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Role of Feedstock and Process Conditions on Biomass Gasification for Synthesis Gas Production

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ROLE OF FEEDSTOCK AND PROCESS CONDITIONS ON

BIOMASS GASIFICATION FOR SYNTHESIS GAS PRODUCTION

(TITLE)

BY

Mayoorey Murugathasan

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF


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IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

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**Role of feedstock and process conditions on
biomass gasification for synthesis gas
production**

By

Mayoorey Murugathan

Abstract

In this study gasification of three different biomasses were performed to study the impact of process conditions and different feed stocks on final syngas composition. Final composition of the syngas determines the energy value of the resulting syngas and the suitability of syngas in chemical synthesis applications. Three kinds of feedstocks studied include switch grass pellets: wood chips 50:50 mixture, wood pellets:wood chips 50:50 mixture and wood pellets.

The effect of process conditions including temperature and feed stock composition on syngas composition were studied. Gas chromatography was used to analyze the final gas composition of syngas samples collected at five different temperature between 650 and 850 °C, in 50 °C intervals. A significant increase in CO and H₂ was observed with increasing temperature which results in increasing energy values of syngas ranging from 4.60 to 6.30 MJ/Kg for wood pellets, and from 4.79 to 6.06 MJ/Kg for the grass pellets:wood chip mixture. Increasing temperature also has a significant influence in CO/H₂ and CO₂/(CO₂ +CO) ratios which influences product selectivity in chemical synthesis. Different types of biomass also showed significant differences in gas composition. Differences in elemental composition, for example grass pellets contain high Na, K and Mg, and wood chips containing high Ca and Fe, can explain the increased H₂ and CO₂ content in the gasification of grass pellets:wood chips 50: 50 mixture. These metal elements may also enhance the water gas shift reaction which produces H₂ and CO₂ from H₂O and CO. High moisture content found in grass pellets and the presence of relatively high amounts of metal elements may enhance the water gas shift reaction in the grass pellets:wood chips 50: 50 mixture. However high alkaline content along with high Si content forms clinkers which cause problems in gasifier operation.

Three kinds of thermal efficiency methods were used to evaluate the thermal efficiency of gasification of different types of biomasses: equivalence ratio method, elemental balance method and stoichiometric ratio method. From the results obtained, equivalence ratio method was predicted to be most suitable for the gasification system used in this study.

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Chapter 1: Introduction

1.1 Background

1.1.2 Energy resources

One of the major problems that the world is going to face in the next 50 years is an energy crisis due to a rapidly emerging population, heavy industrialization, urbanization and human life style changes. Annual energy production of the world was 1.02×10^5 TW h, 1.16×10^5 TW h and 1.49×10^5 TW h in 1990, 2000 and 2010; respectively. Extrapolated statistics show that the energy production in 2015, 2020, 2030 and 2035 will be around 1.68×10^5 TW h, 1.81×10^5 TW h, 2.11×10^5 TW h and 2.25×10^5 TW h; respectively. An energy shortage of 12 TW in 2050 in the world is predicted from these statistics, it is double the current energy consumption.¹

Currently, world energy consumption 78% of the energy is provided by non-renewable energy resources such as fossil fuel, nuclear energy, and natural gas. The remaining 22% ($4.3E6$ kW h as of 2011) is from renewable resources including hydro (16.6%), wind 3.2%, biomass 1.4%, Solar photovoltaics (0.5%) and geothermal (0.4%).¹

Regarding nonrenewable energy resources such as coal, oil and natural gas, they are limited and won't be able to contribute a significant part in facing the future energy demand. Another challenge associated with nonrenewable sources is global climate changes resulting from accumulation of greenhouse gas emissions in the atmosphere. In addition air pollution associated with these sources causes health issues such as respiratory diseases, cardiovascular diseases and mortality.² Nuclear energy is a mature and cleaner technology compared to coal, oil and natural gas. Nuclear fission can provide more than 600 ZJ of energy, which is 1500 times the current world annual energy

consumption. However installation and maintenance costs are significant. Given projected world energy requirements it has been estimated that a 12 GW plant must be constructed every day for the next 50 years in order to meet the 12 TW energy demand deficit. In addition waste disposal and accidents are other major concerns of nuclear power plants. Thus these non- renewable energy resources are undesirable options to face the energy crisis.¹

Renewable energy sources includes solar, wind, hydro, geothermal and biomass. Hydro is a promising energy source which can provide sufficient energy to small countries having enough dams and waterfalls but only certain regions of the world has sufficient hydro resources to meet demand. Wind is a rapidly growing energy source in the United States, but it has its own limitations. These include seasonal changes in energy production and finding suitable and acceptable locations for windmills. Geothermal energy production involves a huge investment and needs expert research of the land forms. Geothermal is also associated with problems such as escape of poisonous gases to the atmosphere, earthquakes and landslides.¹ Though solar energy production is rapidly emerging, it also has limitations due to intermittent sunshine in many areas, and high installation costs. However it was reported in 2012 that the price of photovoltaic panels has decreased significantly from 1.2 \$/W to 0.9\$/W in just that year.³

Biomass is a non- fossilized biodegradable renewable resource and has been used as an energy source in many parts of the world. Most European countries and developing countries such as China, India, Brazil, Costa Rica, Mexico, Tanzania, Thailand and Uruguay have all utilized biomass as an energy source. For example China has increased its energy production from biomass in 2009 to 3.2 GW which represents a 14% increase.

China has further plans to increase biomass energy production to 30GW by 2020. By late 2009 India had installed 835 MW of solid biomass capacity and increased this capacity to 1.7 GW by 2012. The US market is small compared to Europe's, but 80 biomass projects operated in 20 different states by late 2009 produced approximately 8.5 GW of power, making the United States the leading country for total capacity. Many coal and gas fired power plants in the U.S are changing partially or completely to biomass by co-firing fuels in conventional power plants.⁴

Biomasses can be converted into commercially value added products using either thermochemical or biochemical processes. The majority of bio-fuel produced biochemically in the USA by 2013 was derived from either ethanol fermented from corn grain or biodiesel from soy-bean oil. Cellulosic (plant) biomass contains mainly cellulose, hemicelluloses, lignin and smaller amounts of proteins and pectin. However the increasing demand for energy exposed several barriers with respect to biochemical methods to overcome such as the need for conversion of biomass of high cellulosic and low lignin content. It may be achieved by enzymatic processes and are challenging.⁵

Three main thermochemical methods are pyrolysis, combustion or gasification. Pyrolysis is an endothermic process which decomposes the biomass into gaseous, liquid and solid products in the absence of oxygen. The liquid product is called bio or pyrolysis oil that can be upgraded into fuel or useful chemicals. The solid product is called char which can be used as either fuel or soil amendment. Limited uses of bio-oil and difficulties in the downstream processing limit the usage of this technology.⁵

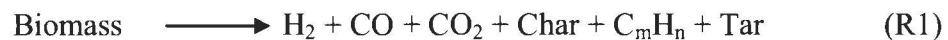
Combustion is usually used in industrial scale to supply heat and power worldwide, but it includes many environmental problems. Incomplete combustion releases environmental

pollutants such as CO and CH₄, and the fuel bound nitrogen and sulfur are emitted as SO₂ and NO₂ at high temperatures where combustion occurs. Efficiency of electricity generation from combustion of biomass is also very low, within the range of 20% to 40%.⁵

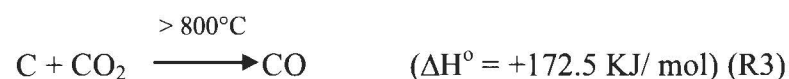
The gasification process is the partial oxidation of biomass in to synthesis gas which has further combustion potential. Synthesis gas is a gaseous mixture consisting of H₂, CO, CO₂, CH₄, N₂ and O₂.⁵

1.1.3 Biomass gasification

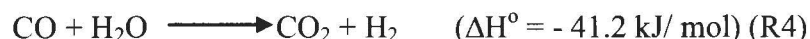
Biomass gasification includes four major steps in the process: drying, pyrolysis, combustion and reduction. Figure 1 shows the cross-section view of a down draft gasifier. In the drying process moisture in the biomass is evaporated at temperatures above 100°C which occurs in the drying zone as shown in Figure 1. The pyrolysis reaction (R1) occurs under anaerobic conditions in the pyrolysis zone producing charcoal, volatile matter and tar.



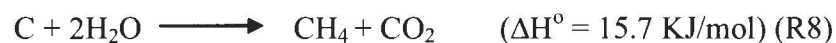
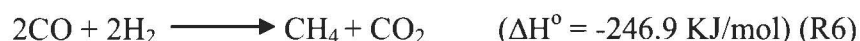
In the combustion zone charcoal and the tarry substances are oxidized to CO₂ and H₂O which are to be reduced at the reduction zone producing CO and H₂ by reaction with hot char (i.e. Carbon) (R2 and R3). Hot char in the reduction zone is highly reactive with oxygen; partially reducing the gases CO₂ and H₂O and reduces them in to CO and H₂.^{6,7,8}



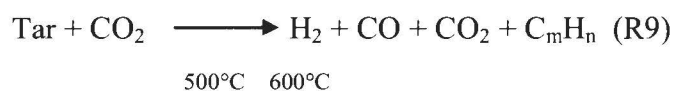
In addition to the above reactions, the water gas shift reaction can occur increasing the concentrations of H₂ and CO₂ (R4). This reaction can be enhanced using catalysts such as alkali and alkaline earth metal oxides.⁹



Methanation reactions that may occur in the reactor are shown in R5 –R8. As can be seen in the reaction most of the methanation reactions are exothermic and therefore they are viable mostly between 300 – 450°C.⁶



Tar and C_mH_n reforming reactions occur at higher temperatures (R9 and R10). Catalysts can enhance these reactions and increase the H₂, CO and CO₂ content, as well as improve the quality of syngas by removing tar and small hydrocarbons.⁶



The gasifier used in this project is a fixed bed-down draft gasifier (Figure 1). In a down draft gasifier air, feedstock and gas, all flow in the same direction (down flow).¹⁰

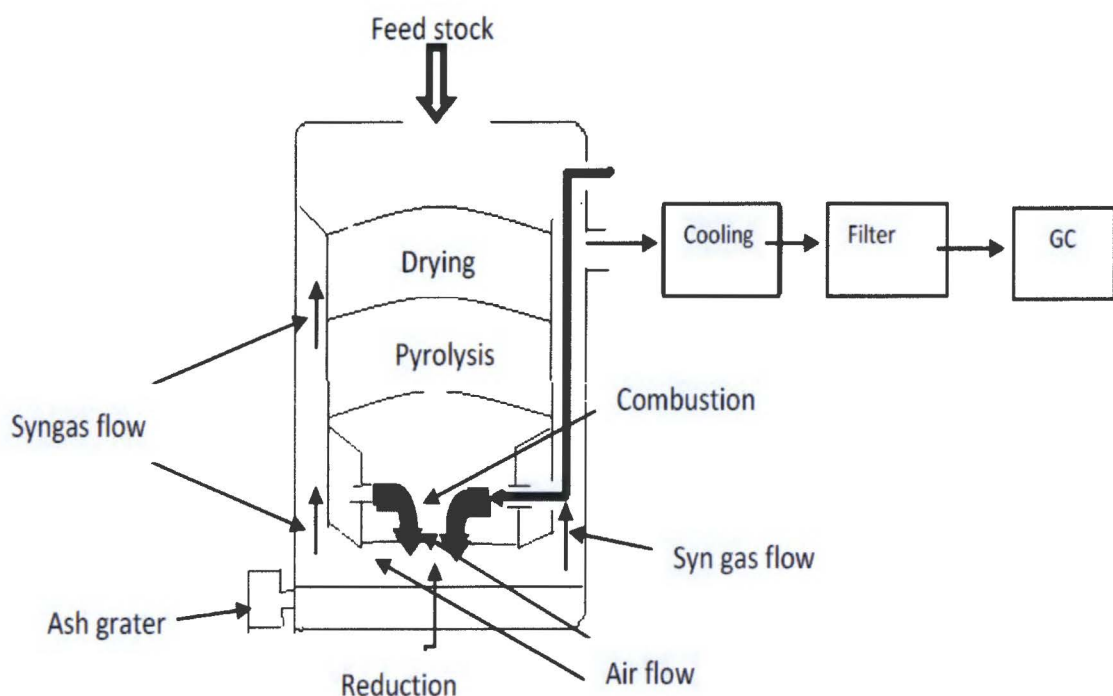


Figure 1: Cross section view of down draft gasifier.

Gasification of biomass has significant environmental advantages over combustion. In gasification, fuel bound sulfur and nitrogen are released as H_2S and N_2 , whereas combustion releases SO_x and NO_x that are causes of smog. Gasification also releases less heat to the environment compared to combustion.⁶

Synthesis gas composition varies with process conditions such as temperature and pressure and thus plays an important role in syngas utilization such as energy production and chemical synthesis. For example the energy value of the resulting gas is determined by the amount of gas components with further combustion potential; such as H_2 , CO and CH_4 . Further chemical synthesis from syngas is also influenced by the CO/H_2 ratio and $CO_2/(CO_2 + CO)$ ratio of the syngas. In this project, the composition of syngas in mole percentage was analyzed using Gas Chromatography (GC).

1.1.4 Gas chromatography

Gas chromatography (GC) is a separation technique for a gaseous mixture. Samples that are being analyzed by GC must have sufficient volatility and thermal stability. GC column has two phases: the mobile phase and the stationary phase. The mobile phase is also called the carrier gas that transports the gaseous analyte in the column. Commonly used carrier gases are hydrogen, helium and nitrogen. Interaction of the analyte with the stationary phase is the main factor that determines the retention time of analyte since these are all gases at very low temperatures. This interaction can occur due to hydrogen bonding, dispersion interactions, and dipole interactions. The setup of the GC and the overall brief process is given in Figure (2).^{11,12,13}

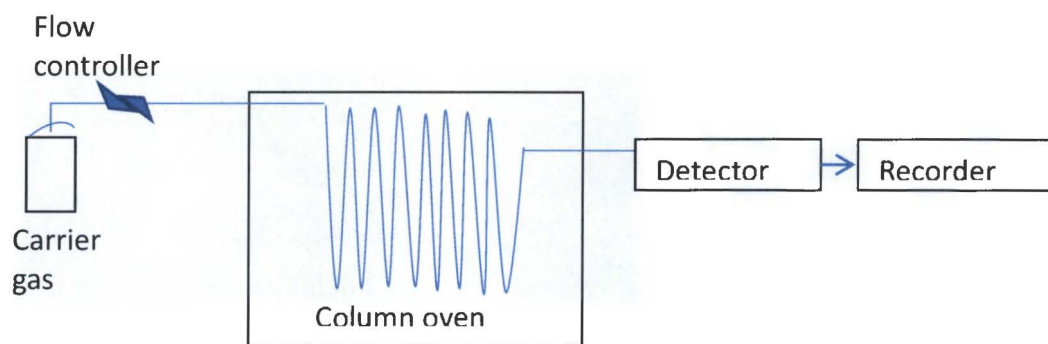


Figure 2: Set up of Gas chromatography.

1.1.5 Influence of feed stocks in syngas composition

Biomasses typically used in the gasification can be mainly classified as woody and nonwoody biomasses. The woody biomass category includes trees, shrubs and bushes. The nonwoody biomass category includes grasses, straw, stems, roots, leaves, water plants, starchy fruits such as bananas and plantains, fibrous seed plants such as cotton, fleshy root plants such as cassava, and energy crops such as sugarcane.⁶

Important characteristics of biomasses that influence the efficiency of the gasification are energy content of the fuel, bulk density, moisture content, dust content, tar content and ash and slagging characteristics. The higher the energy value and bulk density of the biomass, the greater amount of synthesis gas or power can be generated per unit volume of the biomass. In contrast moisture content of the biomass causes significant heat loss due to the evaporation of moisture which, as an endothermic process impairs the thermal efficiency of the gasification. Dust content in the synthesis gas can cause instrumental problems in the internal combustion engine and also in the instrumental analysis of the gas.¹⁰

Tar is one of the other undesirable components produced during the pyrolysis reaction causing operational problems in the subsequent gas analysis phase, as well as impacting on the quality of the synthesis gas. Tar can be removed using filters. The down draft gasifier removes the tar produced in the pyrolysis reaction in the following combustion zone as well.¹⁰

Remaining mineral content of the biomass in its oxidized form is called ash. Elemental composition of the feed stocks including C, H, O and N content along with mineral content such as alkaline and alkaline earth metal and Si also play important positive and negative roles in the resulting gas composition, and in the gasification operation. For instance presence of the elements iron and calcium in the feed stock helps in catalysis of the gasification reaction.⁹ Elemental composition of feed stocks varies with type of biomass.

Ash also causes problems in the gasifier operation in two ways. It fuses together and forms slag or clinkers which interfere with the downward flow of the biomass, or it melts at higher temperatures and shelters the biomass which can block the points where the ignition is initiated. However the above behaviors of the ash are normally based on the composition of ash which is actually based on the elemental composition of the biomass.¹⁰

Energy value, bulk density, moisture content and the elemental composition of the biomasses and ash samples were investigated in this project. Tar and the dust content ends up in the syngas has been minimized using filters during gasifier operation.

Energy value or Higher Heating Value (HHV) of the feed stocks has been determined by bomb calorimetry. HHV, also known as calorific value, is the amount of energy liberated during the complete combustion of the biomass, in other words the energy available in the feed stocks under constant volume condition.

1.1.5.1 Bomb calorimeter

Bomb calorimetry is a widely used method to measure the heating value of the feed stocks. Principle behind this analysis is the first law of thermo dynamics.

$$\Delta U_{\text{System}} = Q \quad (W = 0 \text{ when } \Delta V = 0)$$

Where ΔU_{System} is the internal energy or energy content of the biomass, Q is the heat energy liberated from combustion, W is the work done by the system and ΔV is the volume change.

Usually in the heating value measurements, two different heating values are reported: Higher Heating Value (HHV) and Lower Heating Value (LHV). HHV is the heat of combustion which includes the heat of vaporization of water. LHV value does not include the heat absorbed by the vaporization of water produced during combustion. In this project HHV was used to measure the energy content of the fuel.^{13, 14, 15}

$$\text{HHV} = \text{LHV} + (m_{\text{water}} / m_{\text{fuel}}) H_{\text{fg}} \quad \text{kJ/kg}$$

Where m_{water} is the mass of water produced in the combustion, m_{fuel} is the mass of fuel used, and H_{fg} is the latent heat of vaporization of water.

Moisture content was analyzed using a thermogravimetric based analysis. Bulk density, the mass of the feed stock per unit volume, was determined using a known volume bucket and an electronic gravity mass balance. The C, H, O and N composition was analyzed using combustion analysis. Elemental composition of Na and K is analyzed using Flame Atomic Emission Spectroscopy (AES) and Si was analyzed using Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES) analysis and it is an Atomic Emission Spectroscopy (AES) technique. The composition of other elements such as Ca, Fe and Mg were also investigated using Atomic Absorption Spectroscopy (AAS).

1.1.5.2 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is a technique widely used in quantitative analysis of elements in environmental samples. The atoms absorb ultraviolet or visible light and go from ground state to excited state. Frequency of the photon which is absorbed to make this electronic transition is specific for each atom due to the unique electronic configuration

in their outer shells. Therefore each element absorbs a characteristic wavelength and this enables the quantitative analysis of the elements in the sample.

The form of analyte in the sample should be converted from an ionic solution to atomic gas for excitation to happen in the flame and the amount of light absorbed during this excitation is measured. There are four main steps involved in this process that are nebulization, desolvation, volatilization and atomization. Nebulization makes the sample into small droplets and makes a mist of the sample, and desolvation removes the solvent from it. Volatilization makes the solid molecules into gas, and the gas molecule will be atomized in the flame where the excitation of the atom using the energy from the light source takes place. The overall setup of the atomic absorption spectroscopy is shown in Figure 3 below.^{13, 16}

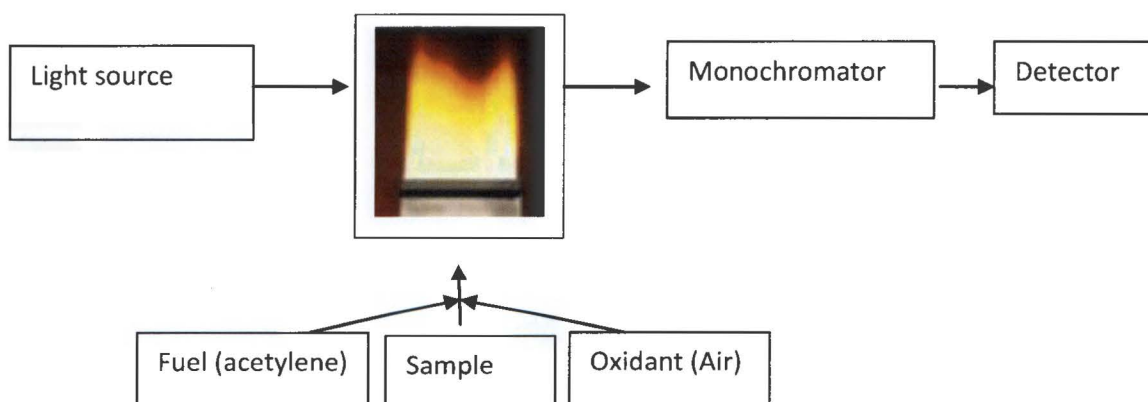


Fig 3: Diagram of Atomic Absorption Spectroscopy (AAS).

The sensitivity of this technique is usually high so that it can measure down to concentrations of ppm (mg/L) of analyte. Selectivity of this technique is usually increased by using monochromators and a narrower band width hollow cathode lamp than the absorbing species.

1.1.5.3 Atomic Emission Spectroscopy

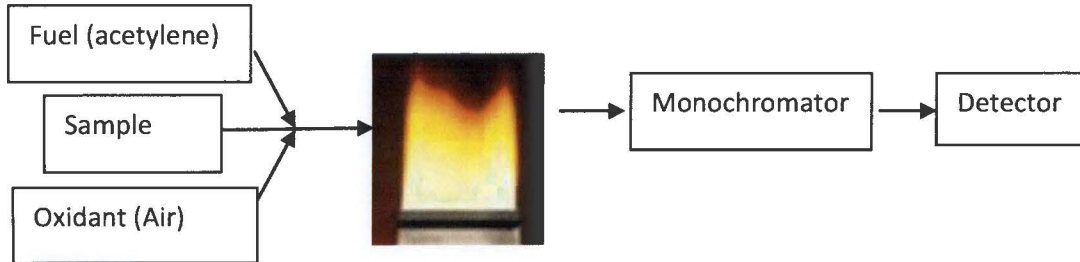


Fig 4: Diagram of Atomic Emission Spectroscopy (AES).

Similar to atomic absorption spectroscopy, flame atomic emission spectroscopy utilizes the same process to produce gas phase atoms from the sample. However the flame is used as the excitation source and emission of the excited state gas phase atoms are detected. Emitted light from the excited atoms by spontaneous emission will go through the monochromator that will select the particular emission which is going to be quantified. A diagram of an Atomic emission spectrometer is shown in Figure 4. In this project flame excitation method was used to detect Na and K and ICP (Inductively Coupled Plasma) was used for Si analysis.¹³

Sensitivity of these emission techniques are high so that it can measure down to concentrations of ppm (mg/L) of the analyte. Selectivity is high since each element usually emits at characteristic wavelengths.

1.1.6 Influence of process conditions in syngas composition

Temperature is one of the important process conditions which influence the syngas composition. Gasification at higher temperatures improves the syngas composition by increasing concentrations of H₂, CO and CH₄.⁸ Therefore the HHV of the syngas

increases. However the maximum achievable temperature is gasifier dependent.⁹ Different locations of the reactor used in this work where the temperature and pressure measured are shown in Figure 5.

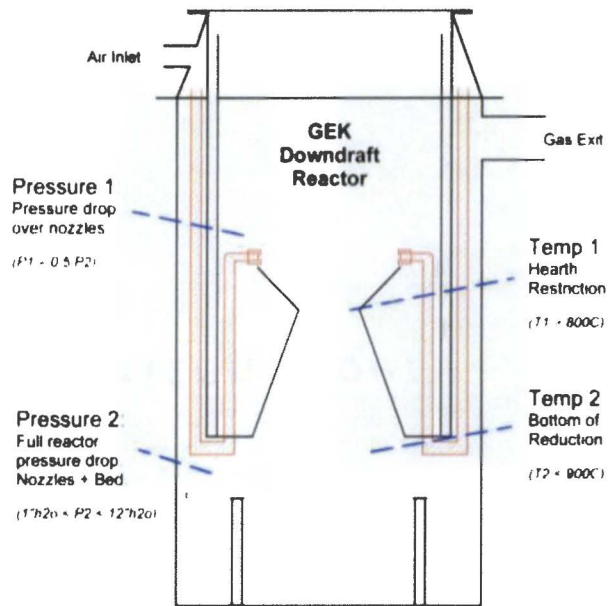


Figure 5: Schematic diagram of the temperature and pressure sensors of down draft reactor.

The other important factor having an impact on the gas composition is the equivalence ratio (ER); the ratio of actual air to fuel ratio in the gasifier to the stoichiometric air to fuel ratio for complete combustion of the fuel in the gasification system (Eq. 1).¹⁷

$$ER = \frac{M_{\text{oxidant}}/M_{\text{biomass}}}{M_{\text{oxidant stoichiometry}}/M_{\text{biomass}}} \quad (\text{Eq. 1})$$

The gasifying agent also plays an important role in syngas composition and in the thermal efficiency of gasification.

Different kinds of gasification oxidants include air, pure O₂, and steam. Air as the gasifying agent is cost effective but decreases the energy value by leaving a large amount of N₂ in the resulting synthesis gas. In contrast pure O₂ increases the heating value, but also increases the operating cost significantly. Steam gasification enhances the production of H₂ during the gasification by R4 and thus increases the heating value of the synthesis gas. In this project air was used as the gasification fuel.

1.2 Syngas utilization

There are two broad categories of use for syngas: energy production and use as a feed stock for chemical synthesis. Examples include Fischer-Tropsch syntheses, H₂ production and other chemical syntheses including biochemical conversion of syngas to chemicals that have commercial value.⁷

1.2.1 Energy production

Energy efficiency or thermal efficiency of the gasification process is important. Three different approaches have been used to evaluate the thermal efficiency of gasification of different biomasses by the comparison of syngas energy value produced from a particular amount of biomass, with the energy value of that particular amount of biomass. The three methods will be described below.¹⁸

1.2.2 Thermal efficiency or energy efficiency calculations

1.2.2.1 Method 1: Equivalence ratio method

The equivalence ratio (ER) is an important parameter which describes the ratio of actual air to biomass ratio in the reactor at a given set of conditions, divided by the

stoichiometric air to biomass ratio (Eq. 1). Stoichiometric oxidation or complete combustion takes place when the $ER=1$.^{4, 17, 18}

Step 1: Calculation of volume of synthesis gas produced from 1kg of feed stocks:

In this calculation pressure in the reactor is assumed to be proportional to the ER since the negative pressure applied in the reactor is responsible for the air intake as it sucks the air inside (Eq. 2).

$$ER = K * P_{react} \quad (\text{Eq. 2}) \quad (K \text{ is a constant, } P_{react} = \text{Pressure in the reactor})$$

The ER of wood biomass of an ideal gasification is 0.25,⁴ by assuming that the wood chip gasification at a pressure of 35 (inches of water) above 850°C approaches ideal gasification, and by using it as a base line, ER of the other biomasses can be calculated using Eqs. 3, 4 and 5.

$$ER_{woodchips} = K * P_{rw} = 0.25 \quad (P_{rw} = P_{react} \text{ wood chips}) \quad (\text{Eq. 3})$$

$$K = 0.25 / P_{rw} = 0.25/35 \quad (\text{Eq. 4})$$

$$ER_{biomass} = K * P_{rb} = 0.25 / 35 * P_{rb} \quad (\text{Eq. 5}) \quad (P_{rb} = P_{react} \text{ biomass of concern, } ER_{biomass} = \text{ER of biomass of concern})$$

The mass of air necessary for complete combustion of 1 kg biomass, is 4.58 kg.¹⁷ From this the actual air mass can be calculated in kg (Eq. 6)

$$\text{Mass of Air used in gasification} = ER * 4.58 = M_{Air} \text{ used} \quad (\text{Eq. 6})$$

and by mass balance the mass of syngas that is produced from 1 kg of biomass can be calculated (Eq. 7).

$$\text{By balance: Mass of syngas} = 1\text{kg} + M_{Air} \quad (\text{Eq. 7})$$

Volume of the syngas can be then calculated using the density of syngas (Eq. 8) and the mass of syngas calculated (Eq. 9).

$$\text{Density of the syngas (at 25°C, 1atm)} = (\%H_2 \cdot d_{H_2} + \%O_2 \cdot d_{O_2} + \%N_2 \cdot d_{N_2} + \%CH_4 \cdot d_{CH_4} + \%CO \cdot d_{CO} + \%CO_2 \cdot d_{CO_2}) \quad (\text{Eq. 8})$$

d= density of gas components

$$\text{Volume of syngas produced from 1 kg of biomass} = \frac{\text{Mass of syngas (kg)}}{\text{Density of syngas}} \quad (\text{Eq. 9})$$

Thermal efficiency of gasification can be then calculated using equations Eq. 10 and Eq. 11.

Step 2: Thermal efficiency

$$\eta_{\text{Gas}} = \frac{\text{Calorific value of gas/kg of fuel}}{\text{Avg. calorific value of 1 kg of fuel}} \quad (\text{Eq. 10})^{10}$$

$$\text{HHV of syngas} = H_2 \text{ HHV} \cdot \% \text{ of } H_2 + CO \text{ HHV} \cdot \% \text{ of } CO + CH_4 \text{ HHV} \cdot \% \text{ of } CH_4 \text{ MJ/m}^3$$

Avg. calorific value of 1 kg of fuel was obtained from bomb calorimeter measurement (HHV of fuel)

$$\eta_{\text{Gas}} = \frac{\text{HHV of syngas (MJ/m}^3) \cdot V_{\text{syngas}} \text{ (from 1 kg of syngas)}}{\text{Avg. calorific value of 1 kg of fuel}} \quad (\text{Eq. 11})^{10,18}$$

1.2.2.2 Method 2: Elemental balance method

In this method the mass of syngas is calculated using the mole % composition of syngas obtained from GC. Mole fractions of each component can be calculated from GC results (Eqs. 12-16).

X is mole fraction, MW is Molecular weight, and ΣX_{mc} is total C mole fraction.

$$X_{CO} = a / (a + b + c + d + f + g) \quad (\text{Eq. 12})$$

$$X_{CO_2} = b / (a + b + c + d + f + g) \quad (\text{Eq. 13})$$

$$X_{H_2} = c / (a + b + c + d + f + g) \quad (\text{Eq. 14})$$

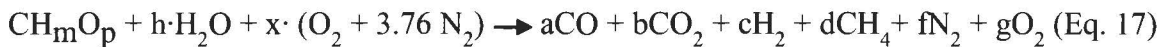
$$X_{CH_4} = d / (a + b + c + d + f + g) \quad (\text{Eq. 15})$$

$$X_{O_2} = g / (a + b + c + d + f + g) \quad (\text{Eq. 16})$$

Step1: Calculating the volume of syngas

The number of moles of C involved in the reaction is assumed as one (Eq.17) and the number of moles of each component or the coefficients of each component can be calculated using equations Eqs. 18–24.^{18, 19}

Assume that the resulting syngas is moisture free, ash free and contains no tars, no remaining carbon or other minor compounds.



$$\Sigma X_{mc} = X_{CO} + X_{CO_2} + X_{CH_4} \quad (\text{Eq. 18})$$

$$a = X_{CO} / \Sigma X_{mc} \quad (\text{Eq. 19})$$

$$b = X_{CO_2} / \Sigma X_{mc} \quad (\text{Eq. 20})$$

$$c = X_{H_2} / \Sigma X_{mc} \quad (\text{Eq. 21})$$

$$d = X_{CH_4} / \Sigma X_{mc} \quad (\text{Eq. 22})$$

$$f = X_{N_2} / \Sigma X_{mc} \quad (\text{Eq.23})$$

$$g = X_{O_2} / \Sigma X_{mc} \quad (\text{Eq. 24})$$

The mass of syngas produced from the gasification of CH_mO_p can be obtained by substituting the coefficients into Eq. 25, and the volume can be calculated using Eq. 9.

$$\text{Mass of syngas produced from 1 kg of biomass} = a \cdot \text{MW of CO} + b \cdot \text{MW of CO}_2 + c \cdot \text{MW of H}_2 + d \cdot \text{MW of CH}_4 + f \cdot \text{MW of N}_2 + g \cdot \text{MW}_{O_2} / \text{Mass of } CH_{1.43}O_{0.69} \quad (\text{Eq. 25})$$

Then the thermal efficiency can be calculated using Eq. 11 as in the equivalence ratio method.

Step 2: Thermal efficiency – similar as equivalent ratio method

$$\eta_{\text{Gas}} = \frac{\text{HHV of syngas (MJ/m}^3\text{)} \cdot V_{\text{syngas}} \text{ (from 1 kg of syngas)}}{\text{Avg. calorific value of 1 kg of fuel}} \quad (\text{Eq. 11})^{10}$$

1.2.2.3 Method 3: Stoichiometric ratio method

The stoichiometric ratio method also uses the same calculations as the elemental balance method to calculate the coefficient of N_2 . It can be noticed from Eq. 17 and the reactions involved in the gasification that N_2 from air does not participate in any reactions. N content of the feed stock is also negligible compared to the N_2 amount in the air. Therefore the number of moles of air can be determined using Eq. 26 and f in this equation refers to the number of moles of N_2 (Eq. 23).¹⁹



$$\text{Number of air moles used} = \frac{f \text{ moles}}{3.76} \quad \text{(Eq. 26)}$$

From Eq. 26, the mass of air used for gasification of 1 kg can be calculated using molecular weight of air and the empirical formula of feed stocks. By balancing the mass and using Eq. 9 and Eq. 11 as in the equivalence ratio method, mass and the volume of the syngas can be found and the thermal efficiency can be obtained.

1.2.3 Chemical synthesis from syngas

The CO/ H₂ and CO₂/(CO₂ + CO) ratios play important roles in product selectivity for chemical synthesis in syngas feedstocks.^{20, 21, 22}

One of the main example for direct usage of syngas as feed stock for fuel synthesis is Fischer-Tropsch synthesis which uses a catalyzed chemical reaction to synthesize liquid hydrocarbons from syngas. Commonly used catalysts in these types of reactions are Fe based and Co based; Ni and Ru are also used.²¹ In general cobalt- based catalysts utilize lower CO/H₂ ratios than iron- based catalysts.

CO₂/(CO₂ + CO) ratios also affect the product selectivity in F-T synthesis. Higher CO₂ content in the syngas generally leads to increased synthesis of CH₄ which is undesirable. Therefore tuning the gasification reaction to produce desired amounts of CO, H₂ and CO₂ is important. Normally variability in concentration of these components occurs due to process conditions such as temperature and the presence of catalysts. The type of biomass and its moisture content also influences the CO/ H₂ ratio of the resulting syngas.

1.3 Motivation and objectives

Motivations of this study include investigations of the energy efficiency of the gasification process of locally (i.e., central Illinois, USA), and to study the applicability of the resulting syngas for further chemical synthesis applications. In this study three types of biomasses were used for gasification including wood pellets, switch grass pellets and wood chips. Influence of process conditions and types of feed stocks in the composition of syngas was studied and composition analysis was performed for the syngas collected at five different temperatures from 650°C to 850°C in 50°C interval. Results of composition analysis are then used to evaluate the thermal efficiency of the gasification of each biomass at all temperatures. From the composition analysis and the values reported in the literature for CO/H₂ ratio and the CO₂/(CO₂ + CO) ratio, suitability of the syngas for further chemical synthesis application is also discussed. Furthermore the elemental analysis of the feed stocks and the ash samples collected from gasification of each biomass was performed to study the influence of elemental composition of feed stocks and ash in the syngas composition.

Chapter 2: Materials and Methods

2.1 Materials

Feed stocks wood chips, wood pellets and switch grass pellets were purchased from EIU renewable Energy Center, Rural King and FDC Enterprise, respectively. NaCl, KCl, Iron, Mg, CaCO₃ and concentrated nitric acid were purchased from Fischer. Ash from wood chips, wood pellets and grass pellets were obtained from the reactor after gasification reaction.

All glassware was cleaned with Alconox and tap water and a final rinse was given with deionized, water then air dried at 150°C.

2.2 Methods

2.2.1 Characterization of feed stocks

2.2.1.1 Higher Heating Value (HHV)

A microprocessor controlled Isoperibol model 6200 Calorimeter manufactured by Parr Instrument Company, USA was used to analyze Higher Heating Values (HHV) or heat of combustion of the feed stocks.

About 1.0 gram of each feed stock was ground and pelletized. The pelletized sample was loaded into the capsule part of the bomb and the bomb was closed and filled with oxygen. The water handling system was used to measure 2 liters of water at 25°C. After sample ignition the operation pressure in the bomb was released, and the bomb was cleaned and dried for the next experiment.

Replicate measurements were done for each sample; the corresponding mean and standard deviation values are reported.

2.2.1.2 Moisture content

A Denver IR-60 Moisture Analyzer was used to analyze moisture contents of the feed stocks.

Approximately 5.0 g of sample was randomly chosen and ground, then loaded on the balance pan. The pan was then placed on the balance and the moisture content was measured as the weight loss percentage at 130°C. The same procedure was repeated for each sample and the averaged results are reported.

2.2.1.3 Bulk density

Bulk density of the biomass was determined using a 7.5 liter bucket and an electronic 3 point balance. The bulk density was calculated using the following equation:

$$\text{Bulk density} = (M_{fb} - M_b) \text{ kg}/7.5 \text{ liters} \quad (\text{Eq. 26})$$

where M_{fb} is mass of feed stock plus mass of bucket and M_b is mass of bucket.

For each feed stock, replicate experiments were performed and the average values are reported.

2.2.2 Gasification

A laboratory scale down draft gasification system from All Power Labs, USA was used for gasification reactions. The gasifier contains a Gasifier Control Unit (GCU) that displays the temperature and pressure conditions measured at two locations inside the system.

In each run syngas was collected at temperatures of 650°C, 700°C, 750°C, 800°C and 850 °C by controlling the reactor pressure. Equilibrium was established at each temperature which was assessed by a stable temperature for a minimum of 5 minutes.

2.2.3 GC analysis

Instrumentation

A 490 micro Gas Chromatograph by Agilent Technology containing two columns was used to analyze the syngas. Column 1 consists of Molsieve 5Å (Carrier gas- Argon: 5.0 Ultra high purity) that separates H₂, O₂, N₂, CH₄, and CO; the stationary phase of this column is 5Å molecular sieve zeolite. Column 2 separates CO₂ utilizing a polystyrene divinylbenzene (PPQ) stationary phase. Genie membrane filters by Agilent Technology were used to further filter the moisture from the carrier gases.

EZchrome software was used to control the gas analyzer. Gas samples were collected at reactor temperatures of 650 °C, 700 °C, 750 °C, 800 °C and 850°C in poly vinyl fluoride gas sampling bags (size- 3.8 liter) purchased from Fischer Scientific by connecting to a hand pump air-out port in the gasifier (Figure 6 A, B). The syngas in the bags was injected in to the GC automatically with a micro machined injector controlled by EZchrome software. There are three steps involved in the analysis. Prior to each experiment GC columns were baked out overnight at a pressure of 1.45 kPa and 180°C in the corresponding carrier gas. The instrument was then calibrated using standard syngas with known composition, shown in Table 1, at 0.965 kPa initial pressure and 90°C for MS5Å column, and 1.45 kPa initial pressure and 100°C for PPQ column. Standard instrument software was used to obtain the calibration. Finally the sample gas was analyzed under the same conditions as the calibration. After the analysis columns were

cooled down to 30°C to the initial pressure of 1.45 kPa before shutting down. Five GC runs were performed for each sample, with the last two runs averaged to avoid error due to trapped air between sampling bags and the columns.

All data was analyzed using standard instrument software. In some cases the reaction times were shifted giving erroneous results. In such cases manual integration methods were used using instrument software.



A



B

Figure 6: A: Collecting gas in sampling bag, B: Sampling bag connected to GC injector using couplers.

Table 1: Composition of standard syngas used in GC calibration

Components of Syngas	Composition (Standard) Mole %
H ₂	25 %
CO	25 %
CH ₄	5.0 %
CO ₂	10 %
O ₂	1.0 %
N ₂	34 %

2.3 Elemental analysis

2.3.1 Standard solutions preparation

A 1000 ppm standard stock solution of each element to be tested was prepared according to Table 2. CaCO₃, NaCl and KCl were oven dried over night at around 110°C and cooled in a desiccator before weighing on an electronic analytical (4 point) balance. Appropriate dilutions were made to prepare solutions for a calibration curve using standard volumetric glassware.

Table 2: Amount of materials used in standard solution preparation

Source	Source amount	Dissolved with	Diluted with	Total volume
CaCO ₃	1.2485 g	6.0 M HCl	Deionized H ₂ O	500.0 ml
Fe (99% pure)	0.5050 g	(1+1) HNO ₃	Deionized H ₂ O	500.0 ml
Mg ribbon	0.5000 g	(1+1) HCl	1% HCl	500.0 ml
NaCl	0.2542 g	Deionized H ₂ O	Deionized H ₂ O	100.0 ml
KCl	0.1907 g	Deionized H ₂ O	Deionized H ₂ O	100.0 ml

2.3.2 Sample preparation

Ash samples were first ground in a clean, oven dried mortar and pestle, and then further ground using a SpectroMill Ball Pestle Impact grinder (Model 1100, USA) for seven minutes. Then the ground samples were oven dried overnight at 110°C and cooled in a desiccator. A portion of 1.0000 g of each sample was refluxed in 100 ml of concentrated nitric acid for six hours. Then the resulting mixture was filtered and diluted in a 250.0 ml volumetric flask with Millipore® water. The resulting solutions were

diluted as needed to obtain measurements that fit within the range of the calibration standards.

Similar procedures were followed for feed stock sample preparation, except the wood pellet and grass pellet samples were oven dried and ground by mortar and pestle only. The wood chips were ground using a magic bullet grinder (model MB 1001C, SGS, USA).

2.3.3 Atomic spectroscopy

Atomic absorption spectrometer by Perkin-Elmer model number 2380 was used for elemental analysis. Acetylene and Air were used as fuel and oxidant respectively.

2.3.3.1 Atomic absorption spectroscopy

Hollow Cathode Lamps were used for Ca (422.7 nm), Mg (248.3 nm) and Fe (285.2 nm). A calibration curve was plotted for each element using standard solutions and the concentration of samples with unknown concentration was determined. The uncertainty of one standard deviation of x axis values in the calibration curves were calculated using linear regression.^{23,13}

2.3.3.2 Atomic emission spectroscopy

Atomic emission values of Na and K were measured at wavelengths of 589.0 nm and 766.5 nm, respectively. Calibration curves were plotted for both elements using standard solutions and the concentration of samples with unknown concentration were determined. Uncertainties of one standard deviation of x axis values in the calibration curve were calculated using linear regression.^{23,13}

2.3.4 CHN- Combustion analysis

CHN analysis was performed in the UIUC Micro analysis lab in Champaign, IL using a CE440 by Exeter Analytical, Inc. N. Chelmsford, MA, USA.

2.3.5 Si analysis

ICP- OES was done at UIUC microanalysis lab in Champaign using an OES Optima 2000 DV by Perkin Elmer Norwalk, CT USA.

2.3.6 Clinker analysis

Mineral content of the clinker was obtained by EDXRF in ALS, Springfield, IL.

Chapter 3: Results and discussion

3.1 Feed stock characterization

The moisture content of feed stocks was characterized for each biomass sample by a thermogravimetric based analysis. Table 3 shows the moisture content of the feed stocks where it can be noticed that grass pellets have approximately twice the moisture of wood chips and three times that of wood pellets.

The higher the moisture content in the feed stock, the lower the energy value of the syngas produced due to the heat loss from evaporation during gasification. Higher moisture content also increases the tar content in the resulting gas as it reduces the temperature in the combustion zone where tar cracking mostly occurs in the down-draft gasifier. Moisture content above 30% also makes for ignition difficulties, but the feed stocks used in this study are below 15%. In addition the water gas shift reaction (R4) also becomes viable in the presence of excess water which may cause differences in the CO/H₂ ratio that can be undesirable in particular instances.²⁴

Table 3: Moisture contents of the feed stocks.

Feed stocks	Moisture content %
Wood pellets	4.19
Grass pellets	12.70
Wood chips	6.29

Table 4 shows the bulk density of the feed stocks. Bulk densities of the wood pellets and grass pellets are closer to each other compared to the low bulk density of wood chips.

The bulk density trend is wood pellets > switch grass >> wood chips. This is due to the particle size of the feed stocks. Pelletized biomasses contain similar particle sizes. The larger the size the larger the void spaces which decreases the bulk density (Figure 7).

Larger particles can cause blocks in the down flow of the feed stock, while smaller particles also tend to clog and cause difficulties in air flow, called bridging, leading to large pressure drops resulting in the shutdown of the gasifier. Bulk density also influences the transport and storage costs of the feed stocks. Therefore feed stock particle size is important.²⁴

Table 4: Bulk densities of the feed stocks (n= number of replicates).

Feed stock	Bulk density	Standard deviation
Wood pellets	0.77kg/l	0.01 (n=3)
Grass pellets	0.68 kg/l	-
Wood chips	0.22 kg/l	-



(a)

(b)

Figure 7: Pictures of non-pelletized and pelletized biomass (a) Wood chips and (b) Wood pellets.

Higher Heating Values (HHV) of feed stocks obtained from bomb calorimetry per unit volume and unit mass basis are shown in Table 5. Wood chips show the lowest HHV or internal energy with wood pellets the largest, also reflecting their bulk density differences.

Table 5: Higher Heating Value of the feed stocks (n= number of replicates).

Feed stocks	Number of repetition	(KJ/l)	(KJ/g)	
		HHV	HHV	Standard deviation
Wood pellets	1	1.362×10^4	17.76	-
Grass pellets	3	1.183×10^4	17.41	0.40 (n=3)
Wood chips	4	3.551×10^3	16.07	0.75 (n=3)

Table 6 provides data from combustion (CHN) analysis for the feed stocks. The % of O₂ was determined by neglecting the amount of all other metal elements. It is interesting to note that while switch grass has a slightly higher N content than the other two feed stocks; wood pellets have a much smaller oxygen content. From this data empirical formulas of the feed stocks were calculated and are shown in Table 7.

Table 6: Mass % of C, H, N and O in feed stocks (Calculated by assuming the other mineral contents including S and Si are negligible).*

Feed stock	%C	%H	%N	%O*
Wood pellets	48.85	5.85	0.28	44.85
Grass pellets	46.15	5.80	0.62	46.47
Wood chips	47.62	5.84	0.34	46.14

Table 7: Results of empirical formula calculation for biomasses by normalizing to C.

Feed stock	C	O	H	N
Wood pellets	1	0.60	1.43	0.005
Switch grass pellets	1	0.76	1.50	0.011
Wood chips	1	0.73	1.46	0.006

3.2 Analysis of syngas composition

Preliminary studies showed that storage of syngas in the sample bag for one hour did not show a significant loss in any of the gas components (each run takes 4 minutes).

Base line conditions for pelletized biomass gasification were established using wood pellets. The composition of syngas collected at five different temperatures: 650°C, 700°C, 750°C, 800°C, 850°C were analyzed using gas chromatography. Reproducibility of the gasification reactions were also confirmed using the experiments with wood pellets.

A sample chromatogram is shown in Figure 8. It can be noticed that there are two chromatograms representing the two column separations in the GC. The chromatogram on the top belongs to MS5Å column where the peaks, in order of increasing retention time correspond to H₂, O₂, N₂, CH₄ and CO. The small peak observed in the PPQ column corresponds to CO₂ and other peaks correspond to other gases present in the syngas. A brief GC/MS study of other components in the syngas (results not shown) indicates a small amount of ethane and furans are produced.

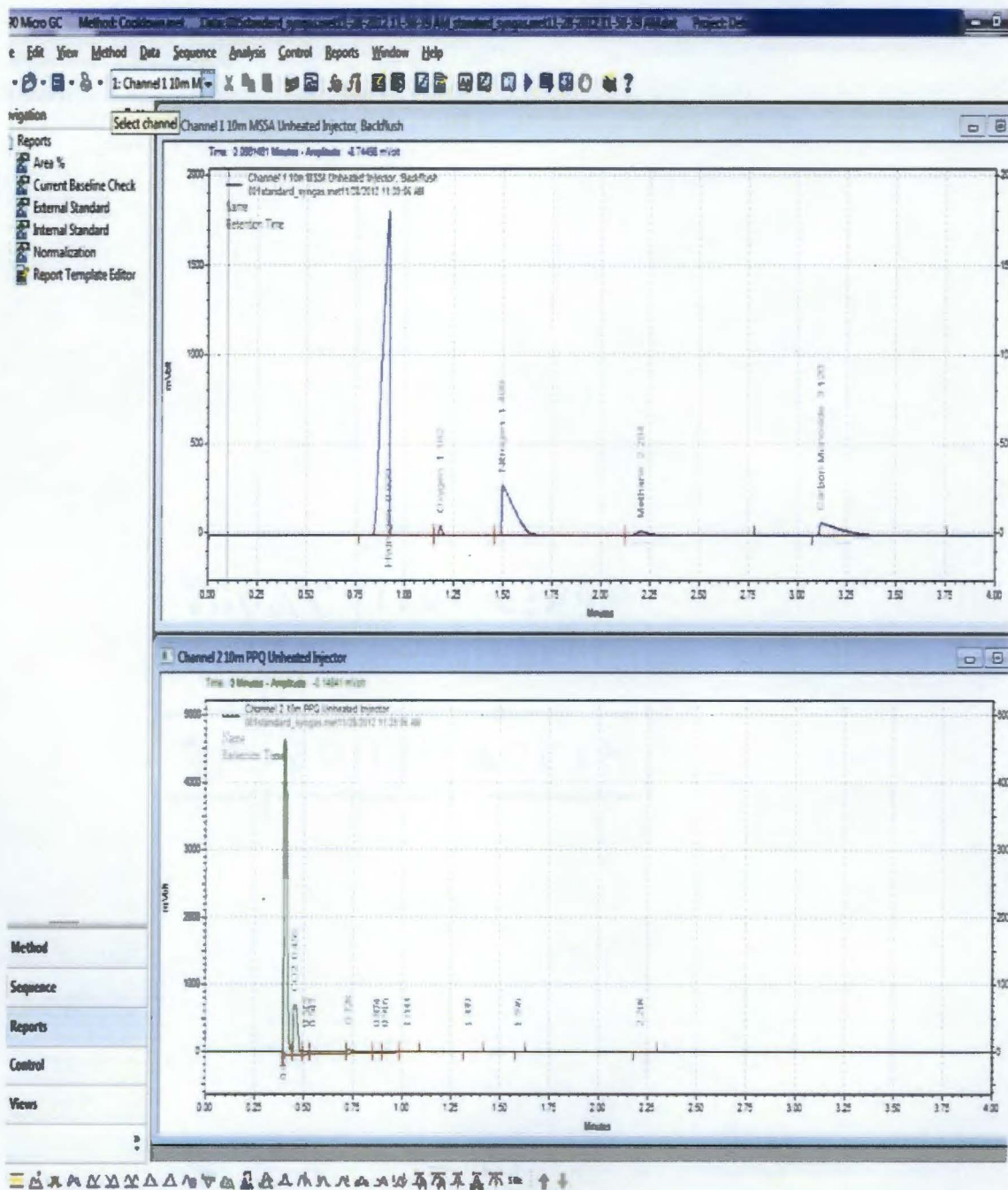


Figure 8: Sample chromatogram of syngas.

A sample external standard report is shown in Figure 9. The external standard report provides the corresponding retention time, peak area and mole % of each gas component

of the standard. Mole %, derived from the peak area, is calculated using the external standard's chromatogram from standard syngas with known mole % of components.

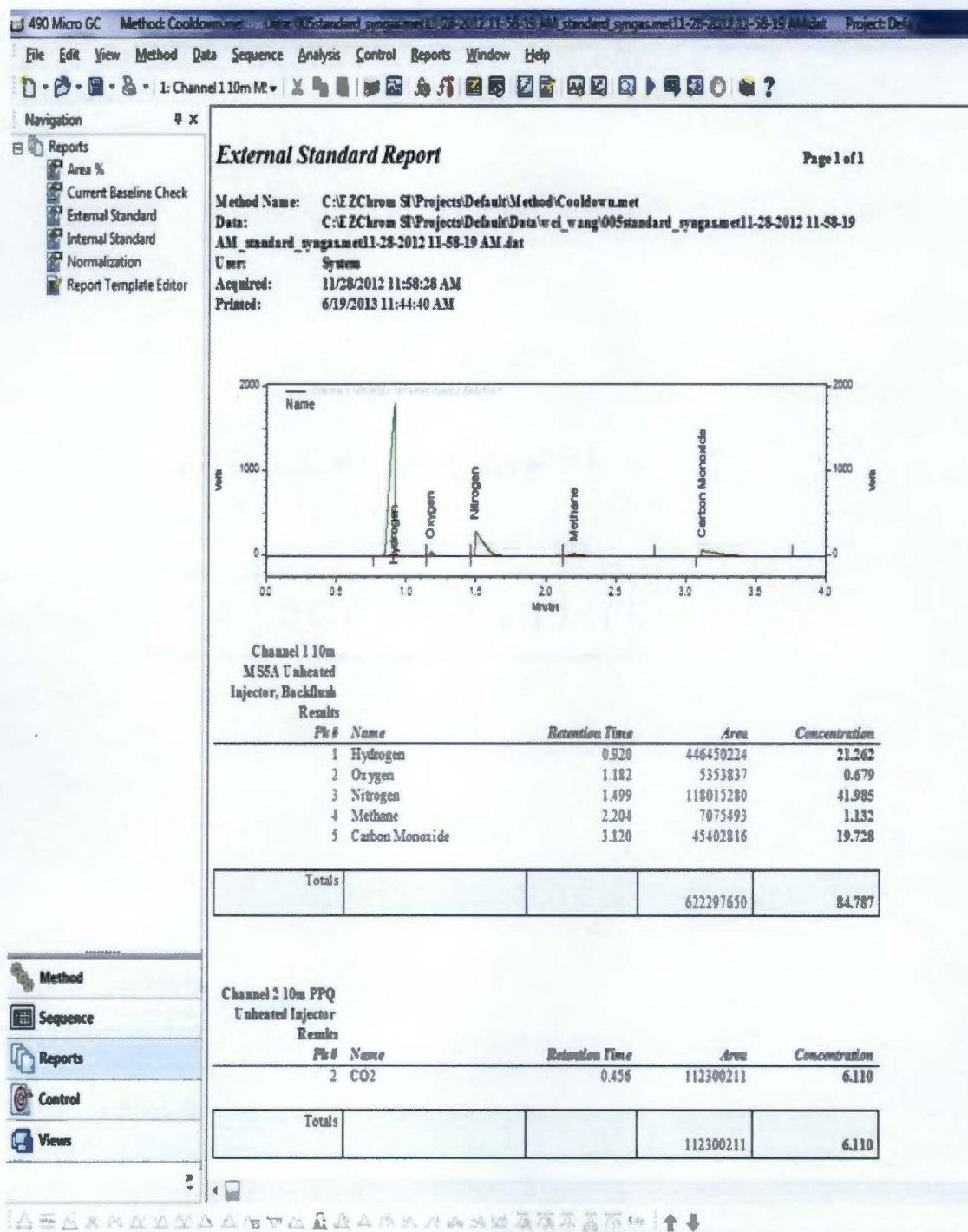


Figure 9: Sample external standard report of GC analysis from EZchrom software.

3.2.1 Establishing base line conditions for pelletized biomasses using wood pellets

Distributions of mole % of gas components of syngas produced in wood pellets gasification are shown in Figures 10 and 11. Figure 10 shows the distribution of mole percentage of H₂ and CO with increasing temperature. A significant increase in mole percentage was observed for both gases with increasing temperature between 650 and 850°C.

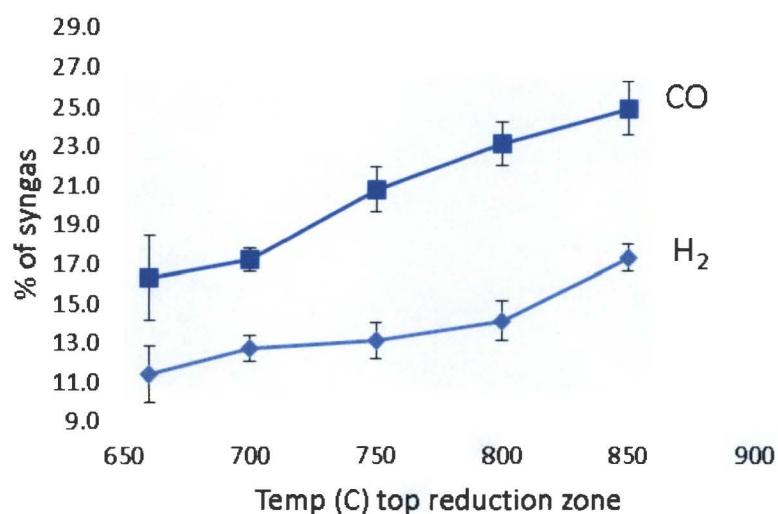


Figure 10: Distribution of H₂ and CO mole % in syngas produced from wood pellets with increasing temperature. Error bars represent one standard deviation of three gasification runs.

Figure 11 shows the distribution of mole percentage of CO₂, CH₄, O₂ and other and lost gas components. Other gas components of syngas normally consist of trace amounts of water, hydroxyacetaldehyde, acetic acid, methyl and hydroxy-ketone and aldehyde compounds, phenol and furan derivatives and species possessing guaiacyl and syringyl structures, some of which we have confirmed by a preliminary GCMS analysis (results not shown).²⁵

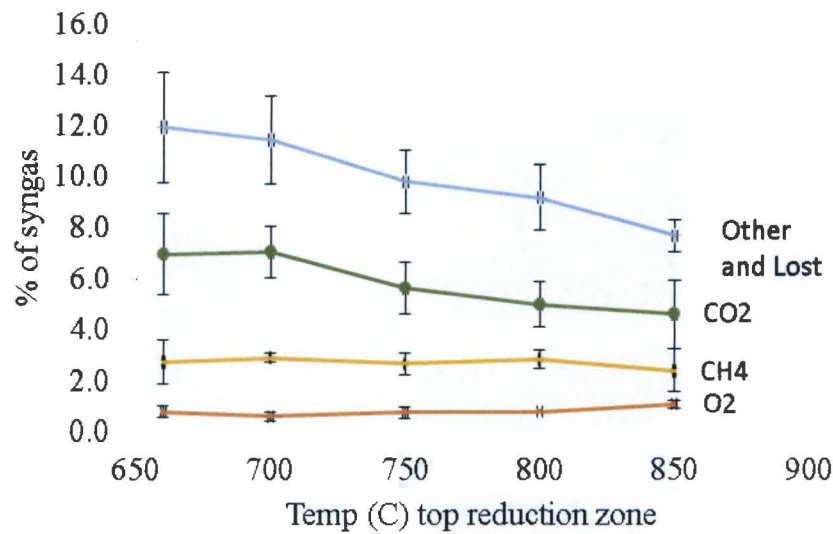


Figure 11: Mole % of O₂, CH₄, CO₂ and other gas constituents. Error bars represent one standard deviation of three separate runs of wood pellets.

3.2.2 Comparison of the composition of syngas produced from different feed stocks

One of the main objectives of this project was to study the influence of different kinds of biomasses in the final gas composition. Concentrations of H₂, CO and CH₄ in the syngas play an important role in the energy value of the syngas since they have further combustion potential. Wood pellets, wood pellets: wood chips 50:50 mixture, and switch grass pellets: wood chips 50:50 mixtures, were used as feed stocks. Co-gasification of wood chips with pelletized biomasses was necessary due to biomass bridging problems observed with grass pellets.

Figures 12 - 15 show the distribution of H₂, CO, CO₂ and CH₄ respectively in syngas, produced from wood pellets, wood pellets: wood chips 50:50 mixture, and switch grass pellets: wood chips 50:50 mixture.

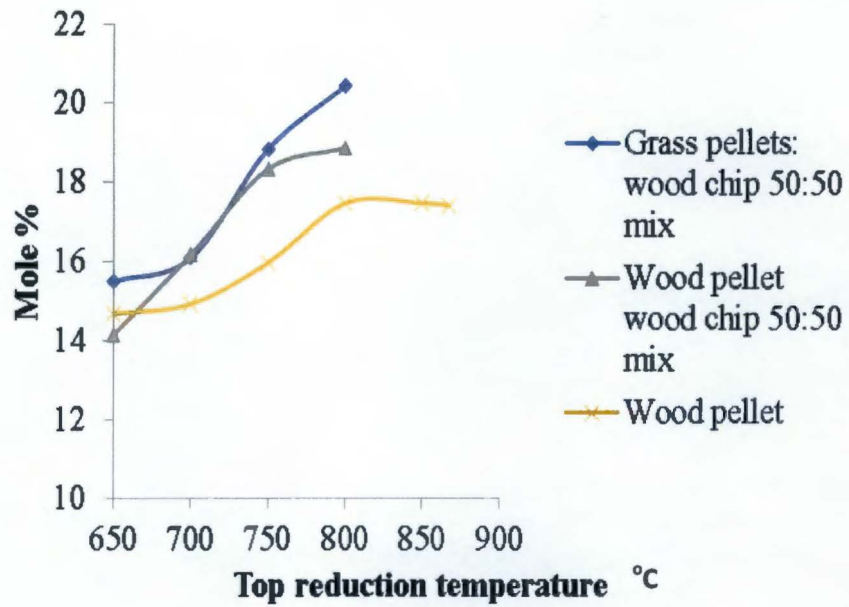


Figure 12: Mole % of H_2 of three biomasses as a function of temperature.

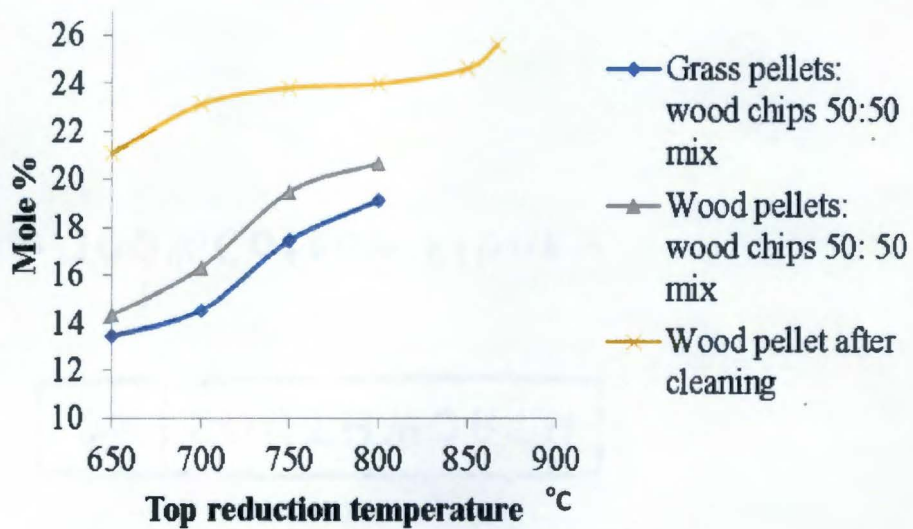


Figure 13: Mole % of CO of three biomasses as a function of temperature.

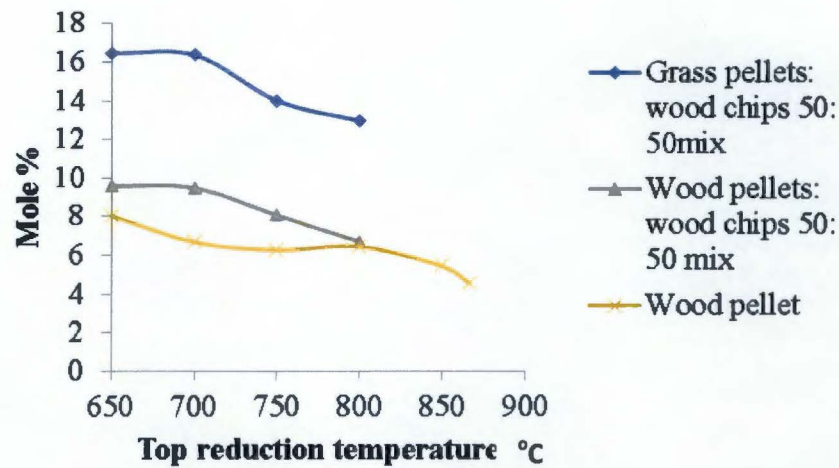


Figure 14: Mole % of CO₂ of three biomasses as a function of temperature.

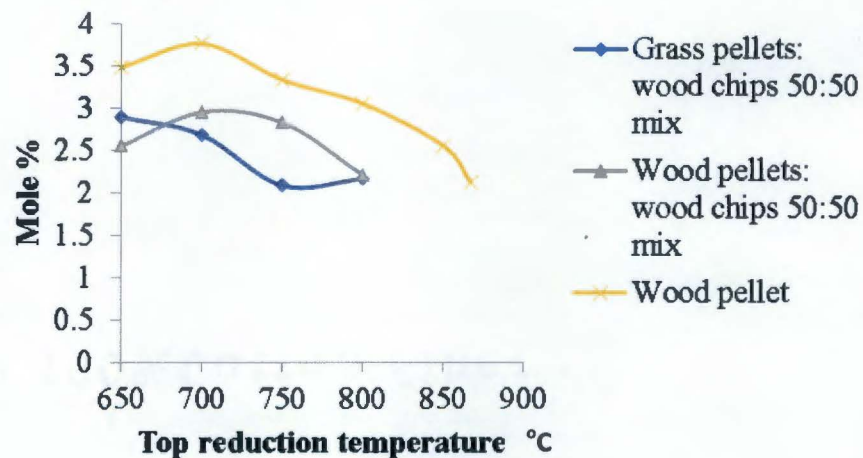


Figure 15: Mole % of CH₄ of three biomasses as a function of temperature.

At higher temperatures, the concentration of H₂ is highest in the grass pellets: wood chips mixture, compared to the other two. Mixing 50% of wood chips with wood pellets also increases the hydrogen content in the resulting syngas. Furthermore a similar

increasing trend in H₂ gas with increasing temperature was observed for all three feed stocks used (Figure 12).

A similar increase in CO content of syngas with increasing temperature was observed for all feed stocks, but the opposite trend was observed in terms of the biomass types (Figure 13). Wood pellets showed the highest CO content and grass pellets showed the lowest at the temperatures studied.

Figure 14 shows the CO₂ concentrations of syngas decreasing with increasing temperature for all feed stocks. With respect to feed stock comparison the trend is similar to H₂. The CH₄ data in Figure 15 shows a seemingly large decrease for wood pellets, with the other two feed stocks exhibiting no discernable pattern with temperature.

The significance of changes in mole percentage produced from three different biomasses at five different temperatures was tested by ANOVA (Analysis of Variance) analysis. Two factor ANOVA without replication was performed to test the gas distribution as a function of temperature. ANOVA analysis compares the variance (Eq. 27) which measures scatter in the data set.

$$\text{Variance} = \frac{\sum(x - \bar{x})^2}{n - 1} \quad (\text{Eq. 27})$$

Two factor ANOVA analysis is performed when the data set contains two variables; in this case reactor temperature and feedstock type. The data for H₂ production as an example are shown in Table 8. Table 9 presents the descriptive statistics of the data of rows and columns in Table 8.

Table 8: Sample data arrangement for two factor ANOVA analysis for mole % of H₂.

Temp (°C)	WP	WC:GP 50:50 mix	WC/WP 50:50 mix
650	11.37	15.50	14.13
700	12.71	16.10	16.16
750	13.09	18.82	18.31
800	14.09	20.41	18.84

Table 9: Sample output of descriptive statistic for the rows and columns in Table 8.

Summary	Count	Sum	Average	Variance
650	3	41.01	13.67	4.440
700	3	44.98	14.10	3.895
750	3	50.22	16.74	10.06
800	3	53.34	17.78	10.81
Wood pellets	4	51.26	12.82	1.268
Woodchips/grass pellets50:50 mix	4	70.83	17.71	5.311
Woodchips/wood pellets50:50 mix	4	67.46	16.86	4.662

Table 10 shows the output of the statistical calculation. To be significantly different at the 95% confidence level, the F value in the output should be greater than the F critical value, and P- value should be smaller than 0.05. These results show that there is a significance difference in mole % of H₂ gas between the temperatures studied because the F value is greater than F critical value, and the P value is lower than 0.05. It can also be said that syngas produced from different biomasses also show a significant difference in the mole% of H₂ by inspecting results from the columns (refer to Table 8).

Table 10: Sample inferential output of two factor ANOVA analysis.

Source of Variation	SS	df	MS	F	P-value	F critical
Rows	29.99	3	9.997	16.07	0.002838	4.757
Columns	54.67	2	27.34	43.95	0.0002608	5.143

Similar ANOVA analyses were performed for each gas including H₂ (also shown above), CO, CO₂ and CH₄. Table 11 shows the average data values of three wood pellets gasification runs, as well as single runs for other two feedstocks used in the ANOVA analysis. Table 12 summarizes the output of all of the analyses performed. Each component except CH₄ shows a significant difference in mole % with increasing temperature at the 95% confidence level.

Table 11: Data for ANOVA test - mole % of each gas against temperature for three feedstocks.

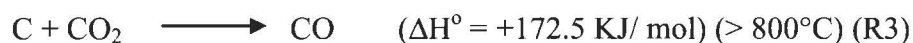
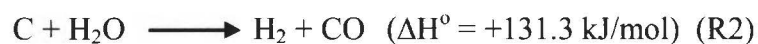
Temp °C	WP				WC:GP 50:50 mix				WC/WP 50:50 mix			
	H ₂	CO	CO ₂	CH ₄	H ₂	CO	CO ₂	CH ₄	H ₂	CO	CO ₂	CH ₄
650	11.37	16.29	6.95	2.74	15.50	13.48	16.45	2.89	14.13	14.37	9.58	2.55
700	12.71	17.22	7.04	2.92	16.10	14.56	16.35	2.68	16.16	16.34	9.47	2.95
750	13.09	20.76	5.61	2.68	18.82	17.47	13.98	2.08	18.31	19.50	8.06	2.83
800	14.09	23.10	4.99	2.85	20.41	19.11	12.94	2.16	18.84	20.66	6.71	2.22

Table 12: Results of ANOVA analysis for syngas components for three feedstocks.

Gas components		df	F	P	F critical
H ₂	Rows	3	16.07	0.002838	4.757
	Columns	2	43.95	0.000261	5.143
CO	Rows	3	137.3	6.44E-06	4.757
	Columns	2	56.47	0.000128	5.143
CO ₂	Rows	3	35.5	0.000323	4.75
	Columns	2	527	1.81E-07	5.14
CH ₄	Rows	3	1.48	0.311	4.75
	Columns	2	1.52	0.293	5.14

With ANOVA demonstrating that there is a significant increase in H₂, CO, and CO₂ as a function of temperature (rows), and feedstock (columns) as shown in Table 12, possible chemical implications of these data will now be discussed.

The increasing trend in H₂ and CO, and the decreasing trend in CO₂ suggest that the following reactions may be important.



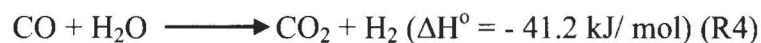
Being endothermic, reactions R2 and R3 may become more prominent (i.e.; the equilibrium constant increases) at high temperatures where CO₂ is consumed and H₂ and CO are produced.⁶ Endothermic reactions absorb heat energy from the environment and thus become more viable at higher temperatures. In addition reaction rates also increase as temperature is increased.

ANOVA analysis also indicates that methane production does not change at temperatures between 650°C and 850°C. The following methane formation reactions have been reported to be most favorable at temperatures between 300°C and 450°C.⁶



This same study also reported a similarly consistent mole fraction of methane at temperatures above 600°C, with higher concentrations of H₂ and CO at higher gasification temperatures similar to the results reported here.

It can also be noticed that in the distributions of CO, H₂ and CO₂ (Figures 10 and 11 resp.), a very slight decrease in gradients of CO and CO₂, and a small increase in the gradient for H₂ were observed between 650 to 700 °C compared to other temperatures. This may be due to the slightly exothermic water gas shift reaction which is thermodynamically more viable at low temperatures. It should be noted that the reaction rate increases at higher temperatures, which may partially offset the lowering equilibrium constant to the extent that the system does not reach equilibrium. It was also reported in the literature that the water gas shift reaction is not very prominent above 700 °C.⁸



Pairwise comparisons of mole % of the syngas components as a function of temperature produced from different feed stocks were performed using a similar two-factor ANOVA analysis without replication. Results show there is a significant difference

in evolution of gases H₂, CO and CO₂ between biomasses except for wood chips:grass pellets 50:50 mixture vs. wood chips:wood pellets 50:50 mixture for H₂ production. Methane did not show a significant difference between different biomasses except for the wood chips:grass pellets 50:50 mixture vs. wood chips:wood pellets 50:50 mixture comparison (Tables 13- 16).

Table 13: ANOVA test results - testing the significant difference in H₂ mole percentages between different biomasses at temperatures between 650 °C and 800 °C.

Feed stocks	F	P value	F critical
W.CH/GP50:50 mix VS. WP	51.6	0.00555	10.1
W.CH / WP 50:50 mix VS. WP	50.5	0.00573	10.1
W.CH/GP 50:50 mix VS. W.CH/ WP 50:50 mix	4.89	0.114	10.1

Table 14: ANOVA test results - testing the significant difference in CO mole % between different biomasses at temperatures between 650°C and 800°C.

Feed stocks	F	P value	F critical
W.CH/GP50:50 mix VS. WP	113	0.00176	10.1
W.CH / WP 50:50 mix VS. WP	21.9	0.0184	10.1
W.CH/GP 50:50 mix VS. W.CH/ WP 50:50 mix	40.6	0.00783	10.1

Table 15: ANOVA test results - testing the significant changes in CO₂ mole % between different biomasses at temperatures between 650 and 800.

Feed stocks	F	P value	F critical
W.CH/GP50:50 mix VS. WP	558	0.000166	10.1
W.CH / WP 50:50 mix VS. WP	134	0.00138	10.1
W.CH/GP 50:50 mix VS. W.CH/ WP 50:50 mix	723	0.000113	10.1

Table 16: ANOVA test results - testing the significant changes in CH₄ mole % between different biomasses at temperatures between 650°C and 800°C.

Feed stocks	F	P value	F critical
W.CH/GP50:50 mix VS. WP	3.23	0.170	10.1
W.CH / WP 50:50 mix VS. WP	0.891	0.415	10.1
W.CH/GP 50:50 mix VS. W.CH/ WP 50:50 mix	10.1	0.652	0.478

To summarize the feedstock comparison data, when the biomass was switched from 100% wood pellets to the 50:50 wood pellets:wood chips mix, and then to the 50:50 grass pellets:wood chip mix, H₂ content and the CO₂ content in the resulting syngas increases and CO content decreases. These observations could also be explained by the water gas shift reaction.



The water gas shift reaction is most prominent in the 50:50 switch grass pellets:wood chips mixture. The moisture content of wood chips and grass pellets are high compared to wood pellets which may help shift the equilibrium of this reaction to products.

3.2.2.1 Elemental analysis of feed stocks

Data of mineral content of the feed stocks are presented in Table 17. It can be noted that the Ca and Fe content are high in wood chips and low in wood pellets; whereas K and Mg are high in grass pellets and low in wood chips. Na content did not vary significantly in the different feedstocks.

Table 17: Results of elemental analysis of feed stocks .Error values represents one standard deviation of x axis values in the calibration curve. ($\pm S$).

Elements	Wood pellets		Grass pellets		Wood chips	
	Mass %	($\pm S$)	Mass %	($\pm S$)	Mass %	($\pm S$)
Ca	0.089	0.005	0.195	0.006	0.375	0.005
Fe	0.012	0.004	0.022	0.004	0.048	0.004
Mg	0.013	0.001	0.146	0.001	0.022	0.001
Na	0.023	0.008	0.026	0.008	0.020	0.008
K	0.101	0.006	0.650	0.006	0.162	0.006

This result can further support the discussion that the water gas shift reaction is most prominent in the 50:50 switch grass pellets:wood chips mixture. Alkali and alkaline earth metal oxides as well as Fe_2O_3 enhance the water gas shift reaction.¹³ It can be noticed that Ca and Fe content is high in wood chips, and K, Na and Mg is high in grass pellets (Table 17). At high temperatures during gasification these elements are converted in to oxides and they may act as catalysts for enhancing the water gas shift reaction in the grass pellets: wood chips mixture.

3.2.2.2 Elemental analysis of the ash

Table 18 shows the mass % of C and Si in the ash samples. Carbon content of the ash samples vary from 32.68% to 70.24% which affects the mass % of the mineral content. The large difference in C values is due to how the fuels react in the gasifier. Ash content varies with different feed stocks for many reasons such as the shape and texture of the feed stocks and feed stock composition. In addition the ash collected from gasification is a mixture of ash collected throughout a gasification run. Therefore mineral content of the

ash samples were calculated excluding the carbon content in order to avoid the large influence of varying carbon levels in the mass % calculations.

Table 18: Mass % C and Si content of ash samples.

Sample	%Si	% Si (excluding C)	%C
Wood pellets	7.48	11.1	32.68
Switch grass pellets	5.21	9.98	60.64
Grass pellets: Wood chips 50: 50 mix	3.01	13.2	70.24
Wood chips	0.27	0.907	69.84

Results of elemental analysis of ash samples are summarized in Table 19, and some of these values are also presented along with values obtained from the literature for comparison in Table 20.⁴ Literature values present the chemical properties of switch grass pellets and the poplar wood biomass, which are mostly consistent with the results reported in this study.

Table 19: Results of elemental analysis of Ash samples and error values represents one standard deviation of x axis values in the calibration curve ($\pm S$).

Elements	Wood pellets		Grass pellets		Wood chips		Grass pellets : Wood chips mix	
	Mass %	($\pm S$)	Mass %	($\pm S$)	Mass %	($\pm S$)	Mass %	($\pm S$)
CaO	11.503	0.247	5.012	0.431	3.738	1.275	12.908	0.564
FeO	3.255	0.082	0.581	0.142	0.111	0.199	0.254	0.193
MgO	3.559	0.002	2.403	0.003	0.114	0.005	3.363	0.004
Na ₂ O	67.196	0.024	12.744	0.043	5.656	0.049	14.428	0.054
K ₂ O	1.377	0.031	0.614	0.055	0.199	0.070	0.978	0.078

Table 20: Chemical composition of feed stocks and ash samples- comparison with the literature values.

Elements	Feed stocks of this study (Mass %)			Literature values (Mass %)	
	Wood pellets	Wood chips	Grass pellets	Switch grass	Poplar (wood)
Feed stocks					
C	48.85	47.62	46.15	42-53	47-52
H	5.85	5.84	5.80	4.9-6.5	5.6-6.3
O	44.85	46.14	46.47	36-49	40-46
Ash					
CaO	11.503	3.738	5.012	5-14	29-61
Fe ₂ O ₃	3.255	0.111	0.581	0.35-3.6	0.3-1.4
MgO	3.559	0.114	2.403	2.6-6.5	0.1-18
Na ₂ O	1.377	0.199	0.614	0.1-1.9	0.1-0.4
K ₂ O	67.196	5.656	12.744	5-28	10-34

It can be noticed that CaO content in the ash decreases in the order grass pellet:wood chips mixture > wood pellet >> wood chips > pure switch grass. Fe₂O₃ content decreases in the order wood pellet >> pure switch grass > wood chips > grass pellet:wood chips mixture. MgO, Na₂O and K₂O decrease in the order wood pellet > grass pellet:wood chips mixture > pure switch grass >> wood chips. The difference trends in elemental composition between feed stocks and ash samples can be explained.

Normally alkali components in the biomass become volatile at higher gasification temperatures and end up in the resulting gas.²⁴ Different colors of syngas flames were observed in the flare during gasification in this study suggesting this occurred. The formation of metal silicates in the presence of Group I and Group II metals and Si can

produce a sticky liquid phase which can deposit on the char particles and the side walls of the gasifier. This sticky liquid metal silicate phase can solidify forming clinkers or slag when the temperature decreases below the melting point of the metal silicate. While important in its own right, this can also cause differences in the elemental composition in the ash.^{4, 23, 26} Therefore finding a correlation between the amount of elements present in the feed stocks and ash is not expected.

Clinker formation was observed during grass pellets gasification in this study. The K content is high in wood pellets compared to grass pellets and Na content is high in wood pellets and low in wood chips. Therefore the alkaline content of the ash sample or in the feed stock alone cannot explain the formation of slag or clinker during the gasification process. Along with alkali metal content, Si content in the ash plays an important role in clinker formation.⁴ Clinker elemental composition data shows that silicon and K₂O are very high, 55.6% and 12.25% respectively (Figure 16), and it is high in grass pellets feed stock (Table 21).

Table 21: Mass % of Si in feed stocks

Feed stock	% Si
Wood pellets	0.175
Grass pellets	0.965
Wood chips	0.056

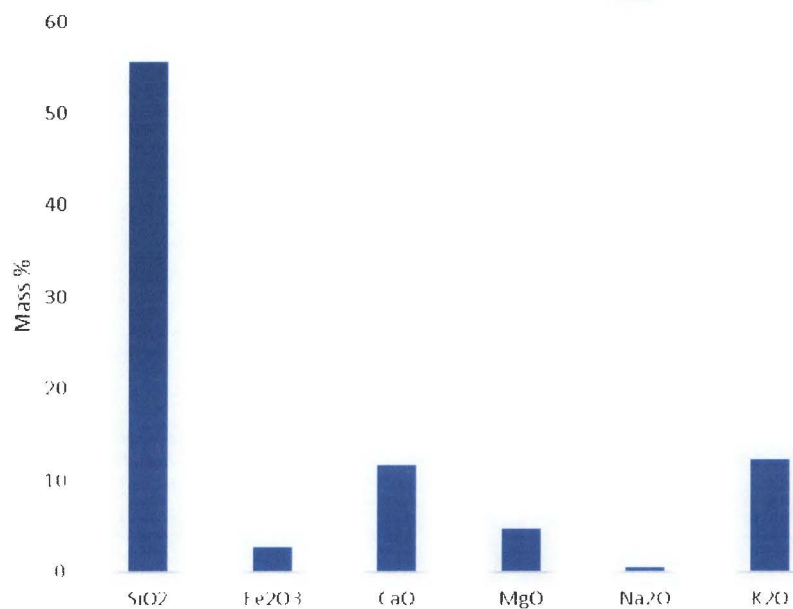


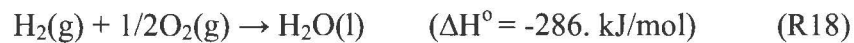
Figure 16: Elemental composition of Clinker obtained by EDXRF.

3.3 Applications of syngas

Two main applications of syngas are generation of clean energy and the synthesis of commercially value added chemicals.

3.3.1 Energy production

Considering energy production, syngas is the product of partial oxidation of biomass hydrocarbons containing gases which have further combustion potential, mainly H₂, CO and CH₄. Standard heat of combustion values and reactions of these components are shown in R17 – R19.



The amount of methane produced in the gasification is low compared to H₂ and CO, being less than 4 % (Figure 15). There are no significant changes in CH₄ mole % observed among feed stocks except W.CH/GP 50:50 mix VS. W.CH/ WP 50:50 mix and against temperature (Table 16). Therefore the amount of H₂ and CO in syngas plays the most important role in comparing the energy values of the syngas with higher amounts of CO and H₂ resulting in higher HHV.

3.3.1.1 HHV of the syngas

The energy value or HHV of the syngas was calculated using standard HHV values of gas components having further combustion potential, and the gas composition obtained from GC. HHV values of syngas produced from wood pellets and grass pellets:wood chips 50:50 mixture increases with increasing temperature as the mole % of CO and H₂ increase significantly, except for the decrease from 800 to 850 °C for grass pellets:wood chips mixture as shown in Figure 17. HHV values of the syngas produced from grass pellets:wood chips mixture remain high compared to wood pellets syngas until 850 °C.

The HHV or energy value of the syngas depends on its composition which in turn depends on the reactor temperature, feed stock type and equivalence ratio (ER) value.^{27,28} The decrease in HHV from 800 to 850°C for grass pellets:wood chips mixture may be due to problems associated with gasifier operation using grass pellets. Here the pressure was increased which may have led to eventual dilution of the resulting gas with air to decrease HHV. An increase in temperature normally increases the mole % of H₂ and CO, but in this study the temperature was controlled by controlling the pressure. An increase in pressure increases the ER or air flow rate which decreases the energy value of the resulting gas by increasing the mole % of N₂.^{29, 30}

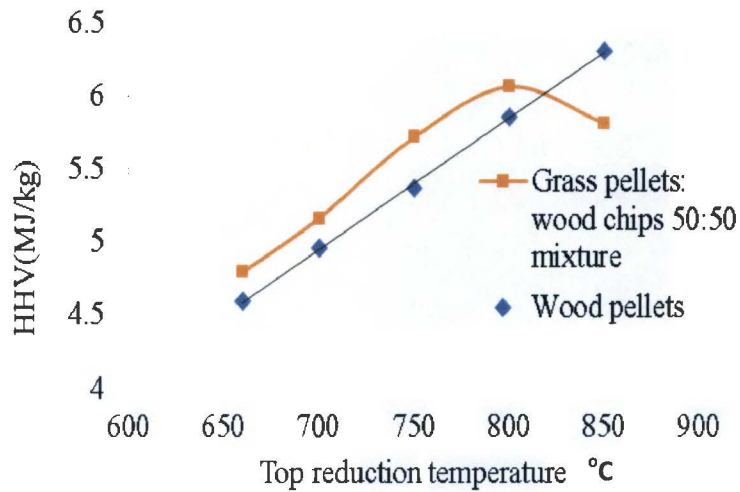


Figure 17: HHV of syngas produced.

3.3.1.2 Thermal efficiency calculations

Three different approaches¹⁸ were used to evaluate the thermal efficiency of the gasification of wood pellets, and grass pellets:wood chips mixture. Recall that thermal efficiency is defined as the ratio of heat produced from complete combustion of syngas produced to the HHV from complete combustion as measured by bomb calorimetry. In all three methods the idea is to compare the energy value of the syngas with the energy value of the feed stock from which it was produced. The three approaches differ by the methods of calculation used to determine the volume of syngas produced per unit biomass. As described in the introduction the equivalence ratio and stoichiometric ratio methods both calculate the volume of syngas by mass balance; that is the total mass of feed stock used and the mass of air used will be equal to the mass of syngas produced. From the calculated mass volume is derived from the syngas density. In the elemental balance method syngas mass was calculated directly from the moles of each component.

Figures 18, 19 and 20 show the result of volume calculations from the above three methods. Results from the equivalence ratio method show volume increasing with increasing temperature (Figure 18); the other two methods show a decreasing trend in gas volume with increasing temperature (Figures 19 and 20).

Considering the conditions in the reactor in view of the individual gas laws, Charles's Law states that an increase of temperature would result in an increase in volume. Avogadro's Law similarly states that as the number of moles of gas is increased, as we know to be the case from our GC analysis, the volume will also increase. Finally Boyle's Law state that a decrease in pressure results in an increased volume of gas. Since all individual gas laws predict an increase in gas volume, the decreasing volume derived from the elemental and stoichiometric ratio methods contradict the ideal gas law. This may be due to the gasifier being an open system, regardless of the reason these methods are unsuitable for thermal efficiency calculations. However the stoichiometric ratio and elemental balance methods may be useful for calculating the thermal efficiency in a closed gasification system where the amount of total excess C in the ash content and the total amount of air molecules in the syngas can be evaluated. For the system used in this study equivalence ratio method appears most applicable since this method calculates the ER of the gasification based on the known experimental ER and the experimental operational conditions. Thus the results obtained from elemental balance and stoichiometric ratio methods are not consistent with gasifier operation and process, therefore these two methods will not be used in thermal efficiency calculations.

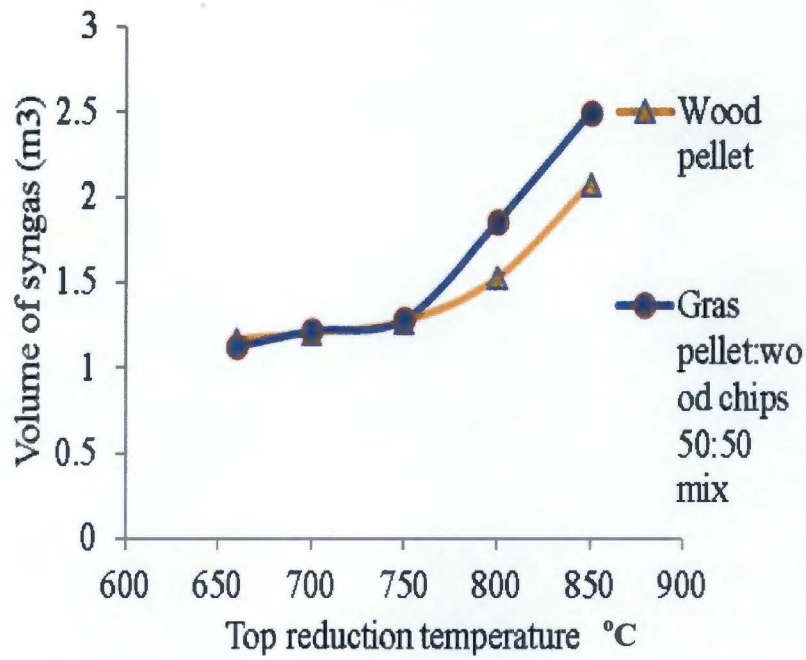


Figure 18: Volume of the syngas from 1kg feed stocks - equivalence ratio method.

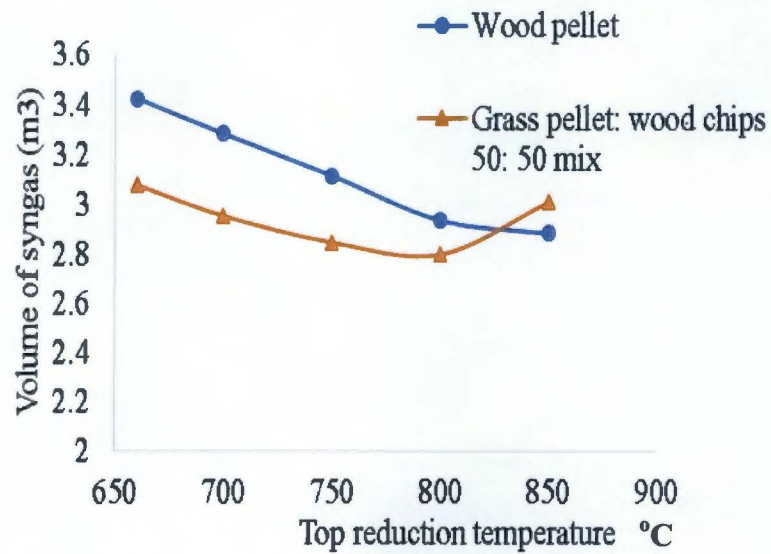


Figure 19: Volume of the syngas from 1kg feed stocks – Elemental balance method.

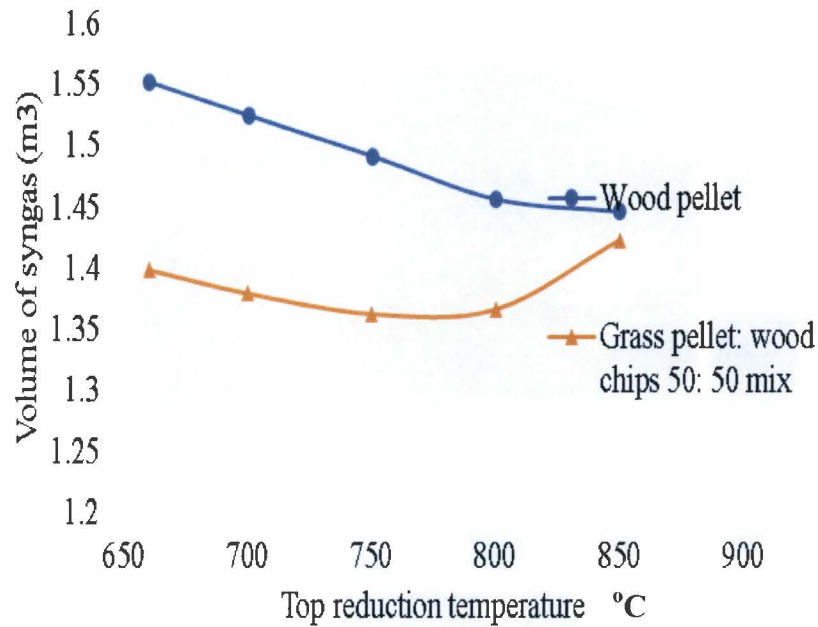


Figure 20: Volume of the syngas from 1kg feed stocks - stoichiometric ratio method.

Figure 21 shows the thermal efficiencies of two different feedstocks during gasification, switch grass:wood chips 50:50 mixture showed a higher thermal efficiency at all temperatures. And both feedstocks show an increasing trend with increasing temperature.

Thermal efficiency decreases in the presence of high moisture content due to heat loss during the evaporation process of gasification. Table 4 shows the moisture content of the feed stocks; grass pellets contain the highest moisture content. Therefore preprocessing of grass pellets to remove moisture may increase the thermal efficiency of grass pellets.

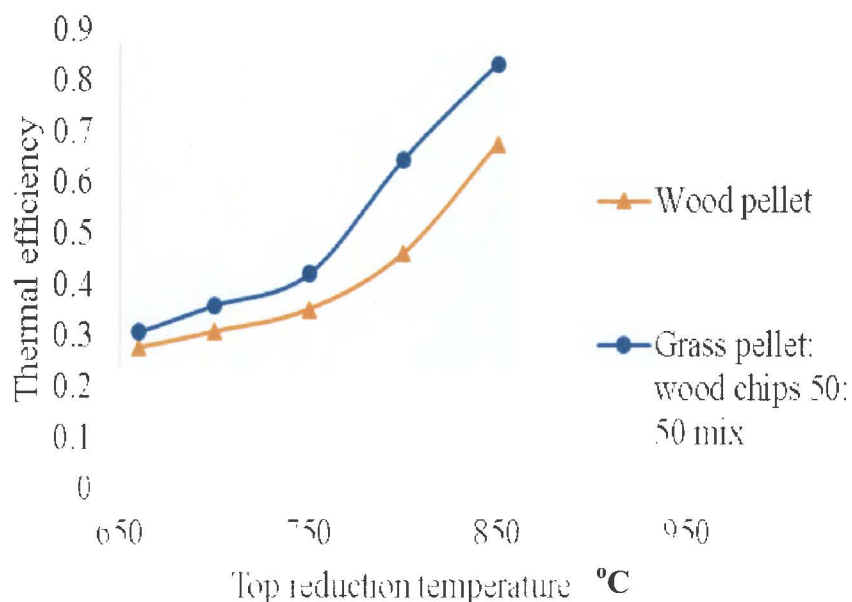


Figure 21: Thermal efficiency of gasification of different biomasses - equivalence ratio method.

3.3.2 Chemical synthesis

Fischer-Tropsch (F-T) synthesis involves a collection of catalyzed chemical reactions that synthesize liquid hydrocarbons from syngas. In the literature, conversion of CO₂ along with CO in F-T synthesis with a cobalt-based catalyst was reported with higher concentrations of CO₂ in the feed gas.²² However, product selectivity of the synthesis is strongly dependent on the composition of syngas. At high concentrations of CO₂, (CO₂/(CO+CO₂)>50%), the product is mainly methane. In contrast at lower concentrations of CO₂ (CO₂/(CO+CO₂)<50%), most products are higher hydrocarbons. CO₂ mainly plays a diluting role at lower concentrations. In summary the undesired methane selectivity increases with increased partial pressure of CO₂.²²

Figure 22 shows that for all three biomasses, the $\text{CO}_2/(\text{CO}+\text{CO}_2)$ ratio is less than 50%, wood pellets having the lowest ratio. These results suggest that the wood pellets may be most favorable for Fischer-Tropic synthesis.

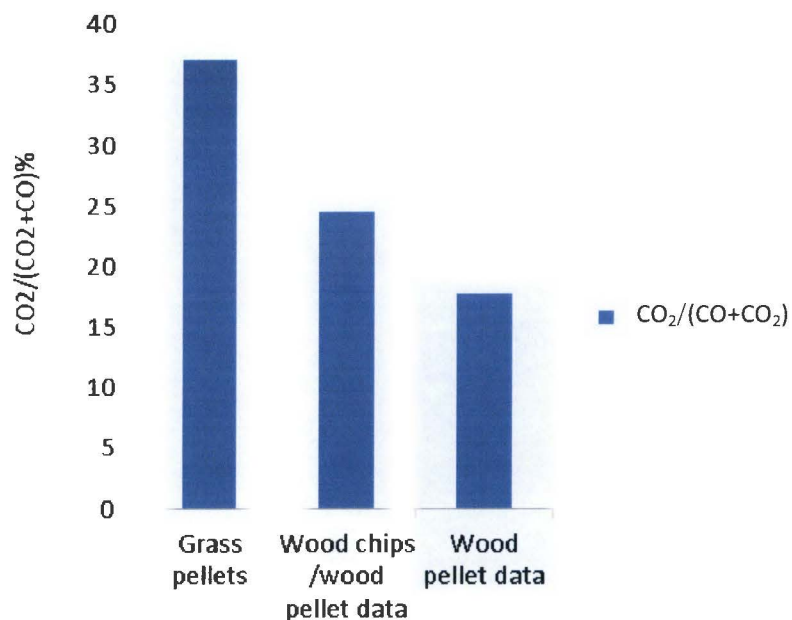


Figure 22: $\text{CO}_2/(\text{CO}_2+\text{CO})\%$ at 800°C for three kind of biomasses used.

Considering the influence of CO/H_2 ratio in low temperature F-T synthesis, the desired ratio for a cobalt-based catalyst is slightly lower than 0.5. However for iron based catalysts the desired ratio is about 1.4.

Figure 23 shows the CO/H_2 ratios of syngas from different biomasses at five different temperatures. The CO/H_2 ratio of the grass pellets:wood chip mixture is less than 1, indicating that this feed stock may be preferential for a cobalt-based catalyst for F-T synthesis. In contrast the CO/H_2 ratio of syngas produced from wood pellets is closer to 1.4, more preferable for iron-based catalysts used in F-T synthesis.²¹

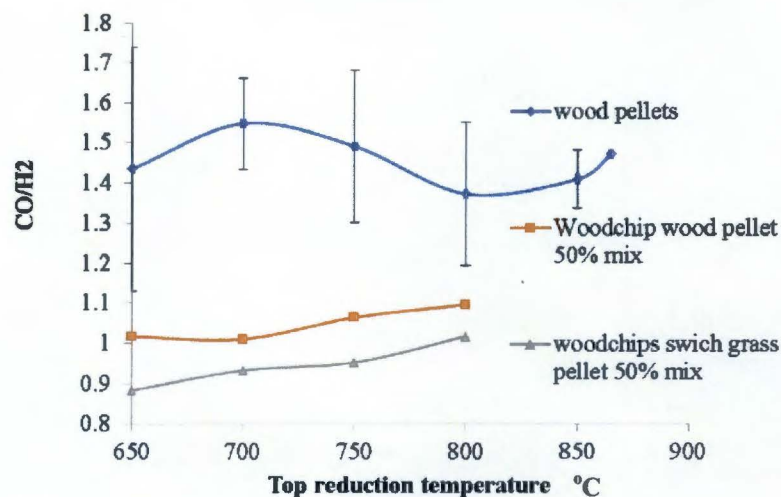


Figure 23: Distribution of CO/H₂ for different biomass feed stocks with increasing temperature. Error bars are 1 standard deviation of 3 separate runs.

The F-T synthesis of oxygenates such as ethanol, acetic acid, ethylene glycol etc., prefer specific CO/H₂ ratio reflecting the stoichiometry of the reactants CO and H₂. Some examples are listed in Table 22.²⁰

Table 22: CO/H₂ ratio in chemical production.

Product	CO/H ₂ ratio
Methanol	1:2
Ethylene glycol	2:3
Acetic acid	1:1
Acetic anhydride	1:1
Ethyl acetate	2:3
Vinyl acetate	4:5
Ethanol	1:2
Ethylene	1:2
BTX	2:3

Alkali metal carbonates and alkaline earth metal oxides (AEMO), dolomite and sepiolite present in the gasification reactor increase the yields of H_2 and CO_2 , and improves the decomposition of tar and light hydrocarbons (C_nH_m).¹³ Transition metals and olivine enhance the reforming reaction of tar and C_nH_m , which result in increases of H_2 , CO and CO_2 in the produced syngas. Furthermore AEMO and Fe_2O_3 , olivine and dolomite also have been reported to enhance the water gas shift reaction (Reaction 4) increasing H_2 and CO_2 production.¹³ Though the effect of catalysts in the gasification was not studied, increases in H_2 and CO_2 content in the presence of high amounts of alkali and alkaline earth metals as well as iron may have been evidenced in the grass pellets:wood chips mixture (Table 18).

Further work is warranted by incorporating different catalysts to effect changes in CO/H_2 and $CO_2/(CO+CO_2)$ ratios with the goal of increasing yields for targeted value added chemicals from biomass gasification.

Chapter 4: Conclusions

Three main factors that influence the final composition of the syngas include gasification temperature (changes effected by ER) and biomass type are studied. A temperature increase resulted in significant increases in the H₂ and CO content, which also influenced significantly in CO/ H₂ and CO₂/(CO₂ + CO) ratio.

Different types of biomass also showed significant differences in the syngas composition. Grass pellets:wood chips mixture and wood pellet were mainly compared. Grass pellets have a moisture content of 12.70%, which is 3 times higher than wood pellet (4.19%). Differences in elemental composition of different feed stocks were also reported which can cause changes in syngas composition as well. For example grass pellets have high K, Na and Mg content, and wood chips have high Ca and Fe content. All of these elements can act as catalysts for the water gas shift reaction below 700°C which increases the H₂ production and decreases CO content. This changes the CO/H₂ ratio which was evidenced for the grass pellets:wood chips mixture.

Considering energy production, amounts of H₂, CO and CH₄ in the final syngas dictate further combustion potential. It is clear from results in this study that the concentration of the above components increase with increasing temperature. the HHV values of the syngas increased from 4.60 up to 6.30 MJ/Kg for wood pellets and from 4.79 up to 6.06 MJ/Kg for grass pellets: wood chip mixture. Considering the chemical synthesis also it is clear that CO/ H₂ ratio and CO₂/(CO₂ + CO) ratio plays important roles in product selectivity in F- T synthesis and other chemical synthesis.

On the other hand, presence of high moisture content and high Si content along with alkali metals can result in formation of metal silicates. This can result in the formation of clinkers or slag causing problems in gasifier operation. Switch grass pellets have higher amounts of silicon 0.965% which is about 10 times higher than the other feedstocks, and SiO₂ content in the clinker which was produced during grass pellet gasification was an extremely high 55.6%. Therefore maintaining low Si content is important for feasible gasifier operation.

Considering the thermal efficiency calculation methods, equivalence ratio method could be applicable to the gasification system used in this study as the method uses the experimental conditions and known experimental ER values for optimum gasification of wood biomass.

References

- 1) Reddy, G. K.; Deepak, G. T.; Anjusree, S. G.; Thomas, S.; Vadukumpully, S.; Subramanian, V. R. K.; Nair, V. S.; Nair, S. A. On global energy scenario, dye-sensitized solar cells and the promise of nanotechnology. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6838—6858.
- 2) Jacobson, Z. J.; Masters, M. G. Exploiting Wind Versus Coal. *SCIENCE*, **2001**, *243*, 1438.
- 3) Albie Fong; Jesse Tippett (5 December 2012). *Project Development in the Solar Industry*. CRC Press. pp. 230—. ISBN 978-0-415-62108-3.
- 4) Bhavanam, A.; Sastry, C. R. Biomass gasification Process in Downdraft Fixed Bed Reactors: A review. *International Journal of Chemical Engineering and Applications*, **2011**, *6*, 425- 433.
- 5) Tanger, P.; Field, L. J.; Jahn, E. C.; DeFoort, W. M.; Leach, E. J. Biomass for thermochemical conversion: targets and challenges. *frontiers in PLANT SCIENCE*, **2013**, *4*, 1- 20.
- 6) Butterman, C. H.; Castaldi, J. M. Syngas Production via CO₂ Enhanced Gasification of Biomass Fuels. *ENVIRONMENTAL ENGINEERING SCIENCE*. **2009**, *26*, 703 – 713.
- 7) Wang, L.; Weller, L. C.; Jones, D. D.; Hanna, A. M. Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. *BIOMASS AND BIOENERGY*, **2008**, *32*, 573-581.
- 8) Yan, F.; Luo, S.; Hu, Z.; Xiao, B.; Cheng, G. Hydrogen-rich gas production by steam gasification of char from biomass fast pyrolysis in a fixed-bed reactor:

- Influence of temperature and steam on hydrogen yield and syngas composition. *Bioresource Technology*. **2010**, *101*, 5633 – 5637.
- 9) Xie, R. Y.; Shen, H. L.; Xiao, J.; Xie, X. D.; Zhu, J. Influence of Additives on Steam Gasification of Biomass. 1. Pyrolysis Procedure. *Energy Fuels*. **2009**, *23*, 5199 – 5205.
- 10) Rajvanshi, A. K. *Biomass Gasification. Alternative Energy in Agriculture*, D ed.; Yogi Goswami: Maharashtra, 1986; Vol. 2, pp 83-102.
- 11) Agilent J&W GC Column Selection Guide by Agilent technology, 2007, USA.
- 12) User manual for Agilent 490 Micro GC Biogas Analyzers by Agilent Technologies, Inc. 2012, USA.
- 13) Harris, C. D.; *Quantitative Chemical Analysis*, 7th ed.; Craig Blayer: New York, 2007.
- 14) Instruction manual for 6200 Isoperibol Calorimeter by parr instrument company, USA.
- 15) Konda, R. E.; Sulaiman, S. A.; Ariwahjoedi, B. Syngas production from gasification of oil palm fronds with an updraft gasifier. *Journal of Applied Sciences*. **2012**, *12*, 2555-2561.
- 16) Hollas, M. J. *Modern Spectroscopy*, 4th ed.; John Wiley & Sons: England, 2004.
- 17) Dion, M. L.; Lefsrud, M.; Orsat, V.; Cimon, C. Biomass Gasification and syngas Combustion for Green house CO₂ Enrichment. *BioResources*, **2013**, *8*, 1520-1538.
- 18) Wang, Wei, "A Thermal Conversion Efficiency Study on Biomass Gasification of Arundo Donax and Woodchips" (2013). *Masters Theses*. Paper 1149.

- 19) Melgar, A., Perez, J., & Horrilo, A. Biomass gasification process in a downdraft fixed bed gasifier: a real time diagnosis model based on gas composition analysis. *Rev. Fac. Ing. Univ. Antioquia N.º 49*, **2009**, 9-18.
- 20) Sheldon, A. R.; Chemical Synthesis from Synthesis Gas, d. Rediel publishing company: Venlo, 1983.
- 21) Lu, Y.; Lee, T. Influence of the Feed gas Composition on the Fischer- Tropsch Synthesis in Commercial Operations. *Journal of Natural Gas Chemistry*, **2007**, *16*, 329-341.
- 22) Yao, Y.; Hildebrandt, D.; Glasser, D.; Liu, X. Fischer-Tropsch Synthesis Using H₂/CO/CO₂ syngas Mixtures over a Cobalt Catalyst. *Ind. Eng. Chem.Res*, **2010**, *49*, 11061-11066.
- 23) Kumar, A.; Singh, P. R.; Singh, P. N. Analysis of macro and micro nutrients in some Indian medicinal herbs grown in Jaunpur (u.p.) soil. *Natural Science*, **2011**, *3*, 551-555.
- 24) McKendry, P. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology*, **2002**, *83*, 55-63.
- 25) Kanaujia, K. P.; Sharma, K. Y.; M.O. Garg, O. M.; Tripathi, D.; Singh, R. Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. *Journal of Analytical and Applied Pyrolysis*, **2014**, *105*, 55-74.
- 26) McKendry, P. Energy production from biomass (part 1): gasification technologies. *Bioresource Technology*, **2002**, *83*, 37- 46.

- 27) Couto, N.; Rouboa, A.; Silva, V.; Monteiro, E.; Bouziane, K. Influence of the biomass gasification processes on the final composition of syngas. *Energy Procedia*, **2013**, *36*, 596-606.
- 28) Costa, M.; Massarotti, N.; Cappuccio, G.; Chang, T. C.; Shiue, A.; Lin, J. C.; Wang, T.; Y. Modeling of Syngas Production from Biomass Energy resources Available in Taiwan. *Chemical engineering transactions*, **2014**, *37*, 343-348.
- 29) Cao, Y.; Wang, Y.; Riley, T. J.; Pan, W. A novel biomass air gasification process for producing tar-free higher heating value fuel gas. *Fuel Processing Technology*, **2006**, *87*, 343-353.
- 30) Kumar, A.; Jones, D. D.; Hanna, A. M. Thermochemical Biomass Gasification: A Review of the Current Status of the Technology. *Energies*, **2009**, *2*, 556-581.