figure 2.2. Increase in CO_2 emissions have been linked to increase in global temperatures, causing global warming and melting of ice caps in the Arctic and Antarctic regions. The CO_2 when released from use of fossilized biomass has caused an alarming climate change in several parts of the world. The CO_2 thus released through consumption of biofuels can be reabsorbed by the newly growing biomass via photosynthesis, thus reducing the threat to climate.

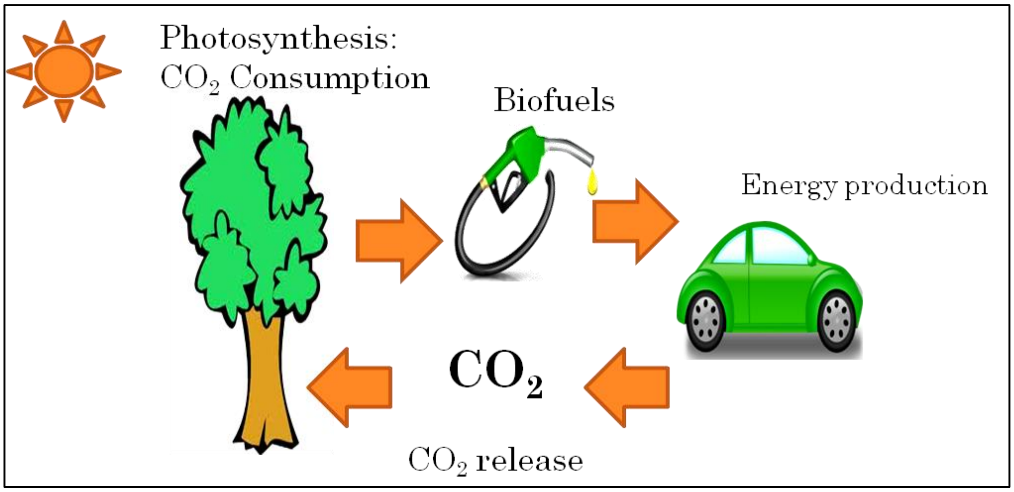


Figure 2.2: Pictorial depictions of Carbon dioxide recycle.

. The fossil fuels have high sulfur and nitrogen content. When energy is obtained from these sources the sulfur and nitrogen compounds are released in the atmosphere, which react to produce acids rain. The emission of carbon dioxide and methane from these sources are reason for increasing temperatures around the planet, which has led to climate change in many parts of the world.

Biomass is the widely available energy resource around the world, thus reducing the dependency on certain countries for fulfillment of energy demand. In the developed world the production of excess food crops resulting in surplus has resulted in restriction on cultivable land use. Energy crops could be grown on these lands and provide additional income for farmers. Depending on the type of crop chosen, the energy crops can help improve the quality of soil and reduce the amount of fertilizers and pesticides. Biomass cultivation for energy purposes can also help increase employment and benefit the economy,

Several technologies have been successfully implemented in obtaining energy from biomass. A conversion technique is selected based upon the type of biomass, form of energy desired and the end product. Energy from biomass can either be converted to heat/ power, or can be converted into liquid fuel. Industrial grade chemicals can also be derived from biomass via conversion processes.

As mentioned in the previous chapter, there are three main conversion techniques, biochemical, trans-esterification and thermochemical. In biochemical techniques, the biomass cellulosic (sugar cane, corn, wheat) and lignocellulosic biomass (switchgrass) is converted into liquid fuel (mostly ethanol) via fermentation or into gaseous fuel (mixture of CO_2 and CH_4) via digestion. Another method called trans-esterification, converts vegetable oil (used or produced via mechanical extraction) into biodiesel. Glycerol is a valuable by-product of this process. In thermochemical processes, heat is applied to the biomass in either presence or absence of oxygen, steam or carbon dioxide. Figure 2.3 gives a quick glance at these conversion technologies. The following section discusses the thermochemical conversion techniques in detail.

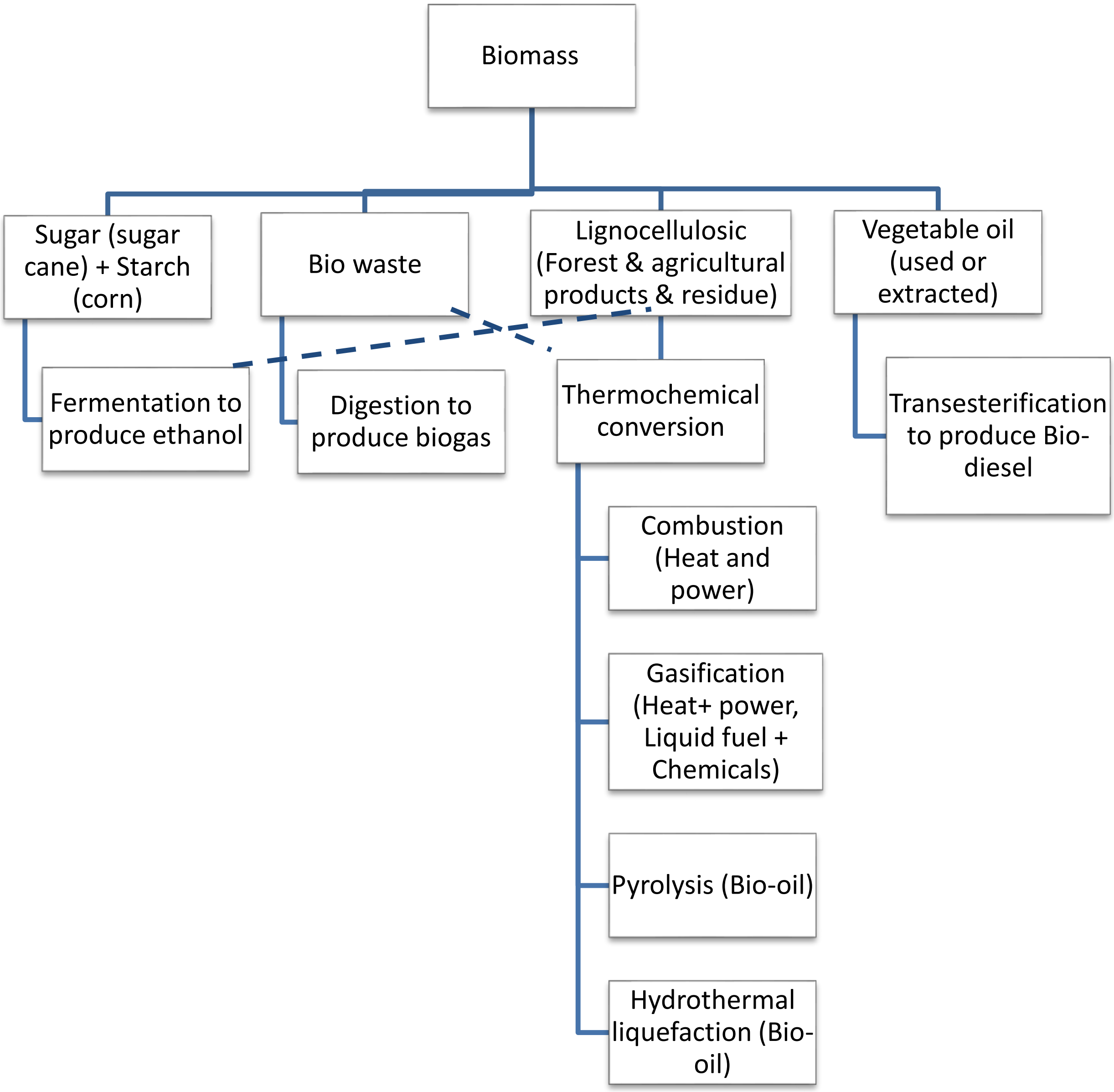


Figure 2.3: Various biomass conversion technologies and the respective bio-products obtained.

2.3 Thermochemical conversion techniques

Combustion is one of the oldest processes known to mankind to obtain energy for cooking and heating. It is an exothermic reaction between biomass and oxygen to produce H_2O and CO_2. The heat released during combustion is the largest source of energy for mankind. The heat obtained can be converted in to mechanical or electrical power. Technically any type of biomass can be used as feedstock for combustion, however, lower moisture content biomass is preferred. The biomass combustion usage ranges from small scale (e.g. domestic fireplace) up to large-scale power plant (up to 3000 MW)(Basu, 2010). Co-combustion of biomass with fuel in large-scale power plant has been determined as an attractive option by several studies(Baxter, 2005; Bridgwater, 1995)

In contrast to combustion, pyrolysis takes place in the absence of oxygen. It can be defined as a thermal decomposition of biomass into condensable and non-condensable gases and char. Condensable gases yield a liquid product stream referred to as bio-oil. The heating rate, residence time and temperature of pyrolysis can be selected to control the product distribution. There are three variations of pyrolysis: fast pyrolysis, slow pyrolysis and mild pyrolysis. Fast pyrolysis takes place at higher temperature relative to mild and slow pyrolysis (450-600°C) and higher heating rates (up 10,000°C/min).(Bridgwater and Peacocke, 2000; Diebold and Bridgwater, 1997)The aim of fast pyrolysis is to maximize liquid product or bio-oil. This achieved primarily by optimizing the temperature and using a short residence time (< 1s). Slow pyrolysis or carbonization is carried out between 300-450°C with slow heating rates between 5 to 10°C/min. It produces lower liquid and gas products and higher char yield relative to fast pyrolysis. The residual char has properties similar to charcoal and as such this process is often used to produce biomass-derived charcoal. Mild pyrolysis, or torrefaction, occurs at temperatures between 230-300°C. Mild pyrolysis is used as pretreatment step to alter the chemical composition of the biomass in order to improve fuel properties such as energy density, grindability and hygroscopic nature. The major product is the pyrolyzed or torrefied biomass followed by gases with virtually no liquid product.

Hydrothermal liquefaction is a process of obtaining liquid fuels from biomass by directly mixing biomass with water at high temperatures (300-350°C) and pressure (12-20MPa). Superheated water can also be used for this process. This process is well adapted to biomass feedstocks with high moisture content as it avoids the need for drying.

Gasification fits between combustion and pyrolysis in terms of oxygen utilization. Gasification produces predominantly a gaseous product referred to as producer gas or synthesis gas (syngas) when biomass is decomposed between 700-1000°C in limited supply of oxygen.(Basu, 2010) Syngas can either be directly burned to obtain heat power or can be converted into liquid fuels like gasoline and diesel by various synthetic routes. The syngas produced can also be expanded in a gas turbine to obtain electricity, combusted in the internal combustion engine or can be integrated with the combustion cycle to result in more efficient commercial technology. These various applications give gasification technology an edge over other thermochemical conversion processes. However, there are several challenges associated with development of this technology for large-scale energy production.(Basu, 2010; Bridgwater, 2003)

In the southeastern U.S., the extensive forest cover and ability to grow a winter crop (energy crop: switchgrass) provide us with year around supply of feedstock for energy from biomass. However, to develop gasification of biomass into a fully developed technology, it is important to understand the performance of different feedstocks during gasification, study the effect of pretreatment (torrefaction) on syngas composition and select the best available bed material.

2.4 Gasification

Gasification takes place in temperature range of 600 to 1100°C. During gasification the biomass is decomposed at high temperature and in oxygen deficient atmosphere. The resulting synthesis gas (syngas) is rich in CO and H_2. Some CO_2 and CH_4 are also obtained in syngas. There are several other contaminants and higher hydrocarbons generated in the syngas.

$$\text{Biomass} + O_2\ (\text{partial}) \longrightarrow CO + CO_2 + CH_4 + H_2 + \text{HCs} + \text{Tar} + \text{Contaminants}$$

Inside a gasifier the reactions are taking place simultaneously. The gasification steps can be categorized into four steps as shown in Figure 2.4.

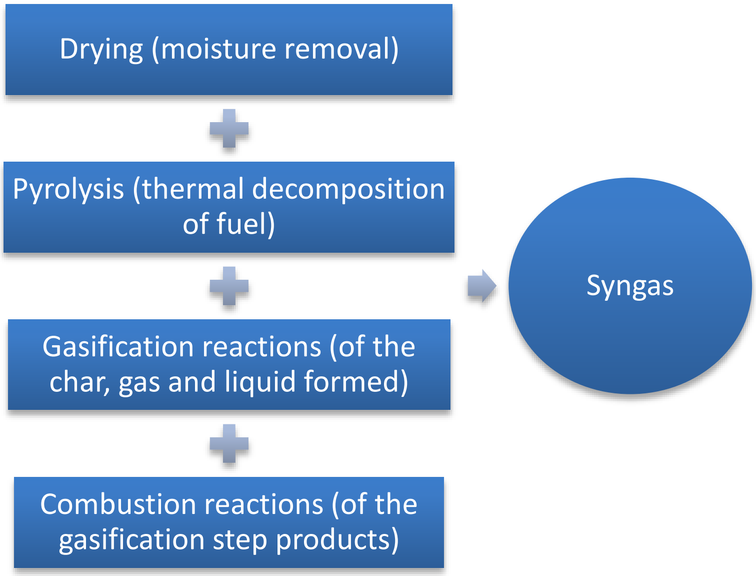


Figure 2.4: Steps involved in the gasification process.

The first step is drying or dehydration of biomass feedstock. Thermal conversion requires low moisture content (< 50%) biomass. Moisture removal requires 2260 kJ/ kg of energy during gasification, which is not recoverable and hence low moisture content is desirable. Thus for gasification the biomass moisture content should be ideally between 10 and 15% (McKendry, 2002b). Drying takes place as biomass is heated up inside the gasifier causing moisture evaporation from biomass at or above 100°C.

Biomass devolatilization mainly occurs during the pyrolysis step occurs between 150°C and 700°C. During this step, biomass is thermally broken down in the absence of oxygen, resulting in the formation of solid residue (char), gaseous products and "tars". Tars are defined as condensable hydrocarbon containing all organic compounds higher than molecular weight of benzene (78). (Haas et al., 1957) Partial oxidation or the gasification step occurs around 700 to 1500°C. During this step products formed at the previous step (thermal decomposition) undergo further partial oxidation to produce, carbon monoxide, steam, carbon dioxide, oxygen and hydrogen in the gasifier. The last step in gasification is char combustion which lead to the formation of carbon dioxide and carbon monoxide. These char combustion reactions are exothermic in nature and provide part of the heat required for the drying and pyrolysis steps. These reactions occur between 800°C to 1100°C.

At the particulate level, the thermal decomposition beings when the biomass particles enter into the gasifier. The particles lose the moisture, followed by devolatilization and release of volatiles, char particles, and liquid condensate (tars). The char produced undergoes the char further reaction with oxygen and hydrogen producing CO, CO_2, CH_4 and these gases react with each other in the gas phase determining the gas concentration. Figure 2.5 depicts these steps at the particulate level and the corresponding reactions taking place are explained below.

The carbon present in the char formed during pyrolysis (thermal decomposition) step undergoes reactions with oxygen to produce CO and CO_2 as shown by Equation (2.1) and (2.2). The CO reacts with the oxygen to produce CO_2. Further, the CO_2 undergoes reaction with char (C) to produce more CO (the Boudouard reaction) as shown in Equation (2.4). The carbon in char also reacts with the steam produced during gasification via a reversible reaction known as the water gas reaction, to produce CO and H_2, two of the main components of syngas and is shown in Equation 5.

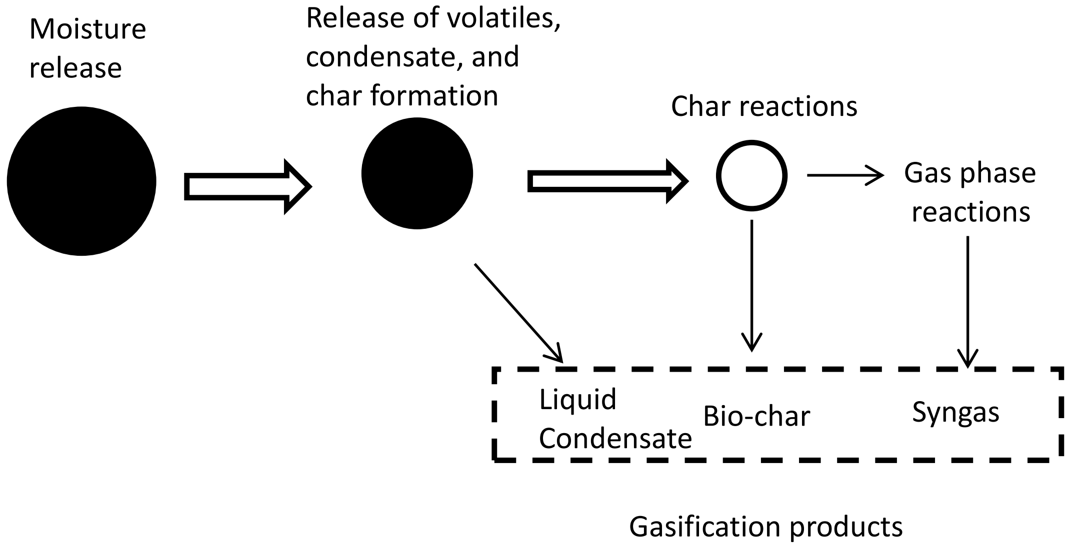


Figure 2.5: Gasification of biomass particle and release of gasification products

$$C + 0.5\,O_2 \longrightarrow CO \tag{2.1}$$

$$C + O_2 \longrightarrow CO_2 \tag{2.2}$$

$$CO + 0.5O_2 \longrightarrow CO_2 \tag{2.3}$$

$$C + CO_2 \longrightarrow 2CO \tag{2.4}$$

$$C + H_2O \longrightarrow CO + H_2 \tag{2.5}$$

The hydrogen released during devolatilization undergoes reactions with oxygen to produces steam as shown in Equation (2.6), which reacts with other gasification products. The hydrogen also reacts with the char in reactor to produce methane as represented by Equation (2.7).

$$H_2 + 0.5O_2 \longrightarrow H_2O \tag{2.6}$$

$$C + 2H_2 \longrightarrow CH_4 \tag{2.7}$$

Equations (2.8) through (2.10) represent the various methane formation reactions. The methane formed can undergo an oxidation as shown in Equation (2.11) or undergo reforming with steam or CO_2 to produce more CO and H_2 as shown via reversible Equation (2.8) and Equation (2.12).

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O \tag{2.8}$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \tag{2.9}$$

$$2CO + 2H_2 \longleftrightarrow CH_4 + CO_2 \tag{2.10}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{2.11}$$

$$CH_4 + 0.5O_2 \longleftrightarrow CO + 3H_2 \tag{2.12}$$

Most char reactions are endothermic, except for reactions (2.1), (2.2), (2.6) & (2.7), which are exothermic in nature. Increase in temperature favors the Boudouard reaction and reverse methanation thus increasing CO & H_2(Di Blasi, 2009), while increase in ER increases the combustion of char, methane and hydrogen leading to an increase in complete combustion products (carbon dioxide and steam) concentrations. Along with temperature and ER the reactions are also influenced by the gasifying media. The rate of char-oxygen reaction (2.1) is fastest of all the oxygen reactions and thus consumes the oxygen quickly. The rate of char-steam reaction follows char-oxygen reaction (3 to 8 times slower), while the char-CO_2 reaction (Boudouard reaction) is six to seven orders of magnitude slower (Smoot and Smith, 1985) than char-oxygen Thus indicating oxygen is most reactive of all the gasifying agents.

2.5 Parameters affecting gasification

There are several parameters that affect the gasification process. The concentration of syngas obtained depends on the type of gasifier, the type of feedstock used, the gasification parameters etc. Selection of feedstock is dependent up on the availability of biomass in any region. The desired downstream application defines the syngas composition. This section presents a thorough review of the parameters affecting gasification and the syngas composition.

2.5.1 **Types of gasifier**

There are several types of gasifiers. They are primarily categorized into three main categories based on the type of bed used inside the gasifier. The categories are as shown below.

I. Fixed or moving bed
  i. Updraft gasifier
  ii. Downdraft gasifier
II. Fluidized bed
  i. Bubbling bed gasifier
  ii. Circulating bed gasifier
  iii. Twin bed
III. Entrained flow

The fixed bed or moving bed gasifiers as they are called could be further classifier as updraft or downdraft depending on the direction of biomass feed and direction of syngas flow as shown in Figure 2.6. In an updraft gasifier, the biomass is fed from the top and syngas is collected from the top as well. However, in the downdraft configuration, the biomass is fed from top and the syngas produced is also collected at the bottom of the gasifier.

An updraft gasifier is easy to construct and use. The reactor is heated and biomass is fed from the top of the reactor as shown in Figure 2.6, decomposing while moving downward in the reactor to produce the syngas., This syngas moves up through the reactor to the exhaust. However, during this process, it interacts with the biomass particles at lower temperature, which are undergoing pyrolysis or devolatilization. This infuses the condensable liquid with vapors released during the pyrolysis phase into the escaping syngas, while the biomass particles absorb the heat from the syngas. Thus the syngas obtained from the updraft gasifier is at lower temperature and with higher amount of tar. The updraft gasifiers can effectively handle high ash and moisture content feedstock.(Basu, 2010)

On the other hand, the downdraft gasifiers produce syngas at higher temperature and lower tar content, this is a result of design of a downdraft gasifier, in which the biomass is fed from the top of the gasifier and syngas is collected at the bottom. The high temperatures at the bottom of the reactor cause thermal cracking of the tar particles producing relatively cleaner gas. Use of high ash content biomass causes agglomeration, leading to blockage of syngas exhaust. Downdraft gasifiers can handle forest and agricultural biomass and residue efficiently. Since the syngas has low ash content, it can be further used as a fuel in IC engines(Basu, 2010).

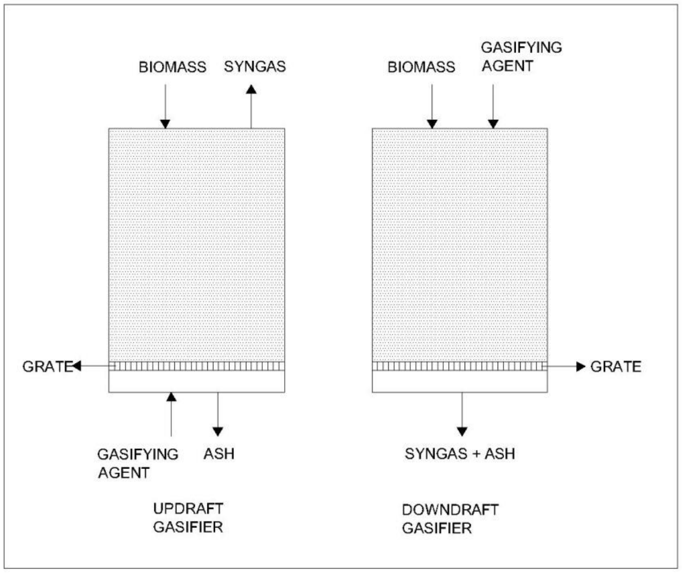


Figure 2.6: Fixed bed gasifiers.

Fluidized bed gasifiers are more tolerant with respect to the feedstock when compared with fixed bed gasifiers. Granular material is used for the bed, which is fluidized using a gasifying medium such as air, steam or nitrogen. There is an excellent mixing and temperature uniformity in the bed, and the gasification zones cannot be distinguished. There are two types of fluidized bed gasifier: the circulating fluidized bed and bubbling fluidized bed gasifier (shown in Figure 5). The fluidized bed gasifiers are more tolerant towards high ash content material, this is because the fluidized bed does not let the ash melt inside the gasifier due to lower operating temperatures (700 to 1000°C), thus making ash removal relatively easy. Thus high ash samples can be gasified easier with fluidized bed gasifiers than with fixed bed. One of the major disadvantages of fluidized bed gasifiers is lower solids conversion due to intermixing of completely gasified particles and partially gasified particles.

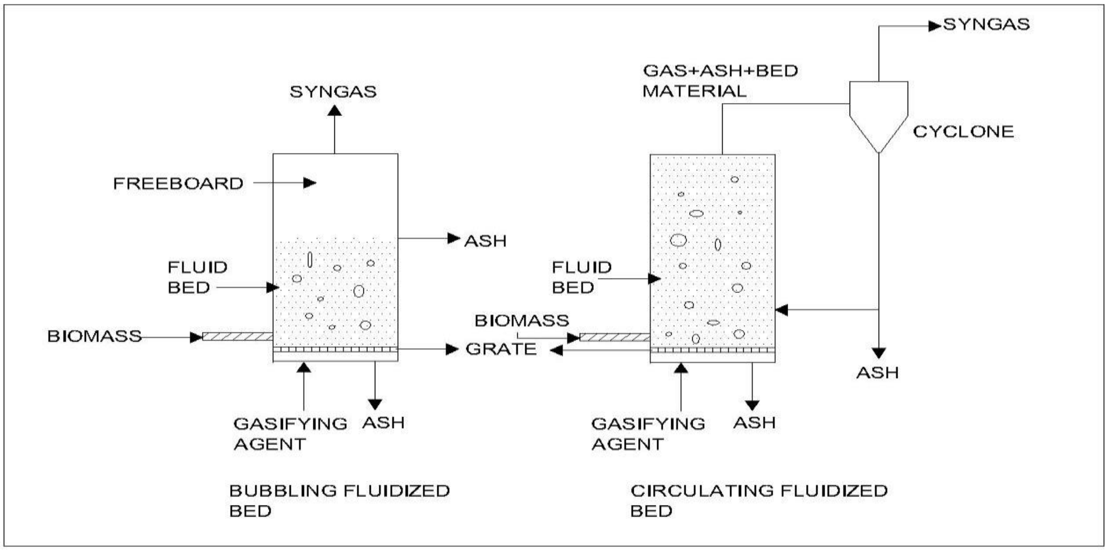


Figure 2.7: Fluidized bed gasifier

Bubbling fluidized bed gasifiers:

In a bubbling fluidized bed gasifier (as shown in Figure 2.7), a solid material like sand is used as a bed material. A fluidizing media like air or steam is flown over a grind to help fluidize this material. The minimum velocity at which this material shows fluidity is called minimum fluidization velocity (U_{mf}). When this velocity is further increased, a bubbling regime is obtained inside the bed material, and is called minimum bubbling velocity (U_{mb}). In the literature, the superficial velocity (U_s) used was reported to be 2-4 times the U_{mb} to ensure proper fluidization. A bed material like sand, which can be classified as Geldart's group B material (Appendix A), has minimum fluidization velocity equal to the minimum bubbling velocity. The bubbling of bed material provides excellent mixing and heat transfer to the fuel which results in decomposition of biomass and release of gasification products. A comparison of fluidization parameters of some fluidized bed gasifiers used for research purposes and as reported in literature has been listed in Table 2.1.

Table 2.1 Comparison of various fluidization parameters.

Author	Size	Bed material	Fluidization parameters
Lim and Alimudin(Lim and Alimuddin, 2008)	Gasifier 0.4 dia x 3 m ht, free board ht 0.9	Sand, 425 to 600 µm, ρ = 1520 kg/m³	Static bed height = 0.5 m, 50 to 200 kg/hr, Umf = 0.24 m/s, wood chips (30mm x 30mm) size.
Gil et al(Gil et al., 1999a).	Gasifier 0.15 m dia x 3.2 m ht	Dolomite0.4 to 1.0 mm, or sand -500 to 320 µm.	Umf ~ 2m/s (residence time 1.3 to 1. S)Biomass feed rate: 5.20 kg/hr

			Sand Umf = 0.1 m/s, Us = 0.19 to 0.22 m/s
Makwana et al.(Makwana et al., 2015)	Gasifier: dia 0.21m and ht 1.6 m	Sand, 400 to 600 μ,ρ = 1470 kg/m$_3$	Bed ht 0.3m, Umf = 0.11 m/s, Us = 0.31, Ut = 3.2, Uff = 1.9 m/s (Biomass: Rice husk ground)
Boateng et al.(Boateng et al., 1992)	Gasifier: 0.078 m dia, ht 0.52m	Sand, 655 μm,	Umf = 0.23 m/s, Us = 0.65 m/s, Biomass feed = 2.2 kg/h, (Pyrolysis)
Lv et al.(Lv et al., 2004b)	Gasifier: dia 0.040 m, ht 1.4 m, freeboard = 0.6m	Silica sand (30 g)	Flow rate of air: 83 LPM to 11.8 LPM

In an entrained flow gasifier, the pulverized fuel particles are suspended in a stream of oxidant. Entrained flow gasifiers are widely used for coal gasification. The fuel used in an entrained flow gasifier needs to be very small in size, as residence time is very low and it is very difficult to grind the biomass into such fine particles (Basu, 2010). Table 2.2 lists the characteristics of various gasifiers. It can be seen that though construction of fixed bed gasifiers is much easier, they have issues of plugging and slugging. On the other hand, fluidized bed gasifiers are difficult to construct and have better fuel mixing, although with entrainment issues.

Table 2.2. Advantages and disadvantages of different types of gasifiers(Bridgwater, 1995)

Type of gasifier	Advantages	Disadvantages
A. Downdraft gasifier	Simple and reliable, Easy construction, Clean gas (low tar), High exit temperature.	Design specific for feedstock, low moisture fuel needed, high ash can cause slugging & plugging

		scale up potential low
B. Updraft gasifier	Simple robust Low exit temperature High thermal efficiency Can accommodate moderate ash content Good scale-up potential	High tar content Gas clean up needed downstream
C. Bubbling fluidized bed gasifier	Can tolerate wide range of feedstock and particle size Good temperature control and gas solid mixing In bed catalyst use possible	Moderate amount of tar in gas High particulates in product gas.
D. Circulating fluidized bed gasifier	Greater tolerance to particle size than fixed bed Good temperature control and gas solid mixing Good carbon conversion Good scale up potential	In bed catalyst use not possible Operation can be difficult than fixed bed
E. Entrained flow gasifier	Feed preparation costly Good gas quality Good scale up opportunity	Low feedstock options Ash content can cause slagging.

With respect to power generation, the selection of gasifier is made depending on the capacity of the desired power generation. Updraft and downdraft gasifiers are used as smaller units, with a capacity up to 10 MWth power. Fluidized beds are used for medium capacity (5-100 MWth) power and entrained flow configurations are used for larger capacity (>50 MWth) applications. Downdraft, updraft, bubbling fluidized bed and circulating fluidized bed gasifiers are the most common gasifiers. A higher throughput can be obtained from fluidized bed than fixed bed gasifier (Basu, 2010).

2.5.2 **Types of biomass**

Forest biomass and residue: The southeastern United States is rich in forest reserves. Around 214 million acres of Southern United States is under forest cover. This forest cover provides a habitat for wildlife, protection for the watershed areas, public recreational areas, and wood for timber production (Galik et al., 2009). The economy in the southern states is heavily dependent upon forest related industries like timber and, the paper and pulp industry. The decline in paper demand has resulted in closing of mills; corresponding loss of jobs, and has affected this area, which is still more than 60% rural(Conrad Iv et al., 2011). The development of a sustainable renewable energy source through conservation and cultivation of forest will help develop the rural economy. If the trees and wastes from sawmills are used for bioenergy production through biochemical processes, then around 6.5 million gallons of transportation fuel can be obtained for the nations' supply(Johnson and Steppleton, 2007). As per a study performed on electricity production from logging residue in the south, it was projected that around 33 TWh (Terra watt hours) of electricity can be obtained(Gan and Smith, 2006). This shows the potential that woody biomass possesses for energy production in this region. A good example energy production from biomass waste is the electricity generation from black liquor in the paper pulp industry. A byproduct of the pulping process, black liquor, is combusted and the heat is used to produce steam. The electricity is further produced using a steam turbine; this electricity produced in turn runs the pulp mill.

However, if the energy production from forest products is limited to the residual wood then the forest biomass would have a smaller role in renewable energy production(Galik et al., 2009), and the entire potential of the forest reserve will not be explored. In recent years the demand for pelletized saw dust has increased in the European market which has led to the use of entire trees for pellet production(Administration, 2011). This could possibly result in harvesting wood at higher rate which could reduce the capacity of the forest soil to hold the carbon in the trees and soil(Mitchell et al., 2009). The southern forest future project report of 2011(Wear and Greis, 2012), states that there are four major factors influencing the forest in the southeast namely the growing human population, timber market, climate change and invasive species. It also asserts that the use of forest reserves to meet bioenergy demands could impact forest conditions, markets and management. It also warms against possible decrease in water reserves and degradation of water quality. The report states the increase in human population would result in reduction of southern forests, with increase in need for forest in form of recreational areas, timber wood resource and energy resource. Even though use of forest biomass for energy production is attractive resource, complementing it with agricultural residue and energy crops could result in a complete alternative to fossil fuels. As mentioned before, in the southeastern United States, pine cultivations are common for the paper pulp industry. There is extensive research taking place to obtain bioenergy from pine via various conversion techniques as well. Since the cultivation of pine is already well established, using pine for energy production can be a complement to the pulp industry. However, this might further increase pine planting, thereby posing a threat for several other plant species and pushing them to extinction.

Energy crops: Energy crops are defined as crops grown for the sole purpose of energy production. These energy crops are carbon negative, i.e. they help sequester carbon back into soil, thus reducing the impact of greenhouse gas emissions. Usually these are perennial grasses which grow easily on agricultural land or non-fertile lands. As per a study by Tilman et al.2006(Tilman et al., 2006), a combination of various prairie grasses in U.S., which are suitable and native to the region under consideration, provides the best option as an energy crop. In another study of 17 different species as possible source of bioenergy production, it was concluded that the choice of crop and cultivation method have to be driven by energy evaluation and the economic potential of the given energy crop(Berndes et al., 2003).

Switchgrass (*Panicum virgatum*), which is a prairie grass which has various sub species growing naturally from southern Canada to northern Mexico in the North American continent. In the Southeast, a variant named Alamo is found to have natural resistance to pest and insects found in the south. It can be easily grown in drought and stand tall in floods, helping prevent soil erosion. As mentioned before, switchgrass, just like other energy crops, help incorporate carbon and nitrogen back into the soil, thus improving quality of soil. It can be grown with very low investment and can provide an excellent resource in the winter months for farmers in the southeast(Bransby and Sladden, 1991).

Composition of biomass: Lignocellulosic biomass primarily consists of cellulose, hemicellulose and lignin. The cellulose is the most common organic compound in biomass. It is a long chain polymer, and is represented by chemical formula $(C_6H_{10}O_5)_n$ and molecular weight around 500,000. It is crystalline in structure, and composed primarily of thousands of molecules of d-glucose (C6 sugar Hexose), which gives it the strength to provide skeletal structure to various terrestrial biomass (Klass, 1998). Carbohydrates are highly insoluble and indigestible by humans, however, some enzymes like cellulase can digest them post hydrolysis(Mosier et al., 2005).

Hemicellulose has amorphous structure and lower degree of polymerization as compared with cellulose. It resistant to hydrolysis and is comparatively much lower strength. It is represented by the chemical formula $(C_6H_8O_4)_n$ Hemicellulose consists of simple sugars predominantly d-xylose along with small quantities of d-glucose, d-xylose, d-galactose, I arabinose and d-mannose.

Lignin on the other hand is the cementing agent for biomass, holding adjacent cell walls together and acts like a glue. Diebold and Bridgewater(Diebold and Bridgwater, 1997), reported that the lignin is a 3 dimensional structure of 4-propenyl-2-methoxy phenol, and 4-propenyl-2.5-dimethoxy phenol. It is the second most widely available component of biomass after cellulose.

Table 2.3 shows the composition of some of biomass samples used for gasification as reported in literature(Keshwani and Cheng, 2009; Nepune, 2014). It can be seen that the woody sample has higher cellulose and lignin percentages compared with switchgrass sample(Demirbas and Demirbas, 2004).

Table 2.3 Composition of some biomass samples

Biomass sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Pine	39.08	24.41	30.29
Switchgrass	33.48	26.10	17.35
Wheat straw	39.1	28.8	18.6
Corn stover	30.7	51.2	14.4
Walnut shell	22.7	25.6	52.3

Ultimate and proximate analysis of biomass: At the elemental level, the primary components of biomass are carbon, hydrogen, nitrogen, oxygen, sulfur, and chlorine. Some alkali metals are present in biomass ash. Table 2.4 shows elemental analyses of some biomass components as reported in the literature(Demirbas and Demirbas, 2004). It can be seen that these raw biomass samples have high amount of oxygen. Low C/O ratio corresponds to lower heating value of biomass. Also the high oxygen content is indication of higher moisture content. The high moisture content (10-30%) of raw biomass leads to biomass decomposition during storage. Biomass also has low bulk density and thus results in low energy density. Along with this, a large amount of energy is required for grinding the biomass to desired size. All these factors make biomass an expensive fuel. In order to overcome these issues, biomass pretreatment is suggested. There are three major pretreatment methods of interest, these are acid pretreatment, steam pretreatment and thermal pretreatment. The thermal pretreatment is called torrefaction is of special interest.

Table 2.4 Elemental and proximate analysis, and heating value of few biomass samples

Biomass sample	C	H	N	O	Volatile matter	Fixed Carbon	Ash content	HHV MJ/kg
Pine	50.90	6.11	0.48	41.84	80.79	18.49	0.72	20.18
Switchgrass	49.76	5.96	0.36	42.01	81.41	17.2	1.39	19.65
Wheat straw	41.8	5.5	0.7	35.5	66.3	21.4	13.7	
Torrefied pine	55.45	4.65	0.87	31.16	59.75	39.17	1.08	24.01
Torrefied switchgrass	59.68	4.71	0.63	32.88	60.02	37.8	2.18	22.67

Torrefaction or roasting is a process in which biomass is heated at 200 to 300°C for 15 to 45 minutes in the absence of oxygen. Bergman et al(Bergman et al., 2005b) divide this process into five regimes. In the first regime, called the nonreactive drying, takes place between 50-120°C, during this step moisture is removed without any change in chemical structure. In next step (between 120-150°C), lignin undergoes a softening process. In the following regime (150-200°C), reactive drying takes place. During this step the structural deformity in the biomass takes place, along with initiation of hemicellulos de-polymerization by breaking the C-H bond. Further, in the regime between temperatures 200-250°C, hemicellulose is torrefied, it results in breakage of C-C and C-O bonds leading to formation of condensable liquids and non-condensable gases. In the last regime between 250-300°C, hemicellulose is extensively decomposed into volatiles, and on the other hand lignin and carbohydrates do not undergo major decomposition, while the biomass cell structure is completely destroyed. Concisely, the thermal pretreatment destroys the biomass structure and the change is appearance of raw and pre-treated biomass is as shown in Figure 2.8

below. Final composition of torrefied biomass has high amount of cellulose and lignin with very low amounts of hemicellulose as shown in Table 2.3.

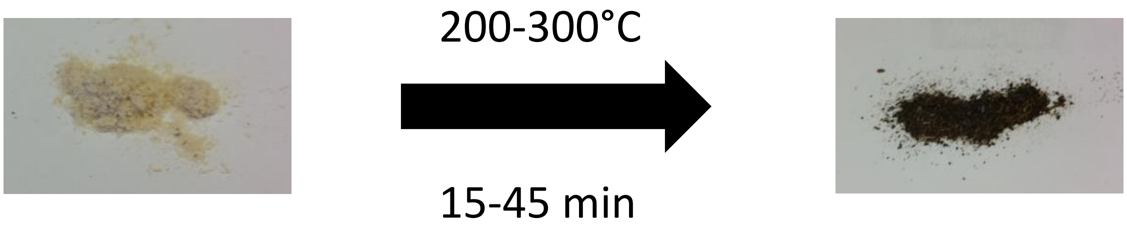


Figure 2.8 Effect of thermal pretreatment on biomass structure

Torrefaction helps improve the biomass properties. The hygroscopic nature of biomass is lost, thus biomass can be stored for longer period of time than raw biomass sample without decomposing. The higher the torrefaction temperature, the lower is the moisture absorption ability. During the torrefaction process, around 30% of mass of the sample is lost while 90% energy is retained; this increases the energy density of the sample. The loss of moisture and breakage of C-O bonds, help increase in C/O ratio as shown in Table 2.4, which corresponds to increase in energy content of biomass. The HHV of torrefied pine is around 20-25 MJ/kg(Carter, 2012) , while that of raw biomass is around 16-18 MJ/kg. The thermal pretreatment increases the grindability of the biomass, thereby reducing the cost of processing. To further reduce the cost of transportation, densification following torrefaction is suggested. Sarkar et al.(Sarkar et al., 2014a) have reported that densification actually helps improve the carbon conversion and cold gas efficiency for torrefied switchgrass.

Composition of biomass plays an important role in during gasification. Even under similar conditions, different biomass samples produce syngas with different compositions. A study by Carpenter et al.(Carpenter et al., 2010a), reported a comparison between gasification of corn stover, Vermont wood (mixture various woody biomass), wheat straw, and switchgrass at a fluidized bed temperature of 650°C with steam at steam to biomass ratio (S/B) of 1.0, (S/B ratio is defined as ratio of kg of steam used per kg of biomass) followed by use of a thermal cracker set at 850°C. The results are tabulated below in Table 2.5. It was observed that switchgrass yield highest amount of CH_4 and CO, followed by wheat straw, corn stover, and Vermont wood respectively. Vermont wood yielded the highest amount of H_2 and highest gas yield. Thus it is important to study and compare different types of biomass species to gain a thorough understanding of their performance at various operating conditions.

Table 2.5 Performance of four types of biomass samples under similar conditions(Carpenter et al., 2010a)

	Corn stover	Vermont wood	Wheat straw	Switchgrass
CO, Vol %	24.7	23.5	27.5	33.2
CO_2, Vol %	23.7	24	22	19.4
CH_4, Vol %	15.3	15.5	16.3	17
H_2, Vol %	26.9	28.6	25.4	23.5
C_n, Vol %	1.07	28.6	25.4	23.5
Gas yield (kg/ kg of feed)	0.54	0.74	0.54	0.62

2.5.3 **Gasifying media**

Gasifying medium plays a very important role on yield of syngas. Air, oxygen and steam are usually used as gasifying media. Air is a widely used for gasification, low cost and ready availability makes it an obvious choice. The amount of air needed to gasify is defined by a ratio called equivalence ratio (ER). ER is defined as ratio of supplied air to stoichiometric air (Basu, 2010). As gasification is partial oxidation, only a portion of stoichiometric air is supplied. The stoichiometric air is calculated based on the ultimate analysis of the sample. Downdraft gasifiers operate efficiently at ER 0.25(Basu, 2010). Updraft gasifiers are operated at ER < 0.25 (ref). Low ERs (< 0.15) result in high concentration of condensable liquids in the syngas. Fluidized bed gasifiers operate in the ER range of 0.2 to 0.3. The higher ERs (< 0.5) lead to increased combustion products in the syngas and are therefore not generally used. The effect of ER on the gasification products has been reported in the section below. Pure oxygen is also used as a gasifying medium, however it is accompanied by nitrogen or steam as fluidizing agent. It is one of the most expensive oxidizing media since a lot of energy is required to separate oxygen from air. Oxygen is supplied mainly to supply energy for the endothermic oxidizing reactions. Superheated steam is also used as a gasifying medium. Use of steam promotes hydro gasification as shown in the reaction below leading to an increase in concentration of CO and H_2 syngas.

$$C + H_2O \longrightarrow CO + H_2 \tag{2.13}$$

The quantity of steam required is calculated from steam to carbon ratio (S/C) or steam to biomass ratio (S/B). Thus it can be assumed that increasing the quantity of steam would give more CO and H_2. However, if an S/C ratio of three or more is used, excess steam would escape without reacting. Table 2.6 compares the performance of air, steam-O_2, and steam as gasifying agent using a bubbling fluidized bed gasifier. It can be seen that steam-O_2 produce syngas with highest amount of CO, CH_4 and H_2, followed by steam and air respectively. Air produces the lowest amount of C_2H_n compounds. The tar yield was highest for pure steam, along with highest amount of energy content. The presence of oxygen with steam in steam-O_2 gasification, helped reduce the tar content. This was due to oxidation of tar compounds with oxygen. The highest gas yield was obtained with air as the gasifying medium. Steam and Steam-O_2 produced syngas with a higher amount of energy than that with air. The higher amount of CH_4 and CO present in the syngas causes the higher energy content.

Table 2.6 Comparison between performance of air, steam and steam-oxygen as gasifying media

	Air(Narváez et al., 1996)	Steam-O_2(Herguido et al., 1992)	Steam(Corella et al., 1991; Herguido et al., 1992)
ER	0.18 - 0.45	0	0.24 – 0.51
S/B	0.08 – 0.66	0.53 – 1.10	0.48 – 1.11
Temperature, °C	780 – 830	785 – 830	750 - 780
Gas composition, vol %			
CO	9.9 – 22.4	17 – 32	42.5 – 52.0
CO_2	9.0 – 19.4	13 – 17	14.4 – 36.3
CH_4	2.2 – 6.2	7 – 12	6.0 – 7.5
H_2	5.0 – 16.3	38 – 56	13.8 – 31.7
C_2H_n	0.2 – 3.3	2.1 – 2.3	2.5 – 3.6
Steam	11 – 34	52 – 60	38 - 61
N_2	41.6 – 61.6	0	0
Yields			
Char (g/kg daf)	3.7 – 61.9	60 – 95	2.2 - 46
Tar (g/kg daf)	n/a	95 – 110	5 - 20
Gas (Nm^3/kg daf)	1.25 – 2.45	1.3 – 1.6	0.86 – 1.14
LHV MJ/Nm^3	3.7 – 8.4	12.2 – 13.8	10.3 – 13.5

Typically, when air is used for gasification the heating value is obtained in the range of 4 to 6 MJ/N•m^3. Similarly when oxygen and steam are used for gasification the heating value of resulting syngas is between 12 to18 MJ/N•m^3. Steam gasification in a bubbling fluidized bed was performed on sawdust, at five different steam to biomass ratios in the range of 0.5 to 2.6 at 750^{o}C (Herguido et al., 1992). It was observed that the gas yield increased with increase in ratio, char and tar reduced with increase in the ratio, the amount of hydrogen obtained increased and amount of carbon monoxide decreases with increase in the ratio. The percent of methane in the gas decreased and LHV of the syngas reduced from 14MJ/N•m^3 to 9 MJ/N•m^3 with an increase in the ratio(Gil et al., 1999b).

Using carbon dioxide (CO_2) as a gasification medium for biomass has been proposed recently. One of the advantages of CO_2 as gasification medium is it's consumption without being released to the atmosphere from other industrial processes. With CO_2 as gasifying medium, increased CO can also be obtained. Also it would decrease the H_2/CO ratio for various grasses that would lead to better Fisher-Tropsch fuel (Butterman and Castaldi, 2009). The typical temperature range for gasification with CO_2 is 700^{o}C-1000^{o}C. Gasification of low grade fuel has been carried out with combination of CO_2 and steam being used as gasifying medium either directly in a gasifier or with a thermal gravimetric analyzer (TGA)(Butterman and Castaldi, 2009; Everson et al., 2006; Ye et al., 1998; Zhang et al., 2006). It was concluded from these studies that concluded that the activation energy was lower for CO_2 than for steam.

2.5.4 **Operating parameters**

Temperature: The temperature at which gasification is carried out influences all chemical reactions involved in the processes of gasification. Increase in temperature influences the Boudouard reaction and methane decomposition reaction, thus resulting in an increase in CO and H_2 production, while reducing the CO_2 and CH_4 content(Narváez et al., 1996). The effect of bed temperature on primary syngas components and energy of syngas from 700^{o}C to 850^{o}C for four studies carried out on a fluidized bed gasifier as shown in Figure 2.9. The four studies included one by Lv et al.(Lv et al., 2004b), on gasification of pine sawdust with air (ER 0.22) and steam

(S/B 2.7), Corella et al. (Corella et al., 1991) , on gasification of cellulosic waste with steam (S/B 0.8), Xue et al. (Xue et al., 2014) on the gasification of torrefied miscanthus with air (ER 0.21), and Narveaz et al (Narváez et al., 1996) on the gasification pine sawdust with air (ER 0.30).

Overall, an increase in H_2 and CO and corresponding decrease in CH_4 and CO_2 were expected. However, Lv et al. reported decrease in CO while CO_2 concentration remained unchanged. It was mentioned in the study that conditions in the reactor did not favor production of CO. Corella et al. reported no effect of temperature on CO, and a slight decrease in CO_2. The studies with air as gasifying media, showed a clear trend of increase in CO, and an equally prominent trend of the decrease in CO_2. These studies also depicted a clear trend in increase in hydrogen at the cost of methane. These primary syngas components affected the syngas energy as well. It was seen that with an increase in temperature energy content of the syngas increased for gasification with air and it did not affect those with steam as gasifying media. C_2 and C_3 compounds, though not shown here, were reported to reduce with an increase in temperature due to decomposition to produce CO ad H_2. Xue et al. and Lv et al. reported that an increase in temperature helped increase in carbon conversion into gas.. It also helps improve the energy efficiency due to increase in the heating value of syngas.

Temperature variation also influenced total gas yield. The gas yield increases as temperature increases. The increase in temperature also helped reduce the total tar yield by thermal cracking of the tar compounds at high temperature. Figure 2.10 shows the effect of increase in temperature on tar as adapted from Narveaz et al. At higher temperature the primary and secondary components formed during gasification decompose and convert to the tertiary tar products. These tertiary tar products further completely decompose above 1200°C(Milne et al., 1998a).

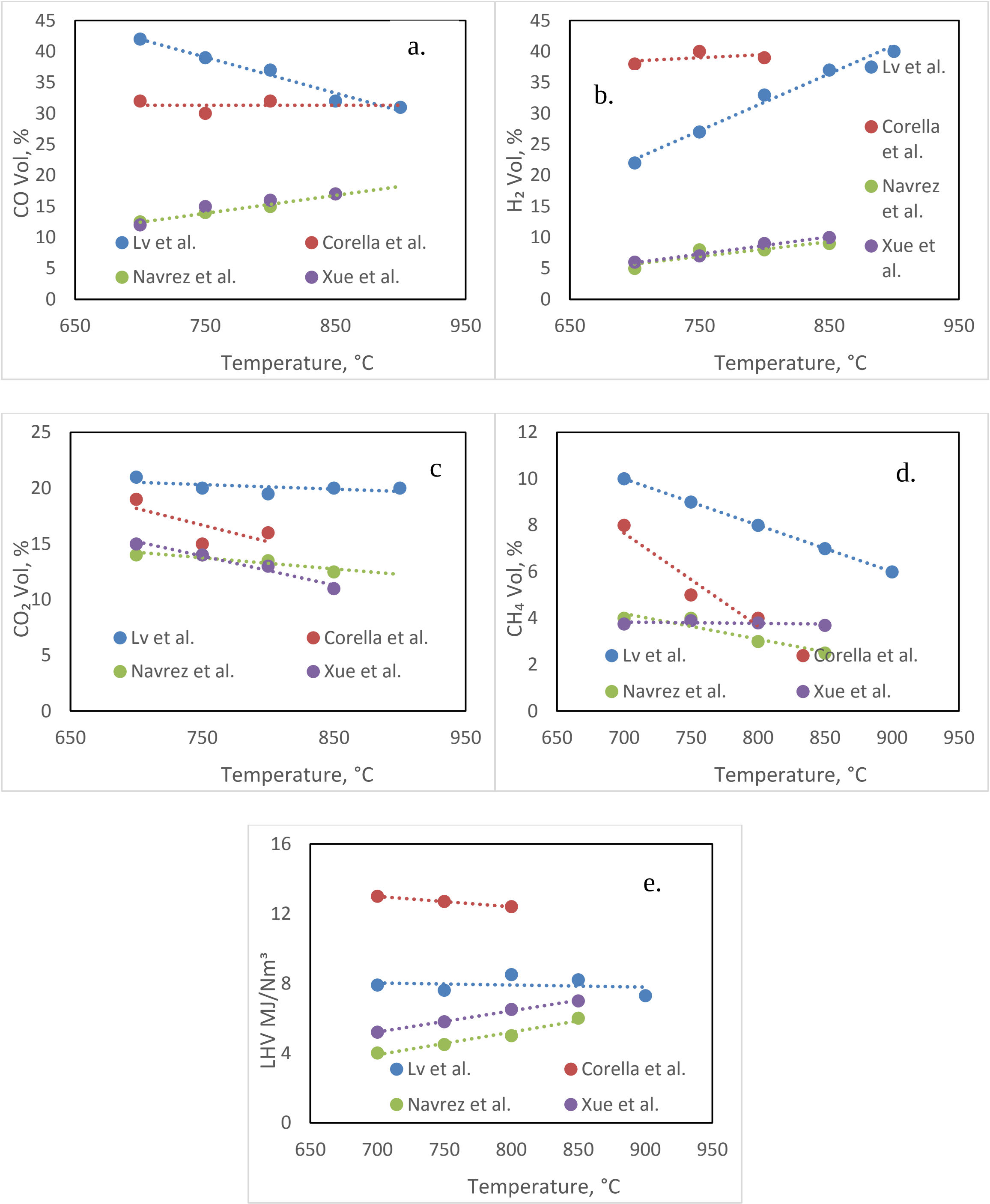


Figure 2.9. Effect of temperature on gas composition (a, b, c &d) and heating value (e), data obtained from Lv et al.(Lv et al., 2004b), Corella et al.(Corella et al., 1991), Narveaz et al.(Narváez et al., 1996), and Xue et al.(Xue et al., 2014)

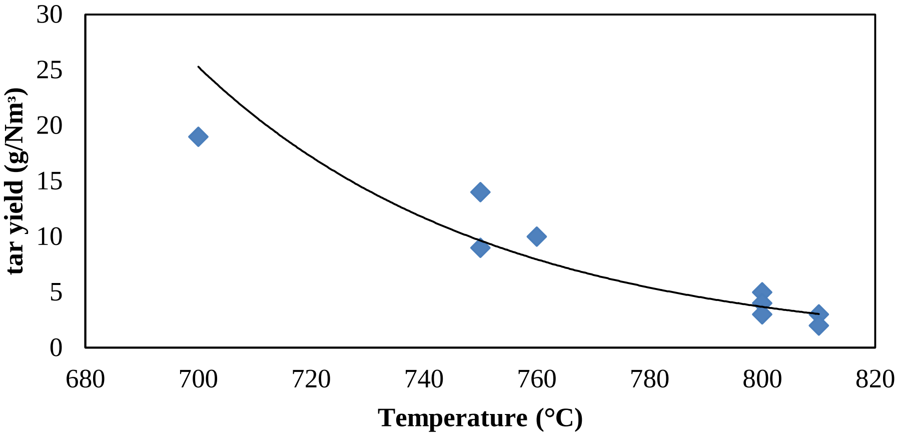


Figure 2.10. Effect of temperature increase on tar yield (reproduced from **(Narváez et al., 1996)**)

Equivalence ratio (ER): ER is an important parameter in the gasification study. Typically gasification is carried out between ER 0.2 and 0.4. Increase in ER corresponds to an increase in oxygen supplied. As the ER increases combustion products i.e. concentration of CO_2 and H_2O increases in the syngas. Since more air/ oxygen is available for gasification the syngas yield increases as shown in Figure 2.11(Narváez et al., 1996). Figure 2.12 shows the effect of ER on syngas components and heating values for four studies. Lv et al.(Lv et al., 2004b) carried out the study with steam and air, the S/B ratio used was 1.56 at 800°C bed temperature with pine sawdust as gasification fuel. It was observed that CO, showed a peak at ER 0.23 and then decreased, CO_2 followed exact opposite trend and increased past ER 0.23. The energy content of syngas reduced from 8.8 to 7.2 MJ/N•m³. In a study on gasification of torrefied miscathus(Xue et al., 2014), it was observed that increase in ER increases CO_2 significantly along with slightly increase in CO. This resulted in decrease in energy content and increase in carbon conversion, the Authors reported carbon conversion between73.5 to 82.5%. Narveaz et al. reported decrease in tar yield with an increase in tar yield. Increase in ER causes decomposition of tar compounds due to oxidation(Milne et al., 1998a) and thus helps reduce tar, however this is accompanied by decrease in heating value and increase in CO_2 concentration of syngas, which is not desired. Narveaz et al. also reported an reduction in CO and H_2 while CO_2 concentration increased(Gil et al., 1999b) and the corresponding LHV of the gas decreased as ER increases. Increase in ER results in higher CO_2 production, this results in higher carbon conversion. However, it results in reduction in energy efficiency. Thus higher equivalence ratios (> 0.50) are not used for gasification processes.

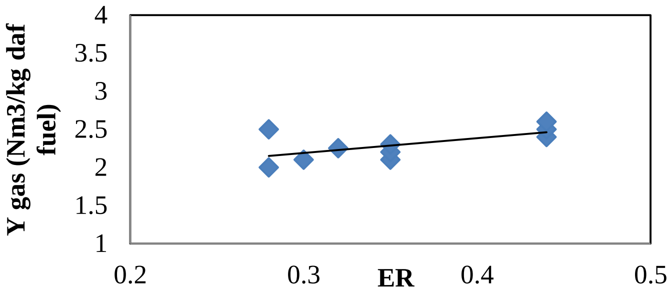
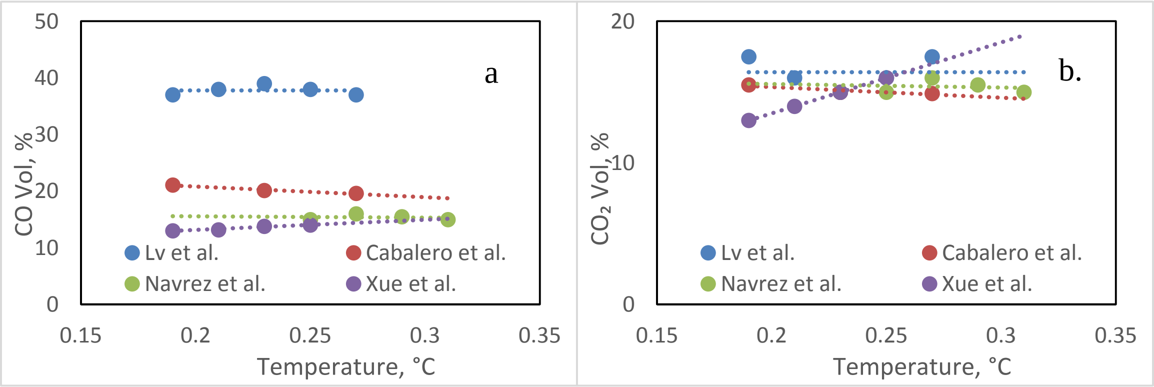


Figure 2.11. Effect of ER on gas yield (reproduced from **(Narváez et al., 1996)**).



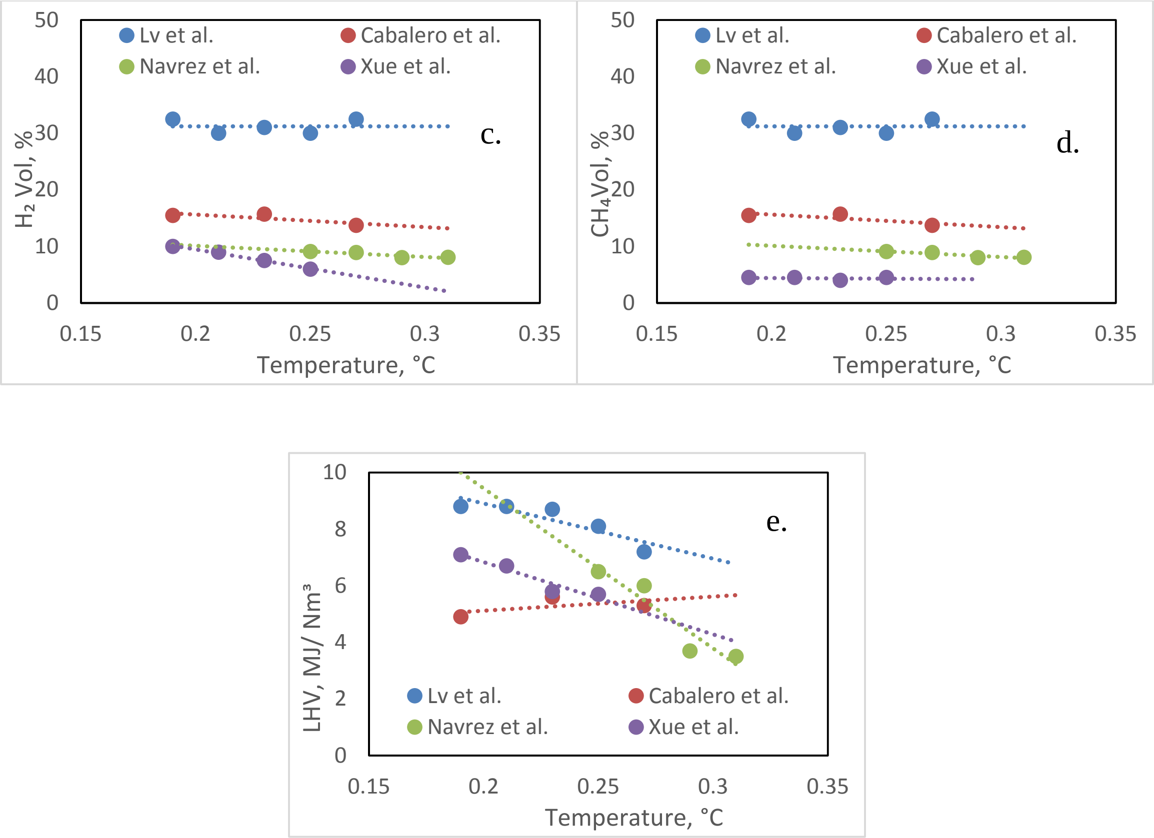


Figure 2.12 Effect of increase in ER on syngas components (a, b, c &d) and heating value (e), data obtained from Lv et al.(Lv et al., 2004b), Cabalero et al.(Caballero et al., 2000), Narveaz et al.(Narváez et al., 1996), and Xue et al.(Xue et al., 2014)

2.5.5 Type of bed material

In fluidized bed gasifiers, fine particles like silica sand are used as bed materials at temperature around 700 to 1100°C. When the solid fuel particles interact with these bed particles they exchange heat and rapidly undergo drying and pyrolysis. They provide good mixing during gasification processes(Basu, 2010). Catalysts are added in the bed to reduce tar formation via catalytic decomposition. . Ni-based catalysts, calcined dolomite, magnesite, zeolite, and iron catalysts are some examples of tar reducing catalysts(Devi et al., 2005). The catalysts accelerate the steam reforming reaction and the dry reforming reaction, thus increasing hydrogen and carbon monoxide content. In a study performed to understand effect of using Fe-impregnated CaO as a catalyst in gasification of sawdust, it was found that the Fe-impregnation of CaO increased hydrogen yield (Huang et al., 2012). To understand the working of various catalysts on tar decomposition, one of the tar constituents is selected as a model representation of the tar and decomposition of that particular constituent is studied (Devi et al., 2003).

Dolomite is a carbonated mineral of calcium and magnesium ($CaCO_3$ and $MgCO_3$). It is inexpensive and readily available catalyst. It works better to increase dry reforming than steam reforming. Dry reforming is a reaction between methane and carbon dioxide to produce H_2 and CO. Similarly steam reforming is reaction of methane with steam to produce H_2 and CO. Equations 13 and 14 represent these reactions.

$$CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2 \quad (2.14)$$

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad (2.15)$$

Naturally occurring particles of olivine, which is a mineral containing magnesium and iron oxides and silica ($(Mg, Fe)_2SiO_4$), have more attrition resistance due to their crystalline form than dolomite, and bed activity comparable to dolomite. In an attempt to understand the difference between sand, calcined dolomite, and olivine, fluidized bed gasification of crushed almond shells was performed with steam as the gasifying medium (S/B ratio 1) (Rapagnà et al., 2000). It was concluded that HHV of syngas was highest for dolomite bed (7% more than olivine bed), tar reduction was almost similar for both but the major advantage of olivine was that only small amount of fines were collected. When dolomite was used, fines caused problem in smooth operation of the run, by increasing pressure drop across the filter. In yet another study, the performance of olivine was compared with that of calcined olivine (1200°C) and sand in a circulating fluidized bed gasifier at 750 and 800°C. It was observed that calcined olivine helped increase hydrogen concentration and helped reduce the tar. The tar further decreased for calcined olivine with an increase in temperature(Christodoulou et al., 2014). When compared with dolomite, the attrition resistance and lower elutriation are the most important benefits of olivine.

2.6 Contaminants

Tar: Tar is an undesirable and unavoidable product of gasification. It condenses in the low temperature zone as a thick black viscous fluid. In a gasifier it can clog the gas path and lead to system disruption. The U.S. DoE identifies all of the syngas components that have molecular weight more than benzene as tar (Knoef and Ahrenfeldt, 2005). Tar is classified as primary, secondary or tertiary (detailed tar classification shown in Appendix B). The classification is primarily based on its molecular structure. The pyrolysis step in the gasification process produces primary tar from breaking down of hemicelluloses, cellulose, and lignin present in the biomass. These are phenols, acids, sugars, ketones etc. The secondary tars are formed from rearranging of molecules in the primary tars at temperature above 500^{o}C. Tertiary tars, formed at higher temperatures, are methyl derivatives of aromatics. They condense to form poly aromatic hydrocarbons (PAH). Milne et al.(Milne et al., 1998a) stated in their renowned work that the tertiary hydrocarbons are formed at expense of primary hydrocarbon. At high temperature above 750-800^{o}C the primary tars are completely consumed and tertiary and secondary tars remain. However, complete removal of tar via thermal cracking does not take place below 1100°C(Milne et al., 1998a).

Application of syngas in direct combustion, internal combustion engine, gas turbine and hydrogen production pose tight limits for tar. Table 2.7 gives the limitations on the tar content in the syngas based on its end use. It should be noted that direct combustion has no limitation on the tar content and that in gas turbine tar in vapor form is acceptable. Internal combustion engines are more tolerant than gas turbines(Milne et al., 1998b).

Table 2.7. Acceptable limit of biomass tar **(Basu, 2010)**

End use application	**Permissible tar content (g/ Nm^3)**
Direct combustion	No limit specified
Syngas production	0.1
Expansion in gas turbine	0.05-5
Internal combustion engine	50-100
Pipeline transport	50-500 for compressor
Fuel cells	<1.0

Tar concentration can be reduced during gasification (in-situ tar reduction) or after the syngas is obtained (secondary reduction of tar). The important measures of tar elimination include selection of proper gasification temperature, use of bed material, catalyst and gasification medium. The operating parameters also play an important role in tar elimination (Devi et al., 2003). A parametric test on tar formation was conducted by varying the temperature, ER and residence time on a bench scale fluidized bed gasifier (diameter 89mm and height 2500mm, feed rate up to 2.4 kg/hr) with saw dust (8.2% moisture content) as biomass (Kinoshita et al., 1994). It was observed that number of tar species reduced with increase in temperature (700^{o}C to 900^{o}C). Tests also suggested that lower temperature (below 800^{o}C) favored formation of aromatic compounds. Increase in ER decreased the number of tar species, as there was more oxygen available for char combustion; however according to the authors’ ER could not be increased beyond a certain point as that would lead towards complete combustion. It was also observed that tar concentration was not much influenced by residence time.

Nitrogen contaminants: The NH_3 and HCN concentrations in syngas are proportional to fuel nitrogen content (Zhou et al., 2000). In addition, these concentrations are affected by oxidizing agent (steam/O_2 or air), temperature and ER (Aljbour and Kawamoto, 2013b; Zhou et al., 2000). In general, as temperature and ER increase, NH_3 and HCN concentrations were reported to decrease(Abdoulmoumine et al., 2014; Leppälahti, 1993; Zhou et al., 2000). However, there have been instances where NH_3 and HCN did not follow this behavior (Aljbour and Kawamoto, 2013b; Van der Drift et al., 2001). Reported NH_3 and HCN concentrations vary widely. In the only instance of NH_3 and HCN reports for switchgrass gasification, the investigators reported NH_3 and HCN concentrations ranging from 10000 to 5800 ppm and 2500 to 400 ppm, respectively (Broer et al., 2015). Van der Drift *et al.* (2001) reported NH_3 concentration of 12500 ppm for verge grass with nitrogen content of 0.18 wt % (dry ash free basis (daf.)) NH_3 and HCN concentrations in this study are closer to values reported for woody biomass feedstock with lower nitrogen content were reports ranged from near 300 to 1800 ppmv for NH_3 and less than 70 ppmv for HCN (Abdoulmoumine et al., 2014; Aljbour and Kawamoto, 2013a; Van der Drift et al., 2001). The primary incentive for ammonia removal is the reduction in the NOx emission during downstream combustion application.

***Sulfur contaminants**:* SO_2 is a product of complete combustion of fuel sulfur and present in lower concentration during gasification compared to combustion(Basu, 2010). The combustion of coal produces much higher amounts of SO_2. In a study on a fluidized bed combustor at around 700 to 800°C, the SO_2 emission values for coal and coal-biomass co-feeding (up to 23% by weight.) were reported to be around 400 to 500 ppm (Xie et al., 2007) The oxygen deprived conditions of gasification, around 93 to 98% of the sulfur is converted into the H_2S and most of the remaining in to Carbonyl sulfide (COS) (Higman and van der Burgt, 2008).The sulfur contaminants need to be removed for downstream application since they can cause catalyst poisoning and equipment corrosion, as well as compliance with SOx emissions.

Hydrogen Halides: The HCl and HF concentrations are direct results of reaction of these halides present in the biomass with hydrogen in the biomass. These halides also react with the alkali metals like Na and K, found in the biomass ash to form their respective salts. Coal gasification reported leads to HCl values around 600 ppm(Duong et al., 2009). Since biomass consists of much lower amounts of halides these values are much lower. However, due to high reactivity of HCl, concentrations even in a few ppm volume, could cause corrosion on filters, heat exchangers and turbine blades during downstream applications.

2.7 Summary

In summary, it can be stated that biomass has a potential to provide renewable liquid fuel as well as electric power. Use of lignocellulosic biomass for bio-energy production provides a carbon neutral energy cycle due to consumption of carbon dioxide released during photosynthesis. Bioenergy can be obtained from biomass via several techniques including thermochemical conversion. Thermochemical conversion techniques use thermal energy for chemical transformation of biomass to bio-fuels. Gasification is one such technique where, biomass is heated in limited supply of oxygen to produce gas called syngas, which is a mixture of carbon monoxide, hydrogen, methane, carbon dioxide, and contaminants including tar. Gasification of lignocellulosic biomass has been studied in details in literature. However, variety of biomass species are obtained worldwide and hence it is important to study the performance of biomass available in the geographic location.

In Southeast U.S, energy crop like switchgrass can be grown during the warm winter months which could help the soil by incorporating the carbon and nitrogen from air and helping improve the soil erosion. The switchgrass has high content of ash. However, the storage and transportation of raw biomass is a challenge, thus thermal pretreatment of biomass called torrefaction has been proposed. Torrefaction is a process where biomass is heated at 200 to 300°C, from 15 to 45 minutes, this helps lose the moisture and the hygroscopic nature of biomass, thus enabling the storage of biomass for longer time, increasing the energy density of biomass and improve the grindability of biomass. This torrefied biomass has a potential to be co-fed with coal in coal fired power plants to reduce emissions.

During a thorough investigation of a type of gasification fuel, the oxidizing media plays an important role, air is used widely due to easy and cheap availability. The type of gasifier used also plays an important. The fluidized bed gasifiers are one such type, where biomass is fed into a bed of sand like particles, which is fluidized with a fluidizing medium. The oxidizing agent sent into this bed, causes decomposition of the biomass particles to form syngas. Fluidized bed gasifiers, due to excellent mixing are best suited for high ash content feedstock.

In order to obtain syngas with desired composition, it is important to study performance of fuel at various temperatures and ERs. Several studies have reported effect of temperature and ER on different types of biomass species. Generally it has been seen that with an increase in temperature, the carbon monoxide and hydrogen increase, while carbon dioxide and methane decrease. The tar also reduces due to thermal cracking. Whereas, with an increase in ER, the carbon dioxide and steam increases due to higher complete combustion of syngas products, while methane, carbon monoxide and hydrogen reduce. The tar also under go oxidation thus reducing the amount of tar obtained. Some studies have reported reduction in ammonia with an increase in ER.

Another important parameter to be studied is the type of bed material used in fluidized bed gasifier. Silica sand is widely used as bed material. However, use of in-bed catalyst like olivine or dolomite has been suggested to help reduce the tar formation. Olivine, has better attrition resistant and elutriation properties, though dolomite has been reported to perform better in tar reduction.

In conclusion it can be said that from the literature review, there is a need to thoroughly investigate performance of an energy crop like switchgrass which can be easily grown in the Southeastern U.S. Along with this there is a need to study the performance of switchgrass with an in bed catalyst to study the effect of high ash. Along with this it is important to investigate the pretreated biomass as a gasification fuel, which has excellent grindability and longtime storage benefits, and has excellent potential to be co-fed in a coal-fired power plants.

Chapter 3

Switchgrass Gasification

3.1 Introduction

Presently, the majority of the world's energy requirements are fulfilled by fossil fuels. However, the excessive use of fossil fuel has led to an increase in greenhouse gases and other pollutant emissions that are harmful for the environment and human health. Crude oil, the major source of transportation fuel, has seen a steady rise in its cost due to increasing consumption over the last few years although the price has been relatively low due to recent developments in fracking technology. Furthermore, the largest crude oil reserves are concentrated in turbulent regions of the world, which has led to questions about energy security in the longer run. In order to reduce dependence on fossil fuels, it is vital to develop an alternative technology to convert biomass to electricity and transportation fuel since these are the major sectors in which fossil fuels are used (EIA, 2012). Gasification provides an advantage over all other methods in this regard. It can be used to produce to synthesis gas, which contains essential building blocks (H_2, and CO) for fuel and chemical synthesis or it can be used as a substitute for natural gas for power generation.

Because of the abundant availability of biomass, it has been extensively investigated as a potential gasification feedstock with much attention devoted to woody biomass feedstocks. However, other biomass types such as energy crops are equally viable low-cost alternatives and are poised to play a major role in bioenergy projects. Energy crops are defined as crops grown specifically for energy production and include perennial grasses, like switchgrass and miscanthus.

Switchgrass is of particular interest in the southeastern U.S. where it can be easily grown on farmland during the winter months thus providing farmers with extra income (Bransby and Sladden, 1991). In addition, it requires low care (i.e., low fertilizers and pesticide usage) and can help incorporate nitrogen and carbon into the soil to improve soil fertility (Liebig et al., 2005). It also has higher yield and pesticide resistance variants (Bransby and Sladden, 1991; Sanderson et al., 1996b).

One of the major concerns of using switchgrass in gasification is high ash content which is known to impede feeding and fluidization due to ash melting and bed agglomeration (Broer et al., 2015). However, inorganic elements in ash can play a catalytic role in gasification as demonstrated by Brown *et al.* (2000) in a study where alkali elements from switchgrass char and ash enhanced char conversion eightfold. Gasification of switchgrass has been reported in the literature using various types of gasifiers (Broer et al., 2015; Carpenter et al., 2010a; Moutsoglou, 2012; Sarkar et al., 2014a). A computational study to compare gasification of prairie cordgrass and switchgrass concluded that switchgrass gasification resulted in higher yields of CO and H_2 (Moutsoglou, 2012). Carpenter and coworkers (2010a) conducted a parametric study of switchgrass along with three other biomass feedstocks in steam gasification. When compared to Vermont wood, switchgrass resulted in lower H_2 and CO_2 but higher CO and CH_4 concentrations. Furthermore, switchgrass resulted in higher tar and H_2S content when compared to woody biomass. Broer *et al.* (2015) investigated steam/oxygen gasification of switchgrass and reported primary gas compositions far below predictions obtained by equilibrium modeling. The investigators also quantified contaminants (tar, NH_3, HCN, H_2S, COS, CS_2). With the exception of tar which was measured at higher levels than typically reported (43-56 g/m^3), all other contaminants were detected at levels similar to those reported for woody biomass. The effect of torrefaction and densification on switchgrass air gasification was studied at various temperature (Sarkar et al., 2014a). Based on the gas composition, energy content and process efficiencies, the authors concluded that combined torrefaction and densification yielded the best performance. No analysis on contaminants was conducted in that study.

Although several switchgrass gasification studies have been conducted, the knowledge on contaminants is limited particularly in air gasification. Furthermore, the impact of ash content in this process is not clearly understood. Therefore, this present study aimed to evaluate the performance of switchgrass in air gasification in a bench scale bubbling fluidized bed reactor. The performance was analyzed based on the primary gas composition, gas heating value and contaminants for different temperatures, equivalence ratios (ER), ash content and feeding rates.

3.2 Methods and materials

3.2.1 **Materials**

Three switchgrass samples were used in this study: SG made locally available at Auburn University, and SG19 & SG33 provided by the University of Tennessee, Knoxville. These three samples were used to study the effect of ash content. For all other experiments, only switchgrass sample SG was used. All samples were dried and ground using a hammer mill and then sieved through an 850 µm sieve before carrying out proximate, ultimate and energy content analyses. Heating value and ultimate analysis were carried out using a calorimeter (IKA Bomb Calorimeter, Model C-200, Wilmington, NC) and CHNS/O analyzer (Perkin Elmer, Model 2400, Waltham, MA), respectively. The ash content (ASTM D1102), volatile matter (BS EN 15148:2009) and moisture content (ASTM E871) were performed according to the standard tests methods indicated in parenthesis.

3.2.2 **Experimental set up**

Experiments were carried out using a bench scale bubbling fluidized bed gasification rig shown in Figure 3.1 and described in detailed elsewhere (Abdoulmoumine et al., 2014). Briefly, the set-up consisted of a hopper, an auger feeder, a fluidized bed gasifier, a high temperature filter unit (HTF), a pair of condensers, an electrostatic precipitator and a tar analysis impinger train. The bubbling fluidized bed gasifier had a diameter of two inches (0.0508 m) and a freeboard with diameter of four inches (0.1016 m). The overall height of the gasifier was 30 inches (0.762 m), while the freeboard was 6 inches (0.1524 m) high. The biomass was stored in the hopper and fed into the gasifier with the help of the auger feeder.

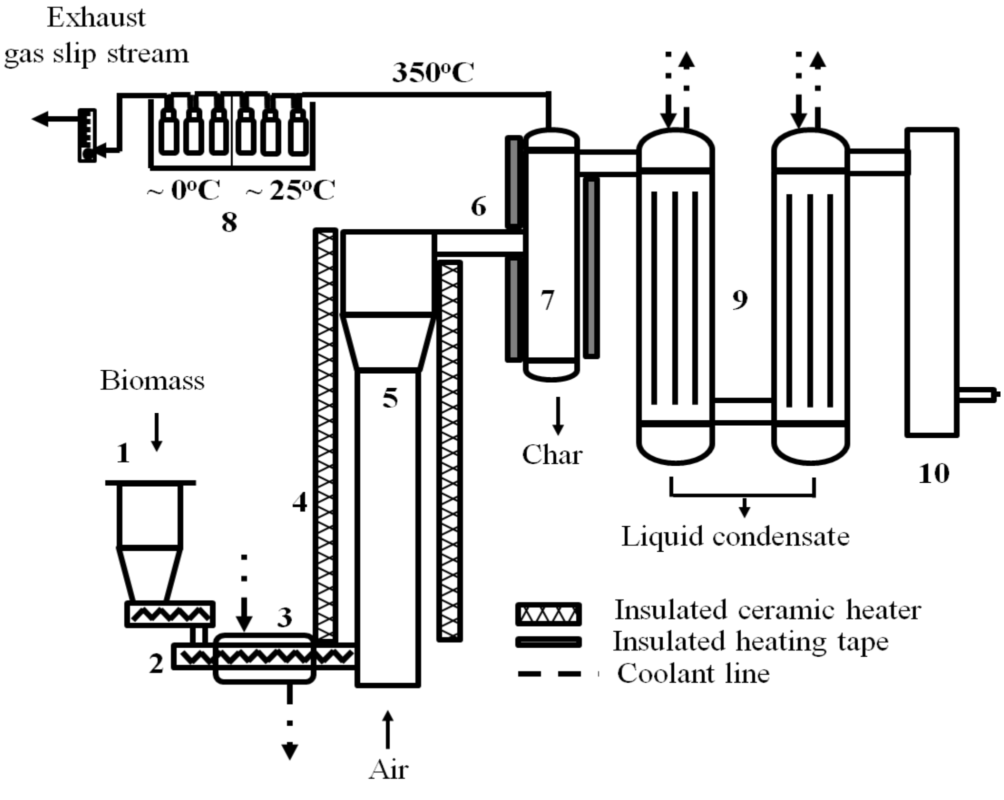


Figure 3.1: Schematic of the bench scale bubbling fluidized bed (BFB) gasifier assembly. **1.** biomass hoper, **2**. injection screw, **3.** heat exchanger, **4.** gasifier heaters, **5.** fluidized bed gasifier,

6. filter heaters, **7.** high temperature filter, **8.** impinger train for tar sampling, **9.** condensers, and **10.** electrostatic precipitator

For gasification of switchgrass, oxygen and nitrogen were used as oxidizing and fluidizing agents, respectively. The flow rate of nitrogen supplied for fluidization was 15.84 ±0.14 l/min and was kept constant for all other runs. The flow rate of oxygen supplied was varied to achieve the targeted equivalence ratio. The equivalence ratio (ER) was defined as a ratio of the actual amount of oxygen supplied to the gasifier to the amount of oxygen required for complete combustion of a given quantity of biomass and is defined in equation 3.a (Abdoulmoumine et al., 2014).

$$\mathrm{ER} = \frac{\left(\dot{\mathrm{m}}_{\mathrm{O_2}}/\dot{\mathrm{m}}_{\mathrm{biomass_{dry}}}\right)_{\mathrm{actual}}}{\left(\dot{\mathrm{m}}_{\mathrm{O_2}}/\dot{\mathrm{m}}_{\mathrm{biomass_{dry}}}\right)_{\mathrm{stoichiometric}}} \qquad (3a)$$

3.2.3 **Data sampling and analysis**

Temperature of the gasifier was measured with a thermocouple placed vertically inside the reactor from the top in the gasifier bed. The output of this thermocouple was used to control the heaters heating the gasifier. The bench scale gasifier could be heated up to 1025 °C without damaging the heaters. Thus, the maximum temperature used for study was maintained at 1000^{o}C. The gaseous product from switchgrass gasification was analyzed continuously through in-line measurements. The primary gas and light hydrocarbon were measured continuously using TC (H_2) and NDIR (CO, CO_2, CH_4) detectors (NOVA, Niagara Falls, NY) and an FTIR with a four meter gas cell (IMAAC, Austin, TX) for C_2H_2 and C_2H_4. The gaseous syngas contaminants (HCN, NH_3, and SO_2) were measured in-line using the aforementioned FTIR gas analyzer. The NOVA and FTIR gas analyzer are shown in Figure 3.2 below. For all gases measured continuously, only the steady state data points were chosen for calculation where steady state was deemed achieved when the primary gas profiles (CO, CO_2, CH_4, and H2) did not exhibit significant variation over time. In addition to the gaseous contaminants listed above, syngas tar was collected using an impinger setup and qualitatively analyzed by gas chromatographic analysis of the impinger solvent. The impinger setup consisted of five iso-propanol filled impinger bottles through which syngas was bubbled, followed by an empty impinger bottle to trap carried over solvent. The first three impingers were maintained at room temperature while the last three were cooled in an ice bath. The impinger solvent analysis was carried out on using an Agilent GC (Agilent, Santa Clara, CA) equipped with a flame ionization detector and a DB-1701 column (30m, 0.25mm, 0.25um, Agilent, Santa Clara, CA) and is shown in Figure 3.2 below. The GC inlet and FID detector temperature were both maintained at 280^{o}C and the oven ramped at 5^{o}C/min to 45^{o}C.

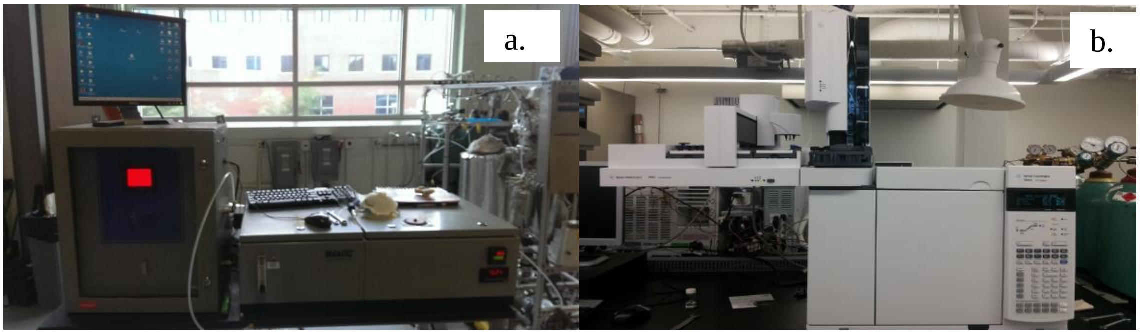


Figure 3.2 Data sampling instruments, Nova and FTIR gas analyzer(a) and GC FID (c)

Other than the gas product, char collected in the high temperature filter and in the bed, and liquid condensate collected from the condensers, were measured gravimetrically to determine their corresponding yield. Samples of char collected were further analyzed by CHNS/O for elemental composition.

The carbon balance or the carbon conversion efficiency was defined as the ratio of carbon obtained in the syngas to the amount of carbon fed into the gasifier (i.e. carbon in biomass feed), and is expressed in percentage form. Carbon monoxide, carbon dioxide, hydrogen and methane are major carbon compounds in syngas. Ethylene and acetylene were measured with help of FTIR and were included in the carbon balance calculations. The energy content of the syngas is defined as the sum of the heating values of the component gases. Heating value plays an important role when heat power application is the downstream application for the syngas. In gasification, the goal is to convert the highest amount of carbon present in the biomass to syngas components; hence, higher carbon conversion values are desirable. The carbon conversion efficiency or the carbon balance, expressed in Equation 3.b, was carried out for all experiments by considering the following carbon containing species in syngas: CO, CO_2, CH_4, C_2H_2 and C_2H_4.

$$\mathrm{Conversion_c} = \frac{(\text{mass carbon in syngas+mass of carbon in char})}{\text{mass carbon in sample}} \times 100 \qquad (3.b)$$

The cold gas energy efficiency (CGE) was defined as the ratio of sum of the heating values of primary syngas components to that of the LHV of the biomass., LHV was calculated from the HHV of biomass. This was efficiency of how much energy in biomass was converted in the useful syngas components and is shown in equation 3.c.

$$\mathrm{CGE} = 100 \times \frac{(\sum(\text{HV of comp. gas}x\left(\frac{\text{vol conc of comp. gas}}{100}\right)))\text{ x Syngas yield}}{\text{LHV of biomass}} \qquad (3.\mathrm{c})$$

3.2.4 **Experimental design and statistics**

ER and temperature are the primary control parameters during air gasification and range typically from 0.2 to 0.4 and from 600° to 900°C, respectively, although temperatures lower than 700°C are uncommon (Narváez et al., 1996). However, several biomass studies have been carried out at temperature and ER outside those ranges (Bingyan et al., 1994; Narvaez et al., 1996; Narváez et al., 1996). In this study, ER varied from 0.21 and 0.27 while temperature ranged from 790 to 1000°C.

Since the purpose of the study was to determine the effect of temperature and ER, experiments were designed to understand the effect of temperature and the equivalence ratio (ER) on the gasification products. The experiments were carried out at ER of 0.24 at 790, 935 and 1000°C. Three replications of each run were performed to calculate stand derivation. To understand the effect of ER variation, experiments were carried out at 0.21, 0.24 and 0.27 at 935°C. The data presented in the Results and Discussion section is the average of three runs for every ER and temperature, unless otherwise noted. To study the effect of ash content, samples with different ash content were selected, and are denoted as SG, SG 19 and SG 33. Statistical analysis was carried out using 1-way ANOVA with an alpha of 5%. Minitab was used as a tool for statistical analysis. It is important to notice that only one tar data point was collected at every condition, and thus the results presented for tar analysis have a larger error band.

3.3 Results and discussion

The minimum fluidization velocity (Um_f) and terminal velocity (U_t) values were calculated at 25°C and at 790, 935 and 1000°C, and have been reported in Table 3.1, the formulae used are listed in Appendix A. Sand (ρ_p = 2674.2 kg/m^3) was used as a bed material and is classified as a group B particle according to Gelbart's classification. For group B particles, since bubbling takes place at the onset of fluidization, therefore minimum fluidization velocity is equal to bubbling velocity (U_b). Consequently, the superficial velocity must lie between the minimum fluidization velocity (U_{mf}) and the terminal velocity (U_t). The nitrogen flow rate used for fluidization was 15.84 ±0.14 l/ min or a superficial velocity (U_s) of 0.14 m/s at STP between Um_f and U_t.

Table 3.1: Fluidization parameters for the bench-scale fluidized bed gasifier

Temp, °C	**790**	**935**	**1000**	**25**

Air, μ (N s/m^2)	4.44E-05	4.69E-05	4.93E-05	1.94E-05
Ar	67.1	60.14	54.42	1503.77
Re_{mf}	0.05	0.05	0.04	1.11
U_{mf}, m/s	0.031	0.029	0.028	0.069
U_t, m/s	2.27	2.15	2.04	22.21

3.3.1 **Biomass characterization**

Table 3.2 summarizes the properties of switchgrass feedstock used in this study. The physical and chemical properties of this feedstock are consistent with typical values reported for woody biomass with the exception of the ash content. However, ash content varies widely depending on the source, harvesting operation, and variant of the switchgrass. It is generally higher than that for typical woody biomass feedstocks (Carpenter et al., 2010a). Furthermore, the heating values of 18.86, 18.75 and 17.69 MJ/kg (dry basis) were obtained in this study and are in agreement with those reported in literature (Moutsoglou, 2012). The moisture content was reported in the table. When operated between 800-1000°C, the use of fluidized bed gasifiers helps reduce the ash agglomeration in high reactive samples like biomass (Basu, 2010). The particle size distribution of the biomass samples is shown in Figure 3.3.

Table 3.2: Proximate and ultimate analysis of switchgrass samples used in this study.

Analysis	**SG**	**SG 19**	**SG 33**
Moisture, % ar	8.54 ±0.34	8.43 ±0.39	7.95 ±0.31
HHV MJ/ kg, dry basis	18.86 ±0.25	18.75 ±0.23	17.69 ±0.19
Proximate Analysis (wt%, dry basis)			
Ash	2.71 ±0.12	3.48 ±0.19	4.59 ±0.43
Volatile matter	80.52 ±3.40	84.65 ±4.30	80.53 ±1.4

Fixed Carbon	16.77 ±3.31	12.15 ±4.28	14.87 ±1.44
Elemental Analysis (wt%, dry ash free basis)			
Carbon	50.65 ±0.82	50.43 ±0.01	48.50 ±0.28
Hydrogen	5.87 ±0.10	4.95 ±0.10	4.14 ±0.03
Nitrogen	1.74 ±0.12	0.57 ±0.03	1.02 ±0.90
Sulfur	0.33 ±0.01	0.30 ±0.03	0.25 ±0.23
Oxygen	38.65 ±0.81	43.73 ±0.10	46.06 ±0.27
Physical properties			
Bulk density (kg/m^3)	1439.47 ±14.85	1382.83 ±14.98	1165.16 ±9.21
Particle density (kg/m^3)	253.21 ±9.45	224.55 ±2.94	189.56 ±11.44
Particle size (d_{50}, mm)	0.518 ±0.08	0.57 ±0.16	0.651 ±0.78

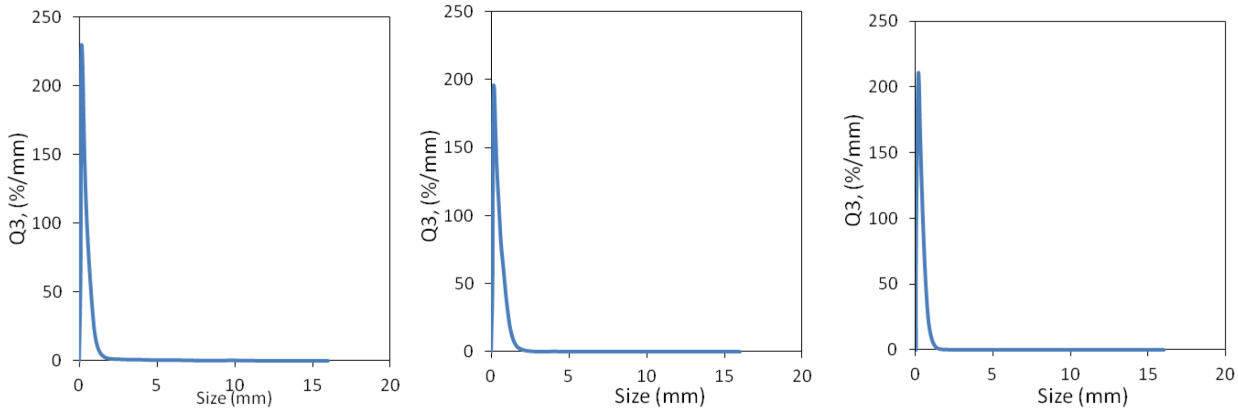


Figure 3.3: Particle size distribution of the switchgrass samples a. SG, b. SG19 and c. SG33

3.3.2 **Syngas profile**

The gasification experiments were carried out at three different temperatures (790, 935 and 1000°C) and at three different equivalence ratios (0.21, 0.24 and 0.27). Figure 3.4 and Figure 3.5 show the syngas profiles obtained during gasification experiments for an ER of 0.24.

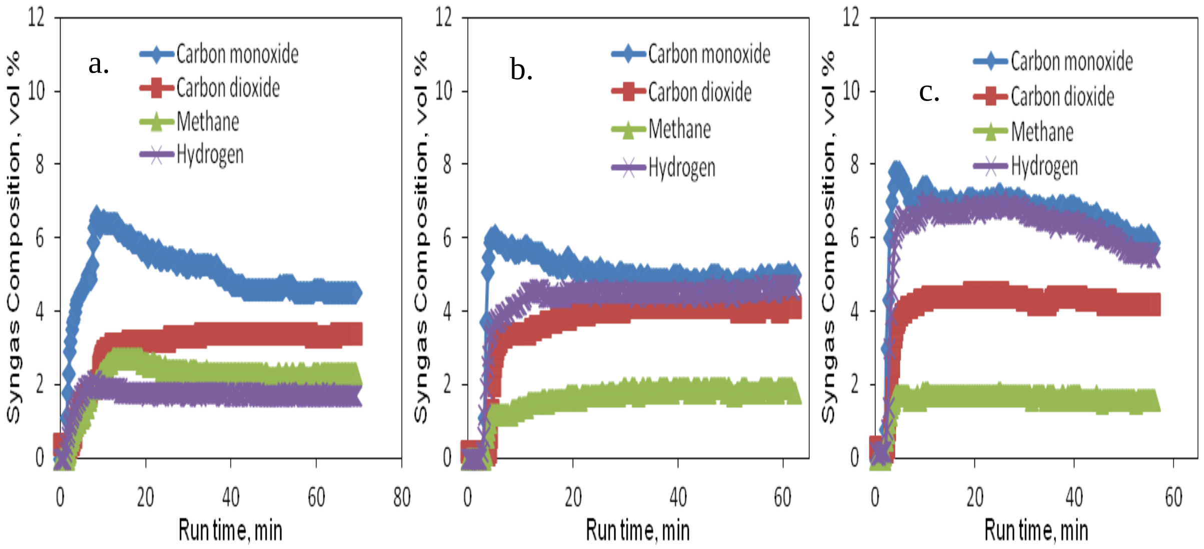


Figure 3.4: Syngas profile for experimental runs at 790 (a), 935 (b) and 1000°C (c) for ER 0.24 ±0.01.

Overall, it was observed that steady state in the syngas composition was obtained faster with an increase in temperature potentially due to faster decomposition of biomass as the temperature increased. While steady temperature control was achieved at 790 and 935˚C, a constant temperature could not be maintained at 1000°C after biomass feeding began. It was noticed in the first run that, when a set point of 1000˚C was set in the temperature controller, the reactor temperature gradually decreased over a typical run by 40˚C during a 60 minute run once the biomass feeding commenced. To attain an average temperature of 1000°C, the experiments were started at 1020°C and, over the course of the run, dropped to 980°C. This decreasing temperature behavior at 1000˚C was observed due the inadequate lower power capacity of the heaters which could not provide the additional heat required to sustain the endothermic gasification reactions. Although a brief steady-state syngas profile is observed as seen in Figure 3.4c , as the temperature decreased so did the concentrations of syngas constituents later in the run.

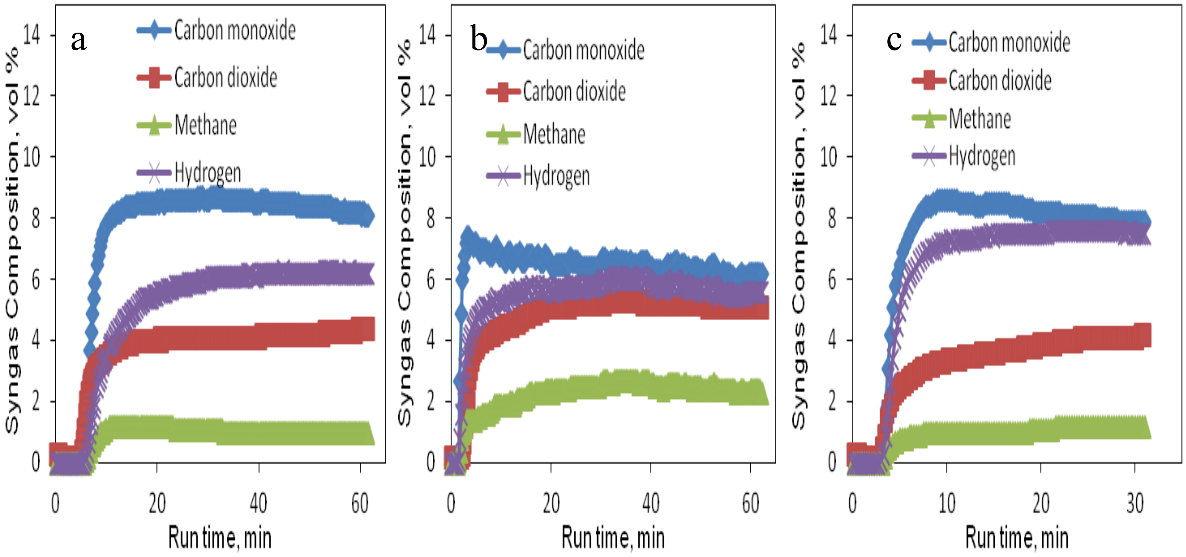


Figure 3.5: Syngas profile for experimental runs at 935°C for ER 0.21 (a), 0.24 (b) and 0.27 (c). Experiments at 0.27 ER were conducted for 30 minutes instead of the run-time of 60 minutes for the other ERs.

As equivalence ratio was varied, the time required to achieve steady state was not affected as illustrated in Figure 3.5. As these experiments were conducted at 935°C, temperature control was stable resulting in a steady gas composition after the first 30 minutes.

Reports of syngas profile are scarce in gasification studies. The effect of temperature and ER on syngas profile has not been widely documented. Carpenter *et al.* (2010a) reported gas profiles from a pilot scale fluidized bed unit with steam gasification. While the authors have not elaborated on the effect of temperature on gas steady state, the profile presented suggests that it does, with transient trends in gas composition following trends in temperature transients. In a pre-cursor to the present study, Abdoulmoumine *et al.* (2014) reported a similar trend of the effect of temperature for pine gasification using the same system. However, that study observed a different trend of the effect of ER, with the time required to achieve steady-state increased as ER increased.

The average values at steady state (typically last 20-30 minutes of the run) were used for further analysis in the present study. The use of study state date for analysis has been reported frequently in the literature(Abdoulmoumine et al., 2014; Carpenter et al., 2010a).

3.3.3 **Effect of temperature and equivalence ratio**

These experiments were performed using switchgrass sample that has ash content around 2.71 wt%. Table 3.3 summarizes the product yield, gas composition, gas energy, carbon conversion and cold gas efficiencies observed in this study as a function of temperature and equivalence ratio. Subsequent sections will further discuss these results, as well as the select contaminants measured in details.

Table 3.3: Gasification products obtained as a function of temperature and ER.

	Temperature, °C			**ER**		
	790	935	1000	0.21	0.24	0.27
Product yield, %						
Gas	73.94 ±9.00^{A}	79.81 ±8.06^{A}	87.65 ±3.57^{A}	76.85 ±5.87^{a}	79.81 ±8.06^{a}	77.33 ±3.78^{a}
Char	13.26 ±3.88^{A}	10.30 ±4.12^{A}	7.95 ±2.56^{A}	12.14 ±0.99^{b}	10.30 ±4.12^{b}	9.77 ±0.51^{b}
Liquid	12.79 ±5.22^{A}	9.88 ±5.26^{A}	4.39 ±2.46^{A}	11.01 ±4.88^{c}	9.88 ±5.27^{c}	12.90 ±3.98^{c}
Composition, vol %						
CO	3.48 ±0.93^{B}	6.13 ±1.02^{A}	6.87 ±0.76^{A}	5.41 ±0.34^{b}	6.13 ±1.01^{a,b}	7.56 ±0.96^{a}
CO_2	3.19 ±0.64^{B}	4.74 ±0.69^{A}	4.19 ±0.11^{A,B}	4.05 ±0.13^{a}	4.74 ±0.69^{a}	4.10 ±0.87^{a}
CH_4	1.67 ±0.52^{A}	1.74 ±0.60^{A}	1.39 ±0.27^{A}	1.85 ±0.09^{a}	1.74 ±0.60^{a}	1.29 ±0.35^{a}
H_2	1.29 ±0.36^{B}	5.51 ±0.87^{A}	6.56 ±0.90^{A}	4.69 ±0.39^{b}	5.51 ±0.87^{a,b}	6.91 ±0.91^{a}
C_2H_2	0.05 ±0.002^{A}	0.08 ±0.003^{A}	0.09 ±0.001^{A}	0.07 ±0.001^{a}	0.08 ±0.003^{a}	0.08 ±0.004^{a}
C_2H_4	1.06 ±0.02^{B}	0.42 ±0.12^{A,B}	0.71 ±0.02^{A}	0.91 ±0.01^{a}	0.42 ±0.12^{a}	0.22 ±0.07^{a}
Efficiency, %						
Carbon conversion	71.50 ±8.68^{A}	85.53 ±10.35^{A}	91.87 ±11.84^{A}	80.40 ±2.22^{a}	85.53 ±10.35^{a}	83.44 ±8.34^{a}
Cold gas	32.83 ±9.95^{B}	60.18 ±7.85^{A}	68.28 ±8.05^{A}	56.00 ±6.25^{a}	60.18 ±7.85^{a}	65.08 ±0.91^{a}
Syngas yield and energy						
Yield , Nm^3/ kg	0.54 ±0.02^{B}	0.89 ±0.11^{A}	1.03 ±0.08^{A}	0.79 ±0.06^{a}	0.89 ±0.12^{a}	0.95 ±0.05^{a}
LHV, MJ/ Nm^3	1.27 ±0.37^{B}	2.17 ±0.31^{A}	2.33 ±0.27^{A}	2.01 ±0.09^{a}	2.17 ±0.32^{a}	2.36 ±0.10^{a}

Effect of Temperature and ER were studied separately. Means with same superscripts are not statistically different (P-value > 0.05) based on a one-way ANOVA test. Means not connected by the same superscript are significantly different at the 0.05 level based on Tukey HSD Post Hoc test.

3.3.3.1 Product yield

The gasification process yields products in solid (char), liquid (liquid condensate) and gaseous (syngas) forms. The yields of these products are shown in Figure 3.6 as a function of temperature variation.

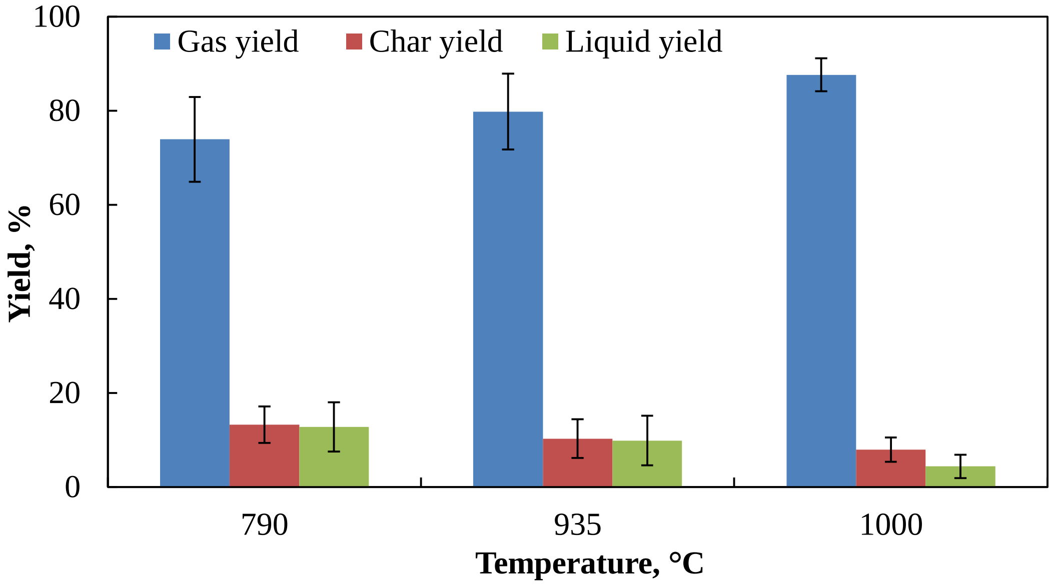


Figure 3.6: Effect of temperature on product yield at ER=0.24.

Increase in temperature is expected to increase the char reactivity and enhance char reactions shown below resulting in char reduction as temperature increased as evidenced in Figure 3.6.

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H^{\circ}_{f298} = +131 \text{ kJ/mol} \qquad (3.1)$$

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H^{\circ}_{f298} = +172 \text{ kJ/mol} \qquad (3.2)$$

H_2O and CO_2 produced at the onset of biomass decomposition further react with carbon rich char to produce H_2 and CO while decreasing the char yield. However, since the char yield was not significantly reduced as temperature is increased; the role of these reactions must be minimal in char conversion. This hypothesis is corroborated by the statistical analysis, which, as shown in Table 3.3, indicated that temperature did not have a statistically significant effect on char yield.

The char yield and decreasing trend as temperature increased is consistent with other studies (Abdoulmoumine et al., 2014; Cui et al., 2013; Narvaez et al., 1996). Nevertheless, these observations contradict findings by Campoy et al. (2008b) who reported increase in char yield with an increase in temperature while maintaining ER constant.

The liquid condensate yield shows a decreasing trend as temperature is increased. This liquid condensate is largely water, which would be in the form of steam at gasification temperatures of concern in this study. Since steam is involved in several gasification reactions including the aforementioned char reaction, it is likely consumed in gasification reactions resulting in the decrease of liquid condensate yield. As with char, temperature did not have a significant effect on the liquid yield. As the gas yield is determined by difference, it is evident that it would increase as temperature is increased since both char and liquid yields decreased. The increase of gas yield as temperature increases is consistent with several studies (Abdoulmoumine et al., 2014; Carpenter et al., 2010a; Narvaez et al., 1996).

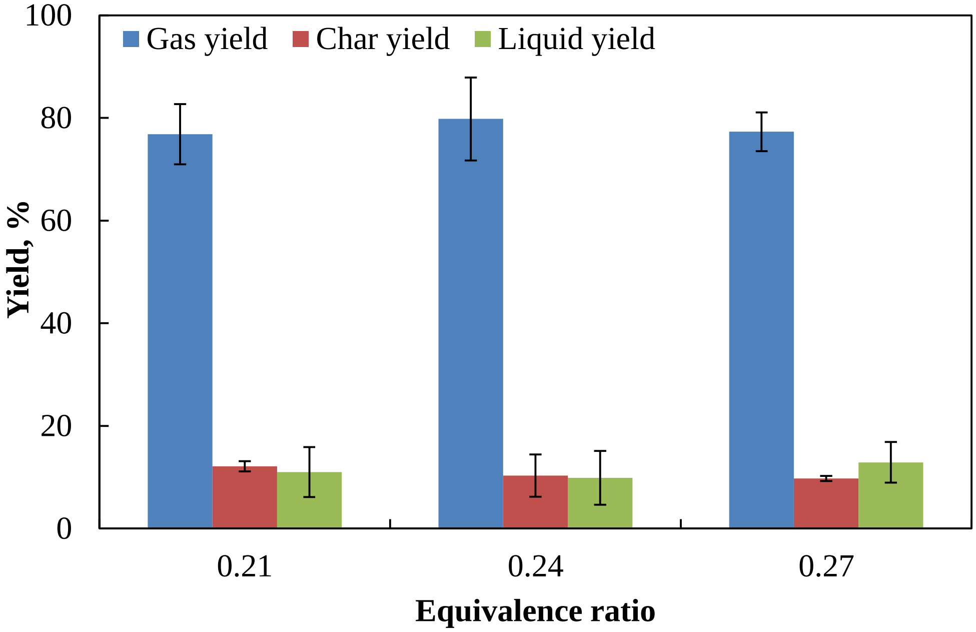


Figure 3.7: Effect of ER on product yield distribution at 935°C.

Figure 3.7 shows the product distribution as a function of ER. As ER is increased, higher oxygen availability is expected to influence the oxidation reactions. Reactions 3.3 to 3.7 are the key reactions that are expected influence the three products as ER is increased (Basu, 2010).

$$C + 0.5O_2 \rightarrow CO \qquad \Delta H^{\circ}_{f298} = -111 \text{ kJ/mol} \tag{3.3}$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^{\circ}_{f298} = -394 \text{ kJ/mol} \tag{3.4}$$

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \Delta H^{\circ}_{f298} = -284 \text{ kJ/mol} \tag{3.5}$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + H_2O \qquad \Delta H^{\circ}_{f298} = -803 \text{ kJ/mol} \tag{3.6}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \Delta H^{\circ}_{f298} = -242 \text{ kJ/mol} \tag{3.7}$$

The reactions above suggest that with increasing oxygen supply, increased oxidation of char and syngas components is expected. Based on reactions (3.3) and (3.4), higher oxygen supplied would result in a reduction in char yield as observed in this study. Furthermore, reactions (3.6) and (3.7) would expectedly lead to an increase in the liquid yield due to the formation of steam. The liquid yield remained more or less the same with an increase in ER as shown in Figure 3.6 due to the small range of ER studied. The gaseous yield also remained constant from ER 0.21 to 0.27. While reactions (3.3) to (3.7) increase CO_2, they also consume CO and H_2 simultaneously thus nullifying any increase in gas yield due to oxidation. The product yields were not significantly different at all levels based on the one-way analysis of variance. Other studies have observed trends similar to those observed in this study for char yield as ER increased (Abdoulmoumine et al., 2014; Campoy et al., 2008b). However, in contrast to the observations in this study, increasing gas yields were observed for increasing ER by other investigators for pine sawdust and unspecified wood pellets (Abdoulmoumine et al., 2014; Campoy et al., 2008b). Product yield obtained for a wide range of ER (0.20 to 0.49) has been shown in Appendix C.

Figure 3.8 further illustrates and compares the trend of gasification products as a function of ER for this study as well as others were char or gas yields were reported. The studies reported used polypropylene plastic (Xiao *et al.*), pine (dust) (Abdoulmoumine *et al*) and wood pellets (Campoy *et al.*). For given temperature (around 800°C) and ER (0.25-0.27), the gas yield was similar to pine, the char yield was slightly higher than those reported in the study and liquid yield was lower than pine study. Overall, the product yields from switchgrass gasification compared well with other studies.

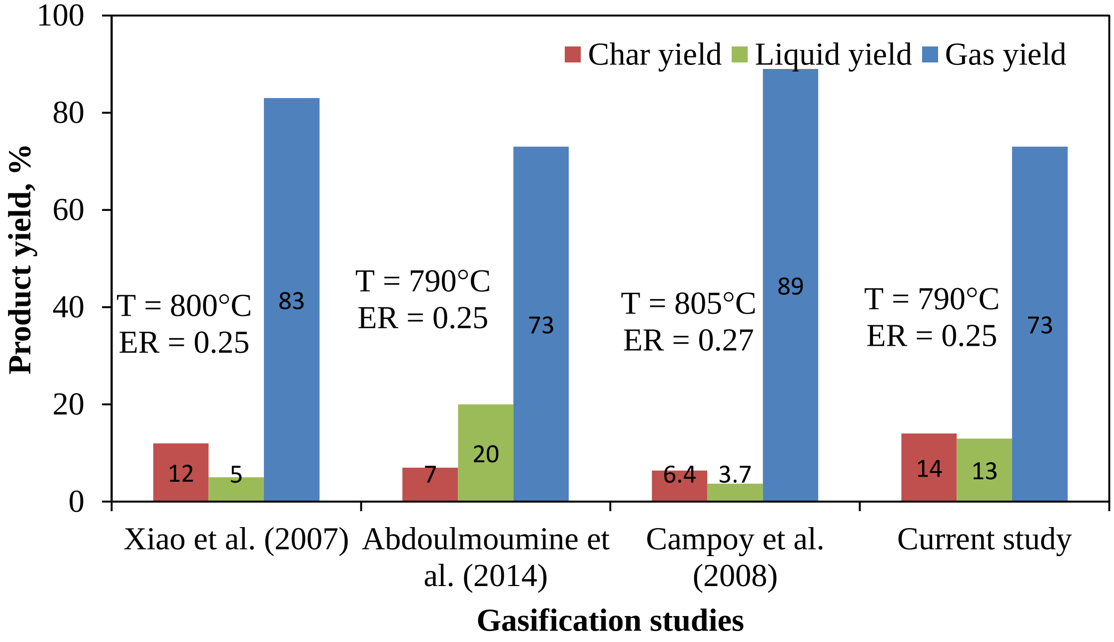


Figure 3.8: Product yield for switchgrass gasification compared with other biomass and waste reported in literature for fluidized bed gasifiers, Xiao et al (polypropylene plastic), Abdoulmoumine et al. (pine) and Campoy et al. (Wood pellets).

3.3.3.2 Syngas composition

Figure 3.9 shows the variation of syngas components as a function of temperature and ER.

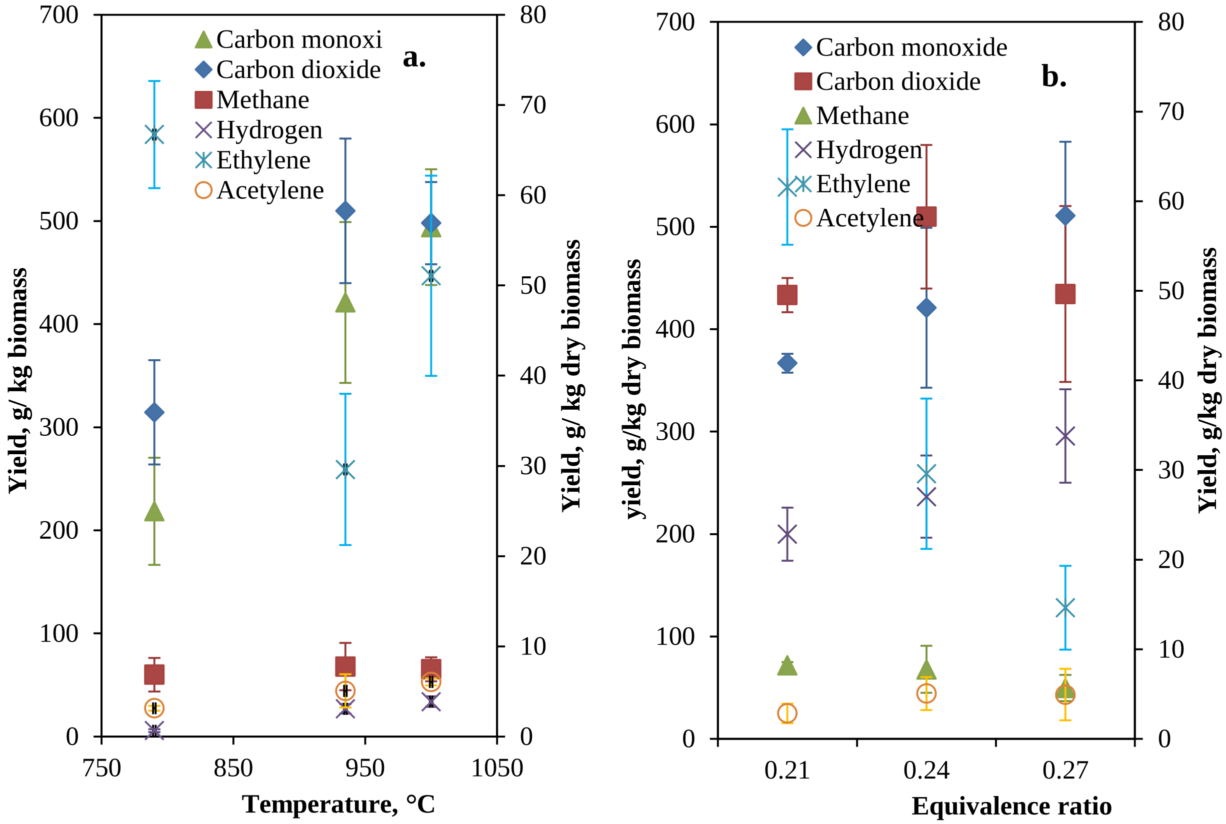


Figure 3.9: Effect of (a) temperature at 0.24 ER and (b) ER at 935°C on syngas composition.

With an increase in temperature from 790 to 935°C, char reactivity increased thereby increasing the yields of CO and CO_2 as shown in Figure 3.9a. With further increase in temperature (1000°C), the increase in CO yield could be explained by the occurrence of the Boudouard reaction which would convert CO_2 into CO. Increasing CO and H_2 is also likely due to the methanation reaction shown below, which would convert CH_4 and H_2O as temperature increased.

$$CO + 3H_2 \leftrightarrow H_2O + CH_4 \qquad \Delta H^{\circ}_{f298} = -206 \text{ kJ/mol} \qquad (3.8)$$

The decrease in liquid yield observed in the previous section further justifies the occurrence of this reaction. The increase in concentration of CO and H_2 agreed with that reported in literature for switchgrass and other biomass feedstocks(Abdoulmoumine et al., 2014; Carpenter et al., 2010a; Narváez et al., 1996; Sarkar et al., 2014a). As temperature increased, CH_4 yield was not statistically affected and remained approximately constant. However, statistical analysis indicated that temperature has a significant effect on CO, H_2, CO_2 and C_2H_4. Acetylene increased slightly, though the increase was not significantly affected by temperature based on statistical analysis. Ethylene yields were lower than previously reported figures for switchgrass (Carpenter et al., 2010a; Smeenk and Brown, 1998) and other biomass types (Van der Drift et al., 2001). However, those studies were carried out at lower temperatures which would typically yield higher concentrations of light hydrocarbons due to lower cracking. As observed in this study, acetylene was present at much lower concentration than ethylene in several reports (Abdoulmoumine et al., 2014; Carpenter et al., 2010a).

Figure 3.9b shows the variation in the yields of syngas components based on ER. Even though a narrow range of ER was studied, a noticeable variation in component yield was observed. CO yield increased with an increase in ER primarily as a result of char partial oxidation (Eqn. 3.3). This increase was statistically significant based on a one-way analysis of variance. From 0.21 to 0.24 ER, CO_2 increased suggesting that oxidation of CO and complete combustion of char was prevalent. However, as ER was further increased, CO_2 decreased while CO increased. This observation suggests two possible explanations: CO oxidation and complete combustion decreased or, more likely, CO_2 was converted to CO via the Boudouard reaction (Eqn. 3.2). Statistical analysis revealed that changes in CO_2 concentrations were significantly affected by the increase in ER. H_2 and CH_4 showed a decreasing trend in yield with increasing ER, consistent with expectation of greater oxidation of these constituents. The decrease in H_2 was statistically significant while that of CH_4 was not. While Carpenter *et al.* (2010a) reported lower CO yield compared to this study, Sarkar *et al.* (2014a) reported similar CO, H_2 and CH_4 yields for switchgrass. The syngas component yields were comparable with those values reported for other biomass feedstocks

(Abdoulmoumine et al., 2014; Campoy et al., 2009b). Equivalence ratio had a statistically significant effect on ethylene which was reduced as ER increased. This decrease is due to ethylene oxidation as shown in the reaction below.

$$C_2H_4 + O_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^{\circ}_{f298} = -273.45 \text{ kJ/mol} \qquad (3.9)$$

On the other hand, acetylene remained more or less constant with an increase in ER and was thus not significantly affected by the increase in ER. Both ethylene and acetylene were present at lower levels than reported for switchgrass (Carpenter et al., 2010a; Smeenk and Brown, 1998). Switchgrass air gasification data reported by Smeenk and Brown (1998) is compared to the results in the study after concentrations are corrected for different N_2 concentrations and shown in Table 3.4. When nitrogen concentrations are similar, the two studies have similar gas composition. Thus, the gas volumetric concentrations and consequently the gas heating values are due to nitrogen dilution.

Table 3.4: Comparison of gas composition from the present study with data reported by Smeenk and Brown (1998) for switchgrass air gasification in a bubbling fluidized bed gasifier

Authors	**Smeenk and Brown (1998)**	**Current study (N_2 corrected)**	**Current study**
Temperature, °C	700	790	790
ER	0.28	0.25	0.25
Composition, vol %			
CO	15.48	14.37	3.48
CO_2	18.04	13.17	3.19
CH_4	4.57	6.92	1.67
H_2	4.24	5.33	1.29
N_2	57.26	55.00	88.49
C_2H_4	1.92	4.38	1.06
HHV(MJ/Nm^3)	5.20	5.25	1.27

3.3.3.3 Syngas energy

The variation of energy content in the syngas with respect to the temperature and equivalence ratio is shown in Figure 3.10. In the Figure, error bars denote the standard deviation.

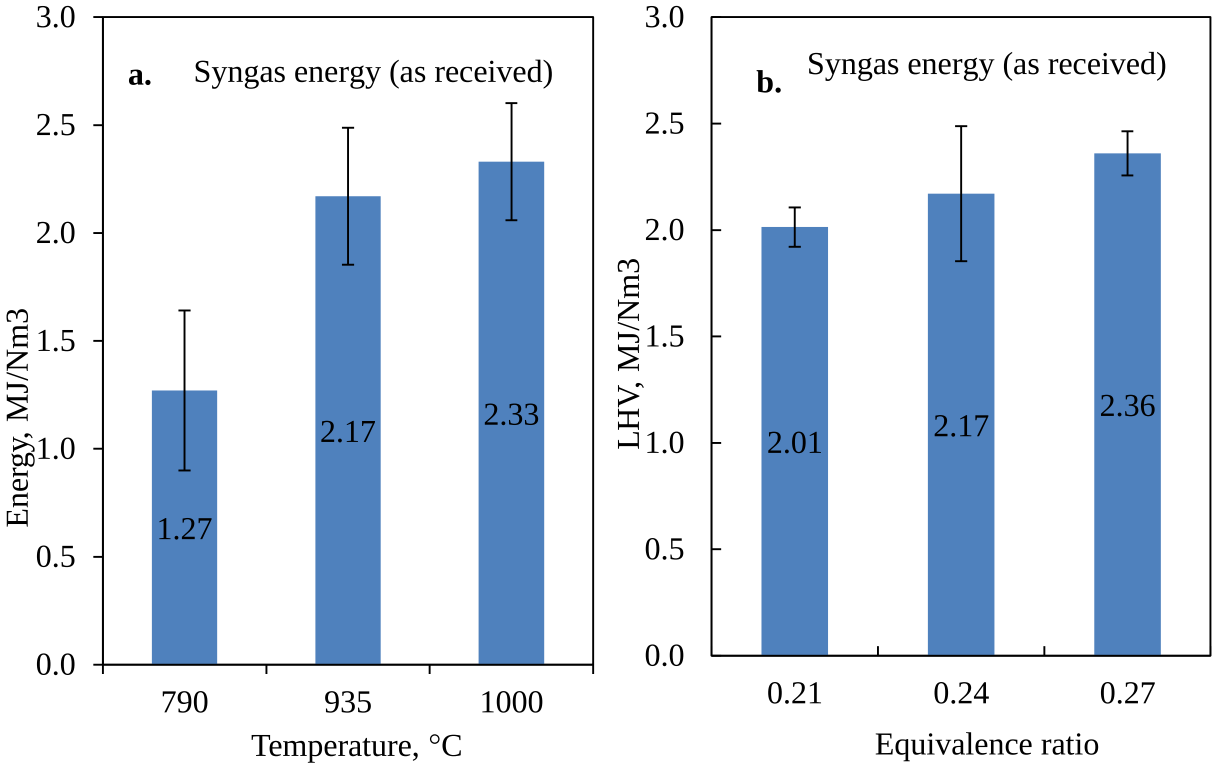


Figure 3.10: Effect of (a.) temperature at 0.24 ER and (b.) equivalence ratio at 935°C on LHV of the syngas on as received basis

As temperature and ER increase, the energy content of the syngas increases although at different rates. The steeper increase of energy content from 790 to 1000°C is a result of the increase in carbon monoxide and hydrogen over the same temperature range as previously discussed and illustrated in Figure 3.10a. This increase is statistically significant. In contrast, while the syngas energy content increased with increasing ER, the increase is lower than observed for temperature and statistically significant. Although carbon monoxide and hydrogen increased as ER increased, the increase was less than in the case of temperature particularly for hydrogen (Table 3.3). This explains the corresponding trend in syngas energy content for ER variation when compared to temperature variation.

When air is used as gasification medium, energy content typically ranges between 4 to 6 MJ/Nm^3 (Basu, 2010). The energy content values in this study are much lower than those reported in an earlier study (Smeenk and Brown, 1998) due to nitrogen dilution effect previously discussed. However, when nitrogen content is adjusted to values typically seen in air gasification for fluidized bed systems (~55 vol%), the energy contents in this study agree with expected values for air gasification as shown in Table 3.5. Furthermore, few studies suggest that with increasing ER, energy content decreases due to higher oxidation products (Abdoulmoumine et al., 2014; Lim and Alimuddin, 2008; Narváez et al., 1996). While over a narrow ER range, the present observations seemingly contradict the earlier reports, further investigation over a wider ER range revealed a downward trend consistent with previous reports for syngas energy as illustrated in Figure 3.11.

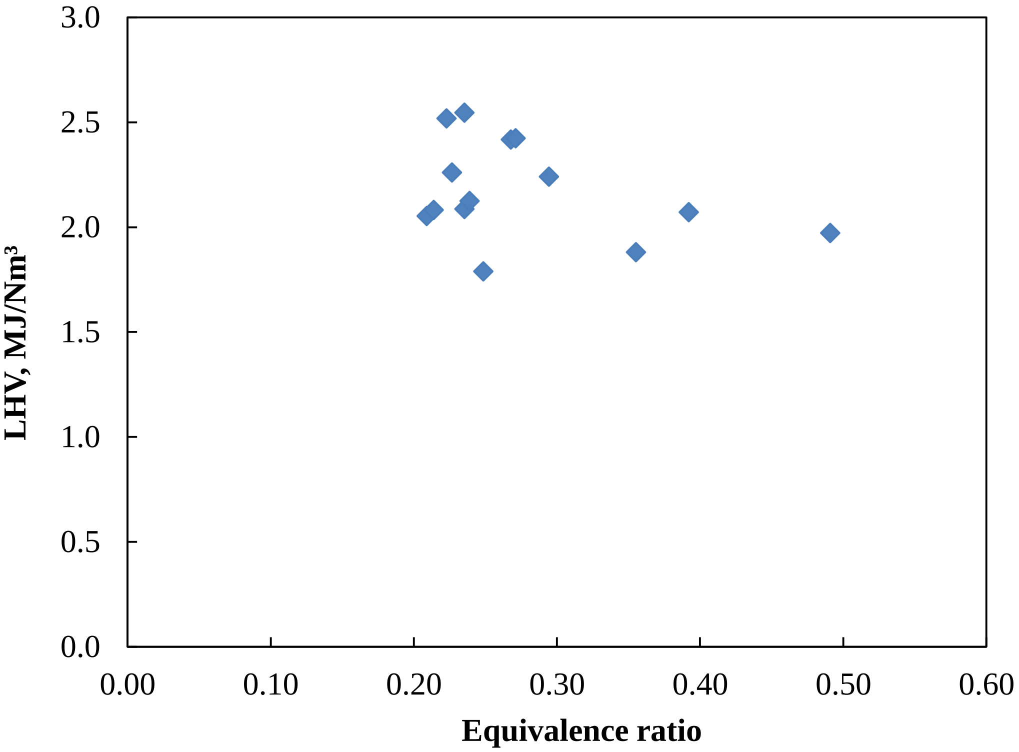


Figure 3.11: Syngas energy content over a wider ER range at 935°C on as received basis.

3.3.3.4 Carbon balance and cold gas efficiency

Figure 3.12 shows the carbon conversion based on temperature and ER. The carbon conversion increased with an increase in temperature due to an increased char reactivity resulting in higher carbon compounds in the syngas at higher temperature. Thus, temperature had a positive impact on carbon conversion. The carbon balance increased significantly from 790 to 935°C, and it further increased at 1000°C but was not significantly different. The total carbon conversion into syngas and char ranged from 71.51 % at 790°C to 91.87 % at 1000°C. With increase in temperature, the carbon in the char reduced indicating higher conversion into carbonaceous gas products as previously discussed. The effect of temperature on carbon that was converted into gaseous form was statistically significant. In contrast, temperature did not have a significant effect on carbon in char. The Broer et al. (2015) reported carbon syngas conversions to syngas ranging from 74 to 82% for temperatures and ERs ranging from 705 -880°C, and 0.21-0.32, respectively, for oxygen gasification of switchgrass in a pilot scale fluidized bed unit. Others reported carbon conversion to syngas for switchgrass between 60 to 81% from 650 to 900°C (Carpenter et al., 2010a; Sarkar et al., 2014a). With the exception of carbon conversion at 790°C which is lower than typically observed for fluidized bed systems, all other temperature and ER levels are comparable to those reported in the aforementioned studies. The carbon conversion into gas for a large ER range has been reported in Appendix C. The lower carbon conversion to syngas at 790°C suggests poorer biomass thermal decomposition potentially due to several reasons: (i) higher nitrogen flow rate leading to partially gasified biomass particle carried out of gasifier, (ii) lower heating rate in the gasification zone due to lower heat transfer between sand and biomass particle and (iii) higher uncertainty in gas product measurements. While all these reasons could explain the lower carbon conversion at 790°C, (i) and (iii) are more plausible in light to the higher char yield and higher standard deviations observed at that temperature.

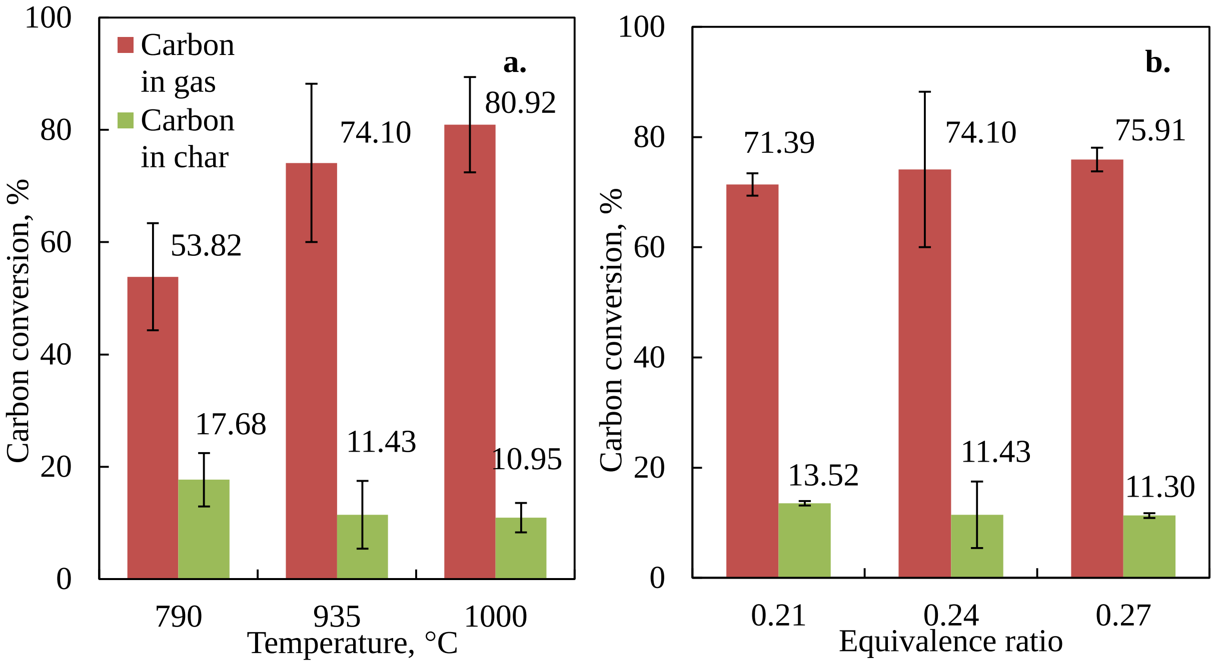


Figure 3.12: Carbon conversion from syngas and char by (**a.**) temperature at 0.24 ER and (**b.**) ER at 935°C

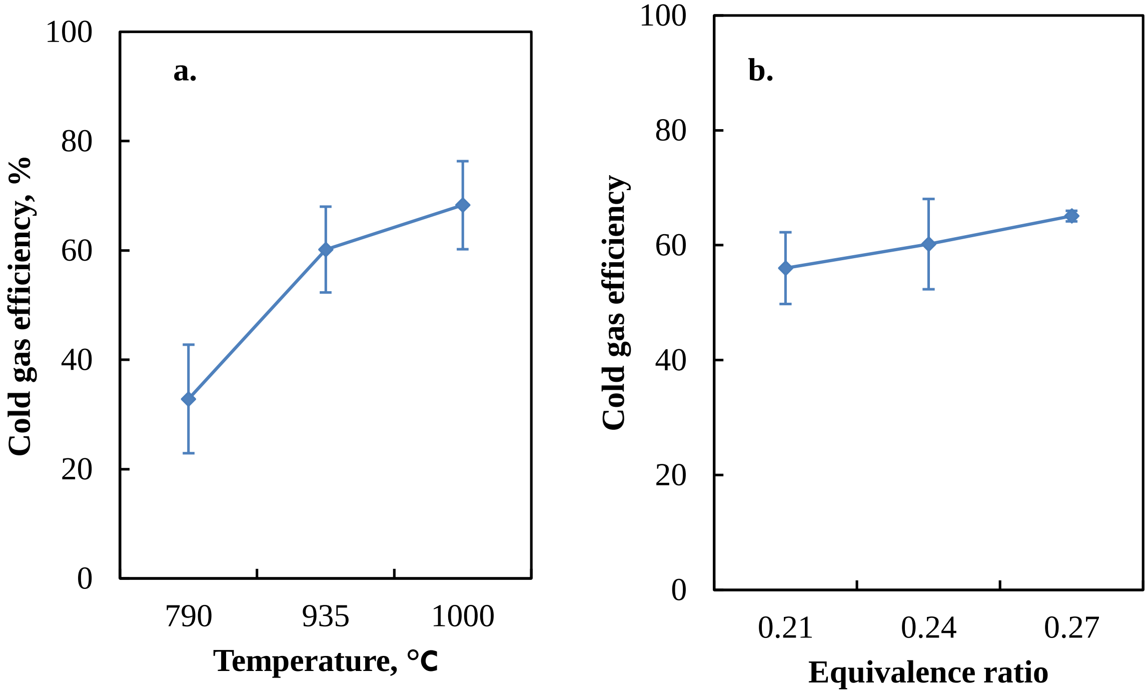


Figure 3.13: Effect of (a) temperature at 0.24 ER and (b) ER at 935°C on cold gas efficiency

Figure 3.13 shows the effect of temperature and equivalence ratio on cold gas efficiency. Cold gas efficiency increased as temperature increased due to the increase in carbon monoxide and hydrogen noted before. For ER, the increase was less pronounced due to lower carbon monoxide increase relative to temperature and the decrease in hydrogen yield. The increase in cold gas efficiency over temperature was statistically significant while it was not over the range ER studied. Cold gas efficiencies achieved in this study compare well with those reported by others where it ranged from 42 to 65 % for switchgrass (Broer et al., 2015; Carpenter et al., 2010a; Sarkar et al., 2014a) and 37 to 69 % for various other biomass types (Campoy et al., 2008b; Cao et al., 2006; Cui et al., 2010, 2013; Lv et al., 2007).

3.3.3.5 Contaminants

Figure 3.14 shows the ammonia, hydrogen cyanide and sulfur dioxide concentrations as function of temperature and ER. Ammonia and hydrogen cyanide increased with increase in temperature and ER. However, in both cases, temperature and ER did not significantly affect these contaminants based on a one-way ANOVA. The NH_3 and HCN concentrations in syngas are proportional to fuel nitrogen content (Zhou et al., 2000). In addition, these concentrations are affected by oxidizing agent (steam/O_2 or air), temperature and ER (Aljbour and Kawamoto, 2013b; Zhou et al., 2000). In general, as temperature and ER increase, NH_3 and HCN concentrations decreased(Abdoulmoumine et al., 2014; Leppälahti, 1993; Zhou et al., 2000). However, there have been instances where NH_3 and HCN did not follow this behavior (Aljbour and Kawamoto, 2013b; Van der Drift et al., 2001). Reported NH_3 and HCN concentrations vary widely. In the only instance of NH_3 and HCN reports for switchgrass gasification, the investigators reported NH_3 and HCN concentrations ranging from 10000 to 5800 ppm and 2500 to 400 ppm, respectively (Broer et al., 2015). Van der Drift *et al.* (2001) reported NH_3 concentration of 12500 ppm for verge grass with nitrogen content of 0.18 wt % daf. NH_3 and HCN concentrations in this study are closer to values reported for woody biomass feedstock with lower nitrogen content were reports ranged from near 300 to 1800 ppmv for NH_3 and less than 70 ppmv for HCN (Abdoulmoumine et al., 2014; Aljbour and Kawamoto, 2013b; Van der Drift et al., 2001). SO_2 is a product of complete combustion of fuel sulfur and present in lower concentration during gasification compared to combustion (Basu, 2010). SO_2 values did not significantly change and were around 50 ppmv. Furthermore, analysis of variance indicated that the concentration of SO_2 was not significantly affected by an increase in the temperature or ER. The combustion of coal produces much higher amounts of SO_2. In a study on a fluidized bed combustor at around 700 to 800°C, the SO_2 emission values for coal and coal-biomass co-feeding (up to 23% by weight.) were reported to be around 400 to 500 ppm (Xie et al., 2007). The current study shows a drastic reduction in SO_2 emission from gasification of biomass. The oxygen deprived conditions of gasification, around 93 to 98% of the sulfur is converted into the H_2S and most of the remaining in to Carbonyl sulfide (COS); this explains the low SO_2 concentrations obtained in the current study (Higman and van der Burgt, 2008).

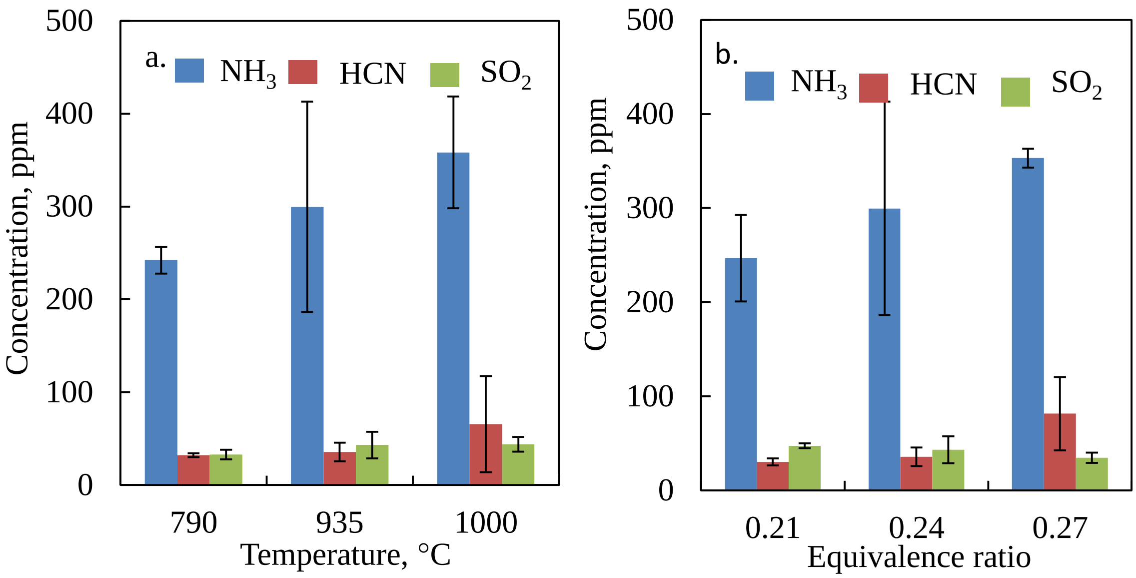


Figure 3.14: Effect of (a) temperature at 0.24 ER and (b) ER at 935°C on contaminants

The effect of temperature and equivalence ratio on tar yield and composition are presented in Figure 3.15 and Figure 3.16, respectively. As illustrated in Figure 3.15, tar yield decreases as temperature is increased presumably due to primary and secondary tar cracking or conversion to tertiary tar compounds (Milne et al., 1998a). In other studies, various investigators have observed a similar tendency for tar concentration as temperature increased (Broer et al., 2015; Carpenter et al., 2010a; Mayerhofer et al., 2012). As ER is increased, tar yields are expected and observed in some studies to decrease due to increasing oxidation (Aljbour and Kawamoto, 2013b; Narvaez et al., 1996). However, in few instances, it has been observed that tar yield increases with ER (Abdoulmoumine et al., 2014; Basu, 2013; Campoy et al., 2008b). Tar yield (g/kg biomass or mg/kg biomass) is the product of tar concentration (g/Nm^3) and gas yield (Nm^3/kg biomass). As gas yield increases with increasing ER, it is plausible to obtain a net increase in tar yield if the rate of increase of gas yield (Nm^3/kg biomass) is greater than the rate of decrease of tar concentration (g/Nm^3). Within the narrow ER range and thus a lower extent of tar oxidation, the above reasoning best explains the observations in this study. The tar yields and concentration are lower than yields reported for fluidized bed systems (2-19 g/Nm^3) (Narvaez et al., 1996). However, as these yields only account for GC detectable compounds, lower values are expected.

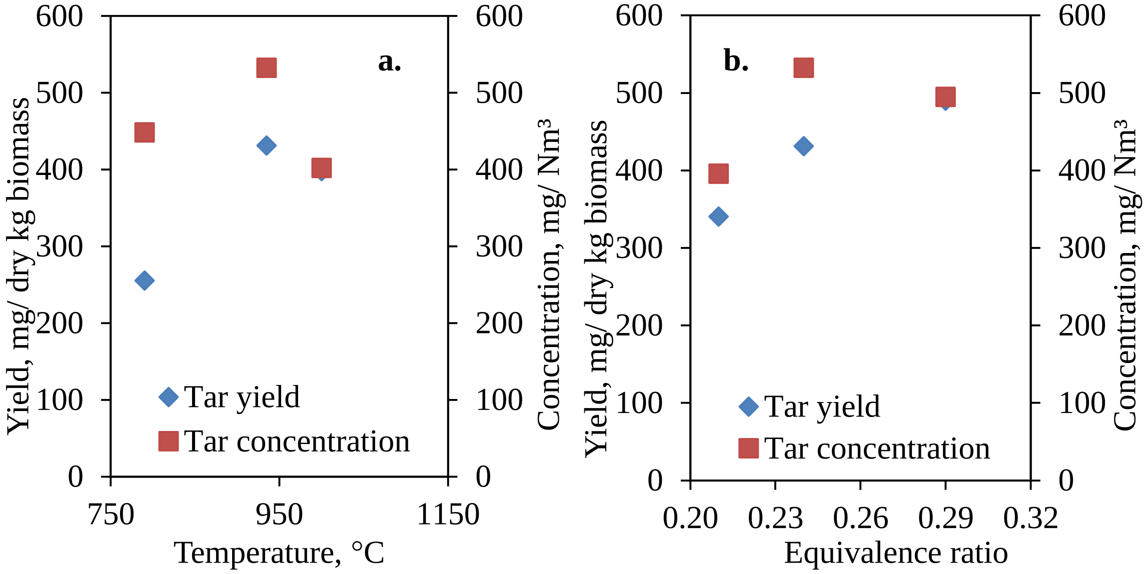


Figure 3.15: Effect of (a) temperature and (b) ER on tar yield and concentration (Note: During the experimental tar run at 0.27 resulted in lower feeding of biomass resulting in ER 0.29, hence it was used in this figure).

The tar compounds detected in the impinger solvents are benzene, toluene, ethyl benzene, o-xylene, styrene, indene, phenol, 3-methyl phenol, naphthalene, 2-methyl naphthalene and bi-phenyl. High concentrations of benzene, toluene and naphthalene were obtained. As temperature increased, the yield of toluene, styrene, indene and phenol decreased. Irrespective of the temperature or equivalence ratio, benzene was consistently observed at high yields than all the other compounds in agreement with other studies followed by naphthalene, phenol and toluene (Abdoulmoumine et al., 2014; Carpenter et al., 2010a; Devi et al., 2003; Mayerhofer et al., 2012). The trends observed for individual compounds are largely aligned with the trends observed for tar yields over temperature and ER. In particular, most abundant compounds like benzene, naphthalene and toluene shows similar trend as observed for tar yields: as temperature increases, they decrease and increase as ER increased.

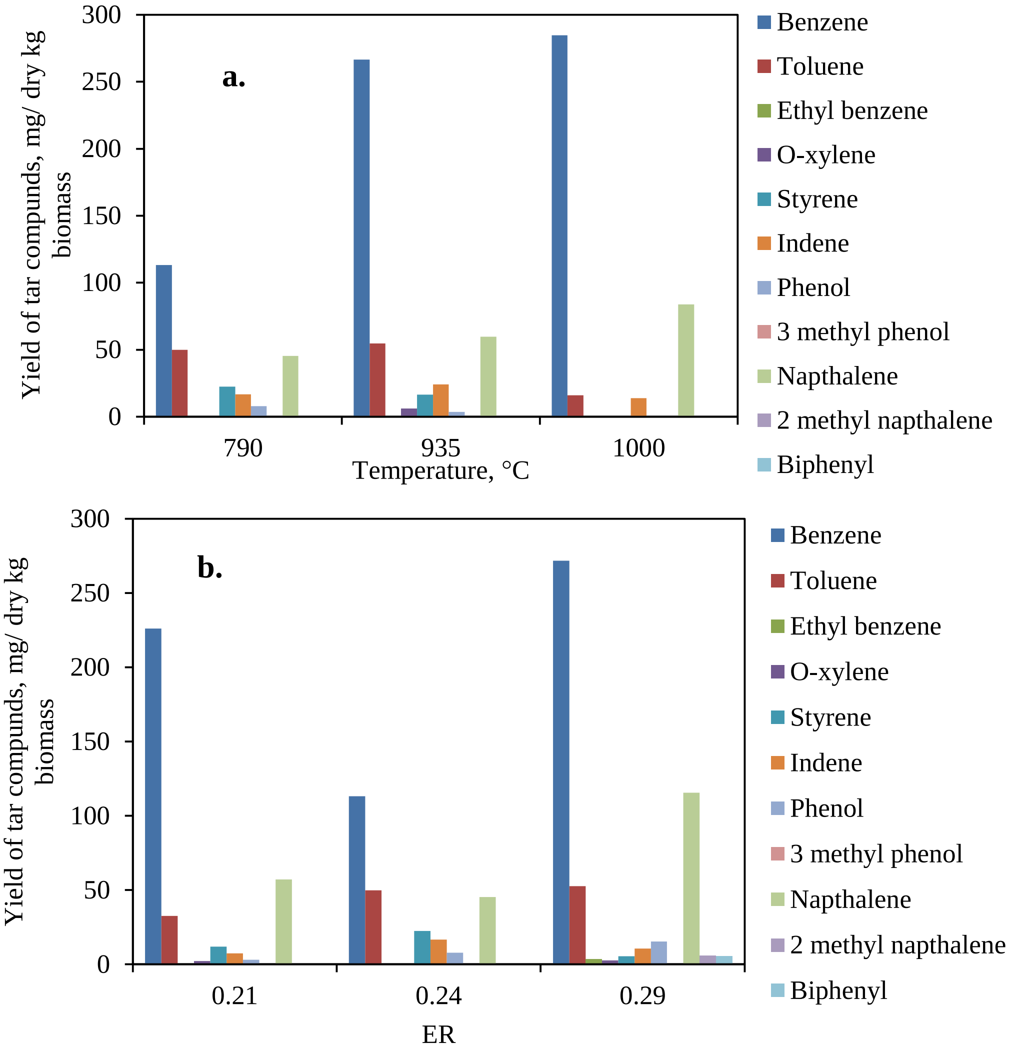


Figure 3.16: Yield of tar components as a function of (a) temperature and (b) ER.

3.3.4 **Effect of ash content**

High ash content in switchgrass is a source of concern in gasification due to its tendency to cause agglomeration and slugging in the reactor. However, for all experiments, no agglomeration or slugging was observed in the reactor in this study despite the high gasification temperature in some experiments (935 and 1000°C). The lack of these issues might be due to the bed turbulence caused by fluidization which would have broken up agglomerates. As opposed to moving bed gasifiers where these issues are more prevalent, it can be concluded that fluidized bed gasifiers are suitable for handling the high ash content materials at least within the range of ash content in this study. Table 3.5 summarizes the product yield, gas composition, gas energy, carbon conversion and cold gas efficiencies observed in this study. Subsequent sections will further discuss these responses as well as the select contaminants measured in details.

Table 3.5: The gasification products obtained as a function of temperature and ER.

	Ash content, wt% dry basis		
	2.71	3.48	4.59
Product yield, %			
Gas	79.81 ±8.06^{A}	82.51 ±3.41^{A}	80.41 ±2.23^{A}
Char	10.30 ±4.12^{A}	12.24 ±2.06^{A}	13.29 ±1.24^{A}
Liquid	9.88 ±5.26^{A}	5.26 ±1.36^{A}	6.29 ±0.90^{A}
Composition, vol %			
CO	6.13 ±1.01^{A}	5.59 ±0.82^{A}	6.08 ±1.52^{A}
CO_2	4.74 ±0.69^{A}	4.07 ±0.32^{A}	3.24 ±0.90^{A}
CH_4	1.74 ±0.60^{A}	1.35 ±0.18^{A}	1.33 ±0.54^{A}
H_2	5.51 ±0.87^{A}	4.97 ±0.78^{A}	5.01 ±1.29^{A}
C_2H_4	0.42 ±0.13^{B}	0.60 ±0.06^{A,B}	0.72 ±0.08^{A}
C_2H_2	0.08±0.03^{A}	0.05 ±0.01^{A}	0.05 ±0.01^{A}
Efficiencies, %			
Carbon conversion	74.10 ±14.09^{A}	80.15 ±6.12^{A}	77.46 ±12.15^{A}
Cold gas	85.53 ±9.12^{A}	76.01 ±5.59^{A}	81.16 ±14.15^{A}
Syngas yield and energy			
Yield , Nm^3/ kg	0.89 ±0.12^{A}	0.92 ±0.03^{A}	0.89 ±0.25^{A}
LHV, MJ/ Nm^3	2.17 ±0.31^{A}	1.89 ±0.24^{A}	1.93 ±0.56^{A}

Means without superscripts are not statistically different ($P\text{-value} > 0.05$) based on one-way ANOVA test. Means not connected by the same superscript are significantly different at the 0.05 level based on Tukey HSD Post Hoc test.

3.3.4.1 Product yield

Product yields from three switchgrass samples with different ash contents ranging from 2.71 to 4.23 wt% (dry basis) are shown in Figure 3.17. The yields varied between 79.81 to 82.51%, 10.30 to 13.29% and 9.88 to 5.26% for gas, char and liquid products. The variation in yields was not statistically significant based on a one-way ANOVA indicating that ash content has no affect the product yields. Unlike for temperature and ER were several gasification reactions govern changes observed in products, only catalytic effects of inorganic elements in ash are expected to influence product yields. However, the results in this study suggest that inorganic elements of ash did not play a catalytic role significant enough to impact product distribution. Based on previous gasification studies of high ash content feedstocks, char yields around 10 wt % were observed, similar to observations in this study (Carpenter et al., 2010a; Cui et al., 2013; Qian et al., 2013). However, liquid condensate yields are lower than previously observed for low ash content woody biomass (Abdoulmoumine et al., 2014). It appears that gas yield decreases with increasing fuel ash content in a linear fashion. Indeed, Carpenter et al. (2010a) quantified the gas yields from switchgrass, corn stover and wheat straw with ash contents of 8, 11.4 and 12.7 wt % dry basis with corresponding gas yields of 62, 54 and 54 %. The plot of these values reveals a linear correlation that holds when the lower ash contents gas yields, like in this study, are included. The decrease in gas yield was followed with an increase in liquid yield as ash content increased (Carpenter et al., 2010a).

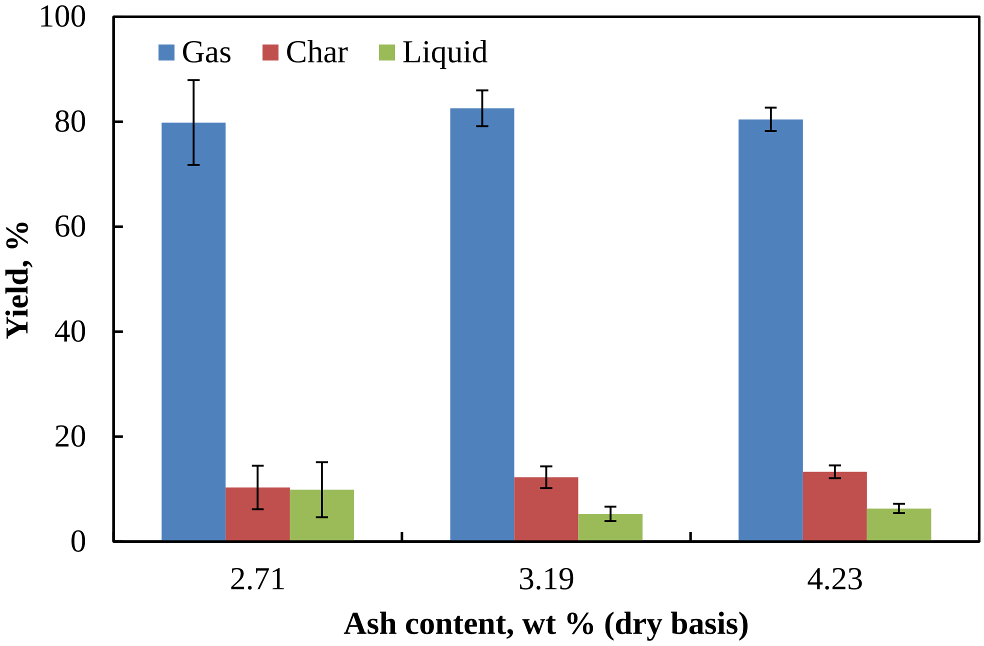


Figure 3.17: Effect of ash content on product yields at 935°C and 0.24 ER.

3.3.4.2 Syngas composition

Figure 3.18 shows the effect of ash content on the syngas composition. Inorganic elements in biomass ash have long been known to have catalytic properties in thermochemical processes (Bridgwater, 1994; Rizkiana et al., 2014). Since all other parameters (temperature and ER) are maintained fixed, it stands to reason that variations in syngas composition are due to the catalytic effect of ash inorganic elements on various gasification reactions.

It was observed that as ash content increased, the concentration of CO_2 decreased while that of CO increased simultaneously suggesting that the Boudouard reaction. likely played a role. It is unlikely that the increase in CO was due to any catalytic effect on ash on the water-gas reaction (Eqn. 4) as H_2 did not vary significantly. CH_4 and C_2H_2 decreased as ash content increased possibly due to ash catalyzed steam and/or dry reforming. Van der Drift et al. (2001) found that for willow and verge grass with ash contents of 2.13 and 17.6 wt% dry basis, CO_2 decreased while CO increased slightly in agreement with the observations in this study. While CH_4 decreased as ash content increased, C_2H_4 was observed to decrease in contrast with this study. In light of the absence of increase in H_2 yield, it is possible that additional H_2 produced as a result of steam and/or dry reforming of CH_4 and C_2H_2 was subsequently consumed in the hydrogenation of C_2H_2 to form C_2H_4. Statistically the increase in C_2H_4 was statistically significant from ash content of 2.71% to 4.59%. For all the other syngas components the ash content had no significant effect.

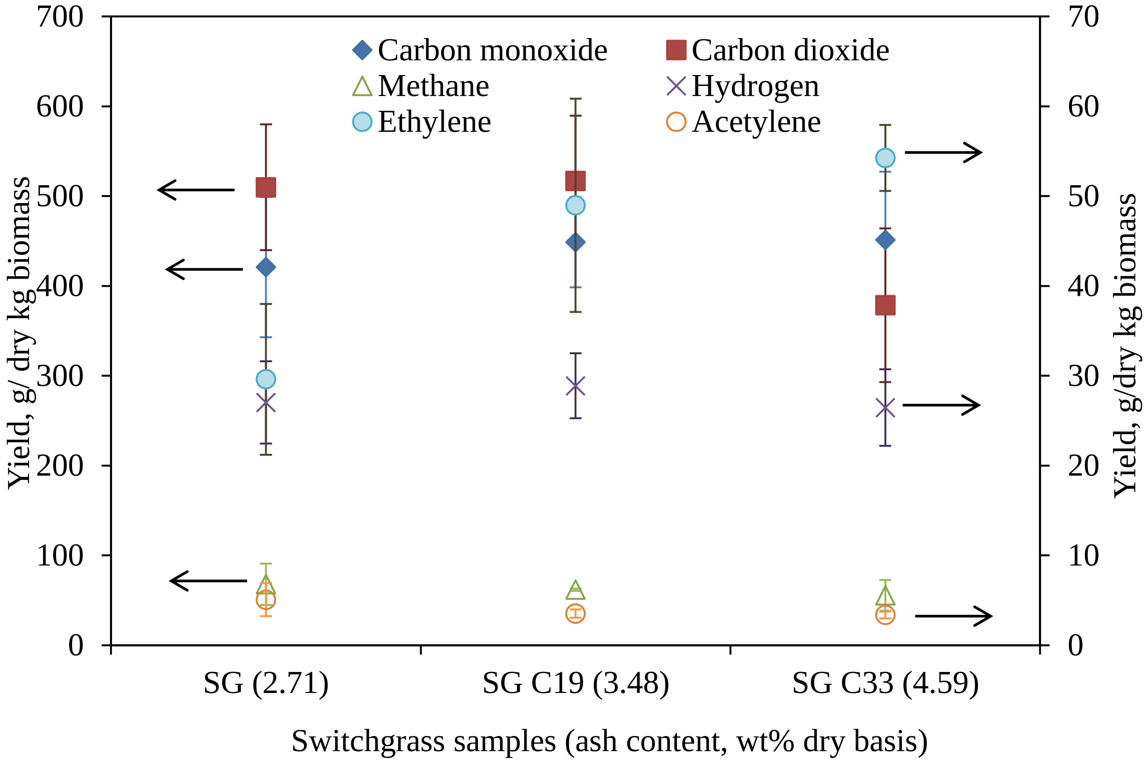


Figure 3.18: Effect of ash content on primary syngas composition at 935°C and 0.24 ER.

3.3.4.3 Syngas energy and yield

The syngas energy content is a function of the syngas composition. Higher concentration of methane in syngas, translates to higher syngas energy content. The syngas energy and yield obtained for the switchgrass samples were reported in Table 3.6. The average values of syngas energy obtained for the switchgrass yield at the given temperature and ER were reported between

2.17 and 1.66 MJ/Nm^3. The ash content did not statistically affect the syngas energy content. The syngas yield was calculated on per dry kg of biomass. The conversion of biomass into syngas was found to be not affected by the ash content either. The average syngas yield ranged between 0.88 and 0.92 Nm^3/ dry kg biomass.

3.3.4.4 Carbon and cold gas efficiency

A high conversion of carbon in the biomass into the syngas is desirable. The study performed showed no significant effect of ash content in the range studied affected the carbon conversion. Similarly, the cold gas energy efficiency was not affected by increase in the ash content. These trends agreed with those reported previously for low ash content green wood and high ash content verge grass (Van der Drift et al., 2001). Figure 3.19 shows the carbon conversion in gas and cold gas efficiency obtained during the ash content variation study. Thus from the previous section and this section, it could be the carbon conversion and cold gas energy are influenced more by the temperature of the gasifier bed than by the ash content of the biomass.

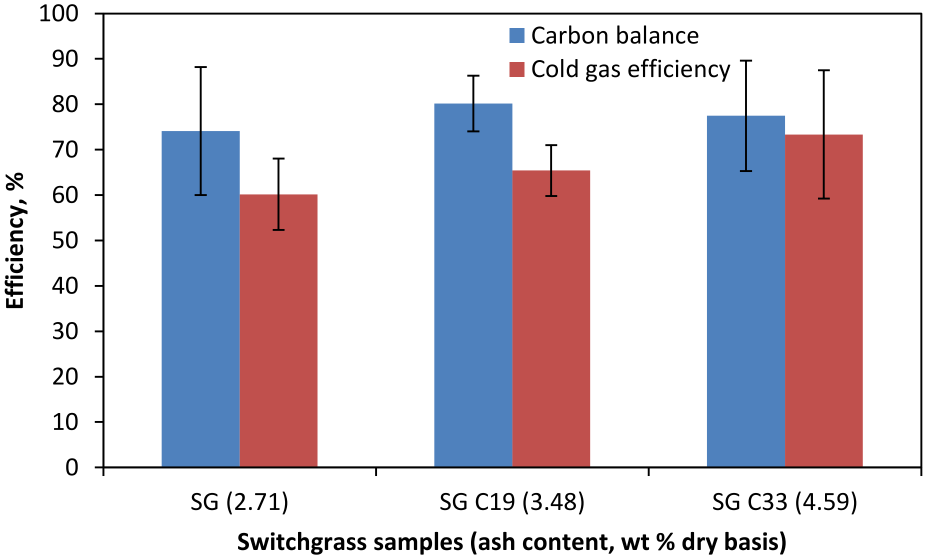


Figure 3.19: Carbon conversion in gas as a function of ash content of biomass.

3.3.4.5 Contaminants

The contaminants obtained from gasification of the three samples of switchgrass have been reported in the Table 3.6. It can be seen that the yield and volumetric concentration of ammonia were not affected by the ash content. This contradicted the findings of a study (Van der Drift et al., 2001), where the high ammonia concentration were obtained for samples with higher ash content (12500 ppmv at 17% ash content). The trend reported in this study could be due to small range of ash content under study. The HCN and SO_2 were also more or less in the same range for the three different biomass samples.

Table 3.6: Yield and concentration of the syngas contaminants obtained for three different samples of biomass

	SG	**SG C19**	**SG C33**
	Volumetric concentration (ppmv)		
Ammonia	299.62 (113.4)^{A}	227.15 (25.18)^{A}	291.01 (90.56)^{A}
Hydrogen cyanide	35.73 (9.99)^{A}	47.84 (14.2)^{A}	91.89 (69.9)^{A}
Sulfur dioxide	43.11 (14.3)^{A}	31.50 (4.91)^{A}	33.49 (10.70)^{A}
	Yield (g/ dry kg biomass)		
Ammonia	1.28 (0.45)^{A}	1.11 (0.12)^{A}	1.30 (0.25)^{A}
Hydrogen cyanide	0.24 (0.06)^{A}	0.36 (0.07)^{A}	0.65 (0.49)^{A}
Sulfur dioxide	0.69 (0.22)^{A}	0.58 (0.06)^{A}	0.57 (0.12)^{A}

3.3.5 **Effect of feed rate**

In previous sections, the dilution of syngas due to higher percentage of nitrogen was observed. In order to reduce this dilution, biomass feed rate was increased, experiments were carried out with switchgrass sample which has ash content 2.71 wt% (dry basis). In this section, the effect of feed rate on the gasification performance is discussed. In order to study this effect, the experimental runs were performed at different speeds of the feeder screw (100, 200 and 300 rpm). Three runs were performed for each speed. Temperature and ER were kept constant at 935°C and 0.25 respectively. Table 3.7 shows the summary of results obtained. These results are further discussed in the following sections.

Table 3.7: Product yield, the syngas composition, yield, energy and efficiency for different feed rate.

Feeding, RPM	**100**	**200**	**300**
Actual feeding rate, g/ min	3.63 ±0.14	6.38 ±0.21	9.34 ±0.31
Feeding rate, dry g/min	4.02 ±0.15	6.98 ±0.23	10.21 ±0.33
Gas yield, %	79.81 ±8.06 ^{A}	73.80 ±0.36 ^{A}	74.75 ±0.39 ^{A}
Char yield, %	10.30 ±4.12 ^{A}	8.05 ±0.86 ^{A}	7.55 ±0.44 ^{A}
Liquid yield, %	9.88 ±5.26 ^{A}	18.14 ±0.98 ^{A}	17.68 ±0.19 ^{A}
Syngas composition			
Composition, vol %			
CO	6.13 ±1.01 ^{C}	9.44±0.57 ^{B}	12.56 ±0.60 ^{A}
CO_2	4.74 ±0.69 ^{C}	7.65 ± 0.23 ^{B}	9.50 ±0.59 ^{A}
CH_4	1.74 ±0.60 $^{`C}$	3.82 ±3.36 ^{B}	5.81 ±0.20 ^{A}
H_2	5.51 ±0.87 ^{B}	6.14 ±0.24 ^{B,A}	7.02 ±0.29 ^{A}
C_2H_4	0.42 ±0.01^{B}	2.6 ±0.08^{A}	2.52 ±0.86^{A}
C_2H_2	0.08 ±0.01 ^{B}	0.11 ±0.02 ^{B}	1.58 ±0.01 ^{A}
Yield, g/ dry kg biomass			
CO	420.99 ±78.13 ^{A}	387.81 ±18.03 ^{A}	407.78 ±13.68 ^{A}
CO_2	509.84 ±70.11 ^{A}	494.34 ±11.68 ^{A}	484.37 ±15.72 ^{A}
CH_4	67.86 ±22.92 ^{B}	89.76 ±3.36 ^{B,A}	107.82 ±1.99 ^{A}
H_2	27.02 ±4.58 ^{A}	18.02 ±0.42 ^{B}	16.28 ±0.54 ^{B}
C_2H_4	29.60 ±8.38 ^{B}	65.10 ±3.35 ^{B,A}	49.59 ±16.23 ^{A}
C_2H_2	5.07 ±1.83 ^{A}	2.80 ±0.10 ^{A}	3.13 ±0.20 ^{A}

Syngas yield and energy			
Syngas yield	0.88 ±0.11 ^{A}	0.83 ±0.02 ^{A}	0.84 ±0.01 ^{A}
Syngas energy	2.17 ±0.31 ^{C}	3.49 ±0.08 ^{B}	4.79 ±0.16 ^{A}
Efficiency			
Carbon conversion efficiency	74.10 ±14.09 ^{A}	87.40 ±1.53 ^{A}	87.17 ±4.50 ^{A}
Cold gas efficiency	60.18 ±7.85 ^{A}	61.998 ±1.03 ^{A}	63.21 ±0.95 ^{A}

Means without superscripts are not statistically

3.3.5.1 Product yield

With an increase in feeding rate, the product yields were expected to increase. Table 3.7 shows that the gas yield was not affected by increase in feeding rate and neither was the char yield. However, a slight decrease in gas and char yield was noticed. The water yield on the other hand, increased significantly with an increase in feeding rate from 100 to 200 rpm. At higher feed7 rate, higher amounts of CO and H_2 were obtained. The methanation reaction, as shown in Equation (11) was favored, resulting in production of higher amounts of steam and methane. This steam was collected by condensers thus resulting in higher water yield.

3.3.5.2 Syngas composition

The volumetric concentrations of primary syngas components increased with an increase in feeding rate as seen in Table 3.7. The nitrogen dilution reduced with an increase in feed rate. It was important to note that with an increase in feed rate, the CO and CO_2 concentration increased. The CH_4 also increased with an increase in feed rate. However, looking at hydrogen trend, it could be observed that at lower feed rate the H_2: CO ratio decreased with an increase in feeding rate. This suggests that higher feed rate favor production of carbon compounds. Also, the data was more comparable with literature due to an increase in the volumetric concentrations of syngas components (Carpenter et al., 2010a; Smeenk and Brown, 1998).

Figure 3.20 shows the syngas component yield on a per kg biomass basis, it could be observed that per dry kg of biomass, the CO and CO_2 yield remain more or less constant. However, the methane yield increased from 100 to 300 rpm and the hydrogen yield reduced with an increase in feed rate. This indicates the tendency of the gasifier to produce higher methane at expense of the hydrogen (methanation reaction) with an increase in feeding rate. The higher concentrations of C2 compounds followed the same trend of that of the primary syngas components.

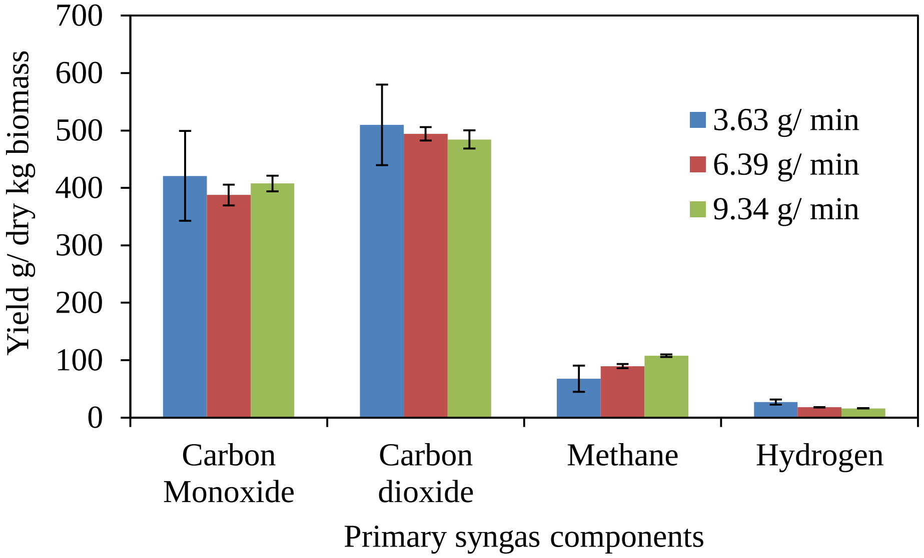


Figure 3.20: Syngas component yield for different biomass feed rates.

3.3.5.3 Syngas energy and yield

The syngas energy content and the syngas yield have been reported in Table 3.7. With the increase in feed rate the primary syngas composition improved and helped reduce the dilution due to nitrogen. The syngas energy around 4.79 MJ/Nm^3, agrees very well with those reported in literature (Basu, 2010; Carpenter et al., 2010a; Narváez et al., 1996; Van der Drift et al., 2001). The syngas yield calculated (on per dry kg biomass) was however, not affected by increase in the feeding rate. The average yield was observed to be between 0.88 to 0.83 Nm^3 per dry kg biomass. Thus meaning that the conversion of biomass into syngas is influenced more by the temperature of the gasifier than by the biomass feed rate. The syngas energy on the other hand increased with an increase in feed rate of biomass, due to higher concentration of methane obtained at higher feed rate as seen in Table 3.7.

3.3.5.4 Carbon and cold gas efficiency

The energy efficiency and carbon efficiencies are a measure of mass and energy conversion. As seen in Table 3.7, it could be noted that the average carbon efficiencies were between 74.10 to 87.17%. The carbon efficiencies reported are comparable to those reported in the literature for bubbling fluidized bed gasifiers (Carpenter et al., 2010a; Sarkar et al., 2014a). The average cold gas efficiencies were reported to be from 60.18 to 63.21% and agree well with those discussed earlier in this chapter (Carpenter et al., 2010a; Van der Drift et al., 2001). The cold gas efficiency and the carbon balance were statistically not affected by increase in feed rate, thus indicating that the energy and carbon conversion are independent of biomass feed rate and are influenced by temperature and ER rather than by the biomass feed rate.

3.3.5.5 Contaminants

The contaminants such as ammonia, HCN and SO_2, could create poisoning of catalyst in the downstream application. Table 3.8 tabulates the concentration (ppmv) and yield (g/ dry kg biomass) of the contaminants measured using a FTIR gas analyzer. A steady increase in the concentration of the contaminants was observed with an increase in feed rate. The ammonia concentration at 9.34 g/min, agreed well with that obtained during gasification of park wood (wood obtained from park). Further the dip was observed for NH_3 at 6.38 g/min feed rate, and a corresponding peak was observed for HCN, indicating that at that feed rate HCN production was favored. However, no such trend was noticed in the literature. The higher concentration of HCN at higher biomass feed rate agreed well with values reported in the literature particularly for switchgrass (Broer et al., 2015). Even with an increase in feed rate, the SO_2 concentrations did not increase as much as NH_3 and HCN concentrations. The values reported for SO2 are much lower than those for coal and coal-biomass gasification (Xie et al., 2007).

Table 3.8: Contaminants obtained at different biomass feed rates.

Feeding rate	**3.63 ±0.14**	**6.38 ±0.21**	**9.34 ±0.31**
Contaminants			
	Concentration (ppmv)		
NH_3	299.62 ±113.4 ^{B}	182.66 ±25.23 ^{B}	1060.6 ±81.85 ^{A}
HCN	35.73 ±9.99 ^{B}	544.97 ±21.35 ^{A}	462.01 ±76 ^{A}
SO_2	43.11 ±14.3 ^{B}	71.25 ±0.64 ^{B,A}	108.2 ±12.28 ^{A}
	Yield (g/ dry kg biomass)		
NH_3	1.28 ±0.45 ^{B}	0.45 ±0.06 ^{B}	2.09 ±0.16 ^{A}
HCN	0.24 ±0.06 ^{C}	2.16 0.11 ^{A}	1.44 0.21 ^{A}
SO_2	0.69 ±0.22 ^{B}	0.66 ±0.02 ^{B,A}	0.80 ±0.09 ^{A}

3.4 Conclusions

It can be concluded that increase in temperature positively affected the gas yield, carbon monoxide and hydrogen production. The carbon monoxide and methane decreased with increase in temperature. The energy content of syngas increased with increase in temperature due to higher concentrations of CO and H_2. The carbon balance and energy efficiencies also increased, thus it can be concluded that high temperature gasification around 900 to 1000°C results in good quality syngas. On the other hand, increase in ER resulted in reduction in CO and hydrogen yield and increased CO_2 production. The syngas gas energy content and the efficiencies reduced with increase in ER. The carbon balance however, increased with increase in ER, due to increase in CO_2 yield. It can be concluded that lower ER 0.21 to 0.24 provided better quality syngas than the higher ER. When compared to pine, switchgrass gasification resulted in lower concentrations of syngas components and lower energy content of syngas. However, the results are comparable to those reported earlier with switchgrass.

The study of varying ash content in the biomass suggested that the primary syngas components, syngas yield, energy content, efficiencies and the contaminants were not affected with an increase in ash content in the range studied (2.71 to 4.59).

The third study was to understand the effect of feeding rate on syngas composition and contaminants. The increase in feeding rate helped improve the concentrations of the primary syngas components and the syngas energy content, thus giving a syngas with higher heating value. However, the yield (per dry kg biomass) was not affected by the increase in feeding rate. The increase in feeding rate also increased the contaminant concentration in the syngas.

Chapter 4

Gasification with Olivine as Bed Material

4.1 Introduction

Gasification of biomass is an important thermochemical technology as it has the potential to produce energy, fuel and chemicals, presently derived from fossil fuels, in a CO_2 neutral cycle.(Vasudevan et al., 2005) While agricultural residues and woody biomass resources are abundant in the United States, the ambitious bioenergy and biofuel goals will inevitably require the cultivation of energy crops.(Sims et al., 2006b) Among energy crops, switchgrass (*Panicum virgatum L.*) occupies a central role. It is a native North American perennial lignocellulosic grass with variants grown throughout the U.S. Its advantages include high crop yield, suitability to various soil types and climatic conditions, low fertilizers and maintenance growth requirements. As a result, in recent years, switchgrass has attracted more attention as a feedstock for gasification and other thermochemical conversion techniques for the purpose of energy and fuel production.

Several switchgrass gasification studies have been reported with sand as a bed material for fluidization.(Carpenter et al., 2010b; Sarkar et al., 2014a; Sharma et al., 2011) However, in lieu of sand, minerals such as dolomite or olivine can be used doubly as a fluidization medium and as catalyst to improve syngas properties. In the past, several studies have reported positive effects of mineral as *in-situ* catalyst during biomass gasification including an increase in H_2(Link et al., 2012; Pérez et al., 1997) and a decrease in tar and other contaminants(Link et al., 2012; Pérez et al., 1997; Simell et al., 1996). These naturally occurring minerals have the added benefit to be cheaper than manufactured catalysts. While dolomite and olivine have reported good performance in previous studies, olivine is more suitable for fluidized bed gasification as it is less likely to attrite and elutriate.(Corella et al., 2004b) Furthermore, most studies focused on the woody biomass gasification using olivine. However, switchgrass, with a higher ash content, might present unique challenges during in-situ catalytic gasification.

Therefore, the aim of this study was to understand the effect of temperature (790, 935 and 1000°C at 0.25 ER) and ER (0.20, 0.25 and 0.30 at 935°C) on the performance of olivine as bed material for catalytic switchgrass gasification. The performance of olivine was compared to that of sand as bed material (Kulkarni et al., 2015b). Comparison was made on the basis of product yield, gas concentration and yield, syngas energy, carbon conversion and the energy efficiencies.

4.2 Method and materials

Methods and techniques used have been described below. Switchgrass char and olivine morphology was analyzed using a (ZEISS EVO 50VP) scanning electron microscope at 1000 and 2000 magnitudes and 20 kV electrode voltage. Furthermore, olivine was analyzed elemental composition using INCA-EDS system. XRD analysis was also performed on the olivine. The XRD plot was analyzed using the Defractor.EVA software to understand the composition and crystalline structure. The switchgrass sample used for experimental work was used in the previous chapter to study effect of temperature and ER on air gasification of switchgrass with sand as a bed material.

4.2.1 **Materials**

Switchgrass sample characteristics and properties have been reported in an earlier study using sand as bed material (Kulkarni et al., 2015a) and summarized in the result section. Along with elemental and ultimate analysis, the composition of biomass i.e. cellulose, hemicellulose and acid soluble lignin have been included in the result section. Olivine samples were obtained via VWR in the form of one inch (1”) rocks, mechanically ground using a hammer and sieved through a 40 mesh size sieve. The ground olivine consisted of irregularly shaped granules and fines with a mean particle size (d_{50}) of 0.295 mm while the particle density was 3238 kg/m^3. In order to elucidate the impact of calcination on the effectiveness of olivine, uncalcined and olivine calcined in air at 900°C for 4 hours was tested as bed material and compared to sand.

4.2.2 **Experimental set up**

The details of the bench scale fluidized bed gasifier used for the bubbling fluidized bed gasification has been reported previously in chapter 1. Nitrogen was used as fluidizing agent while oxygen as oxidizing agent. The fluidization of olivine has been discussed in depth in result and discussion section. The amount of oxygen supplied for gasification was varied to obtain desired equivalence ratio (ER). ER was defined as the ratio of the actual amount of oxygen supplied to the gasifier to the amount of oxygen required for complete combustion of a given quantity of biomass and is shown by Equation 3.a in previous chapter(Kulkarni et al., 2015b):

4.2.3 **Data sampling and analysis**

An inline gas analysis was performed for primary gas components using gas analyzer (NOVA, Niagara Falls, NY) for the measurements of CO, CO_2 and CH_4 using an NDIR detector and H_2 using a TCD. Gas-phase contaminants and higher hydrocarbons were analyzed using an FTIR with a 4 m gas cell (IMAAC, Austin, TX). Tar collection using impinger bottle setup included five bottles in series filled with 50 ml isopropanol each while the last one was left empty to trap carry-over solvent droplets: The first three bottles were maintained in an ice bath maintained near 0˚C while the last three were kept at room temperature. After a run, solvents were mixed and analyzed using a GC-MS. Out of the three gasification products, char, liquid condensate and gas, two (char and liquid) were collected gravimetrically and third was calculated mathematically. The collection and analysis of all the parameters have been discussed in details elsewhere (Kulkarni et al., 2015b).

Definitions:

Carbon conversion efficiency also known as carbon balance is defined as ratio of carbon obtained in the gas to that found in the biomass, as shown in Eq. 4.a. For carbon in syngas, the sum of carbon present in ethylene, acetylene, methane, carbon dioxide and carbon monoxide was considered. The cold gas efficiency, the energy in biomass converted to syngas, is defined as the ratio of the sum of the heating values (LHV) of the primary syngas components to that of the LHV of the biomass as shown in Eq. 3.c.

$$\mathrm{Conversion_c} = 100\ \times \frac{\text{mass carbon in syngas}}{\text{mass carbon in sample}} \qquad (4.a)$$

4.2.4 **Experimental design and statistics**

Gasification experiments to study the effect of temperature were carried out at an ER of 0.25 at 790, 935, and 1000°C, and those to study the effect of ER at a temperature of 935˚C for ERs of 0.20, 0.25, and 0.30. Subsequently, the data was analyzed by a one-ANOVA at an alpha of 5% using Minitab with three data points for response variables at each temperature and ER except for tar for which experiments could not be replicated.

4.3 Results and discussion

4.3.1 Olivine characterization

Figure 4.1 shows the scanning electron microscope (SEM) images of olivine particles. It shows the surface of olivine particle at magnifications of 1000x and 2000x. Morphologically, SEM images of olivine shows similar features previously reported by Sweirczynski, et al.(Świerczyński et al., 2006) and Devi et. al. (Devi et al., 2005)

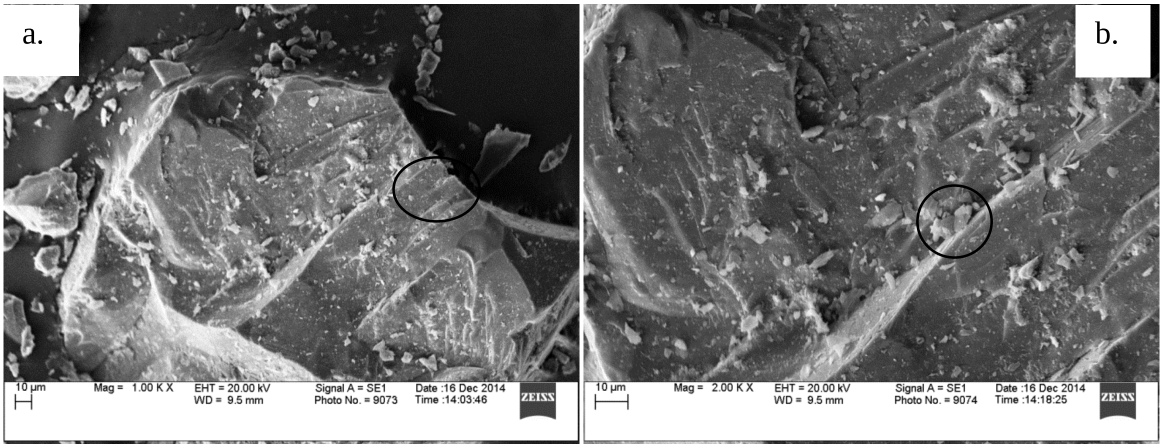


Figure 4.1 SEM images of olivine particle at (a) 1000x and (b) 2000x

Shear marks from grinding of the olivine rocks can be seen in the SEM images on Figure 4.1aas marked circle. Furthermore, it appears that finer particles agglomerated around larger particles Figure 4.1b. EDS analysis of uncalcined olivine revealed that olivine was composed of trace amounts of nickel in addition to strontium, iron, magnesium, silicon and oxygen in increasing concentrations as shown in Table 4.1.

Table 4.1 Elemental composition of the olivine particles as per EDS analysis

Element	*Composition, wt % ± SD*
O	42.73 ± 2.01
Si	22.22 ± 6.9

Mg	11.67 ±7.4
Fe	3.22 ±2.6
Sr	3.66 ± 0.46
Ni	0.37 ± 0.04

XRD analysis was performed on the olivine sample to understand the structure and crystalline structure of the olivine. The XRD powder diffraction pattern, shown in Figure 4.2, is consistent with previous reports in literature for olivine.(Devi et al., 2005; Świerczyński et al., 2006) This plot was analyzed using the Defractor.EVA and it was determined that the olivine has a chemical formula of $Fe_{0.08}Mg_{1.02}Ni_{0.9}O_4Si$, an I/I_{cor} ratio of 1.63 and a rhombic crystalline structure with a coupled 2theta wavelength of 1.5406 Å. Interestingly, peaks corresponding to strontium were not detected in the XRD analysis suggesting that Sr is not chemically bound to olivine and is present in smaller proportion relative to other constituents.

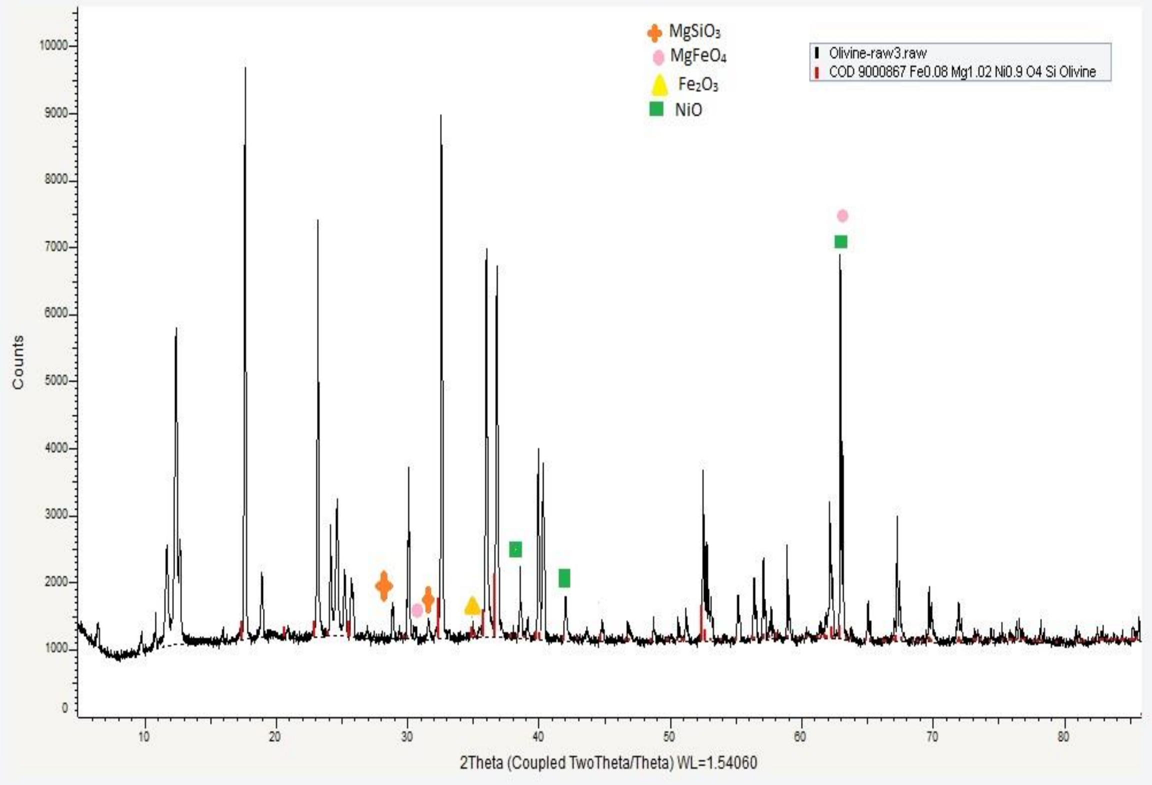


Figure 4.2 XRD analysis of olivine sample

4.3.2 Fluidization of olivine

The minimum fluidization velocity (Um_f) and terminal velocity (U_t) values were calculated at 25°C and at 790, 935 and 1000°C like in Chapter 3, and have been reported in Table 4.2.**Error! Reference source not found.** Raw olivine (ρ_p = 3238.3 kg/m^3) was used as a bed material and is classified as a group B particle, like sand according to Geldart’s classification. For group B particles, the bubbling takes place at the onset of fluidization, therefore minimum fluidization velocity is equal to bubbling velocity (U_b). Consequently, the superficial velocity must lie between the minimum fluidization velocity (U_{mf}) and the terminal velocity (U_t), to minimize the loss of bed material via elutriation. The nitrogen flow rate used for fluidization was 15 l/ min or a superficial velocity (U_s) of 0.12 m/s at STP between Um_f and U_t.

Table 4.2 Fluidization parameters for the bench-scale fluidized bed gasifier

Temp, °C	**25**	**790**	**935**	**1000**
Air, μ (N S/m^2)	1.94E-05	4.44E-05	4.69E-05	4.93E-05
Ar	2569.79	114.6	102.76	93.00
Re_{mf}	1.86	0.09	0.08	0.07
U_{mf}, m/s	0.10	0.047	0.044	0.042
U_t, m/s	12.52	3.46	3.27	3.11

4.3.3 Biomass characterization

A summary of the properties of switchgrass feedstock used in this study have been reported in Table 4.3. Physical and chemical properties of switchgrass are consistent with typical values reported for woody biomass with the exception of ash, which is higher. Although commonly higher than what is typically observed in woody biomass feedstocks, ash content of switchgrass varies widely depending on the source, harvesting operation and variants.(Carpenter et al., 2010a) Heating value was measured to be 18.86 MJ/kg (dry basis) and is in agreement with those reported in literature.(Moutsoglou, 2012; Sarkar et al., 2014a) The average moisture content was observed to be 8.54 wt % (wet basis). The chemical composition analysis, also reported in Table 4.3, indicates that cellulose, hemicellulose and acid insoluble lignin fractions account for 40.44, 21.94 and 26.11%, respectively. As an herbaceous crop, switchgrass has higher hemicellulose content than woody biomass. It provides strength to the biomass cell walls by interacting with the cellulose. The switchgrass chemical composition agrees well with that reported in literature. (Keshwani and Cheng, 2009)

Table 4.3 Proximate, ultimate and composition analysis of switchgrass sample

Analysis	**SG**
Moisture, wt.% ar	8.54 ±0.34
HHV MJ/ kg, dry basis	18.86 ±0.25
Proximate Analysis (wt.%, dry basis)	
Ash	2.71 ±0.12
Volatile matter	80.52 ±3.40
Fixed Carbon	16.77 ±3.31
Elemental Analysis (wt.%, dry ash free basis)	
Carbon	50.65 ±0.82
Hydrogen	5.87 ±0.10
Nitrogen	1.74 ±0.12
Sulfur	0.33 ±0.01
Oxygen	38.65 ±0.81
Physical Properties	

Bulk density (kg/m^3)	1439.47 ±14.85
Particle density (kg/m^3)	253.21 ±9.45
Particle size (mm) (d_{50})	0.518 ±0.08
Composition Analysis (wt.%, extractive free and dry basis)	
Cellulose	40.44 ±3.60
Hemicellulose	21.94 ±4.30
Klason lignin (acid insoluble)	26.11 ±1.11

4.3.4 Effect of calcination

Since the calcination was reported to improve performance of olivine, one part of this study was to understand whether or not calcination of this particular olivine sample has any effect on syngas composition. The comparison was made at 790°C. Mean values obtained for runs with calcined olivine were compared with those obtained for raw olivine. Table 4.4 shows the product yield, syngas composition, yield, energy and efficiencies for calcined and raw olivine. Olivine pretreatment did not have an impact on syngas composition based on the statistical analysis as shown in Table 4.4. This agreed well with that reported by Rauch et.al. (2004).(Rauch et al., 2004) This could be due the fact that the olivine sand (calcined or raw) undergoes heating for 3-4 hours as the gasifier is brought to desired temperature. During this treatment, iron is oxidized to iron oxides, which later catalyze tar decomposition and increase CO_2 and H_2O yield(Corella et al., 2004b). Thus, based on the results presented in this section, raw olivine was used for further gasification experiments.

Table 4.4 Comparison of performance of calcined and uncalcined olivine at 790°C and ER 0.25

	Calcined olivine	Raw olivine	P-Value
	Product Yield, %		
Gas yield	72.90 ±11.67	73.00 ±6.13	0.993

Char yield	15.74 ±1.55	16.01 ±1.99	0.881
Liquid yield	11.36 ±3.22	10.99 ±6.29	0.939
Syngas composition, Vol.%			
CO	3.83 ±0.29	4.76 ±0.38	0.532
CO_2	4.58 ±0.02	4.87 ±0.52	0.436
CH_4	2.53 ±0.22	2.83 ±0.28	0.305
H_2	2.56 ±0.21	2.75 ±0.93	0.766
C_2H_2	0.05 ±0.01	0.04 ±0.001	0.987
C_2H_4	0.82 ±0.01	0.80 ±0.16	0.849
Efficiency, %			
Carbon conversion	64.73 ±5.47	76.71 ±4.06	0.23
Cold gas	56.3 ±6.00	60.5 ±4.00	0.209
Syngas energy and yield			
Syngas energy, MJ/Nm^3	1.82 ±0.15	2.06 ±0.27	0.331
Yield, Nm^3/ dry kg biomass	0.59 ±0.05	0.69 ±0.05	0.360

A t-test was performed for comparison. P-Value >0.05 corresponds to no significant difference. P-value obtained is shown in the right most column

4.3.5 Effect of temperature and equivalence ratio

The effect of temperature and ER is discussed in the following section. Table 4.5 shows the product yield, syngas volumetric composition, heating value, carbon conversion, cold gas efficiency of the process and contaminant yield, as a function of temperature and ER. The statistical analysis is also shown in the table; and was carried using one way ANOVA.

Table 4.5 Gasification products obtained as a function of temperature and ER with olivine as bed material.

	Temperature, °C			**ER**		
	790	935	1000	0.21	0.24	0.27
Product yield, %						
Gas	73.00 ±6.13^{A}	65.92 ±4.78^{A}	71.71 ±0.68^{A}	59.63 ±6.40^{X}	65.92 ±4.78^{X}	67.51 ±4.57^{X}
Char	16.01 ±1.99^{A}	15.82 ±2.87^{A}	12.61 ±0.55^{A}	22.83 ±5.31^{X}	15.82 ±2.87^{X}	14.25 ±0.85^{X}
Liquid	10.99 ±6.29^{A}	18.26 ±5.00^{A}	15.68 ±0.12^{A}	16.54 ±2.34^{X}	18.26 ±5.00^{X}	18.24 ±4.39^{X}
Composition, vol %						
CO	4.76 ±0.30^{A}	5.37 ±0.32^{A}	6.20 ±0.15^{A}	5.50 ±0.36^{X}	5.37 ±0.32^{X}	5.08 ±0.22^{X}
CO_2	4.87 ±0.52^{A}	4.42 ±0.33^{A}	3.86 ±0.27^{A}	3.81 ±0.62^{Y}	4.44 ±0.33^{Y,X}	5.26 ±0.32^{X}
CH_4	2.38 ±0.28^{A}	1.97 ±0.35^{B}	1.51 ±0.07^{B}	2.08 ±0.26^{X}	1.97 ±0.34^{X}	1.72 ±0.24^{X}
H_2	2.75 ±0.93^{B}	4.64 ±0.46^{A}	5.65 ±0.04^{A}	4.51 ±0.45^{X}	4.64 ±0.46^{X}	4.25 ±0.31^{X}
Efficiency, %						
Carbon conversion	76.71 ±4.06A	72.22 ±5.16^{A}	70.95 ±4.29^{A}	76.00 ±6.80^{X}	72.22 ±5.16^{X}	73.23 ±1.79^{X}
Cold gas	60.44 ±4.30^{A}	57.03 ±6.53^{A}	67.15 ±7.61^{A}	62.49 ±1.50^{X}	57.03 ±6.53^{X,Y}	52.26 ±1.86^{Y}
Syngas energy						
LHV, MJ/ Nm^{3}	2.06 ±0.27^{A}	1.88 ±0.11^{A}	2.01 ±0.15^{A}	2.02 ±0.17^{X}	1.88 ±0.11^{X}	1.74 ±0.08^{X}
Contaminants, ppm volume						
NH_3	239.79 ±36.48^{A}	289.19 ±59.92^{A}	328.77 ±85.12^{A}	317.92 ±16.20^{X}	289.19 ±59.92^{X}	398.77 ±11.38^{X}
HCN	46.67 ±16.18^{A}	32.13 ±5.74^{A}	20.59 ±4.79^{A}	34.34 ±8.37^{X}	32.13 ±5.74^{X}	31.43 ±2.38^{X}

SO₂	38.18 ±6.39^{A}	34.80 ±13.4^{A}	31.57 ±7.07^{A}	44.36 ±10.71^{X}	34.80 ±13.4^{X}	44.76 ±3.82^{X}
Tar yield (g/ Nm3)	0.46	0.65	0.55	0.18	0.65	0.48
Tar yield (g/ kg dry biomass)	0.29	0.54	0.48	0.15	0.54	0.37

Effect of Temperature and ER were studied separately. Means with same superscripts are not statistically different (P-value > 0.05) based on a one-way ANOVA test. Means not connected by the same superscript are significantly different at the 0.05 level based on Tukey HSD Post Hoc test.

4.3.5.1 Product yield

Table 4.5 shows the effect of temperature on the product yield with olivine as a bed material. The char yield decreased with an increase in temperature; however, the temperature did not significantly affect the gas, char and liquid yield. The gas and liquid yield showed a dip and peak respectively at 935°C. This could be due to variation in the experiments and not necessarily have an explainable trend associated with it.

Figure 4.3 shows the comparison of product yield between olivine and sand as bed materials. It could be seen that the temperature had no statistical effect on product yield for both bed material. Rapaganà *et al.* reported for steam gasification of biomass with olivine as bed material, a reduction in char and increase in gas yield with an increase in temperature. (Rapagnà et al., 2000) The overall decreasing trend for char and liquid yield agreed well with gasification of other biomass samples as reported by some investigators as well. (Carpenter et al., 2010b; Kulkarni et al., 2015b) When comparison was drawn between sand and olivine as bed material, it can be seen that the gas yield for sand is higher than that that for olivine at 935°C and 1000°C, the liquid yield at same temperatures were comparatively lower. However, a study comparing sand and olivine in steam gasification using dual fluidized bed reported slight increase in gas yield with olivine and reduction in yield of water (Koppatz et al., 2011). This difference in yield could be due to difference in performance of olivine in steam and sand.

Table 4.5 also shows the product distribution as a function of ER. With increase in ER, the gas and liquid yields increased at an expense of the char yield. However, the ER did not significantly affect the product distribution. A higher char yield was obtained at ER 0.20, indicating a lower conversion of switchgrass into gas due to lower oxygen supply. Reduction in char yield and corresponding increase in gas and liquid yield were also observed for pine gasification (Abdoulmoumine et al., 2014) and also for air-steam gasification of wood pellets (Campoy et al., 2009a). When compared with performance of sand, olivine yielded higher liquid and char yield at any given ER. The higher liquid yield could be result of catalytic effect of olivine. Overall, the trends observed in product distribution were similar for olivine and sand as seen in Figure 4.3(b).

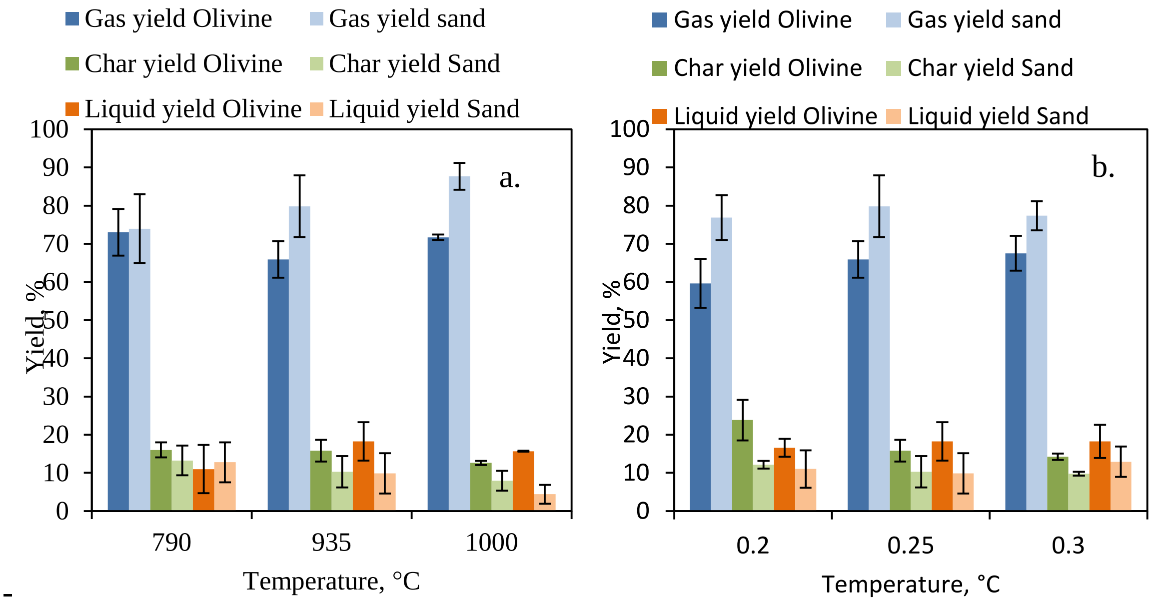


Figure 4.3 Comparison of product yield between olivine and sand as bed materials at different (a) temperatures and (b) ER

4.3.5.2 Syngas composition

As the bed temperature and oxygen supply are important parameters in achieving a desired syngas composition, experimental runs were carried out at different temperatures and equivalence ratio to elucidate their impacts on primary components and higher hydrocarbons (acetylene and ethylene). Several endothermic and exothermic key reactions shown below regulate the gas composition, particularly for CO, H_2 and CH_4, as a result of variation of temperature.

$$C + 0.5O_2 \rightarrow CO \qquad \Delta H^{\circ}_{298} = -111 \text{ kJ/mol (char reaction)} \tag{4.1}$$

$$C + 2H_2 \leftrightarrow CH_4 \qquad \Delta H^{\circ}_{298} = -74.8 \text{ kJ/mol (hydrogasification)} \tag{4.2}$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H^{\circ}_{298} = +131 \text{ kJ/mol} \tag{4.3}$$

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H^{\circ}_{298} = +172 \text{ kJ/mol (Boudouard)} \tag{4.4}$$

$$CO + 3H_2 \leftrightarrow H_2O + CH_4 \qquad \Delta H^{\circ}_{298} =-206 \text{ kJ/mol} \tag{4.5}$$

The variations in concentrations and yields of syngas components as a function of temperature are shown in Table 4.5. It can be seen that with an increase in temperature, CO increased due to increase in char reaction, while CO_2 decreased as CO_2 was converted into CO through the Boudouard reaction. As the char-steam reaction (Eq. 4.3) is endothermic, it would also contribute in increasing the concentration of CO and H_2 as reported in the Table 4.5. As the main methanation reaction, hydrogasification is exothermic; thus CH_4 decomposition would be favored to form carbon radicals and hydrogen with an increase in temperature. The increase in CO and H_2, and corresponding decrease in CO_2 and CH_4 were reported in pine gasification (Abdoulmoumine et al., 2014), these trends also agreed well with those reported previously by Carpenter et. al.(Carpenter et al., 2010b).

The syngas composition and yield were compared at similar conditions with that obtained for switchgrass with sand as bed material and represented in Figure 4.4. It was observed that with increase in temperature the syngas composition obtained from olivine and sand showed some difference. At 790°C, olivine helped produce syngas with higher concentrations of all the component gases. In order to further investigate this, SEM images of char for olivine and sand were compared. Figure 4.5(a &b) shows these images; it could be observed that the char particles were much finer for olivine as bed material (Figure 4.5(a)), indicating higher disintegration of biomass structure during gasification process, on the other hand complete decomposition of char particles did not occur with sand as bed material, this was confirmed by observing the microstructure of biomass as seen in the image in Figure 4.5(b). Though higher concentrations were obtained with olivine 790°C, statistical analysis does not indicate any significant increase with use of olivine rather than sand.

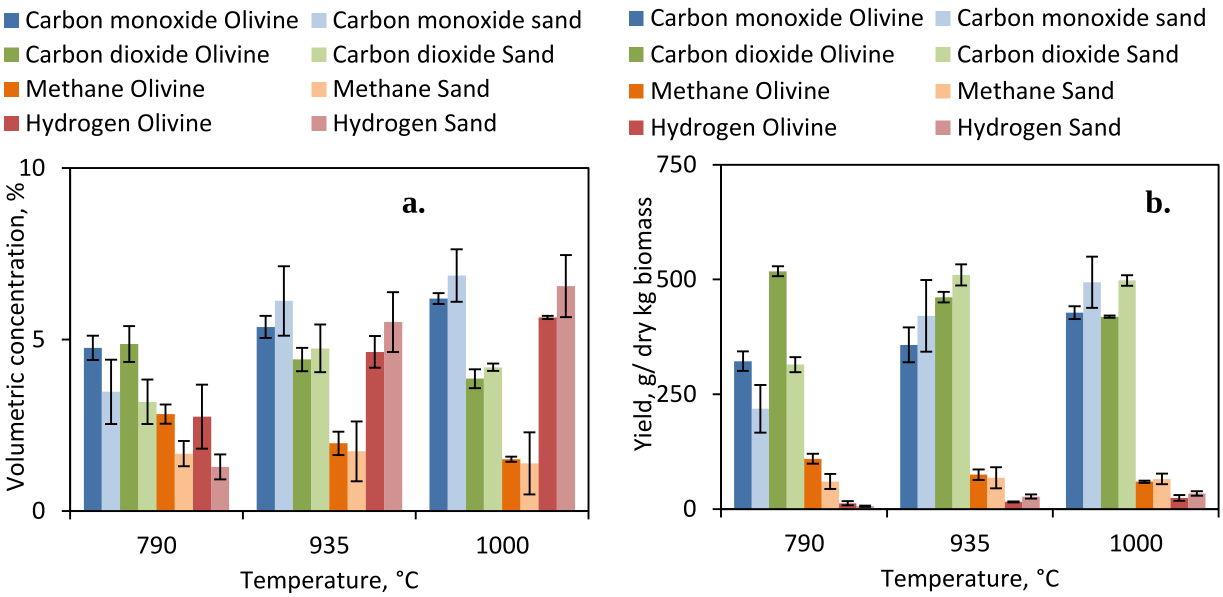


Figure 4.4 Effect of temperature (a) on volumetric composition and (b) yield with olivine and sand as bed material: a comparison

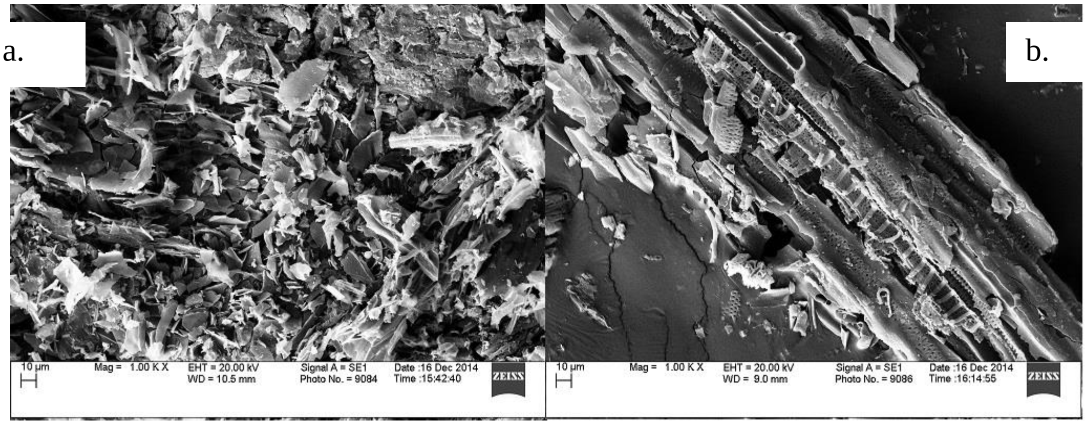


Figure 4.5 SEM images of bio-char obtained with olivine (a) and sand (b) as bed material, at 790°C and ER 0.25.

However, at higher temperatures it was seen that the concentration of primary syngas components were less than that with sand. At higher temperature, though gas concentrations were lower with olivine than with sand, this difference was not statistically significant either. A higher elutriation of olivine fines were observed as compared to sand during gasification experiments. Olivine particles were found in condensers, ESP and also in gas analyzers; elutriation was also observed by Corella *et al.* (Corella et al., 2004b) for olivine and dolomite, the degree of elutriation observed was 4-6 times higher for dolomite than olivine. Also a TGA study performed on olivine indicated 3% loss in mass of olivine at 800°C for one hour long run (shown in Appendix D). This corresponded to loss of 6 grams of olivine during an hour long run due to thermal degradation.

Further, the concentrations and yields of acetylene and ethylene as a function of temperature were reported in Table 4.6. It can be observed that an increase in temperature did not significantly affect the concentrations/ yields, however, a decreasing trend was observed for ethylene, which agreed with that reported for pine and sand due to thermal decomposition of hydrocarbons at higher temperature. (Kulkarni et al., 2015b) (Abdoulmoumine et al., 2014)A comparison is shown in Table 4.6 between sand and olivine as bed material, it was observed that overall, olivine helped reduce the yield and concentrations of acetylene and ethylene. The reduction was a result of steam reforming of higher carbon compounds in the presence of olivine (Corella et al., 2004b). However, it can be seen that the amount of acetylene increased slightly with an increase in the gasification temperature. During the reforming of ethylene (C_2H_4) some amount of C_2H_2 was also produced along with CO and H_2, which resulted in a slight increase in the concentration of acetylene with an increase in temperature.

Table 4.6 Yield and molar concentration of higher carbon compounds as a function of temperature

Compound	**Olivine**			**Sand**		
	Concentration (vol %)					
Temperature, °C	790	935	1000	790	935	1000
Acetylene	475.4 ±96.9	730.9 ±160.6	758.9 ±48.3	534.8 ±25.7	778.2 ±298.6	914.2 ±84.5
Ethylene	8020.8±1609.7	7545.4 ±841.9	4963.9 ±1873.9	10604.10 ±1402.1	4207.36 ±1287.1	7140.76 ±1559.9
	Yield (g/dry kg biomass)					
Acetylene	2.8 ±0.9	4.7 ±1.2	5.6 ±1.5	3.14 ±0.3	5.1 ±1.8	6.1 ±0.4
Ethylene	51.1 ±14.7	50.8 ±7.0	38.4 ±11.9	66.7 ±5.9	29.6 ±8.4	51.1 ±11.1

Table 4.5 shows the effect of ER on the syngas composition and yield. The increase in oxygen resulted in higher oxidation reactions. The equations shown below (3.6 to 3.9) are the oxidation reactions which influence the syngas composition. With an increase in ER, CO was further oxidized into CO_2 leading to a decrease in the CO yield and an increase in CO_2 consistent with Eq. 10. Methane reduced due to oxidation with increase in ER. The hydrogen reduced to produce higher water yield. These trends with H_2 and CH_4 were consistent with pine (Kulkarni et al., 2015b) and switchgrass gasification on the same set up and also with dolomite studies (Gil et al., 1999a; Narvaez et al., 1996)with wood chips.

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^{\circ}_{298} = -394 \text{ kJ/mol} \qquad (3.6)$$

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \Delta H^{\circ}_{298} = -284 \text{ kJ/mol} \qquad (3.7)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O \qquad \Delta H^{\circ}_{298} = -803 \text{ kJ/mol} \qquad (3.8)$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \Delta H^{\circ}_{298} = -242 \text{ kJ/mol} \qquad (3.9)$$

As seen in Figure 4.6, the trends for CO_2, CH_4 and H_2 concentrations agreed well for olivine and sand. However, for sand, the increase in CO was accompanied with an increase in CO_2 from ER

0.21 to 0.27 and with any further increase in ER it decreased. Catalytic effect of olivine helped oxidation of CO to increase concentration and yield of CO_2. An increase in CO_2 and corresponding decrease in CO was observed for pine gasification with sand (Abdoulmoumine et al., 2014) and also for pine chips with dolomite (Gil et al., 1999a)as bed material. Based on the results, it could be concluded that the lower ERs around 0.20, are more suitable for producing syngas rich in CO and H_2 when olivine is used as bed material.

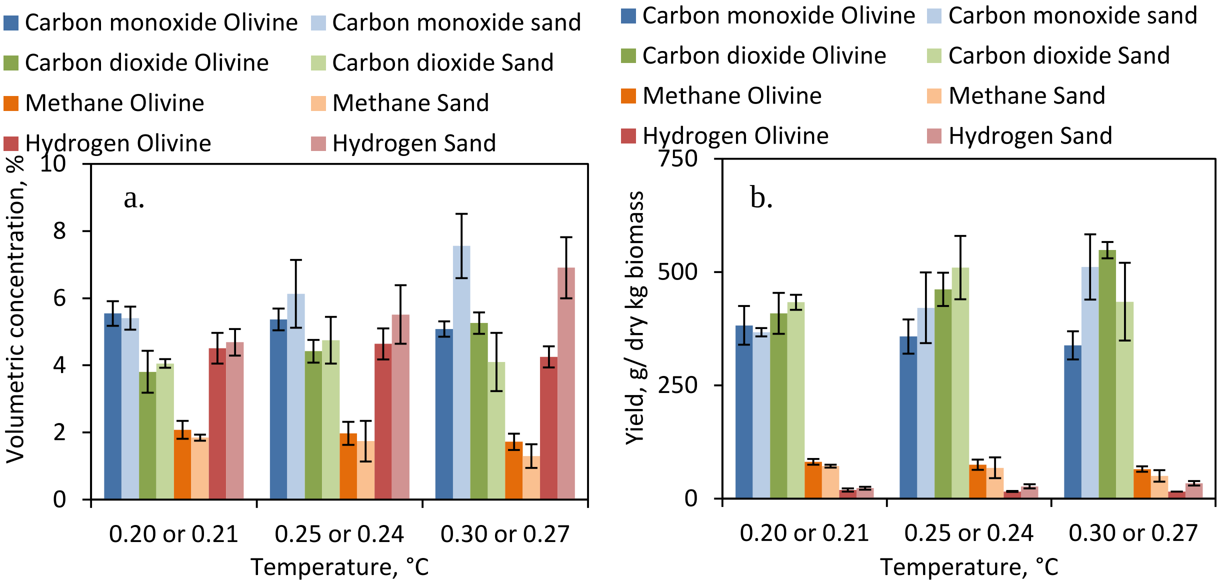


Figure 4.6 Effect of ER on syngas (a) concentration and (b) yield with olivine and sand as bed material

With an increase in ER, the higher hydrocarbons were not affected (shown in Figure 4.7). The yield and concentration showed that increase in supply of oxygen did not influence the further reduction of acetylene and ethylene. For acetylene, similar trends were also observed by Gil *et al.*(Gil et al., 1999a) and Narveaz *et al.*(Narvaez et al., 1996). As these hydrocarbons are present in much lower concentrations than primary gases, it is probable that the additional oxygen at higher

ER was consumed primarily in char oxidation and homogeneous oxidation reactions. A high variation in volumetric concentration and yield was obtained at ER 0.30.

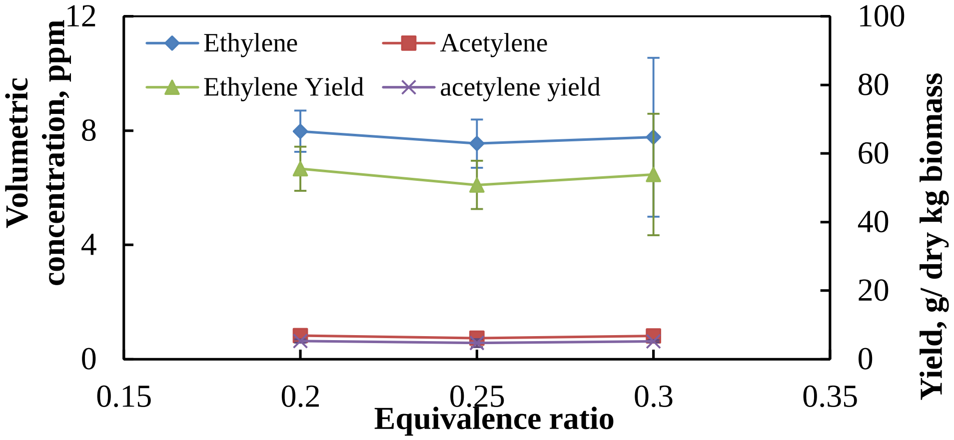


Figure 4.7 Effect of ER on higher hydrocarbon volumetric concentration (ppm) and yield

Table 4.7 shows the comparison between acetylene and ethylene yields obtained with sand and olivine. When olivine was used as bed material, significantly higher concentrations of ethylene were measured as compared with sand at ER 0.24 (p-value 0.019) and 0.27/0.30 (p-value 0.024). As for acetylene, olivine resulted in lower concentrations than sand at all levels. While with sand, a decreasing trend was observed as ER increased; no statistically significant decrease was noticed with olivine partly due to higher uncertainty at 0.30 ER.

Table 4.7 Yields of acetylene and ethylene in syngas as a function of ER

	Bed material					
	Olivine			**Sand**		
ER **g/kg ……..**	0.20	0.25	0.30	0.21	0.24	0.27
C_2H_2	2.86 ±1.09	5.07 ± 1.84	4.94 ± 2.87	5.28 ± 0.48	4.68 ± 1.17	5.20 ± 0.32
C_2H_4	55.55 ±6.39	50.83 ±7.03	53.83 ±17.72	61.57 ±6.44	29.60 ±8.39	14.63 ±4.67

4.3.5.3 Syngas energy

Higher energy content of syngas is required for downstream application like heat power generation. When air is used as gasification agent the nitrogen present in the air dilutes the syngas energy content. In this case, amount of nitrogen used was higher than that obtained through air for fluidization purpose. This further resulted in dilution of syngas energy. Figure 4.8a shows the syngas energy content obtained for experimental runs at different temperatures and ER with olivine and sand as bed material. It was observed that with an increase in temperature the energy content was not affected statistically with olivine as bed material. Even though CH_4 decreased, and concentrations of CO and H_2 increased no significant effect was observed with an increase in temperature. When compared with sand, the trends were different, for sand the heating value increased with an increase in temperature. At 790°C, the energy content of syngas was higher for olivine than for sand, this result was a reflection of syngas composition for the two bed materials as discussed in above sections. With pine gasification (Abdoulmoumine, 2014), an increase in energy content of syngas was observed, however with dolomite (Gil et al., 1999a)(20-30% in bed) a decreasing trend in LHV was observed with an increase in temperature between a narrow range of temperature (800° to 840°C).

The effect of increase in ER on energy content of syngas was shown in Figure 4.8b. It shows a decrease in energy content with increase in ER, which is due to increase in CO_2 concentration in syngas. When compared with sand, the energy content in syngas with sand as bed material was higher at 0.24 and 0.27 ER due to higher carbon monoxide content compared with that for olivine (Kulkarni et al., 2015b). The decreasing trend in energy content with an increase in ER when olivine was used as bed material agreed well with that reported for pine gasification

(Abdoulmoumine, 2014) and also for dolomite as bed material for wood chip gasification with air and steam(Gil et al., 1999a; Narvaez et al., 1996).

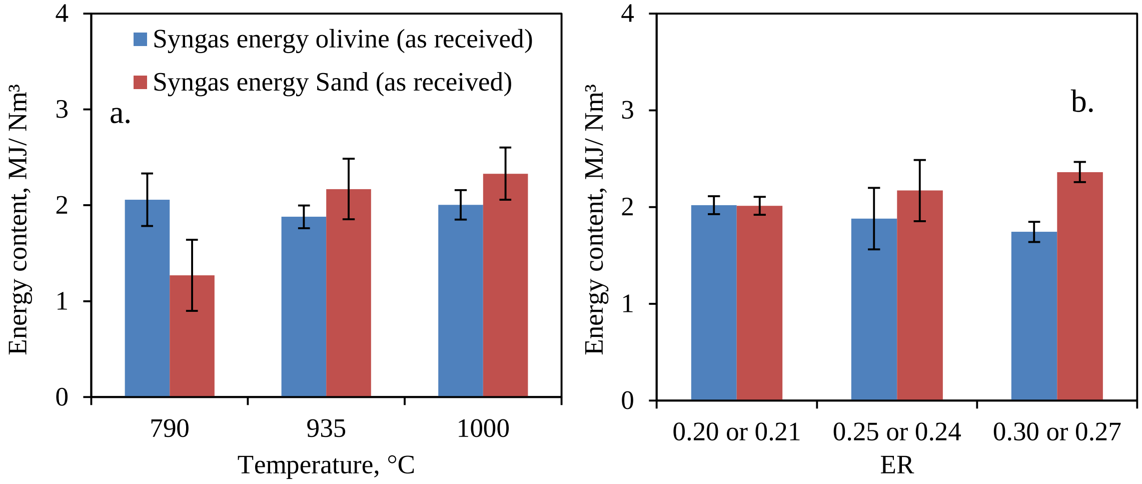


Figure 4.8 Effect of temperature (a) and ER (b) on the energy content of the syngas with olivine and sand as bed material

4.3.5.4 Carbon balance and energy efficiency

Carbon balance or carbon conversion represents the conversion of carbon from biomass into syngas. It is influenced by various factors like type of biomass, type of bed material, temperature and ER at which gasification is taking place. Ideally, a complete conversion of carbon into syngas is desired. However, due to various operational limitations, achieving complete conversion is extremely unlikely for any reactor. Similarly, for energy efficiency, we would like to achieve maximum possible energy efficiency during the process. However, due to several energy losses in the gasifier high energy efficiency values are difficult to obtain.

Table 4.5 shows the effect of temperature on carbon conversion and cold gas efficiency for switchgrass with olivine as bed material. It was observed that the increase in temperature did not affect the carbon balance. The mean carbon conversion values ranged between 76.71 and 70.95%. Table 8 shows the comparison between performance of sand and olivine based on the carbon conversion efficiency. It could be interpreted that when olivine is used as bed material, the carbon conversion was not influenced by the temperature of gasification. As against when sand was used as bed material an increase in carbon conversion was obtained with increase in temperature, implying that with olivine even lower temperatures could yield better carbon conversion.

Statistically, the temperature seemed to have no effect on the cold gas efficiency. The lowest cold gas efficiency was observed at 935°C. It was observed that at 1000°C, the average carbon conversion efficiency was lowest and the cold gas efficiency was the highest. This could be interpreted as at higher temperature lower amount of carbon was converted more efficiently into higher energy syngas.

When this performance was compared with that of sand with bed material (as shown in Table 4.8), it was noted that at lowest temperature under the range of investigation in this study, olivine helped improve the efficiencies at 790°C. With an increase in temperature, the performance with sand as bed material improved. At 935°C, olivine and sand as bed material performed very similar, resulting in very similar carbon conversion and energy efficiency values. At 1000°C, the efficiencies obtained with sand as bed material were higher as compared to that obtained from olivine experiments.

Table 4.8 Effect of bed material on carbon conversion, cold gas and hot gas efficiencies

	Bed material					
	Olivine			**Sand**		
°C **Efficiency, %**	790	935	1000	790	935	1000
Carbon conversion	76.71 ±4.06	72.22 ±5.16	70.95 ±4.30	53.82 ±9.53	74.10 ±14.09	80.92 ±8.50
Cold gas	60.44 ±4.30	57.03 ±6.53	67.15 ±7.61	32.83 ±9.95	60.18 ±7.85	68.28 ±8.05

The increase in ER triggers higher combustion of char thereby producing higher amounts of CO_2. This definitely increases the carbon conversion. However, this would mean reduced energy content of syngas due to increased concentration of CO_2, and in turn reduced energy efficiency. Table 4.9 shows the carbon conversion and cold gas efficiency as a function of ER. It can be seen that even though the CO_2 increased with an increase in ER, the carbon conversion was not significantly affected. The increase in CO_2 was a result of further oxidation of CO and other hydrocarbons. Hence the carbon conversion efficiency did not increase with an increase in ER. There was no significant effect of ER on carbon conversion. However, increase in ER significantly reduced the cold gas efficiency due to increase in concentration of CO_2. Table 4.9 shows the comparison between sand and olivine as bed material over the range of ER tested. It can be seen that even with sand as bed material the carbon balance did not vary much with ER. However, the cold gas efficiency increased with an increase in ER for sand as bed material. This was due to increase in concentration of CO with increase in ER. In case of olivine, reduction of CO to CO_2 was observed with increase in ER. It is important to notice that ER range studied for sand as bed material was 0.20 to 0.27, while that for olivine was 0.20 to 0.30.

Table 4.9 Effect of ER on gasification with switchgrass with sand and olivine as bed material

	Bed material					
	Olivine			**Sand**		
ER **%**	0.20	0.25	0.30	0.21	0.24	0.27
Carbon balance	76.00 ±6.80	72.22 ±5.16	73.23 ±1.79	71.39 ±2.02	74.10 ±14.09	75.91 ±2.16
Cold gas efficiency	62.49 ±1.50	57.03 ±7.17	52.26 ±1.89	56.00 ±6.25	60.18 ±7.86	65.08 ±0.91

4.3.5.5 Contaminants

Ammonia, hydrogen cyanide and sulfur dioxide: NH_3, HCN and SO_2 were the only major contaminants obtained above one ppm volume level for switchgrass with olivine as bed material. The switchgrass gasification with sand (Kulkarni et al., 2015b) also produced primarily these three contaminants which could be measured with FTIR gas analyzer. Pine (Abdoulmoumine et al., 2014)on the other hand, produced notable quantities of COS, HF and HCl along with the above mentioned contaminants.. Table 4.5 shows the concentration of these contaminants in ppmv. It was observed that ammonia increased with an increase in temperature and was accompanied by reduction in HCN concentration. SO_2 was not affected by increase in temperature. With increase in ER, NH_3 increased while, HCN and SO_2did not show any affect.

Figure 4.9a&b shows the yield of contaminants as a function of temperature and Figure 4.9c&d show effect of ER for olivine and sand as bed materials respectively. These figures showed that for sand, with an increase in temperature, the yield of NH_3 increased; overall the ammonia yields were higher at 935 and 1000°C for olivine than with sand as bed material. The ammonia concentrations were much lower than those reported for pine by Abdoulmoumine *et al.*(Abdoulmoumine et al., 2014). Study by Van der Drift *et al.*(Van der Drift et al., 2001) reported the average ammonia concentration to be around 0.58 to 0.64% for wood and grass samples with sand as a bed material at a pilot scale. It was observed that, the HCN released was at lower concentration than that of NH_3, this was observed by several authors in literature (Abdoulmoumine et al., 2014; Aljbour and Kawamoto, 2013a; Kulkarni et al., 2015b).

Increase in ER had a similar effect on the nitrogen contaminants yield, i.e. with an increase in ER, NH_3 increased while that of HCN remained more or less unaffected. The total amount of N_2 contaminants released by the olivine bed was similar to that of sand at any given ER condition.

Corella *et al.* (Corella et al., 2004b)reported NH_3 concentrations around 900 to 1200 ppmv for raw olivine bed in BFB gasifier. In the same study much higher concentrations of ammonia were reported for dolomite (~2000 ppmv), it was argued that this was due to presence of Fe- ions in olivine which help reduce the ammonia. However, in the present study no such effect was noticed when compared with sand. The SO_2 yields were similar for olivine and sand for all conditions. The SO_2 yields were lower than those reported for coal combustion and coal-biomass co-feeding (400 to 500 ppm) as reported by Xie et al (Xie et al., 2007).

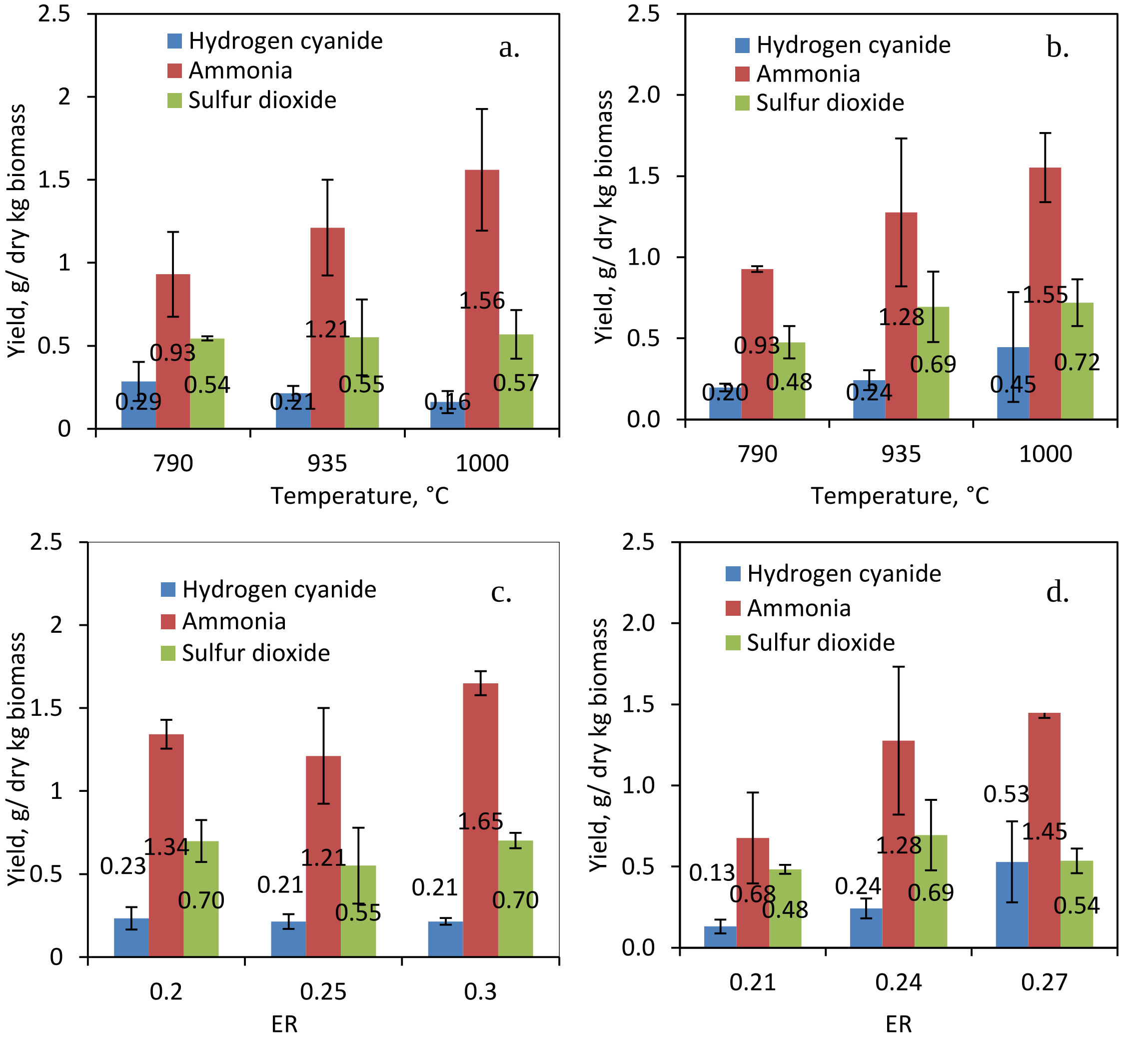


Figure 4.9 Effect of temperature (a&b) and ER (c&d) on contaminant yield for olivine (a&c) and sand (b&d) as bed material

Table 4.5 documents the tar yield obtained per cubic meter of syngas and on per dry kg biomass. When compared with sand(Kulkarni et al., 2015b), total tar yield was higher for olivine than for sand, which was contradictory to what was expected. This was observed due to higher levels of benzene and naphthalene obtained with olivine as bed material. All the other tar compounds were lower or similar in concentration/ yield to those obtained for sand(Kulkarni et al., 2015b). It was noticed that highest yield of tar was obtained at 935°C and 0.25 ER, while lowest was obtained at 935°C and ER 0.20. Figure 4.10a&b show the composition of tar obtained as a function of temperature and ER. It is seen that benzene, toluene and naphthalene are three major tar components at all conditions. Increase in temperature and ER increased benzene and naphthalene, while toluene decreased. The increase in styrene, indene, toluene, benzene, and naphthalene with an increase in temperature was due to the conversion of primary and secondary tars into these tertiary tar compounds at 935°C and agreed well with that reported for sand as bed material (Kulkarni et al., 2015b) and also as reported in literature by Milne *et al.* (Milne et al., 1998b) . Like Milne *et al.* stated the alkyl-tertiary tar compounds (styrene, indene and toluene) thermally decomposed with further increase in temperature from 935° to 1000°C, while, benzene and naphthalene (condensed tertiary compounds) increased. This was exactly what was observed in this case. Narvaez et al. (Narvaez et al., 1996) reported reduction in tar with increase in temperature due to thermal cracking and steam reforming (for runs with steam as gasifying agent).

The increase in benzene and naphthalene with an increase in ER was also observed for sand as bed material(Kulkarni et al., 2015b), however a decreasing trend with ER for naphthalene was also reported in literature (Abdoulmoumine et al., 2014; Aljbour and Kawamoto, 2013a). A study on various wood and grasses by Van der Drift *et al.* (Van der Drift et al., 2001) reported that ER did not have any effect on benzene production and the total tar collected for these samples were around 200 to 600 mg/ Nm^3, while Devi et. al. (Devi et al., 2005) reported significant reduction in tar with use of olivine and dolomite in a secondary fluidized bed reactor. Use of dolomite or olivine in reduction of tar was observed more with steam as gasifying medium than with air. (Devi et al., 2005; Milne et al., 1998b) This could be the reason that in the current study we did not observe a significant impact on tar reduction; also this reason was accompanied by elutriation and thermal breakdown of olivine particles in the reactor. Coking of olivine in the reactor could also be one of the reasons for average performance of olivine in this case.

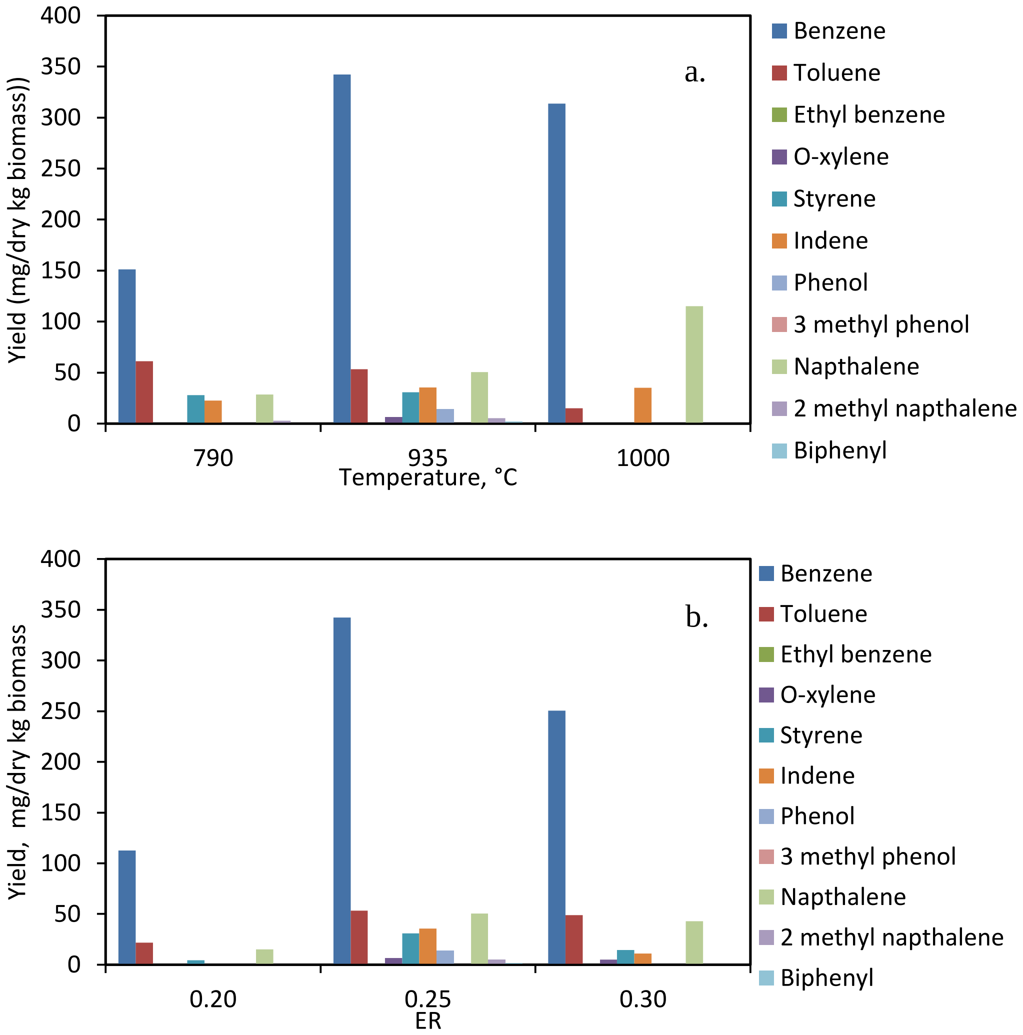


Figure 4.10 Effect of temperature (a) and ER (b) in the yield of tar components

4.4 Conclusion and remarks

It could be concluded that with increase in temperature from 790 to 1000°C, the CO and H_2 increased. The CO_2 decreased at higher temperature. The energy content, carbon conversion efficiency, and cold gas efficiency, were not affected by temperature. Use of olivine was effective in reduction of products into water with increase in temperature. When compared with use of sand as bed material, the olivine use resulted in higher concentration of CO, H_2 and CH_4 at 790°C. However, with increase in temperature the sand performed better, resulting in gas with higher energy content and higher concentration of CO, H_2 and CH_4. Implying that for switchgrass gasification, olivine is better choice bed material at lower temperature. The tar yield was higher for olivine due to higher concentration of benzene in the tar, which was contradictory to what was expected. The increase in temperature resulted in formation of tertiary tar products like benzene and naphthalene due to decomposition of primary and secondary tars resulting in higher yield of tar.

An increase in ER resulted in reduction of CO, H_2 and CH_4. The energy content reduced with increase in ER. The carbon conversion was not affected by increase in oxygen. However, the cold gas efficiency reduced with an increase in ER. A comparison was performed between use of sand and olivine as bed material. It could be concluded that at 935°C, the sand performed better than olivine at any ER. Even with respect to tar yield, olivine performed similar to sand, this could be due to elutriation of olivine particles, accompanied by thermal decomposition at higher temperature and coking of the olivine in bed. At lowest ER though, the olivine and sand performed fairly similar as bed material. In all, more experiments with better quality olivine and use of a secondary reactor for tar reduction could be a future path of study with switchgrass. Finally, it could be concluded that between olivine and sand, olivine performed better at lower temperature; however at higher temperature the in bed catalyst did not produce a better quality syngas.

Chapter 5

Pre-treated Biomass Gasification

5.1 Introduction

At present, there is a heavy dependence on coal for electricity generation globally and coal has been estimated to last for around 125 years.(Shafiee and Topal, 2009) To reduce the dependency on fossil based resources, raw biomass presents an excellent opportunity as a renewable fuel. However, in order to use biomass as a fuel for power production, a transition is necessary. During this transition, biomass can be co-fed along with coal for energy production purposes, which will help reduce CO_2, SO_X and NO_X emissions(Demirbaş, 2003; Ericsson, 2007; McIlveen-Wright et al., 2007). However, there are several issues like low energy density, high moisture content, and low grindability associated with the raw biomass, which makes it a difficult fuel to co-feed with coal (Baxter, 2005; McKendry, 2002a; Zhang et al., 2010). Along with this, the low bulk density and the low energy content also make it an expensive fuel to transport. In order to help in co-feeding, pretreatment of biomass has been suggested in several studies(Bergman et al., 2005a; Phanphanich and Mani, 2011).

The decomposition of hemicelluloses helps increase the grindability of biomass; the energy required for torrefaction followed by grinding is less than that required for the grinding of same amount of raw biomass, thus making the process affordable(Bergman et al., 2005a; Bridgeman et al., 2010; Kokko et al., 2012; Phanphanich and Mani, 2011; Repellin et al., 2010). Torrefaction increases the energy density of biomass by retaining around 90% of the energy and 70% of the weight of the raw biomass. This makes the transportation of biomass inexpensive. Along with this, the properties of the biomass resemble those of coal, especially the carbon content (closer to lower grade coal), grindability, energy content, and the lower hygroscopic nature.(Phanphanich and Mani, 2011) This makes torrefied biomass an excellent choice for co-feeding with coal for power generation purposes.

The easy availability of torrefied pine in the Southeast compared to that of torrefied switchgrass influenced the selection of torrefied pine for the experiment. The objective of this article was to study the torrefied biomass as a fuel for gasification using a bench-scale bubbling fluidized bed with sand as the bed material and compare it with the performance of switchgrass (Kulkarni et al., 2015a) and pine.(Abdoulmoumine et al., 2014)

5.2 Materials and methodology

5.2.1 **Materials**

Torrefied pine was used to understand the behavior of pretreated biomass under different gasification parameters. Torrefied pine was obtained in the pelletized form from New Biomass Energy, Quintman, Mississippi. The pellets were ground and sieved through 850μm sieve before feeding into the gasifier.

5.2.2 **Experimental set up**

The experiments were carried out using a bench-scale bubbling fluidized bed gasification rig as shown in Figure 3.1. The detail description of this set up has been discussed in the published document elsewhere. (Abdoulmoumine et al., 2014)

Oxygen and nitrogen were used for gasification as the oxidizing and the fluidizing agent, respectively. The flow rate of the nitrogen supplied for fluidization was kept constant at 15 l/min and the corresponding superficial velocity was 0.12 m/s with Reynolds number of 0.04. The flow rate of oxygen supplied was varied to achieve the target equivalence ratio (ER), which was defined as the ratio of the actual amount of oxygen supplied to the gasifier to the amount of oxygen required for complete combustion of a given quantity of biomass and is shown by Equation 4a.(Abdoulmoumine et al., 2014)

$$\mathrm{ER} = \frac{\left(\dot{\mathrm{m}}_{\mathrm{O_2}}/\dot{\mathrm{m}}_{\mathrm{biomass_{dry}}}\right)_{\mathrm{actual}}}{\left(\dot{\mathrm{m}}_{\mathrm{O_2}}/\dot{\mathrm{m}}_{\mathrm{biomass_{dry}}}\right)_{\mathrm{stoichiometric}}} \tag{4a}$$

5.2.3 **Data sampling and analysis**

Various parameters that were analyzed are listed below and have been discussed in details by Abdoulmoumine *et al.* (Abdoulmoumine et al., 2014):

1. The primary components were measured using a gas analyzer (NOVA, Niagara Falls, NY) for CO, CO_2, CH_4 using an NDIR detector, and H_2 using a TC detector.
2. Higher hydrocarbons (C_2H_2 and C_2H_4) and other contaminants (HCN, NH_3, SO_2, COS, HCl and HF) were analyzed using an FTIR with a 4 m gas cell (IMAAC, Austin, TX).
3. Tar was collected using impinger setup which included five iso-propanol filled bottles and a sixth empty bottle was used to trap the carried over solvent. This tar was later analyzed using a GC-FID.
4. The char and condenser liquid were collected gravimetrically. The char was further analyzed using Perkin Elmer elemental analyzer for elemental composition.

Detailed calculations have been presented in Appendix E. Carbon conversion efficiency is defined as ratio of carbon obtained in the syngas to the carbon in the biomass and is shown in Equation 4b. Summation of carbon obtained in ethylene, acetylene, methane, carbon dioxide and carbon monoxide made up the carbon in syngas, while the carbon in the biomass was obtained from elemental analysis of sample on dry basis. The char conversion on the other hand is defined as the ratio of amount of carbon obtained in char to that present in the biomass fed. The char conversion efficiency was calculated as shown in Equation 4c.

$$\text{Conversion}_{\text{c}} = 100\ \times \frac{(\text{mass carbon in syngas})}{\text{mass carbon in sample}} \tag{4b}$$

$$\text{Cconversion}_{\text{char}} = 100\ \times \frac{(\text{mass of carbon in char})}{\text{mass carbon in sample}} \tag{4c}$$

The cold gas efficiency was defined as the ratio of the sum of the heating values (LHV) of the primary syngas components to that of the LHV (which was calculated from HHV) of the biomass as shown in Equation 4. This efficiency showed how much energy in the biomass was converted to useful syngas components.

$$\text{Cold gas efficiency} = 100\ \times \frac{\sum \text{Heating values of primary syngas compoenents} * (\frac{\text{vol conc}}{100})}{\text{LHV of biomass}} \tag{4d}$$

5.2.4 **Experimental design and statistics**

Several studies have reported air gasification with an ER ranging from 0.2 to 0.4 and a temperature range of 600 to 900°C. In this study, the experiments were carried out at an ER of 0.25 at 790, 935, and 1000°C and ER of 0.20, 0.25, and 0.30 at 935°C to study the effect of the temperature and the ER on the gasification products, respectively. The data presented in Section 3 is the average of three runs for every ER and temperature unless otherwise noted. Statistical analysis was carried out using 1-way ANOVA with an alpha of 5% to determine the significance of ER and temperature on syngas products, and the analysis was performed using Minitab®. It is important to note that only one tar datum point was collected for each condition

5.3 Results and discussion

In this section, effect of temperature and ER on product yield, syngas composition, syngas energy, carbon balance and contaminants have been discussed thoroughly. The biomass characterization and the syngas profile obtained for various process conditions have also been discussed in depth.

5.3.1 Biomass characterization

Table 5.1 summarizes the properties of torrefied pine used in this study. The physical and chemical properties of this feedstock are consistent with the typical values reported for torrefied biomass. The heating value of 23.60 MJ/kg (dry basis) is in agreement with those reported for the torefied pine by other studies (Doassans-Carrère et al., 2014; Kuo et al., 2014; Phanphanich and Mani, 2011; Shreshtha, 2014).

Table 5.1: Physical, proximate and ultimate analyses of torrefied biomass sample

Analysis	**Torrefied pine**
Moisture, % a.r.[a]	6.73 ±0.26
HHV MJ/ kg, dry basis	23.60 ±0.13
Proximate analysis (wt%, dry basis)	
Ash	1.17 ±0.11
Volatile matter	75.74 ±0.22
Fixed Carbon	23.10 ±0.32
Elemental analysis (wt%, dry ash free basis)	
Carbon	58.61 ±0.40
Hydrogen	6.27 ±0.27
Nitrogen	0.35 ±0.01
Sulfur	0.31 ±0.04
Oxygen	33.36 ±0.17

Physical properties	
Particle density (kg/m^3)	489.91 ±3.88
Bulk density (kg/m^3)	1474.46 ±10.48
Average (d_{50}) particle size (mm)	0.289 ±0.01

[a] wet basis

The raw pine gasification runs were performed at approximately 9 g/min to compare the results with the torrefied pine. The proximate and ultimate analysis of this pine has been reported elsewhere.(Abdoulmoumine et al., 2014) The switchgrass gasification data used for comparison with the torrefied biomass gasification has been reported elsewhere(Kulkarni et al., 2015a). Biomass composition analysis of three samples was performed and is reported in Table 5.2. The hemicellulose content was calculated from summation of sugars (i.e. xylan, galactan, arabinan, and mannan). These data agree well with the values reported in the literature.(Phanphanich and Mani, 2011) It can be concluded that the torrefied pine has high content of Klason lignin, which was formed by decomposition of hemicellulose and some cellulose during the torrefaction process.(Nepune, 2014)

Table 5.2: Component analysis of biomass samples[a]

Biomass sample	**Cellulose %**	**Hemicellulose %**					**Klason Lignin**
	Glucan	Xylan	Galactan	Arabinan	Mannan	Total	%
Torrefied pine	39.51 ±6.97	2.02 ±0.31	1.00 ±0.09	2.52 ±2.15	4.82 ±2.94	10.35 ±6.11	45.00 ±0.02
Pine	50.83 ±0.15	4.23 ±0.05	1.69 ±0.01	1.79 ±0.01	8.68 ±0.06	16.39 ±0.14	29.75 ±0.89
Switchgrass	40.44 ±3.60	16.23 ±1.72	0.44 ±0.07	2.62 ±0.54	2.64 ±1.52	21.94 ±4.30	26.11 ±1.11

[a]Cellulose, hemicellulose and lignin are calculated on extractive free basis.

5.3.2 Syngas profile

Syngas profile comparing the gasification experiments carried out for torrefied pine at three temperatures (790°, 935°, and 1000°C) and three ER (0.20, 0.25, and 0.30) are illustrated in Figure 5.1 and Figure 5.2, respectively.

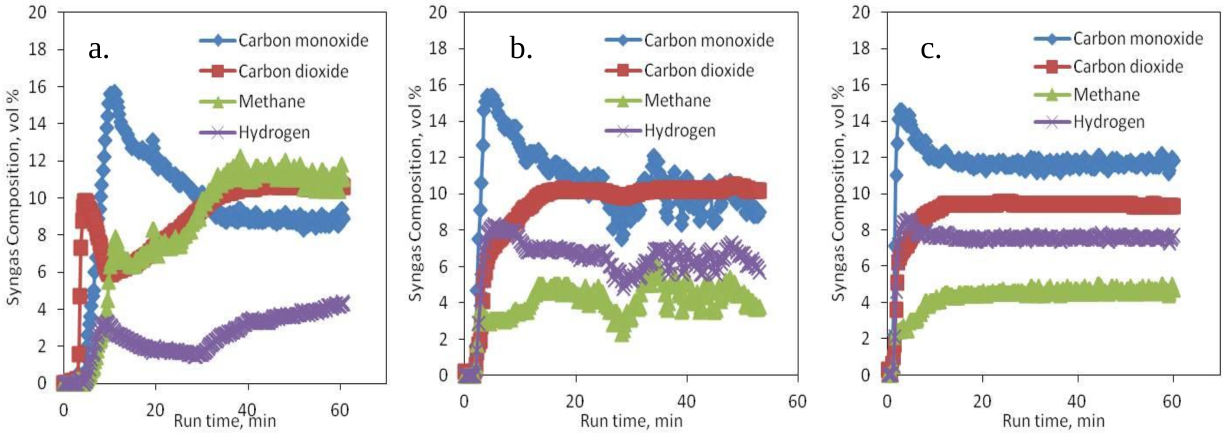


Figure 5.1: Syngas profile for experimental runs at 790 (a), 935 (b), and 1000°C (c) for ER 0.25 ±0.01.

At 790°C, the steady state was obtained after 30 minutes into the run for CO, CO_2 and CH_4; however, the H_2 concentrations increased. This could be a result of hydrogen production via steam reforming of other higher hydrocarbons (like ethylene and acetylene). At 935°C, the steady state was achieved only for CO_2, indicating that the reforming of methane continued throughout the run, resulting in the variations obtained for CO, CH_4, and H_2. However, at 1000°C, the steady state was obtained much faster and the concentrations remained constant throughout the run, which could be due to the high temperature that helped maintain the thermodynamic conditions required for the syngas reactions. During the 1000°C run, the temperature in the gasifier dropped from 1010 to 990°C however, the steady state did not seem to be affected; this temperature drop might not be significant to produce a reduction in syngas concentration.

Figure 5.2 shows the syngas profiles for the runs performed at ER 0.20, 0.25, and 0.30 at temperature 935°C. The steady state time did not vary considerably with ER. With the increase in the ER, the CO_2 concentrations increased while the CH_4 and H_2 concentrations were not affected. Conversely, increase in the temperature did influence these concentrations (Figure 5.1).

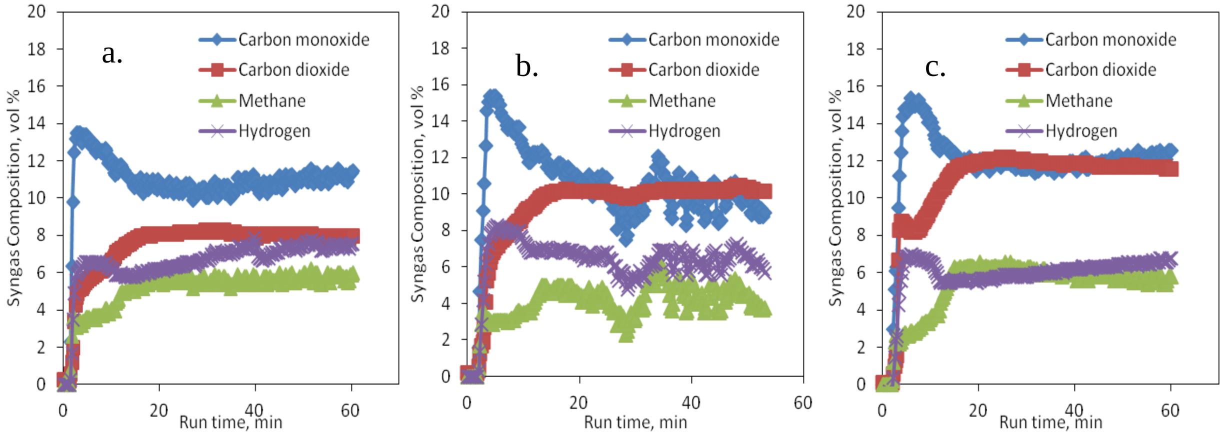


Figure 5.2: Syngas profile for experimental runs at 935°C for ER 0.20 (a), 0.25 (b) and 0.30 (c).

When compared with the pine gasification study, it was observed that the runs performed with raw pine were more steady.(Abdoulmoumine et al., 2014) This could be due to the difference in the feed rate. As mentioned before, the torrefied pine used for this study was ground to the required particle size from pellets, thus the feedstock was much denser and fed faster. The biomass feed rate was around 9 g/min for the torrefied pine as against 3 g/min for raw pine as reported in Abdoulmoumine *et al* (Abdoulmoumine et al., 2014). However, only the steady state data were used for the calculations, which agree well with those reported in some of the previous studies(Carpenter et al., 2010b) (Abdoulmoumine et al., 2014).

5.3.3 **Effect of temperature and equivalence ratio**

Table 5.3 summarizes the product yield, gas composition, gas energy, carbon conversion, cold gas efficiency and energy content of the syngas as obtained in this study. Subsequent sections will further discuss these responses as well as the selected contaminants measured in details.

Table 5.3: Gasification products obtained as a function of temperature and ER for torrefied pine.

	Temperature, °C			**ER**		
	790	935	1000	0.20	0.25	0.30
			Product yield, %			
Gas	69.21 ± 0.85^{B}	79.62 ± 5.17^{A}	80.56 ± 2.57^{A}	77.89 ± 3.46^{X}	79.62 ± 5.17^{X}	79.31 ± 2.54^{X}
Char	12.98 ± 0.80^{A}	7.33 ± 3.12^{B}	6.99 ± 1.19^{B}	9.33 ± 3.38^{X}	7.33 ± 3.12^{X}	5.43 ± 1.43^{X}
Liquid	17.82 ± 0.91^{A}	$13.04 \pm 2.10^{A,B}$	12.44 ± 1.57^{B}	12.77 ± 3.38^{X}	13.04 ± 2.10^{X}	15.04 ± 1.12^{X}
			Composition, vol %			
CO	9.32 ± 0.85^{A}	11.78 ± 2.31^{A}	12.26 ± 1.03^{A}	11.27 ± 0.99^{X}	11.78 ± 2.31^{X}	12.85 ± 1.86^{X}
CO_2	10.97 ± 0.53^{A}	10.09 ± 0.16^{B}	9.39 ± 0.95^{B}	8.39 ± 0.54^{Z}	10.09 ± 0.16^{Y}	11.59 ± 0.39^{X}
CH_4	11.15 ± 0.90^{A}	5.39 ± 0.91^{B}	4.62 ± 0.11^{B}	5.76 ± 0.84^{X}	5.39 ± 0.91^{X}	4.89 ± 0.89^{X}
H_2	3.54 ± 1.03^{B}	6.91 ± 0.76^{A}	7.61 ± 0.31^{A}	7.28 ± 0.05^{X}	6.91 ± 0.76^{X}	6.74 ± 0.99^{X}
C_2H_2	0.05 ± 0.001^{A}	0.11 ± 0.03^{A}	0.10 ± 0.02^{A}	0.11 ± 0.001^{X}	0.11 ± 0.03^{X}	0.11 ± 0.01^{X}
C_2H_4	0.84 ± 0.17^{C}	1.16 ± 0.07^{A}	0.41 ± 0.01^{B}	0.48 ± 0.01^{Y}	1.16 ± 0.07^{X}	0.95 ± 0.2^{X}
			Efficiency, %			
Carbon conversion	70.39 ± 10.9^{A}	68.62 ± 11.2^{A}	62.36 ± 4.53^{A}	60.03 ± 7.5^{Y}	$68.62 \pm 11.2^{Y,X}$	77.02 ± 5.69^{X}
Carbon in char	20.33 ± 0.67^{A}	10.48 ± 4.44^{B}	10.83 ± 1.13^{B}	14.38 ± 5.48^{X}	10.48 ± 4.44^{X}	8.34 ± 2.67^{X}
Cold gas	73.50 ± 11.47^{A}	$52.12 \pm 12.64^{A,B}$	49.67 ± 4.82^{B}	52.55 ± 8.35^{X}	52.13 ± 12.64^{X}	54.14 ± 5.05^{X}
			Syngas yield and energy			
Yield , Nm^3/ kg	0.80 ± 0.12^{A}	0.89 ± 0.15^{A}	0.84 ± 0.04^{A}	0.78 ± 0.08^{X}	0.89 ± 0.15^{X}	0.95 ± 0.09^{X}

Energy content, MJ/ Nm³	6.29 ± 0.23^{A}	4.51 ± 0.69^{B}	4.3 ± 0.13^{B}	4.64 ± 0.45^{X}	4.51 ± 0.69^{X}	4.43 ± 0.37^{X}
Contaminant concentration (ppm Volume)						
Ammonia	459.82 ± 22.64^{A}	637.23 ± 25.07^{A}	529.75 ± 20.10^{A}	564.77 ± 45.65^{X}	637.23 ± 25.07^{X}	622.79 ± 12.04^{X}
Hydrogen cyanide	89.47 ± 4.21^{B}	175.95 ± 13.24^{A}	165.50 ± 19.43^{A}	183.63 ± 30.82^{X}	175.95 ± 13.25^{X}	162.82 ± 19.14^{X}
Hydrogen chloride	2.29 ± 1.09^{A}	0.90 ± 0.15^{A}	0.33 ± 0.03^{A}	1.28 ± 0.07^{X}	0.90 ± 0.15^{X}	1.16 ± 0.25^{X}
Hydrogen fluoride	0.15 ± 0.01^{A}	0.27 ± 0.06^{A}	0.27 ± 0.08^{A}	0.28 ± 0.08^{X}	0.27 ± 0.06^{X}	0.28 ± 0.04^{X}
Carbonyl sulfide	16.41 ± 0.90^{A}	$11.48 \pm 4.25^{A,B}$	5.38 ± 3.24^{B}	6.41 ± 3.72^{X}	11.48 ± 4.25^{X}	11.97 ± 3.9^{X}
Sulfur dioxide	86.29 ± 3.38^{A}	105.44 ± 21.58^{A}	82.09 ± 4.85^{A}	109.29 ± 4.27^{X}	105.44 ± 21.58^{X}	93.13 ± 9.90^{X}

Effect of temperature and ER were analyzed independently and interaction between them was not studied. Means with same superscripts are not statistically different (P-value > 0.05) based on a one-way ANOVA test and are significantly different at the 0.05 level based on Tukey HSD Post Hoc test.

5.3.3.1 Product yield

Gasification products as a function of the temperature and the ER are shown in Table 5.3. The char, liquid and gas yields are a direct result of the reactions taking place inside the gasifier at operating conditions. As expected, the char reactivity increased with the temperature. This resulted in the conversion of higher amounts of char into gas. The liquid yield, which mostly consists of water trapped in condensers along with some condensable hydrocarbons, reduced with an increase in the temperature. This was primarily due to water reacting further with char and other gasification products. This leads to an increase in the gas concentration with an increase in the temperature. Table 5.3 shows that the char yield and the liquid yield decreased while the gas yield increased significantly with an increase in the temperature. Similar trends were observed for switchgrass (Kulkarni et al., 2015a) and pine gasification (Abdoulmoumine et al., 2014) on the same set up. Similarly, an increase in gas yield with increase in temperature was also reported by Narvaez et al.(Narvaez et al., 1996) for pine saw dust and for four biomass samples by Carpenter et al.(Carpenter et al., 2010b)

The increase in the ER directly corresponds to the increase in the oxygen supplied for gasification. As the ER is increased, higher oxygen availability is expected to influence the oxidation reactions, resulting in increase in oxidation products in syngas. Table 5.3 shows that the reduction in char yield and increase in liquid yield with increase in ER are not statistically significant in the range of ER under study. Similarly, an increase in gas yield was not significant. Few other studies have observed trends similar to those observed in this study for the char yield as the ER increased(Abdoulmoumine et al., 2014; Campoy et al., 2008a). The increase in the gas yield was observed for pine gasification and also agreed with simulation results for fluidized bed gasifier (Abdoulmoumine et al., 2014; Campoy et al., 2008a).

As mentioned before, the performance of torrefied pine was compared with pine and switchgrass, under the same gasification conditions (935°C, ER = 0.25, feeding rate ~ 9 g/min). Figure 5.3 shows the comparison between the product yield for torrefied pine, raw pine and switchgrass. It can be seen that the gas yields were comparable for all three whereas the char yield was lowest for the raw pine, thus indicating a higher char conversion for the raw pine. The lower char reactivity noticed in torrefied pine char is comparable to that reported in the literature.(Fisher et al., 2012) The char yield from switchgrass was very close to that obtained from torrefied sample, this could be due to the higher ash content in switchgrass which resulted in higher char yield than raw pine. On the other hand, the liquid yield obtained for the raw biomass samples was significantly higher than that from torrefied pine. This could be the direct result of lower moisture content of the torrefied pine due to the loss of water holding xylan during the torrefaction process.

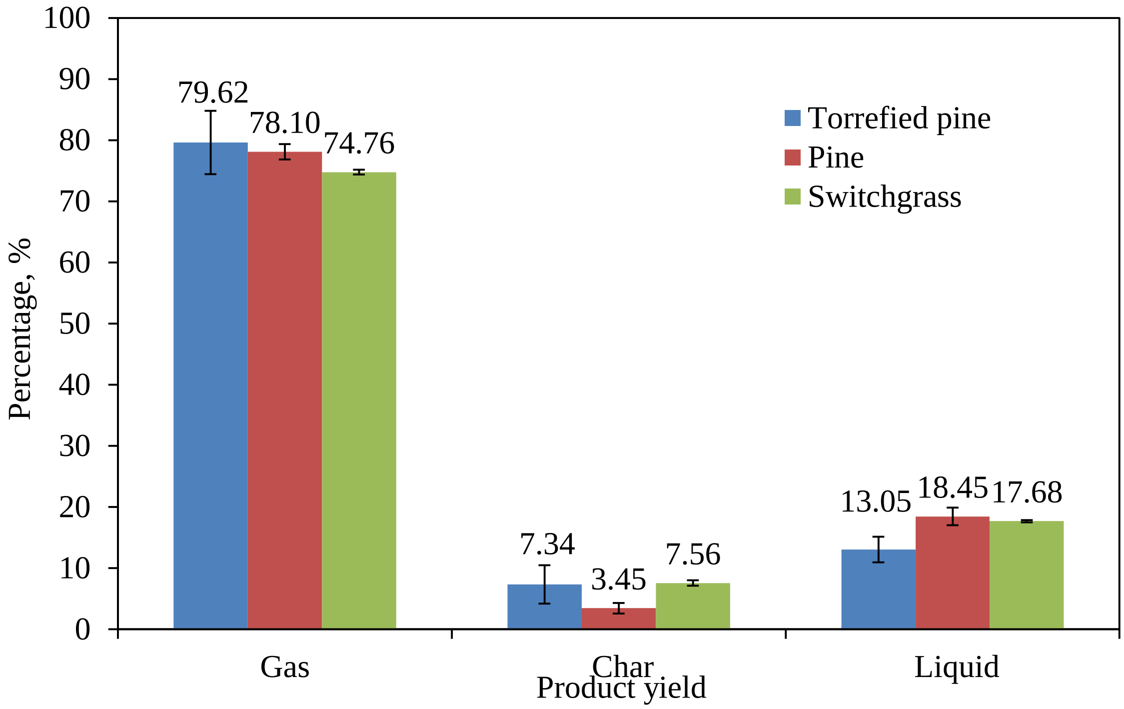


Figure 5.3: Product yield for torrefied pine, pine and switchgrass at 935°C, 0.25 ER and feed rate of approximately 9 g/min.

5.3.3.2 Syngas composition

Table 5.3 shows the volumetric syngas composition as a function of temperature and ER. Figure 5.4 shows the variation of component yield (g/kg dry biomass) as a function of the temperature and ER.

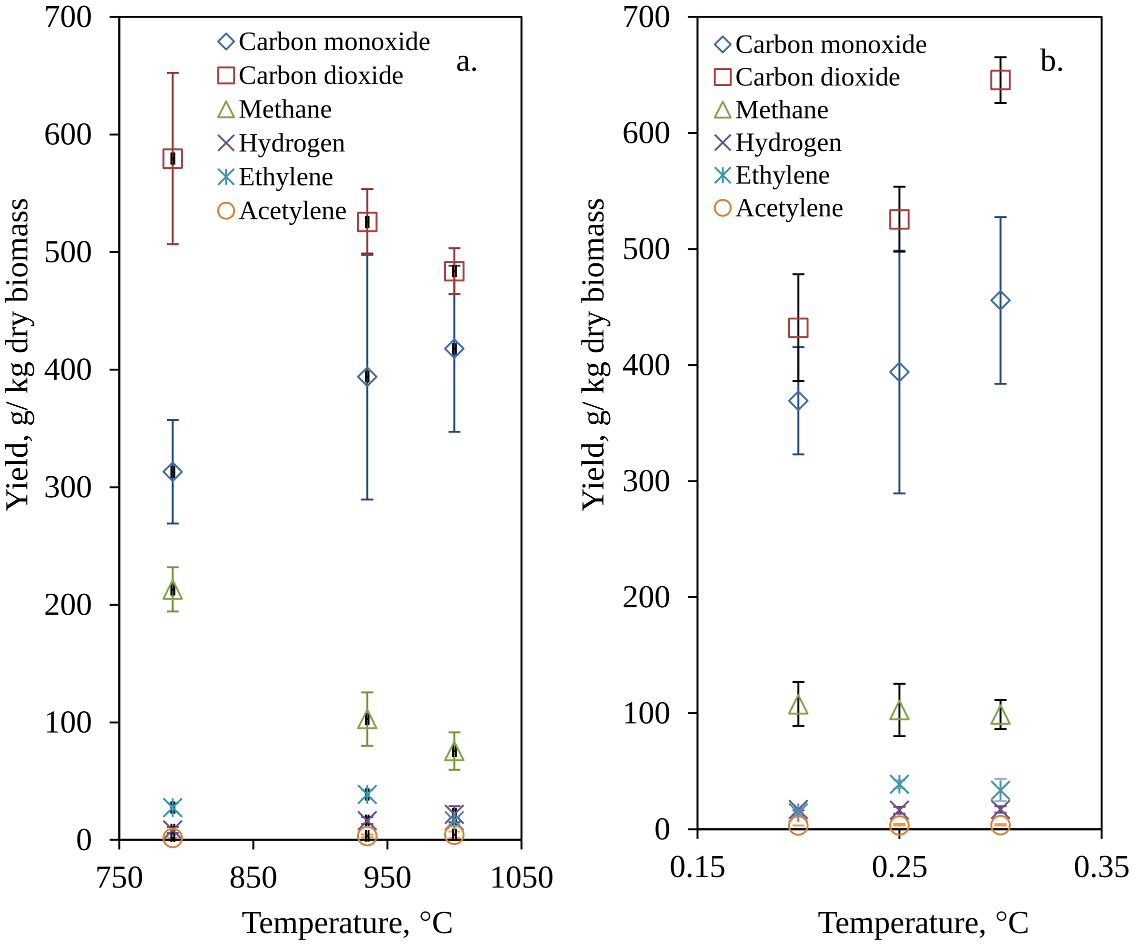


Figure 5.4: Effect of (a) temperature at 0.24 ER and (b) ER at 935°C on syngas composition.

Effect of temperature:

With an increase in temperature, higher amount of char reacted with oxygen, steam (shown in Equation 4.1) as well as CO_2 (Boudouard reaction as shown in Equation 4.2), resulting in an increase in the CO, H_2 yield and decrease in the CO_2 yield as shown in Figure 5.4a. This also resulted in char reduction with an increase in temperature

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = +131 \text{ kJ/mol} \tag{4.1}$$

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H = + 172 \text{ kJ/mol} \tag{4.2}$$

As mentioned above H_2 production increased with an increase in the temperature. One of the contributing factors to the increase in CO and H_2 is the methanation reaction (Equation 4.3), which would convert CH_4 and H_2O into CO and H_2 as the temperature increased. This was confirmed by the reductions in the liquid yield and methane.

$$CO + 3H_2 \leftrightarrow H_2O + CH_4 \quad \Delta H = -206 \text{ kJ/mol} \tag{4.3}$$

The increase in the concentration of CO and H_2 agrees with that reported in the literature for switchgrass and other biomass feedstocks (Abdoulmoumine et al., 2014; Carpenter et al., 2010b; Narvaez et al., 1996; Sarkar et al., 2014b). Although an increase in C_2H_2 was noticed, it was not statistically significant with an increase in temperature. The C_2H_4 yields on the other hand showed a peak at 935°C. The increase in the acetylene and the ethylene production could be due to the reaction of carbon and hydrogen present in the char, which increase with an increase in temperature from 790 to 935°C. It could be proposed that at 1000°C steam reformation of these compounds resulted in a reduced yield of these compounds and their concentrations agree with those reported previously (Abdoulmoumine et al., 2014; Carpenter et al., 2010b; Van der Drift et al., 2001).

Effect of ER:

Figure 5.4b shows the variation in the yields of syngas components as a function ER. Since the increase in the ER corresponds to an increase in the oxygen supply, it resulted in an increase in the liquid yield, as seen in the previous section. Equations 4.4-4.9 are key reactions, which influence the syngas composition and yield as a function of ER

$$C + 0.5O_2 \rightarrow CO \qquad \Delta H = -111\ \text{kJ/mol} \tag{4.4}$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -394\ \text{kJ/mol} \tag{4.5}$$

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \Delta H = -284\ \text{kJ/mol} \tag{4.6}$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + H_2O \qquad \Delta H = -803\ \text{kJ/mol} \tag{4.8}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad \Delta H = -242\ \text{kJ/mol} \tag{4.9}$$

Table 5.3 shows that the CO_2 increased significantly with the increase in ER from 0.20 to 0.30, reaction in Equation 5 explains this increase. The CO increased slightly and was not statistically significant; the slight increase could be due to the higher oxygen availability for the gasification reaction (Equation 4.1). Thus, although the oxidation of methane and hydrogen reduced the concentrations (as seen in reactions 4.8 and 4.9); the effect was not significant over the range of ER. C_2H_2 was not affected at all with the increase in temperature, whereas C_2H_4 showed an increase with an increase in the ER instead of an expected reduction. Pine gasification study indicated a decrease in the CO, CH_4 and H_2 concentrations with an increase in ER since the presence of hemicellulose in raw biomass makes the bio-char more reactive(Fisher et al., 2012). The CO and H_2 agreed well with those reported for torrefied switchgrass gasification using a TGA.(Sarkar et al., 2014b) However, the methane yields were almost twice of those reported in the same study; this could be due to the difference in TGA and bench scale set up.

To clearly understand the effect of torrefaction on the syngas composition, a comparison was made between syngas components obtained from torrefied pine, pine, switchgrass and gasification of torrefied using downdraft gasifiers. Table 5.4 shows the syngas component values for pine, switchgrass and torrefied pine gasified in the same bench scale bubbling fluidized bed gasifier with ER = 0.25 at 935 °C and a feed rate of ~ 9 g/ min. It was observed that the syngas from pine had the highest amount of CO, followed by switchgrass and torrefied pine. The other syngas components were very similar in concentrations. Switchgrass produced the highest amount of C_2H_2. Thus, it was confirmed that the use of torrefied biomass for gasification would not significantly affect the syngas composition, when compared with raw biomass samples. When compared with torrefied pellets gasified in downdraft gasifiers (Doassans-Carrère et al., 2014; Dudyński et al., 2015) with much higher feed rate (almost 30 to 60 times that in bench-scale fluidized bed gasifier) produced significantly higher concentrations of CO and H_2, but much lower CH_4 compared to that obtained from fluidized bed. Also the high amounts of nitrogen present for fluidization reduced the CO and H_2 concentrations.

Table 5.4: Comparison of syngas gas composition obtained from torrefied pine, pine and switchgrass under similar gasification conditions.

Authors	**Torrefied pine**	**Pine**	**Switchgrass (Kulkarni et al., 2015a)**	**Torrefied pine pellets(Shreshtha, 2014)**	**Torrefied Pellets(Dudyński et al., 2015)**
Temperature, °C	935	935	935	800	800
ER	0.25	0.25	0.25	0.28	0.28
Mean Feed rate	9.3 g/min	9.8 g/min	9.63 g/min	23.01 kg/hr	35 kg/hr
			Composition, vol %		
CO	11.8 ±2.3	13.9 ±0.6	12.6 ±0.6	24.5±0.6	29
CO_2	10.1 ±0.2	9.3 ±0.2	9.5 ±0.2	7.9 ±1.3	6.7
CH_4	5.4 ±0.9	6.8 ±0.3	5.8 ±0.2	1.5 ±0.5	1.6
H_2	6.9 ±0.7	6.1 ±0.2	7.0 ±0.3	15.1±0.3	10.3
C_2H_4	1.2 ±0.1	1.3 ±0.3	2.5 ±0.8	n.r.	0.2
C_2H_2	0.1 ±0.04	0.1 ±0.02	0.2 ±0.01	n.r.	n.r.

n.r. not reported.

5.3.3.3 Syngas energy

With an increase in temperature, the CH_4 concentration, which is important for the syngas energy content, reduced significantly and as a result the syngas energy decreased. The decrease in

CH_4 was more influential than the increase in CO and H_2, and was unlike that observed for pine and switchgrass. With raw biomass samples, the energy content increased with the increase in temperature. The CH_4 concentration was much lower for raw biomass samples, and its decreasing trend with the increase in temperature did not significantly affect the energy content. The torrefied pine seems to produce much higher methane at lower temperature, which is excellent for power application. The energy content values obtained were higher than those reported for switchgrass (Kulkarni et al., 2015a) and pine(Abdoulmoumine et al., 2014) due to the higher feed rate of the torrefied pine, and agreed well with those reported previously for air gasification (Carpenter et al., 2010b; Doassans-Carrère et al., 2014; Lv et al., 2004a; Narvaez et al., 1996; Sarkar et al., 2014b). ER did not significantly affect the energy content of syngas. Since the ER did not have any significant effect on CO, CH_4 and H_2, the effect on energy content was justified. For switchgrass and pine studies, an increase in ER resulted in a decrease in energy content.

The gasification experiments carried out for torrefied pine using downdraft gasifiers reported syngas HHV around 5.6 MJ/ Nm^3 at temperature around 800°C.(Dudyński et al., 2015; Shreshtha, 2014) This value is very close to that reported for the current study at 790°C. When compared with pine and switchgrass, the energy content from torrefied pine was slightly lower at 935 °C (Figure 5.5). This was a result of higher CO_2 in the syngas obtained from torrefied pine. Pine seems to produce syngas with the highest energy content at given conditions. At 790°C, on the other hand, torrefied pine produced higher energy syngas compared to pine and switchgrass (Abdoulmoumine et al., 2014; Sarkar et al., 2014b).

5.3.3.4 Carbon balance and cold gas efficiency

The carbon conversion, as defined in this work, only accounts for carbon in biomass converted into CH_4, CO, CO_2, C_2H_2 and C_2H_4. Average carbon conversion (gas) values were 70.39

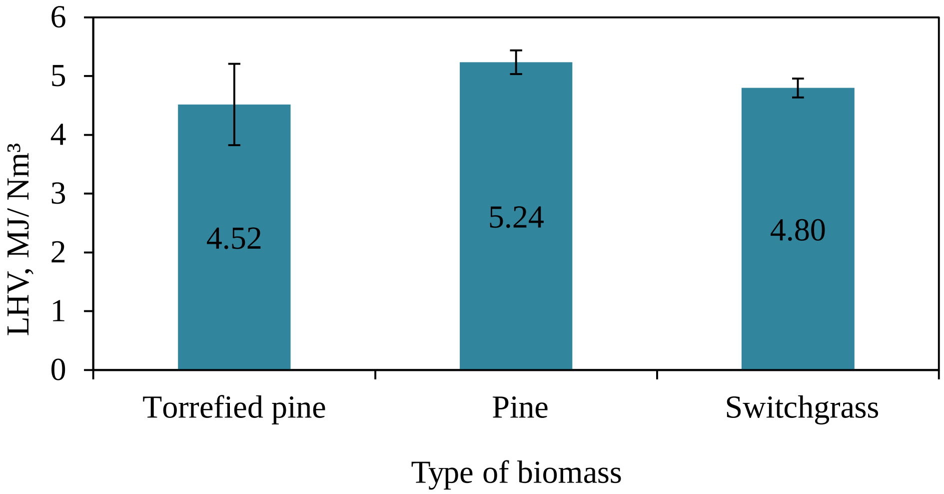


Figure 5.5: Syngas energy content at 935˚C and ER of 0.25 and feed rate of approximately 9 g/min.

±10.9%, 68.62 ±11.2% and 62.36 ±4.53% at 790°C, 935°C and 1000°C, respectively. The effect of temperature on the carbon conversion was not statistically significant. The carbon conversion values were lower than those obtained for raw biomass samples(Abdoulmoumine et al., 2014; Kulkarni et al., 2015a). These lower carbon conversion (in range of 60 to 70%) values were probably due to higher content of lignin in torrefied pine. Previous studies have indicated around 52% of carbon conversion for lignin during TGA (air gasification)(Pasangulapati et al., 2012) and in bench scale fixed bed (air/steam gasification)(Hanaoka et al., 2005) analysis carried around 900°C and at same condition around 97% for cellulose. The decreasing trend however not observed for switchgrass or pine gasification, it was observed due to significant decrease in CH_4 (from average of 11.14% at 790°C to 4.60% at 1000°C) and some decrease in CO_2 (from average of 10.91 at 790°C to 9.39% at 1000°C) concentrations with an increase in temperature. . Lv *et al.* reported the carbon conversion efficiency to be around 77 to 95% using a fluidized bed gasifier using pine saw dust.(Lv et al., 2004a) The values obtained for downdraft gasifier were in the range of 90%. (Shreshtha, 2014) While Sarkar et al. reported carbon conversion values of 67.58% and 58.11% for switchgrass torrefied at 230° and 270°C respectively, when gasified in a bench scale fixed bed reactor (Sarkar et al., 2014b).The average values of carbon conversion into char was 20.33%, 10.48% and 10.83% at 790°C, 935°C and 1000°C, respectively. Temperature had a statistically significant effect in reduction of carbon conversion into char (Table 5.3).

The cold gas efficiency decreased with an increase in the temperature; this was mostly the result of decrease in methane concentration in the syngas with an increase in temperature. This decreasing trend was unlike that observed with the raw biomass samples. The cold gas efficiency for downdraft gasifier was around 65 to 70%.(Sarkar et al., 2014b; Shreshtha, 2014) The range of the cold gas efficiency (30 to 70%) also agreed well with the values reported for fluidized bed gasifiers in the literature.(Dudyński et al., 2015; Sarkar et al., 2014b; Shreshtha, 2014; Van der Drift et al., 2001)

Average carbon conversion into syngas increased with an increase in ER, while that into char reduced. The excess oxygen present resulted in higher CO_2 concentrations; this led to more char conversion. The reduction in char yield was observed with increase in ER, as reported in the product yield section. Also, the carbon present in the char reduced with an increase in ER (Table 5.3).

Carbon compounds, except CO_2, were not affected by the increase in ER and therefore the cold gas efficiency was not affected either. In case of switchgrass, the increase in ER from 0.21 to 0.27 led to an increase in carbon converted into gas, specifically CO, and also slightly increased the cold gas efficiency (Kulkarni et al., 2015a). For pine, the syngas yield (mainly CO_2) increased with the increase in ER, which in turn resulted in a reduced cold gas efficiency.(Abdoulmoumine et al., 2014)

During the gasification of torrefied pine in a 25 KW_{th} downdraft gasifier, the carbon conversion and cold gas efficiency were reported to be around 79% and 63%, respectively at 800°C(Shreshtha, 2014). Yet another study reported carbon conversion and cold gas efficiency around 87% and 75%, respectively(Dudyński et al., 2015). A small-scale study on torrefied switchgrass gasified in a small bench scale downdraft gasifier reported increased carbon conversion at 75 to 80% and cold gas efficiency at 50 to 55%, with increase in temperature(Sarkar et al., 2014b).

When torrefied pine was compared with raw pine and switchgrass at a similar feed rate (~9 g/min), temperature (935°C) and ER (0.25), it was noticed that pine gasification results in the highest conversion of carbon into syngas. Also, pine produced syngas with the highest cold gas efficiency, closely followed by the switchgrass as seen in Figure 5.6. The lower carbon conversion efficiency in torrefied pine was due to high Klason lignin content in torrefied pine.

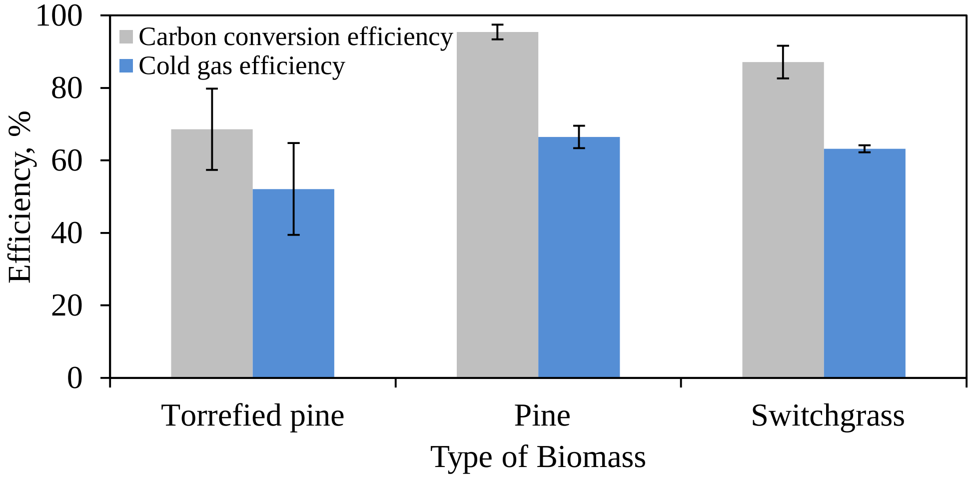


Figure 5.6: Carbon conversion and cold gas efficiency obtained for torrefied pine, pine, and switchgrass at 935°C, ER 0.25 and around 9g/min feed rate.

5.3.3.5 Contaminants

Figure 5.7 and Figure 5.8 show the contaminants yield obtained as a function of temperature and ER. It can be seen that ammonia was the main contaminant obtained during gasification followed by hydrogen cyanide and sulfur dioxide.

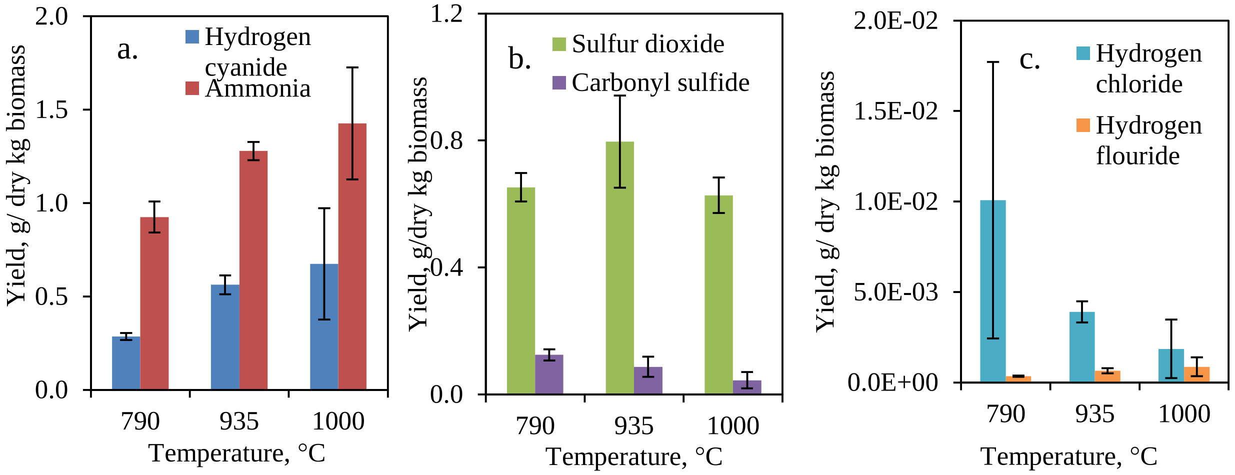


Figure 5.7: Effect of temperature on (a) HCN and NH_3 yield, (b) SO_2 and COS and (c) HCl and HF.

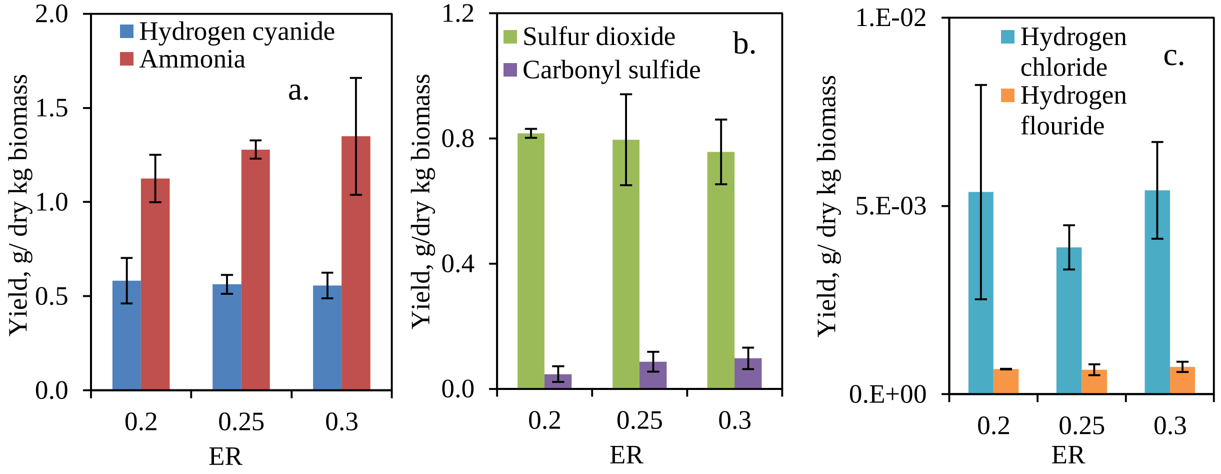


Figure 5.8: Effect of ER on (a) HCN and NH_3 yield, (b) SO_2 and COS and (c) HCl and HF.

Nitrogen contaminants (NH_3 and HCN): The yield and concentrations of nitrogen contaminants (i.e., HCN and NH_3) was directly proportional to the amount of nitrogen present in the biomass samples. With an increase in the temperature, a peak in ammonia concentration was observed at the 935°C, while the HCN concentration increases with an increase in temperature. Figure 8a and Table 5.3 show that with an increase in temperature the yields and concentrations of both NH_3 and HCN increased. This trend agreed well with that reported in the literature (Aljbour and Kawamoto, 2013a; Van der Drift et al., 2001); however, it was opposite of the trend reported for ammonia release from raw pine(Abdoulmoumine et al., 2014). Since the yield is calculated on the dry kg biomass basis, the peak observed for ammonia was a result of slightly higher feed rate of biomass, which was around 9.23 g/min for 935°C run as opposed to 8.3 g/min for the 1000°C run. With an increase in ER, the NH_3 and HCN concentration and yield, however, remained constant over the range of study. This trend was slightly different than that observed for pine, where much higher concentrations of ammonia were reported even at lower feeding rate(Abdoulmoumine et al., 2014), and agreed with that for switchgrass gasification. When the NH_3 and HCN values obtained for all three biomass samples under similar gasification conditions were compared, it was noted that the raw biomass pine produce twice as much NH_3 and one third as much of HCN compared to torrefied biomass (Figure 5.9). The ammonia yield corresponds to the amount of nitrogen present in the biomass. When compared, torrefied pine sample had 0.35% (dry basis), while pine and switchgrass reported 0.44% and 1.65% (dry basis) respectively. Similarly, switchgrass produced as much NH_3 and four times as much HCN as pine.

Sulfur contaminants (COS and SO_2): The effects of temperature and ER on the concentration and yield of sulfur contaminants are illustrated in Table 5.3, and Figure 5.7 and Figure 5.8b. It was observed that with an increase in the temperature, the yield of COS decreased and that of SO_2 increased. This could be due to the reaction of COS with hydrogen in syngas to produce CO and H_2S. With an increase in the ER the yield of COS increased and that of SO_2 was not affected. It is important to note that though the concentrations of SO_2 were reported to be around 100 ppm; this was much lower than that reported for coal and biomass co-feeding in a fluidized bed combustor.(Xie et al., 2007) A study to understand distribution of sulfur species in gasification, reported SO_2 values around 2-4 ppm and COS around 30 ppm, at ER 0.26 and S/B ratio of 1.3 at 1034.9°C for Corn Stover in a bench scale downdraft gasifier. When the concentrations of COS and SO_2 obtained from torrefied pine were compared with those obtained for pine and switchgrass under similar conditions, as shown in Figure 5.9b it was observed that the COS concentrations were around 11.47 ppm for torrefied pine and below detection level for raw biomass samples. This indicated that torrefied biomass favored COS production than the raw biomass. H_2S is the other major contaminant in the syngas; however, it was not reported since the FTIR could not measure it accurately.

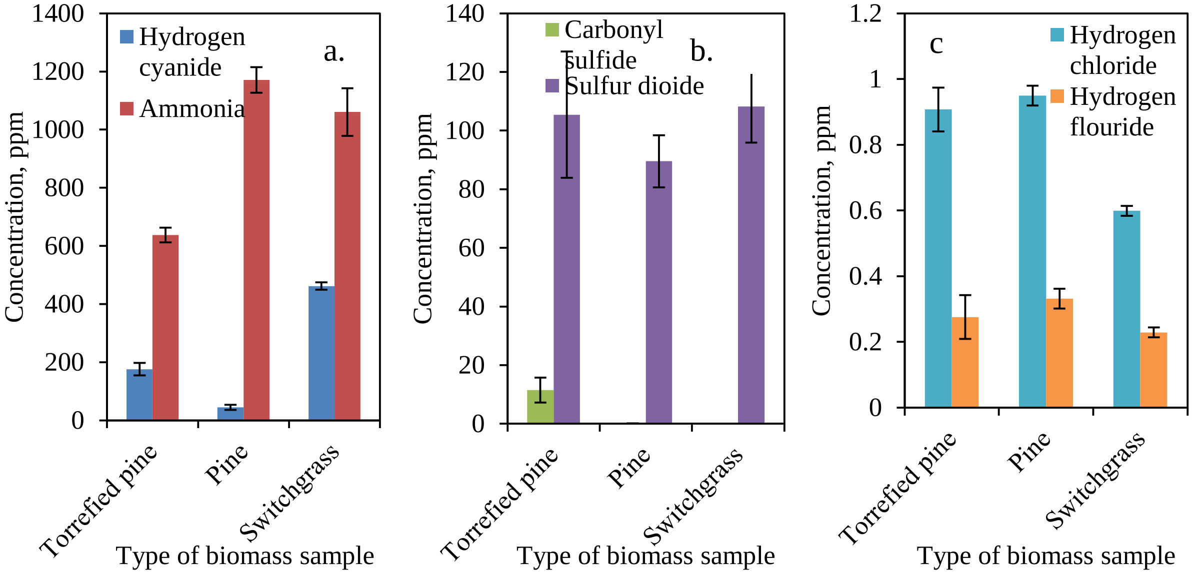


Figure 5.9: Concentrations of contaminants NH_3 and HCN (a), COS and SO_2 (b), and HCl and HF (c) at ER of 0.25 and temperature of 935°C with feed rate of approximately 9 g/min.

Halides (HCl and HF): Biomass consists of various amounts of chlorine and fluorine. The halides present in the biomass reacted with the hydrogen to produce HCl and HF, which are highly reactive acids causing corrosion for downstream processes. The concentrations of HCl and HF have been reported in Table 5.3 in ppm volume and Figure 5.7c and Figure 5.8c show the yield in g/kg biomass on dry basis. It can be seen that with the increase in temperature, the concentration of HCl decreased and that of HF increased. Overall, the concentrations are less than 2.5 ppm. On the other hand, the ER range under study does not seem to have any effect on the halide concentration. During the gasification of raw pine, as reported in by Abdoulmoumine *et al.*, it was observed that the HCl concentration decreased with an increase in temperature, and this trend agreed with that for torrefied biomass. Also, the concentrations of halides for pine and torrefied pine were in a rather similar range. The concentrations of hydrogen halides were below detection limit for switchgrass (Kulkarni et al., 2015a) and hence were not reported. The HCl concentrations for coal have been reported to be around 600 ppm; this corresponds to the higher chlorine content in raw coal (Duong et al., 2009; Krishnan et al., 1999). Since biomass has comparatively much lower halides, lower concentrations are justified. When the hydrogen halides concentrations were compared for pine, torrefied pine and switchgrass under similar conditions, as shown in Figure 5.8c, it was observed that the torrefied pine and raw pine produced approximately the same amount of hydrogen halides. The torrefaction process did not affect the halides present in the raw biomass and hence the similarity in hydrogen halides yields. Hydrogen halide concentrations were much lower for switchgrass syngas; this could be due reaction with alkali metal to form compounds like NaCl and was retained in the char.

Tar: The collected tar was analyzed for benzene, toluene, ethyl benzene, o-xylene, styrene, indene, phenol, 3-methyl phenol, naphthalene, 2-methyl naphthalene, and bi-phenyl. Figure 5.10 shows the yield of each of the above mentioned compounds as a function of temperature and ER, while Figure 5.11 shows the total tar yield as a function of temperature and ER. It is important to note that the data shown in these figures were obtained from single runs and hence, a clear trend was difficult to predict with an increase in temperature and ER. It was seen that with an increase in temperature, the tar yield increased from 1.56 g/kg biomass at 790°C to 3.87 g/kg biomass at 935°C and with further increase in temperature it reduced to 2.08 g/kg biomass at 1000°C. The increase in tar was a result of increase in tertiary compounds like benzene, toluene, indene, styrene and naphthalene. In their seminal work on the nature of tar formation, Milne et al.(Milne et al., 1998b) attributed tertiary tar formation at high temperature to the thermal conversion of primary and secondary tar compounds. However, at sufficiently high temperatures, all tar compounds undergo thermal cracking. Therefore, it is likely that the decrease in tar concentration beyond 935˚C was due to increasing thermal cracking of tar compounds.

The total tar yield reported was 1.94, 3.87 and 2.42 g/dry kg biomass at ER0.20, 0.25 and 0.30 respectively. With an increase in ER from 0.20 to 0.25 the total tar yield increased, which was contradictory to what has been reported in literature (Abdoulmoumine et al., 2014; Basu, 2013; Carpenter et al., 2010b; Milne et al., 1998b). Even though fractions of benzene and naphthalene have been reported to increase(Basu, 2013), other compounds tend to reduce due to oxidation; there seems to be a experimental error and more runs need to be performed at every ER to understand a clear trend. With further increase in ER (0.25 to 0.30) all the compounds and the total tar yield decrease, as expected.

It was observed that the highest yield obtained was that of benzene followed by toluene, indene, and naphthalene for all the conditions. The total and constituent yields agreed well with those reported with literature(Abdoulmoumine et al., 2014; Carpenter et al., 2010b; Devi et al., 2003; Narvaez et al., 1996).

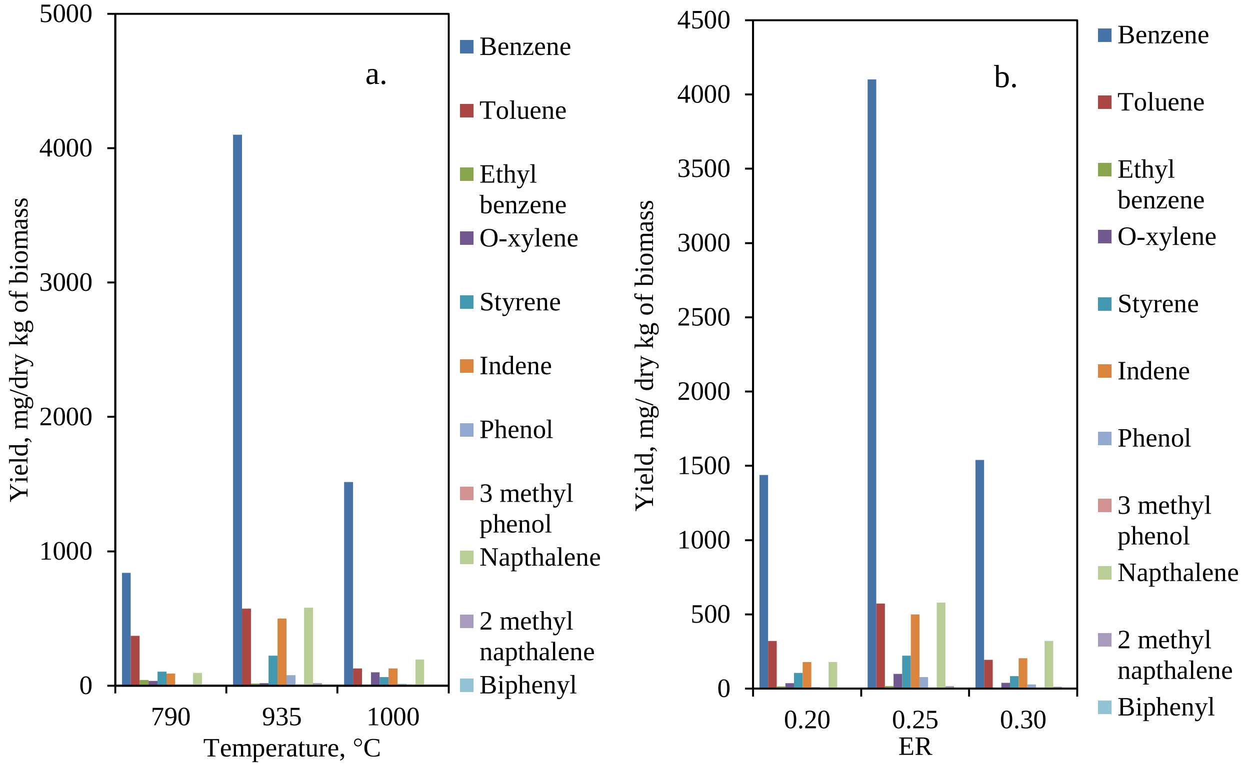


Figure 5.10: Effect of temperature (a) and ER (b) on the tar component yield.

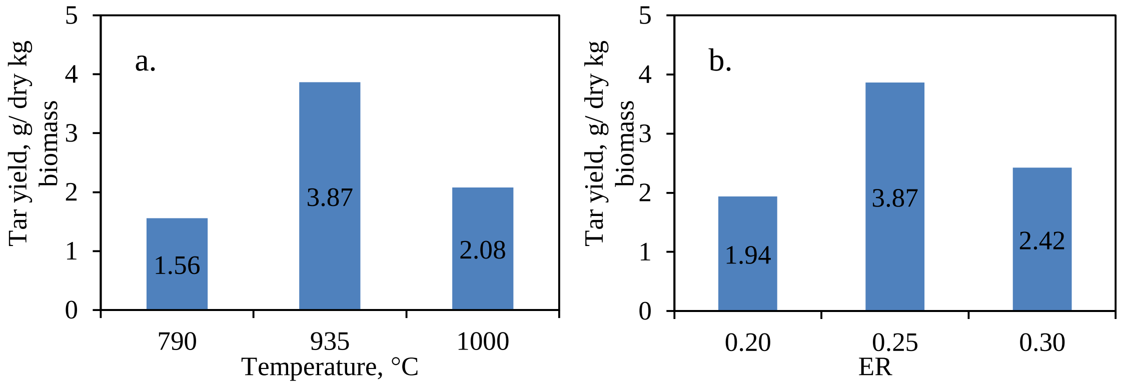


Figure 5.11: Effect of temperature (a) and ER (b) on total tar yield.

In order to compare the tar obtained from torrefied pine with raw biomass, tar data were obtained for switchgrass at feed rate of around 9 g/min, 935°C and ER 0.25, was analyzed and reported. Tar data for pine gasification was reported elsewhere(Abdoulmoumine et al., 2014), under same temperature and ER however lower feed rate. Figure 5.12 shows the total tar yield obtained for pine, switchgrass and torrefied pine. It was observed that the torrefied pine produced less than half the amount of tar obtained for switchgrass. Thus, indicating that the torrefaction of biomass helps reduce the tar yield during gasification and needs to be further investigated.

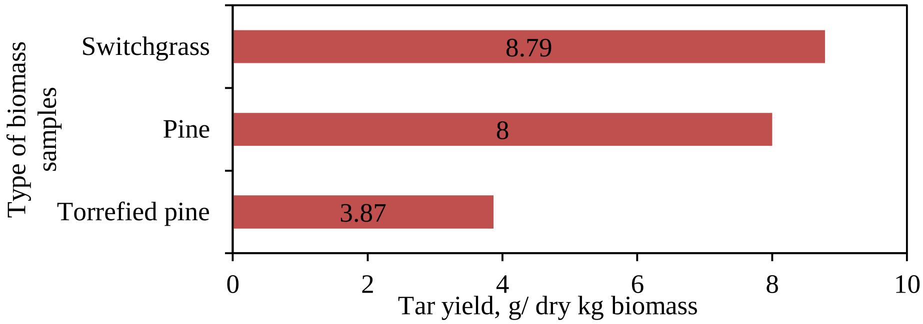


Figure 5.12: Total tar yield obtained for switchgrass, pine and torrefied pine.

5.3.3.6 SEM images of char

In order to understand the effect of gasification parameters on the biomass particles, images from the scanning electron microscope (SEM) were taken. Figure 5.13 shows the raw pine and torrefied pine at 1000x magnification. During torrefaction, the hemicellulose (binding element) decomposes leading to the structure seen in Figure 5.13b. Figure 5.13a shows that the epidermis of the ground biomass is still intact in the raw biomass, while it appears disintegrated for due to torrefaction. This agreed well with that reported previously (Chen et al., 2011; Phanphanich, 2010; Sarkar et al., 2014b).

As seen in Figure 5.14, a higher degradation of the char particles is observed with the increase in temperature. At the microscopic level, the gasification reaction takes place on the epidermis and reveals the vascular tracks like tracheid in the biomass sample. An increase in the number of tracheid pores, visible at the same magnification with an increase in temperature, shows that the degree of disintegration increases as a result of higher char conversion.

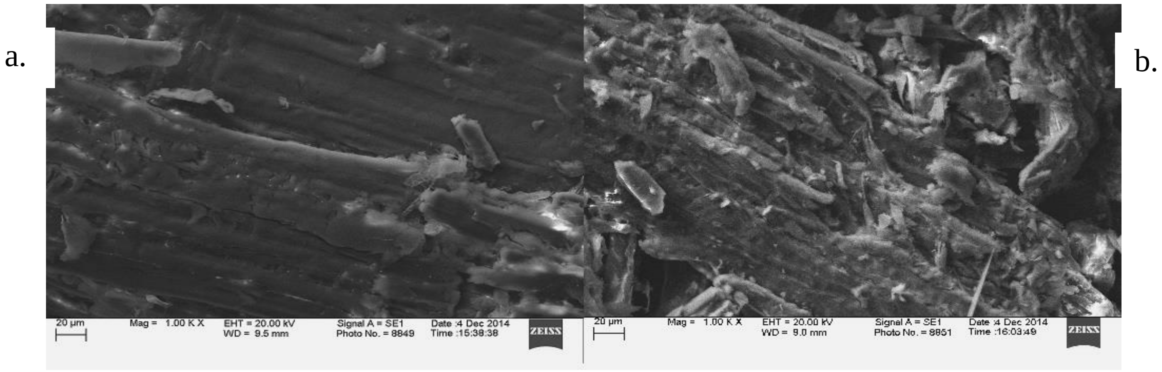


Figure 5.13: SEM image of raw pine (a) and torrefied pine (b).

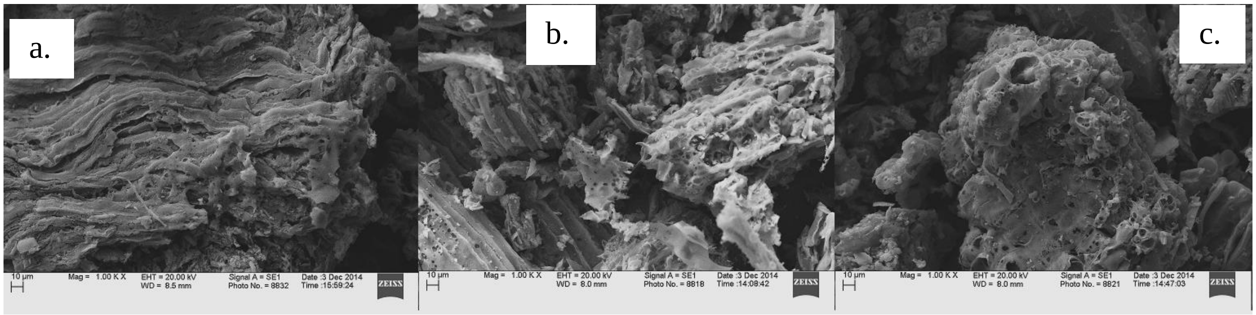


Figure 5.14: Images of char obtained for experimental runs performed at 790°C (a), 935°C (b) and 1000°C (c).

Figure 5.15 shows the microscopic structure of biomass of the char particles obtained through gasification at ER 0.20, 0.25 and 0.30. With higher oxygen supply, the disintegration of the char structure was more prominent, resulting in larger pore openings, which could be result of increase in the char reactivity with increase in ER.

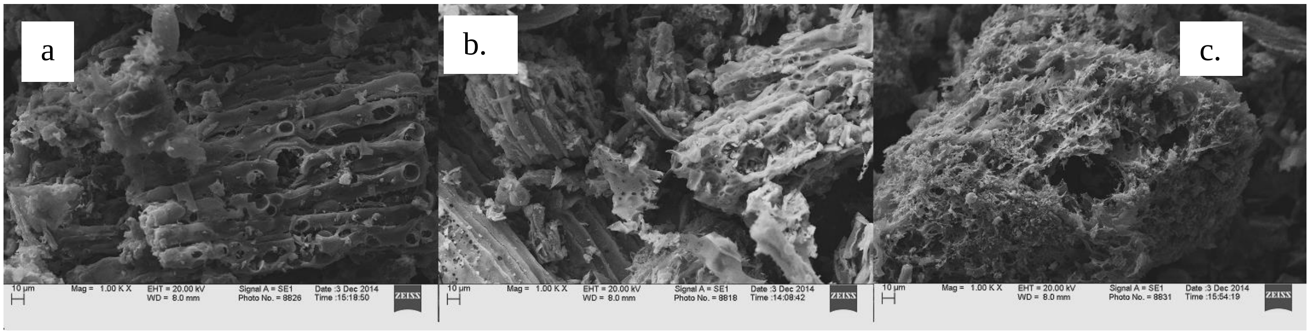


Figure 5.15: SEM images of char obtained for experimental runs performed at ER: 0.20 (a), 0.25(b) and 0.30 (c).

5.4 Conclusions and remarks

The performance of the torrefied biomass can be summarized as follows:

1. Product yield: The gas yield increased with an increase in temperature and also with an increase in ER. Under similar conditions gas yield was similar to those obtained from switchgrass and pine.
2. Primary syngas composition: The CO and H_2 concentration increased with increase in temperature, while the CH_4 and CO_2 decreased. With an increase in ER, the CO_2 concentration increased in syngas. When compared with pine and switchgrass, torrefied pine produced syngas with similar composition under similar conditions. Thus, it can be concluded the torrefaction of biomass does not affect the syngas composition.
3. Syngas energy content: When used for power application, the torrefied pine must be gasified at temperature around 800°C to get syngas with high energy content.
4. Carbon balance and cold gas efficiency: Similarly lower temperatures (around 800°C) lead to energy efficiency.
5. Contaminants: NH_3, HCN and SO_2 were the contaminants with high concentrations. With an increase in temperature HCN concentration increased significantly. On the other hand the increase in ER did not affect the inorganic contaminants. The tar yield showed a peak at 935°C and 0.25 ER. More experimental analysis is recommended to confirm this trend. However, when compared with raw switchgrass, the tar yield in torrefied pine was less than half under similar conditions. Thus, torrefaction helped reduce the tar yield from raw biomass.

6. SEM images: These images proved that with increase in temperature and ER, the disintegration in the bio-char increased. Either larger pores or a higher number of pore sites were observed.

In all it can be said that along with the benefits of torrefied biomass with respect to storage, bulk density and energy density, the performance of torrefied pine as a gasification fuel was better with that of raw biomass samples in tar and ammonia yield, thus indicating that using torrefied biomass for power or fuel application will have an advantage over use of raw biomass.

Chapter 6

Outcomes and Recommendations for Future Work

In conclusion it can be stated that switchgrass performance was comparable to that of pine and other biomass samples that were reported in literature. When gasified in a bubbling fluidized bed gasifier agglomeration due to high ash content was not observed. At temperature around 1000°C, the syngas produced from switchgrass has higher concentration of CO and H_2 concentration, along with lower tar yield due to thermal cracking of tar compounds. The ER in range under study did not significantly affect the syngas composition or contaminant yield. A study conducted to understand the effect of high ash content on the syngas composition was carried out. It suggested that ash content range under study did not have any significant effect on syngas. On the other hand, the switchgrass feeding rate study suggested syngas and contaminant concentration increased with an increase in feeding rate, while the yield per kg of biomass were not significantly affected. This suggested that the conversion of biomass was independent of the feeding rate and dependent on temperature and equivalence ratio during gasification.

From the olivine study it could be concluded at lower temperature around 790°C, the olivine helped improve the syngas yield and concentration. However, at higher temperature, sand behaves better than olivine. A significant amount of elutriation was observed for olivine. The char in reactor might have led to coking of olivine resulting in average performance of olivine.

The study of pretreated biomass as gasification fuel performed equally well as raw biomass samples. It yield much higher concentrations of methane at around 790°C. It also produced high amount of char than raw biomass samples due to presence of higher concentration of lignin..

Torrefied biomass produced lower tar yield when compared with raw biomass samples. Other advantages of torrefied biomass like, high energy density, hydrophilic nature, and high grindability, along with its performance as gasification fuel makes an excellent fuel for gasification or for co-gasification with coal.

Based on downstream applications, it can be concluded that when higher concentration of CO and H_2 are desired (i.e. syngas to be used for Fischer Tropsch synthesis) gasification must be carried out at higher temperature. Similarly, when syngas is to be used for heat and power production, higher CH_4 is desired and hence, from torrefied biomass study it can be concluded that lower temperature must be used.

This chapter contains recommendations for future studies on the bench scale bubbling fluidized bed gasifier, for different fuels or combinations thereof, operating conditions, and bed materials based on the conclusion drawn from the current work..

6.1 Operating conditions

The bench scale bubbling fluidized bed gasifier used in this study was simple and reliable, yet finding an optimum operating condition was a learning experience. There were issues feeding the biomass into the gasifier, especially during the loss of fluidization (when operated below 10 LPM nitrogen flow rate) inside the reactor, the biomass fed into the gasifier would plug the reactor increasing pressure inside and upstream of the reactor, leading to gas-leaks. Thus nitrogen flow rate was maintained at 15 – 16.5 LPM, which resulted in dilution of the syngas thereby reducing the heating value. The char formed during this process was collected in the bed and in the filter, however, some char escaped to the condensers, thereby coating the cooling lines with the char and reducing the efficiency of the condensers. The use of torrefied pine, especially, resulted in high char formation, which created several performance issues when the char was not cleaned out from the condensers after every run. The fines from olivine escaped the HTF, condensers and ESP into the FTIR gas analyzer, resulting in corrosion of one of the mirrors inside the cell. In order to reduce this elutriation and thereby help maintain the costly gas analyzers; it is recommended that a particle trap be added before the syngas enters the gas analyzer.

6.2 Biomass for gasification

Pine, switchgrass and torrefied pine were studied as biomass fuel for gasification. These samples are abundant in the southeastern United States and were hence chosen for the study. However, to fulfill the energy requirements nationwide, it is important to understand the performance of several biomass samples, and co-feeding with coal.

6.2.1 **Co-feeding with coal**

Based on the current investigation, it can be seen that torrefied pine would help reduce the tar and ammonia in the gasification system. Also, torrefied pine has several properties similar to coal, which would make it easier to co-feed with minimal changes in feeding mechanism at large scale. Hence it is recommended that co-feeding of torrefied pine and coal be thoroughly investigated on the bench-scale gasifier. This study will provide an excellent insight into benefits of co-feeding, would provide the necessary background for power companies to look into torrefied pine as a co-feeding fuel.

6.2.2 **Intermixing of biomass species**

Along with co-feeding of biomass, it would be interesting to study the effect of biomass mixing. In real life scenarios, it will be difficult to use a single biomass species as a source of energy or fuel. A combination of available biomass species would provide a sustainable bioenergy supply. Thus it is recommended that a detailed analysis is performed on mixed biomass samples at various experimental conditions to obtain some optimal conditions with respect to efficiency gains contaminant reduction.

6.3 Design changes

To avoid the plugging and pressure build-up issues, redesign of the feed system is recommended. Inclined biomass feeding is an excellent alternative to the current feeding systems. Along with this, use of higher power electric heaters would be recommended to perform high temperature gasification studies. In the present study, the maximum temperature that the gasifier could be heated was 1000°C, and maintaining this temperature was difficult during the run. Replacing the heaters with higher power heaters could help maintain the temperature as well as.

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6.3.1 **Secondary fluidized bed**

Another excellent addition to the system would be designing and adding a secondary fluidized bed reactor to study several in-bed catalysts. During the present study, one of the reasons for the unexpectedly poor performance of olivine was coking due to char in the reactor. However, if a secondary reactor is used in conjunction with the current set-up, coking could be reduced significantly and thus better performance could be obtained.

6.3.2 **Syngas composition and contaminants collection**

There were several issues with the tar collection system, which resulted in negative gravimetric tar collection. Since the gas yields for small scale gasifiers are low, a smaller impinger train needs to be designed to collect the tar samples. Along with this a provision must be made for in-line tar analysis. A MBMS gas analyzer for in-line tar analysis would provide an excellent insight into various tar components and their formation.

Based on the reduction of methane with an increase in temperature, as observed for torrefied pine, a thorough study of methane decomposition during torrefied pine gasification must be performed. Based on the olivine pine study, gasification runs must be performed with uniform size olivine sand. This could help reduce loss of olivine due to elutriation.

In addition, a prior analysis before the experimental analysis is recommended. This could include some thermodynamic modeling or fixed bed bench-scale studies which would help find the parameters and factors of interest which could be studied with several repetitions. This would help better understand the syngas composition and contaminants at these particular conditions and help determine the conditions to be used for pilot/large scale applications.

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Appendix A

Fluidization

This Appendix provides information regarding fluidization including Geldart's chart, and calculations related to fluidization of bed material.

A.1 Fluidization

When a gas is flown through a packed bed of solids (e.g. sand), then the velocity at which the bed material act like a volume of fluid is called fluidization. This technique is used in gasification of coal and biomass, to provide excellent mixing and temperature uniformity in the reactor. The bed particles come in various sizes, the Geldart's chart is used to classify these materials and this classification is further discussed below.

A.1.1 Powder classification by Geldart

Geldart (1972) classified solid particles under four groups, A, B, C and D as shown in Figure A.1 below. This classification helps understand the fluidization behavior of different size particles, since under similar fluidization conditions different size particles behave in different manner. The Y-axis of the chart is difference between particles density of solid and the density of gas at 25°C, while the X-axis is the mean particle diameter of the solid in bed.

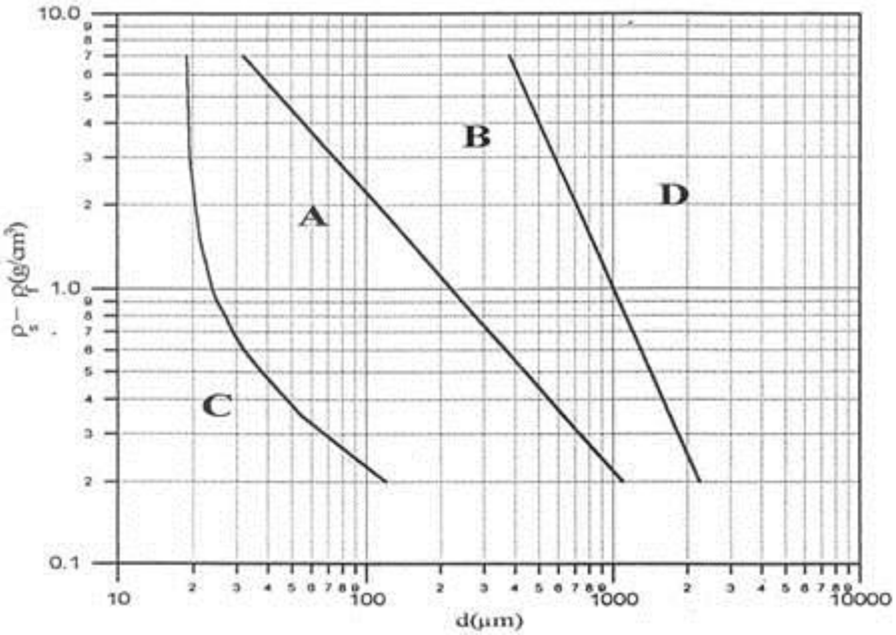

Figure A.1: Geldart's classification of powdered material

Group A: Typical size is in the range of 30 to 100 µm. Though these particles gasify well, and are used by several circulating fluidized bed gasifiers.

Group B: These particles range between 100 to 500 µm in diameter. They fluidize well, for these particles the minimum fluidization and the bubbling fluidization are the same.

Group C: Typically these particles are smaller than 30 µm. The inter particle forces are much higher for these particles and hence difficult to fluidize.

Group D: These particles are greater than 500 µm diameter. These particles need much higher velocity to fluidize.

A.1.2 Calculating minimum fluidizing velocity

As seen above Geldart's classification is used to classify the bed material, it was found that Sand (ρ_p =2776 kg/m^3 & mean particle size d_p= 263 µm) and olivine (ρ_p =3238 kg/m^3 & mean particle size d_p= 295 µm) used in this study belong to Group B. For group B materials fluidization takes place when the superficial velocity, U_s, equals the minimum fluidization velocity, U_{mf}. At this velocity fluid drag force equals the buoyancy of the particles, and the bed of particles behave like a fluid.

When fluid is passed through a packed bed of solid particles, the pressure drop across the bed per unit length of the bed is given by ΔP/L,

$$\frac{\Delta P}{L} = 150\,\frac{(1-\varepsilon)^3}{(1-\varepsilon)}\,\frac{\mu U_s}{(\emptyset d_p)} + 1.75\,\frac{(1-\varepsilon)}{\varepsilon^3}\,\frac{\rho_g U^2}{\emptyset d_p} \quad \text{(A.1)}$$

Where, ε is the void fraction (porosity), φ is the sphericity of the bed solids, µ is the dynamic viscosity, and ρ_g the gas density. However, when the particle of bed fluidizes, the drag forces equal the buoyancy of the particle, thus the drag force is given by

$$F_D = \Delta PA = AL(1-\varepsilon)\left(\rho_p - \rho_g\right)g \quad \text{(A.2)}$$

These equations are solved simultaneously to obtain the minimum fluidization velocity, U_{mf}, as defined in equation A.3:

$$Re_{mf} = \frac{U_{mf}}{\mu} d_p \rho_g = [C_1^2 - C_2 Ar]^{0.5} - C_1 \quad \text{(A.3)}$$

Where, C_1 is 27.2 and C_2 is 0.0408, while Ar is the Archimedes number, calculated as:

$$Ar = \frac{\rho_g\,(\rho_p - \rho_g) g d_p^3}{\mu^2} \quad \text{(A.4)}$$

Using equation A4 and A3, U_{mf} was calculated. For current study the U_{mf} was 0.069 m/s for sand and 0.10 m/s for olivine at 25°C.

A.1.3 Terminal velocity

Terminal velocity is defined as the velocity at which the bed particles would escape the reactor. The U_s is usually kept between, U_t and U_{mf} to avoid particle elutriation, it is calculated as:

$$\mathrm{Re} < 0.4 \qquad \mathrm{U_t} = \frac{\mathrm{Ar}\mu}{\mathrm{d_p U_t}} \tag{A.5}$$

or

$$0.4 < \mathrm{Re} < 500 \quad U_t = \frac{\mu}{d_p U_t}\left(\frac{Ar}{7.5}\right)^{0.666} \tag{A.6}$$

$$\text{Where } \mathrm{Ar} = \frac{3}{4}\mathrm{C_D}\left[\frac{\mathrm{d_p}\rho_g(\mathrm{U}-\mathrm{U_s}}{\mu}\right] \tag{A.7}$$

The U_t obtained for sand was around 2.10 m/s and 2.29 m/s for olivine at 25°C.

A.1.4 Sphericity and voidage:

Sphericity of a particle describes the deviation of a particle from spherical shale and is defined as a ratio of surface are of a sphere with the volume same as the particle to the actual surface area of the particle.

$$\emptyset = \frac{\pi \mathrm{d_v^2}}{\mathrm{S}} \tag{A.8}$$

Where d_v is the volume diameter, which is defined as diameter of the sphere with same volume as particles, while S is the surface diameter of the particle with same surface area as the particle.

Voidage defines the packing characteristics of the bed. When particles are packed in a bed, they rest on each other, in this case depending of the shape of the particles, there is a volume of void between these particles. The Voidage is defined as:

$$\text{Voidage}, \varepsilon = \frac{\text{Void volume}}{\text{Volume of (Particle+void)}} \tag{A.9}$$

Appendix B

Tar Composition in Syngas

This appendix provides a detailed table on classification of tar compounds followed by chart on effect of temperature on primary, secondary and tertiary tar compounds.

B.1 Tar classification

Tar components were classified in a study by Evan and Milne(Evans and Milne, 1997) into primary secondary and tertiary compounds.

Table B.1: List of primary, secondary and tertiary tar compounds

MW	Formula	Name
Primary tar compounds		
Acids		
46	$C_5H_{10}O_5$	Formic (Methanoic)
60	$C_5H_{10}O_5$	Acetic (Ethanoic)
74	$C_6H_{10}O_5$	Propanoic (Propionic)
76	$C_6H_{12}O_5$	Glycolic (Hydroxyacetic)
88	$C_6H_{12}O_5$	Butanoic (Butyric)
102	$C_{12}H_{20}O_6$	
116	CH_2O_2	Pentanoic (Valeric)
116	$C_2H_4O_2$	4-Oxopentanoic
122	$C_3H_6O_2$	Hexanoic (Caproic)
130	$C_2H_4O_3$	Benzoic
254	$C_4H_8O_2$	Heptanoic
Sugars		

150	$C_5H_{10}O_2$	D-Xylose
162	$C_5H_3O_3$	1,6 - Anhydroglucofuranose
162	$C_6H_{12}O_2$	Levoglucosan (1,6-Anhydro-β-D-Glucopyranose)
180	$C_7H_6O_2$	α-D-Glucose (α-D-Glucopyranose)
180	$C_7H_{14}O_2$	Fructose
260	$C_{16}H_{30}O_2$	Cellobiosan
Alcohols		
32	CH_4O	Methanol
46	C_2H_6O	Ethanol
Ketones		
70	$C_4H_6 0$	2-Butenone
72	C_4H_8O	2-Butanone
84	C_5H_8O	Cyclopentanone
96	C_6H_8O	2-Methyl-2-Cyclopenten-1-One
98	$C_6H_{10}O$	3-Methylcyclopentanone
98	$C_6H_{10}O$	Cyclohexanone
112	$C_7H_{12}O$	2-Ethylcyclopentanone
112	$C_7H_{12}O$	Dimethylcyclopentanone
124	$C_8H_{14}O$	Trimethylcyclopentenone
126	$C_{10}H_8O$	3-Methylindan-1-one
Aldehydes		
30	CH_2O	Methanal (Formaldehyde)
44	C_2H_4O	Ethanal (Acetaldehyde)
56	$C_3H_4O_2$	2-Propenal (Acrolein)
84	C_5H_8O	2-Methyl-2-Butenal (Crotonaldehyde-2-methyl
Phenols		
94	C_6H_6O	Phenol
108	C_7H_8O	2-Methyl Phenol o (o-Cresol) 3-Methyl Phenol m (m-Cresol) 4-Methyl Phenol p (p-Cresol)
122	$C_8H_{10}O$	2,3-Dimethylphenol (2,3-Xylenol) 3, 4-Dimethylphenol (2,3-Xylenol) 3, 5-Dimethylphenol (2,3-Xylenol) 2,4-Dimethylphenol (2,4-Xylenol) 2,5-Dimethylphenol (2,5-Xylenol) 2,6-Dimethylphenol (2,6-Xylenol)
122	$C_8H_{10}O$	2-Ethylphenol
136	$C_8H_{12}O$	2,3,5 Trimethylphenol
Guaicols		
124	$C_7H_8O_2$	Guaiacol (2-Methoxyphenol)
138	$C_8H_{10}O_2$	4-Methyl Guaiacol
152	$C_9H_{12}O_2$	4-Ethylguaiacol
164	$C_{10}H_{12}O_2$	4-Propenyl Guaiacol (Isoeugenol)

166	$C_{10}H_{14}O_2$	4-Propylguaiacol
Syringols		
154	$C_8H_{10}O_3$	Syringol (2,6-Dimethoxy Phenol)
168	$C_9H_{12}O_3$	4-Methylsyringol
182	$C_{10}H_{14}O_3$	4-Ethylsyringol
182	$C_9H_{10}O_4$	Syringaldehyde/Benzaldehyde, 4-hydroxy-3,5, dimethoxy
194	$C_{11}H_{14}O_3$	4-Propenylsyringol (4-Allylsyringol)
196	$C_{10}H_{12}O_4$	4-Hydroxy-3,5-Dimethoxyphenyl Ethanone
Furans		
68	C_4H_4O	Furan (Furfuran)
82	C_5H_6O	2-Methylfuran (furan; 2-methyl, 5-methyl furan)
84	$C_4H_4O_2$	2(5H)-Furanone
96	$C_5H_4O_2$	Furfural (2-Furaldehyde 2-furancarboaldehyde)
98	$C_5H_6O_2$	3-Methyl-2(3H) Furanone
98	$C_5H_6O_2$	Furfural Alcohol (2-Furanmethanol)
110	$C_6H_6O_2$	5-Methylfurfural (2-furaldehyde-5-methyl)
126	$C_6H_6O_3$	5-Hydroxymethyl-2-Furaldehyde
Mixed Oxygenates		
58	$C_2H_2O_2$	Glyoxal (Ethanedial, 1-2 Ethanedione)
60	$C_2H_4O_2$	Hydroxyethanal (Hydroxyacetaldehyde; Glycoaldehyde)
62	$C_2H_6O_2$	1,2-Dihyroxyethane (Ethylene Glycol)
72	$C_3H_4O_2$	Propanal-2-One (Methyl Glyoxal,2-Oxopropanal)
74	$C_3H_6O_2$	1-Hydroxy-2-Propanone (Acetol)
74	$C_3H_6O_2$	2-Hydroxypropanal (Methanolacetaldehyde)
86	$C_4H_6O_2$	Butyrolactone (gamma or beta); (2,3-Butanedione)
100	$C_5H_8O_2$	2,3-Pentenedione
110	$C_6H_6O_2$	1,2-Dihydroxybenzene (Catechol)
110	$C_6H_6O_2$	1,3-Dihydroxybenzene (Resorcinol)
110	$C_6H_6O_2$	1,4-Dihydroxybenzene (Hydroquinone)
112	$C_6H_8O_2$	2-Hydroxy-3-Methyl-2-Cyclopentene-1-One
126	$C_6H_6O_3$	2-Methyl-3-Hydroxy-2-Pyrone
152	$C_8H_8O_3$	4-Hydroxy-3-Methoxybenzaldehyde (Vanillin)
Secondary tar compounds		
16	CH_4	Methane
28	C_2H_4	Ethene
30	C_2H_6	Ethane
40	C_3H_4	Propyne
42	C_3H_6	Propene
54	C_4H_6	Butyne
54	C_4H_6	Butadienes
56	C_4H_8	1-Butene, 2-Butene
66	C_5H_6	Cyclopentadiene
67	C_4H_5N	1H-Pyrrole

78	C_6H_6	Benzene
79	C_5H_5N	Pyridine
92	C_7H_8	Toluene
93	C_6H_7N	Methylpyridine
93	C_6H_7N	2.3.4 Picoline
94	C_6H_6O	Phenol
104	C_8H_8	Styrene
102	C_8H_6	Ethynlbenzene
106	C_8H_{10}	Xylene, o, m, p
106	C_7H_6O	Benzaldehyde
107	C_7H_9N	Dimethylpyridine
107	C_7H_9N	o,m,p-Ethylpyridine
107	C_7H_9N	2,4-Lutidine
108	C_7H_8O	p-Cresol
108	C_7H_8O	o-Cresol
108	C_7H_8O	m-Cresol
110	$C_6H_6O_2$	Dihydroxybenzene
116	C_9H_8	Indene
116	C_9H_8	1-Ethynal-4-methylbenzene (indene)
118	C_9H_{10}	Methylstyrene
118	C_9H_{10}	Indan
118	C_9H_{10}	Ethylbenzene
118	C_8H_6O	Benzofuran
120	C_8H_8O	Vinylphenol
121	$C_8H_{11}N$	Trimethylpyridine
122	$C_8H_{10}O$	Dimethylphenol
124	$C_7H_8O_2$	Dihydroxytoluene
128	$C_{10}H_8$	Naphthalene
129	C_9H_7N	Isoquinoline
129	C_9H_7N	Quinoline
130	$C_8H_6N_2$	Quinazoline
132	C_9H_8O	Vinyl Benzaldehyde
132	$C_{10}H_{12}$	Methylindane
132	C_9H_8O	Methylbenzofuran
132	C_9H_8O	1-Indanone
134	$C_9H_{10}O$	Propenylphenol
135	$C_9H_{13}N$	Dimethylethylpyridine
136	$C_9H_{12}O$	Propoxybenzene
136	$C_9H_{12}O$	Methylethylphenol
142	$C_{11}H_{10}$	2-Methylnaphthalene
142	$C_{11}H_{10}$	1-Methylnaphthalene
142	$C_{11}H_{10}$	1,1-Dimethyl-1H-indene
143	$C_{10}H_7N$	Quinaldine

144	$C_{11}H_{12}$	1,2-Dihydro-3-methylnaphthalene
146	$C_{10}H_{10}O$	Methyl-1-indanone
146	$C_{12}H_{10}O$	Dimethylbenzofuran
148	$C_8H_{10}O_2$	Creosole
150	$C_{10}H_{14}O$	Dimethylethylphenol
154	$C_{12}H_{10}$	Vinylnaphthalene
154	$C_{12}H_{16}$	Biphenyl
156	$C_{12}H_{12}$	Dimethylnaphthalene
156	$C_{12}H_{12}$	2-Ethylnaphthalene
166	$C_{13}H_{12}$	Methyl acenaphthalene
168	$C_{13}H_{12}$	Methylbiphenyl
168	$C_{12}H_8O$	Dibenzofuran
168	$C_{12}H_8O$	Naphthofuran
168	$C_{13}H_{12}$	Diphenylmethane
170	$C_{13}H_{14}$	Propylnaphthalene
179	$C_{13}H_9N$	Benzoquinoline
180	$C_{14}H_{12}$	Methylflourene
182	$C_{13}H_{10}O$	Phenylbenzaldehyde ((4-Phenyl carboxaldehyde)
182	$C_{14}H_{14}$	Dimethylbiphenyl
190	$C_{15}H_{10}$	Methylenephenanthrene
192	$C_{15}H_{12}$	Methylphenanthrene
202	$C_{16}H_{10}$	Acephenathrylene
204	$C_{16}H_{12}$	Phenylnapthalene
204	$C_{15}H_{10}$	4H-Cyclopenta [def]phenanthrene
216	$C_{17}H_{12}$	Methylpyrene
216	$C_{17}H_{12}$	11H-Benzo [a,b] fluorene
226	$C_{18}H_{10}$	Benzo [ghi] flouranthene
228	$C_{18}H_{12}$	Benzo [c] phenanthrene
Tertiary tar compounds		
16	CH_4	Methane
26	C_2H_2	Acetylene
66	C_5H_6	Cyclopentadiene
78	C_6H_6	Benzene
92	C_7H_8	Toluene
104	C_8H_8	Styrene
116	C_9H_8	Indene
128	$C_{10}H_8$	Naphthalene
152	$C_{12}H_8$	Acenaphthalene
154	$C_{12}H_{10}$	Acenapthene
166	$C_{13}H_{10}$	Fluorene
178	$C_{14}H_{10}$	Anthracene
178	$C_{14}H_{10}$	Phenanthrene
202	$C_{16}H_{10}$	Pyrene

202	$C_{16}H_{10}$	Fluoranthene
202	$C_{16}H_{10}$	Benzacenaphthalene
216	$C_{17}H_{12}$	Methylpyrene
216	$C_{17}H_{12}$	Benzo [a,b,c] fluorene
226	$C_{18}H_{10}$	Benzo [ghi] fluoranthene
228	$C_{18}H_{12}$	Chrysene
228	$C_{18}H_{12}$	Benz [a] anthracene
228	$C_{18}H_{12}$	Triphenylene
228	$C_{18}H_{12}$	Benzoanthracene
228	$C_{18}H_{12}$	Benzo [c] phenanthrene
230	$C_{18}H_{14}$	2H-Benzo [d] phenathrene

B.2 Decomposition of tar

Primary tars are formed as a result of decomposition of cellulose, hemicellulose and lignin around 500°C as shown in Figure B.1. These undergo decomposition with an increase in temperature 700 to 800°C.

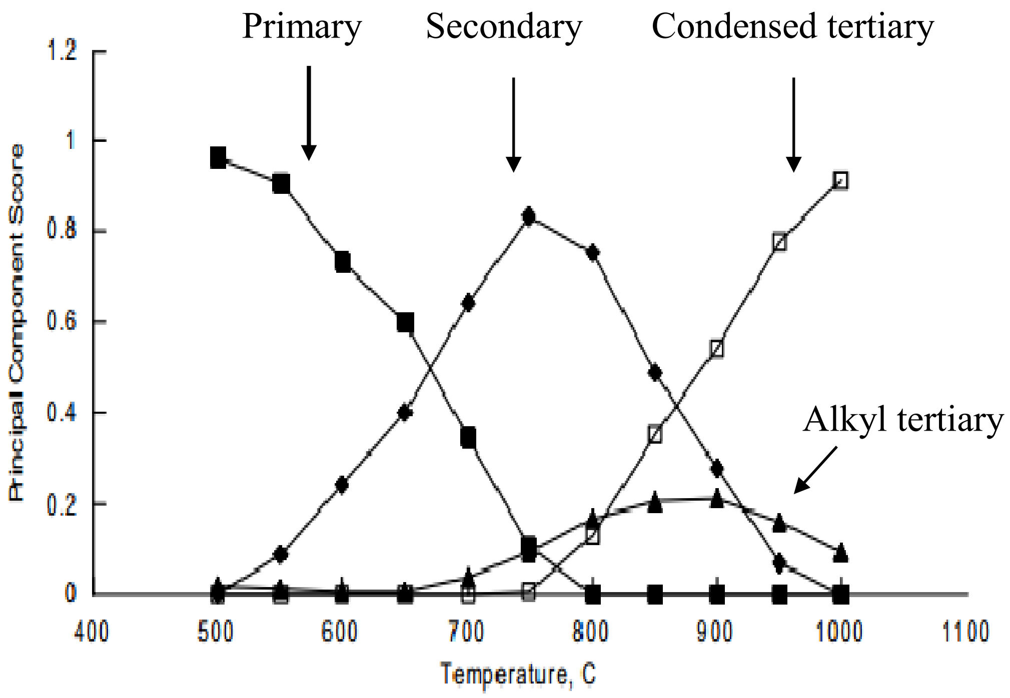

Figure B.1: Variation in tar components with increase in temperature

The secondary compounds formed consist if the Phenolics and olefins. Primary tar compounds decompose at higher temperature to form tertiary compounds like benzene and naphthalene. Figure B2 shows this trend, it can be seen that as temperature increases the component score for primary tar reduces while that for secondary and tertiary increases, indicating conversion of primary tar into secondary and tertiary tar components.

Appendix C

Effect of ER on Product Yield and Energy for Switchgrass Gasification

During switchgrass gasification, several runs were performed at higher ER than that in the range of study (0.20-0.49). This appendix shows the effect of broad range of ER on product yield and on carbon conversion.

C.1 Effect of ER on product yield at all ER values

To better understand the effect of ER on the yield all the ER obtained during gasification of switchgrass were plotted. Figure C.1 shows the variation of gasification product for equivalence ratio from 0.21 to 0.49. It was observed that the highest gas yield values were obtained between ER 0.2 and 0.25. Overall, the gas yield was between 70 to 90%, a decreasing trend could not be confirmed since the runs beyond ER 0.3 were single runs and not duplicates, thus leaving a space for error. The char and liquid yield remained more or less constant. Further experiments need to be conducted with switchgrass to confirm the trend.

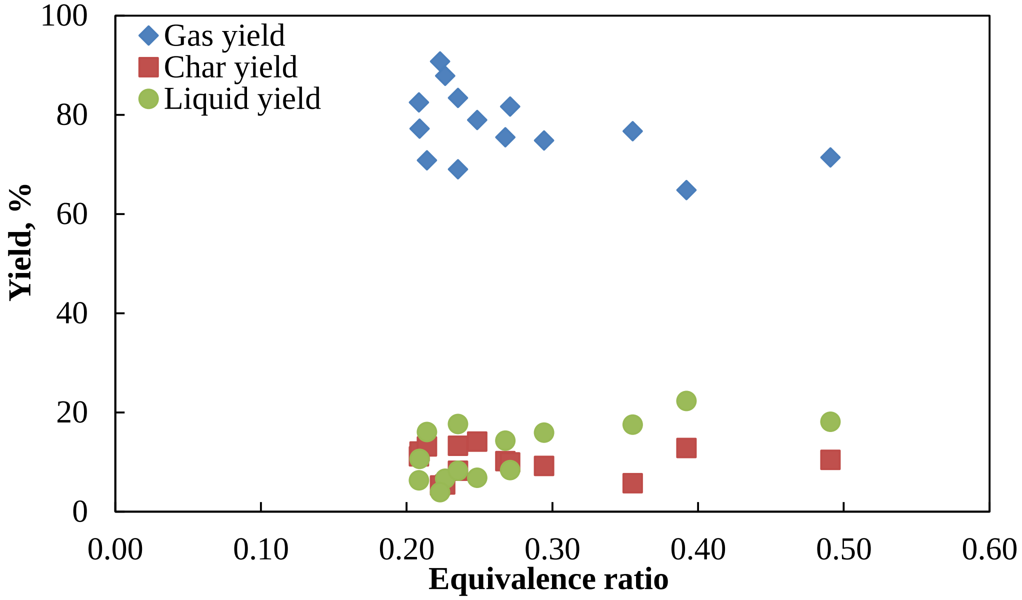

Figure C.1: Product yields observed in this study and others as a function of ER

C.1.1 Carbon conversion as a function of ER.

Figure C.2 shows the overall trend in carbon conversion into syngas. It could be concluded that the ER does not have any particular effect on carbon conversion, which was unlike a peak in carbon conversion reported for circulating fluidized bed gasifier at 0.26 in literature.

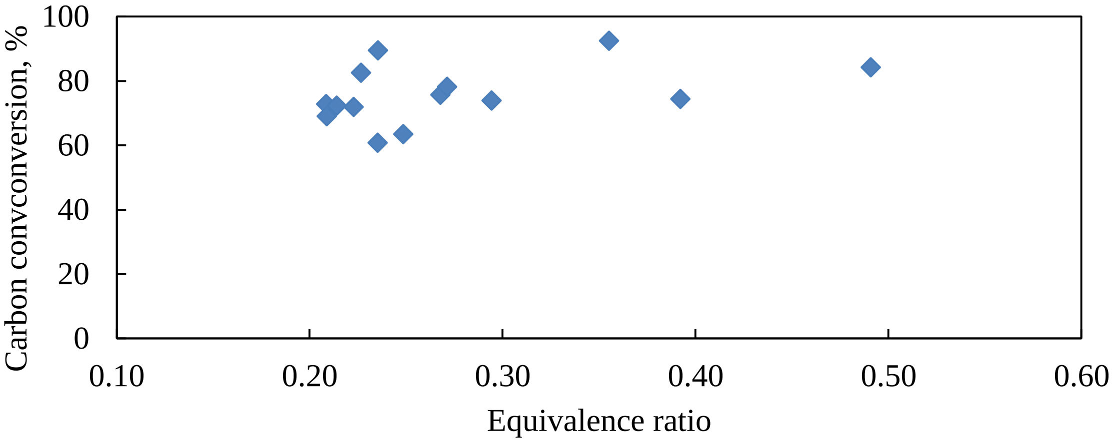

Figure C.2: Carbon conversion into syngas over a wider range of ER

Appendix D

Syngas profiles and TGA of Olivine

Syngas profiles obtained during gasification of switchgrass with olivine have been shown in this appendix. Though similar to those obtained during sand-switchgrass gasification, effects of olivine observed on the syngas profile have been discussed. Second part of this appendix discusses the TGA analysis of olivine.

D.1 Syngas profile obtained as a function of temperature and ER

Syngas profile obtained as a function of temperature and ER.

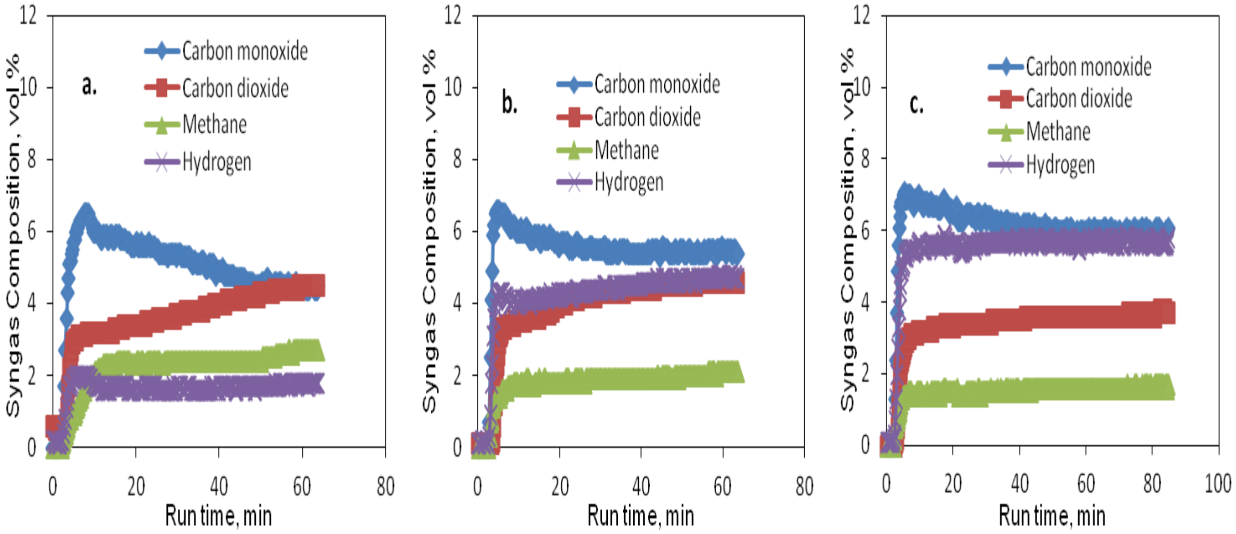

Figure D.1: Syngas profile for experimental runs at (a) 790, (b) 935 and (c) 1000°C for ER 0.25 ±1 with olivine as bed material.

It can be seen in Figure D.1 that the time required to obtain the study state reduced with increase in temperature similarly observed in case of switchgrass and for pine gasification(Abdoulmoumine et al., 2014), due to faster biomass decomposition as temperature increased. It can be seen that at 790°C, the steady state for methane and hydrogen were obtained faster than carbon monoxide and carbon dioxide. However, with the increase in temperature, this gap reduced and the steady state between all the components of syngas were obtained more or less at the same time. It should be noted that at temperature of 1000 (±20°C), even though the temperature reduced from 1020 to 980°C over the period of run time, it did not noticeably affect the concentrations of the gases as it did with sand as bed material. This could be due to better heat transfer achieved with olivine which help maintained the reaction rates even with the reducing temperature.

1. At different ER, as shown in Figure D.2, the time required to achieve steady state varied slightly. However, overall the temperature played a more substantial role in obtaining steady state than ER. This observation is in agreement with what was observed for switchgrass gasification with sand as bed material. However, Abdoulmoumine *et al.*(Abdoulmoumine et al., 2014) noticed that the time required to achieve steady state increased as equivalence ratio increased. The average values at steady state (*i.e.* 20 to 30 minutes into the run) were used for further analysis, as done by previous researchers. (Abdoulmoumine et al., 2014; Carpenter et al., 2010b)

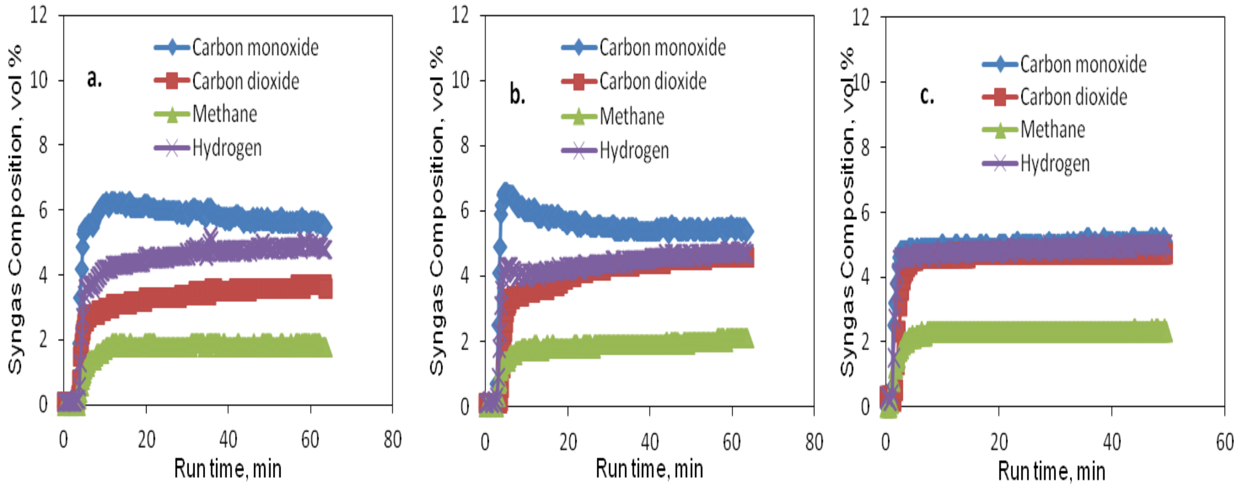

Figure D.2: Syngas profile for experimental runs at 935°C for ER 0.20 (a.), 0.25 (b.) and 0.30 (c.) with olivine as bed material.

D.2 TGA analysis of olivine

The TGA analysis was performed on the olivine samples. The olivine samples were heated from room temperature to around 800°C at 20°C/min rate and total mass loss was measured. Figure D.3 shows that with olivine lost around 2% of mass during this process. This would further increase with increase in temperature, however due to TGA limitations, run at higher temperature were not carried out.

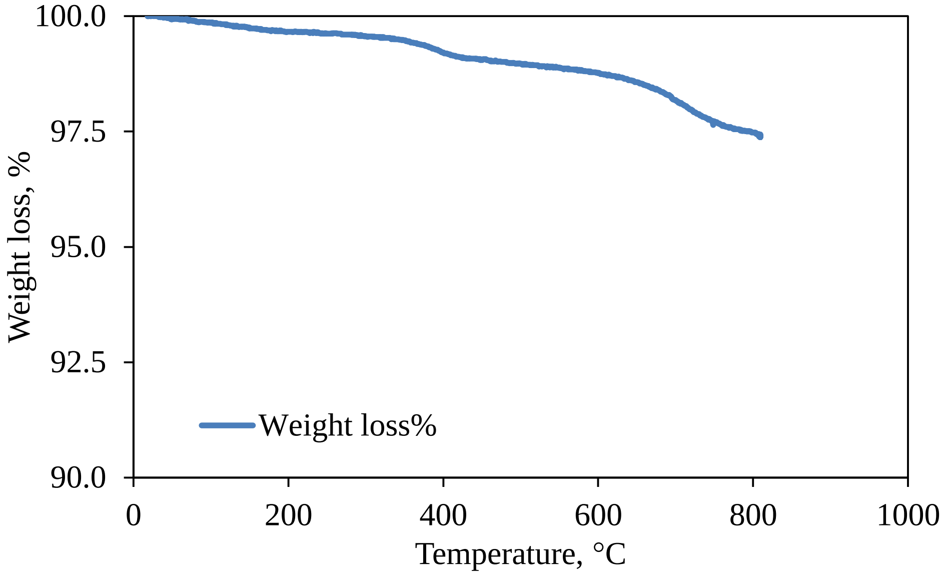

Figure D.3: TGA analysis of olivine for maximum temperature of 800°C

Appendix E

Gasification Calculations

E.1 Calculations for Gasification experiments:

Calculations were performed for torrefied pine at 935°C, ER 0.25.

Data obtained from Run:

Moisture content %	6.5
Biomass Fed (g)	527
Char weighed (g)	60
Liquid weighed (g)	68
Nitrogen (LPM)	15
Oxygen (LPM)	1.8
Run time	60
CO, vol %	10.53
CO_2, vol %	8.10
CH_4, vol %	4.97
H_2, vol %	7.35
C_2H_2, vol %	0.10
C_2H_4, vol %	0.44

N_2 (Calculated) , vol %	69.49

Product yield:

$$\text{Char yield} = \frac{\text{Weight of char from gasifier+filter}}{\text{Weight of biomass fed}} \times 100 \tag{D.1}$$

Char yield = 60/527 =11.29

$$\text{Liquid yield} = \frac{\text{Weight of liquid collected from condenser}}{\text{Weight ofbiomass fed}} \times 100 \tag{D.2}$$

Liquid yield = 68/527 = 12.92

Gas yield = 100 – (char yield +liquid yield) (D.3)

Gas yield = 100-(11.29 +12.92) = 75.79

Syngas and contaminant yield calculations:

Calculations for gas component Ci, where i = CO, CO_2, CH_4 and H_2 or any other contaminants.

$$\text{Yield of Ci} = 1000 \times \frac{(\text{vol\% of Ci})}{100} \times \frac{\text{molar syngas yield}}{\frac{(100-\text{m.c})}{100}} \tag{D.4}$$

$$\text{Molar syngs yield} = \frac{\mathrm{N_2}(\text{kmol/dry kg biomass})}{(\text{Vol\% } \mathrm{N_2}/100)} \tag{D.5}$$

$$\mathrm{N_2}\ (\text{kmol}/\text{dry kg biomass}) = \frac{(\text{syngas } \mathrm{N_2}\text{kg/kg biomass})+(\text{biomass}\mathrm{N_2}/2\times 100)}{28} \tag{D.6}$$

$$Syngas\ N_2(\frac{kg}{kg\ biomass}) = \frac{N_2 for\ fluidization\ (LPM)x1.165}{feeding\ rate\ (dry)} \tag{D.7}$$

Example CO yield:

Dry feed rate = (527- (527 x (6.5/100)))/60 = 493/60 = 8.21 g/min

Syngas Nitrogen = 15x 1.165/ 8.21 = 2.13 kg/kg dry biomass

Nitrogen in biomass = 0.31% dry basis as per CHNS analysis.

Nitrogen (kmol/ dry kg biomass) = (2.13 + (0.31/2))/28 = 0.08

Molar syngas yield (kmol./ dry kg biomass)= 0.08/ 0.69 = 0.11

Yield of CO = (10.53/100) x (0.11/ (1-0.065)) x (1000) =347.10

Carbon conversion

$$C\ conversion\ gas = 100 \times \frac{(\sum Carbon\ in\ CO, CO_2 CH_4 C_2H_4 C_2H_2)\times MW\ of\ Carbon \times Molar\ syngas\ yield}{\%Carbon\ in\ biomass} \quad \text{(D.8)}$$

C gas = ((10.53+8.1+4.2) x (0.1 +0.44))x28x0.11)x100)/58.40 = 55.88%

$$C\ conversion\ char = 100x\ \frac{\%\ Carbon\ in\ char\ x\ weight\ of\ char}{\%\ Carbon\ in\ biomass\ x\ wight\ of\ biomass\ fed} \quad \text{(D.9)}$$

C char = ((75.5x 60) x 100)/ (56.4 x 527) = 13.68 %

Cold gas efficiency

$$Cold\ gas\ efficiency = \frac{Energy\ out\ in\ syngas}{LHV\ of\ biomass}\ x\ 100 \quad \text{(D.10)}$$

LHV of biomass = HHV – 2.26 X ((9H%/100) + (7.94/100)) (D.11)

LHV torrefied pine = 22.07 MJ/ dry kg biomass

$$Energy\ in\ syngas = \left(\sum(\text{HV of Ci}\ x \left(\frac{\text{Vol\% Ci}}{100}\right) \text{x molar volume}\right)\text{) x Syngas yield} \quad \text{(D.12)}$$

Heating value of CO = 12.63 MJ/ m^3

Energy CO = 12.63 x 0.1053 x 22.4 = 29.79 MJ/kmol

Similarly, energy in CH_4 and H_2 is calculated as 45.73 and 20.96 MJ/ kmol respectively

Energy in syngas = (29.79+45.73+20.96) x 0.11 = 10.47 MJ/ dry kg biomass

Energy efficiency = 10.47 x 100/ 22.07 = 47.8 %