

**Experimental Analysis and Modeling of Biomass Gasification using a
Downdraft Gasifier**

by

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Abstract

The call for the use of renewable energy is an urgent one, for not the future but the present. Concerns over depletion of fossil fuels and their negative impact on the global climate have led to much research in this sector. Gasification of biomass for energy production is not only environmentally sustainable but also economically beneficial as it reduces the dependence on imported fuel. Through this thermo-chemical process, biomass is converted into a mixture of combustible gases known as syngas (a.k.a. producer gas) which can be directly used for heat or power, and also synthesized into liquid fuels.

The major objective of this study was to understand the effect of different biomass feedstock on the quality of syngas produced through gasification in a downdraft gasifier. Hardwood, loblolly pine, switchgrass, yellow pine and torrefied pine pellets, pine chips and bark were used as the feedstocks for experiments. Compositions of major gases (H_2 , CO, CO_2 and CH_4) and contaminants (tar and H_2S) were determined, and mass, energy and exergy analyses were performed to substantiate the experimental results. Switchgrass had the highest ash content of 4.66% (d.b.) followed by pine bark (1.59% d.b.) while other feedstocks had lower ash content. Carbon content ranged from 47 to 56% (d.b.), hydrogen from 6.50 to 7.50% (d.b.) and sulfur from 0.32 to 0.40% (d.b.) for all the feedstocks. The higher heating values (HHV) of biomass types ranged from 19 MJ/kg (switchgrass) to 23 MJ/kg (torrefied pine). Syngas obtained from yellow pine showed the highest hydrogen (17.35%) and carbon monoxide (25.05%) fraction and the highest HHV (6 MJ/Nm³), while switchgrass and loblolly pine had significantly lower concentration of H_2 and CO as well as lower HHV. Loblolly pine showed the highest total tar

concentration (2.54g/m^3) along with higher concentration of condensable tar compound, indene ($>0.1\text{ g/m}^3$). The hydrogen sulfide concentration was found to be above 70 ppmv for all the feedstocks, which is higher than the tolerable limit for many syngas applications.

Furthermore, biomass feedstocks that have higher ash content were blended with other lower ash content biomass (switchgrass w/ yellow pine and pine bark w/ pine chips) and similar gasification experiments were carried out. Owing to reduced ash content, gasification of switchgrass/yellow pine blends did not show any ash agglomeration. The hydrogen and carbon monoxide concentrations in syngas obtained from yellow pine/switchgrass blends were higher compared to switchgrass alone, while those from pine chips/bark blends were not significantly different from individual runs. The 75:25 and 50:50 blends of yellow pine and switchgrass showed a total tar concentration of 1.97 g/m^3 and 1.86 g/m^3 , respectively, while the concentrations for the 75:25 and 50:50 blends of pine chips and bark were 1.66 g/m^3 and 1.57 g/m^3 , respectively. The hydrogen sulfide concentration was found to be above 65 ppmv for both the yellow pine/switchgrass and pine chips/bark blends.

In addition, commercial software, Comprehensive Simulator of Fluidized and Moving Bed Equipment (CeSFaMB), was applied to simulate the gasification process. It was able to reproduce the syngas composition within 5-10% deviation for all the major gases except methane. Moreover, a parametric study was conducted to evaluate the effect of factors such as mass flow rate and moisture content of feeding fuel, injected gas/air flow rate, elemental composition and proximate analyses of biomass feedstocks on the program.

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Table of Contents

Abstract.....	ii
Acknowledgments.....	iv
List of Tables	ix
List of Figures	x
1. INTRODUCTION	1
1.1 Rationale	1
1.2 Sources of Biomass.....	2
1.3 Biomass Properties.....	3
1.4 Goals and Objectives	5
1.4.1 Specific Objectives	5
1.4.2 Structure of Thesis	5
1.5 References.....	6
2. LITERATURE REVIEW	8
2.1 Introduction.....	8
2.2 Biomass Energy Conversion: Gasification	10
2.2.1 Drying	11
2.2.2 Pyrolysis.....	12
2.2.3 Char Gasification/Combustion.....	12
2.3 Types of Gasifiers	12
2.3.1 Updraft Gasifier	13
2.3.2 Downdraft Gasifier	14
2.3.3 Fluidized Bed Gasifier	15
2.4 Syngas Quality Considerations	17
2.4.1 Biomass Feedstock.....	17
2.4.2 Moisture Content.....	18
2.4.3 Temperature	19
2.4.4 Equivalence Ratio	20

2.4.5	Particle Size	20
2.5	Syngas Contaminants.....	21
2.5.1	Sulfur.....	21
2.5.2	Nitrogen	21
2.5.3	Chlorine.....	22
2.5.4	Particulate Matter	22
2.5.5	Tar	23
2.6	Comprehensive Simulator of Fluidized and Moving Bed Equipment (CeSFaMB).....	25
2.6.1	Background	25
2.6.2	Working Principle.....	26
2.7	References.....	27
3.	GASIFICATION OF DIFFERENT BIOMASS FEEDSTOCKS	34
3.1	Abstract.....	34
3.2	Introduction.....	35
3.3	Experimental Setup.....	36
3.4	Data Collection	38
3.4.1	Characterization of Biomass	38
3.4.2	Syngas Composition	40
3.4.3	Carbon, Energy and Exergy Analyses	40
3.4.4	Ash Composition Analysis.....	44
3.4.5	Syngas Contaminants.....	44
3.4.6	Experimental Design and Statistical Analysis	47
3.5	Results and Discussion	47
3.5.1	Analyses of Feedstock	47
3.5.2	Gasification Results	50
3.6.2	Carbon, Energy and Exergy Analyses	54
3.6.3	Tar Concentration	55
3.6.4	Hydrogen Sulfide Concentration.....	56
3.7	Conclusions and Remarks.....	57
3.8	References.....	58
4.	GASIFICATION OF BLENDED BIOMASS FEEDSTOCKS	62
4.1	Abstract.....	62

4.2	Introduction.....	63
4.3	Experimental Setup.....	64
4.4	Data Collection	64
4.5	Results and Discussion	65
4.5.1	Analyses of Feedstock	65
4.5.2	Gasification of Biomass Blends.....	67
4.5.3	Carbon, Energy and Exergy Analyses	70
4.5.4	Tar Concentration	70
4.5.5	Hydrogen Sulfide Concentration.....	72
4.6	Conclusions and Remarks.....	74
4.7	References.....	74
5.	COMPREHENSIVE SIMULATOR APPLIED TO DOWNDRAFT GASIFICATION.....	76
5.1	Abstract.....	76
5.2	Introduction.....	77
5.3	Methodology	79
5.3.1	Model Assumptions for a Downdraft Gasifier	79
5.3.2	Program Input	80
5.4	Results and Discussion	85
5.4.1	Calibration of Reaction Kinetics.....	86
5.4.2	Application of Calibrated Program to Other Feeding Fuels	91
5.5	Parametric Study.....	92
5.5.1	Equivalence Ratio (E.R.)	92
5.5.2	Moisture Content.....	93
5.5.3	Biomass Feed Rate.....	94
5.5.4	Properties of Biomass: Proximate and Ultimate Analyses.....	95
5.6	Conclusions.....	97
5.7	References.....	98
6.	SUMMARY AND FUTURE WORK.....	100
6.1	Concluding Remarks.....	100
6.2	Limitations and Recommendations for Future Work.....	101
	APPENDIX A: SUPPLEMENTAL (LABVIEW) DATA FROM GASIFIER	103
A.1	Syngas composition data generated by CAI gas analyzer (torrefied pine pellets).....	103

A.2	Temperature profile inside the reactor (torrefied pine pellets gasification).....	105
APPENDIX B: SAMPLE CALCULATIONS.....		109
B.1	Higher Heating Value (HHV) of Syngas	109
B.2	Carbon, Energy and Exergy Analyses	109
B.2.1	Carbon Conversion	110
B.2.2	Hot and Cold Gas Efficiency	111
B.2.3	Exergy	113
APPENDIX C: TAR COMPOUNDS		115
APPENDIX D: CESFAMB MODEL PARAMETERS.....		116
D.1	Input Parameters	116
D.2	Output Parameters.....	117

List of Tables

Table 1.1 Classification of biomass	2
Table 1.2 Proximate analysis of common biomass (w.b.%)	4
Table 1.3 Elemental analysis of common biomass (as received).....	5
Table 2.1 Syngas composition from different gasifiers	13
Table 2.2 Classification of tar compounds.....	24
Table 3.1 Empirical coefficients of gases	42
Table 3.2 Properties of syngas constituents	43
Table 3.3 Proximate analysis of biomass (d.b.%).....	48
Table 3.4 Elemental (ultimate) analysis of biomass (ash free d.b.%).....	48
Table 3.5 Higher heating value (d.b.) and density of biomass.....	49
Table 3.6 Major inorganic composition (mg/kg biomass).....	50
Table 3.7 Determination of alkali index (AI) and bed agglomeration index (BAI).....	50
Table 3.8 Experimental conditions for different feedstocks	51
Table 3.9 Composition and higher heating value of syngas from different feedstocks	52
Table 3.10 Carbon, energy and exergy analyses of different biomass (%).....	54
Table 4.1 Proximate analysis of biomass blends (d.b.%)	65
Table 4.2 Ultimate analysis of biomass blends (ash free d.b.%)	66
Table 4.3 Higher heating values (d.b.) and densities of feedstock.....	66
Table 4.4 Experimental conditions for different feedstocks	67
Table 4.5 Composition of syngas from different biomass blends.....	68
Table 4.6 Carbon, energy and exergy analyses.....	70
Table 5.1 Gasifier data.....	81
Table 5.2 Characteristics of feeding fuel	82
Table 5.3 Particle size distributions of loblolly, hardwood and switchgrass pellets.....	83
Table 5.4 Particle size distributions of yellow and torrefied pine pellets, and pine chips and bark	84
Table 5.5 Syngas composition (molar d.b. %) produced from loblolly pine pellets obtained during gasification and respective simulation results obtained without calibration	86
Table 5.6 Kinetic parameters of reactions	87
Table 5.7 Syngas composition (molar d.b.%) produced from loblolly pine pellets obtained during gasification and respective simulation results obtained after calibration	87
Table 5.8 Proximate analysis (w.b.%) of switchgrass samples.....	96
Table 5.9 Ultimate analysis (ash free d.b.%) of switchgrass samples	96
Table B.1 Syngas composition (yellow pine) midway through the test.....	109
Table B.2 Properties of syngas constituents.....	112
Table B.3 Empirical coefficients of gases.....	113
Table B.4 Properties of constituent gases.....	114
Table C.1 Retention time of tar compounds.....	115

List of Figures

Figure 2.1 Energy consumption scenario in the United States, 2013	9
Figure 2.2 Updraft gasifier.....	14
Figure 2.3 Downdraft gasifier.....	14
Figure 2.4 Bubbling fluidized bed gasifier	16
Figure 2.5 Circulating fluidized bed gasifier	17
Figure 3.1 BioMax downdraft gasifier.....	37
Figure 3.2 CAI gas analyzer	37
Figure 3.3 Biomass feedstocks used for gasification.....	38
Figure 3.4 Tar collection set up	45
Figure 3.5 Agilent GC FID	45
Figure 3.6 Syngas collection setup for H ₂ S	47
Figure 3.7 Agilent GC FPD	47
Figure 3.8 Effect of E.R. on higher heating value of syngas	53
Figure 3.9 Effect of ash content of biomass on higher heating value of syngas.....	53
Figure 3.10 Tar concentration in syngas from gasification of feedstocks	56
Figure 3.11 H ₂ S concentration in syngas from different biomass feedstock	57
Figure 4.1 Concrete mixer for blending biomass.....	64
Figure 4.2 HHV of syngas from blends of yellow pine and switchgrass.....	69
Figure 4.3 HHV of syngas from blends of pine chips and bark.....	69
Figure 4.4 Tar concentration in syngas from yellow pine/switchgrass blends	71
Figure 4.5 Tar concentration in syngas from pine chips/bark blends	72
Figure 4.6 H ₂ S concentration in syngas from yellow pine and switchgrass blends.....	73
Figure 4.7 H ₂ S concentration in syngas from pine chips and bark blends.....	73
Figure 5.1 Molar fraction profiles of CO, CO ₂ and O ₂ throughout the reactor	88
Figure 5.2 Molar fraction profiles of CO, CO ₂ and O ₂ (Y-logarithmic).....	89
Figure 5.3 Molar fraction profiles of H ₂ O, H ₂ and CH ₄ throughout the reactor	89
Figure 5.4 Reaction rates of homogeneous reactions throughout the reactor	90
Figure 5.5 Reaction rates of reactions throughout the reactor	90
Figure 5.6 Syngas composition: hardwood.....	91
Figure 5.7 Syngas composition: switchgrass.....	91
Figure 5.8 Syngas composition: pine chips.....	91
Figure 5.9 Syngas composition: yellow pine.....	92
Figure 5.10 Syngas composition: torrefied pine.....	92
Figure 5.11 Syngas composition: pine bark.....	92
Figure 5.12 Effect of equivalence ratio on the concentration of syngas constituents	93
Figure 5.13 Effect of moisture content of biomass on the concentration of syngas constituents	94

Figure 5.14 Effect of biomass flow rate on the concentration of syngas constituents	95
Figure 5.15 Simulation of syngas composition from switchgrass samples.....	97
Figure A.1 Hydrogen concentration over time.....	103
Figure A.2 Carbon monoxide concentration over time.....	104
Figure A.3 Carbon dioxide concentration over time.....	104
Figure A.4 Methane concentration over time.....	105
Figure A.5 Temperature profile recorded by thermocouple T1.....	105
Figure A.6 Temperature profile recorded by thermocouple T2.....	106
Figure A.7 Temperature profile recorded by thermocouple T3.....	106
Figure A.8 Temperature profile recorded by thermocouple T4.....	107
Figure A.9 Temperature profile recorded by thermocouple T5.....	107
Figure A.10 Temperature profile recorded at grate.....	108

CHAPTER ONE

INTRODUCTION

1.1 Rationale

Biomass can be a viable replacement of fossil fuels whether it is used as a feedstock for fuels, materials or chemicals production. Although fossil fuels such as oil, coal and gas are easily available and provide a large share of energy at present. However, their finite and non-renewable nature makes them unreliable for the distant future. Adverse effects of fossil fuel use on the environment and high dependence on foreign oil have shifted the focus on to alternative sources of energy. Not only does biomass reduce dependence on imported fuel, it also does not contribute any net carbon to the atmosphere. The Energy Independence and Security Act (EISA) of 2007 has mandated that by 2022, the transportation fuels in the United States must contain at least 36 billion gallons of renewable fuels [1]. Under Title II of the same act, energy security through increased production of biofuels has been significantly emphasized. Development of cellulosic biofuels has been greatly focused to ensure availability of adequate feedstocks to sustain a bioenergy industry.

The purpose of gasification is not just conversion of solid or liquid fuel into syngas; production of chemical feedstocks is also an important application. Another major attraction is the conversion of low cost, and at times waste biomass into high value fuels. Hence, biomass gasification for production of liquid transportation fuels and synthetic chemicals (such as methanol) has been the subject of much research. The process needs to overcome barriers such as

removal of tars and contaminants, issues related to production, logistics, and pretreatment of biomass feedstocks [2]. Production of quality syngas is the most crucial aspect of gasification. The composition and quantity of syngas mainly depends on biomass properties and gasifier operating conditions [3].

1.2 Sources of Biomass

Basically, biomass is grouped according to the sources which include all plants and plant-derived materials. Table 1.1 shows the two major groups of biomass and their subdivisions. Most common sources are from agricultural and forestry operations.

Table 1.1 Classification of biomass [4]

Virgin	Waste
<p><i>Terrestrial:</i> Forest wood, plants and leaves (lignocellulose), grasses, cultivated and energy crops</p> <p><i>Aquatic:</i> Algae, water plant</p>	<p><i>Municipal waste:</i> Solid wastes, sewage landfill gas</p> <p><i>Agricultural solid waste:</i> Livestock manure, crop residue</p> <p><i>Forestry residues:</i> Bark, leaves</p> <p><i>Industrial wastes:</i> Sawdust, waste oil or fat</p>

There is a growing interest in cultivation of lignocellulosic biomass such as miscanthus, switchgrass, willow, and poplar for the sole purpose of energy production [4]. In addition to having a short growth period and high yields, they usually require little to no fertilizer at all, thus providing a quick return on investment. Lignocellulosic material is the non-starch, fibrous part of plants and trees which is not consumable, and thus, its use for bioenergy does not affect the food supply. Short rotation crops of hardwood tree and conifer species in temperate regions have been studied for feasibility of energy plantations [5]. Loblolly pine (*Pinus taeda L.*) is one of the few species that has shown strong economic potential through its rapid growth and established

genetic improvement [1]. According to recent research, advances in loblolly pine breeding and selection has substantially improved the species' productivity for use as bioenergy feedstock [6].

1.3 Biomass Properties

Being derived from diverse sources, biomass materials do not have single unique property that make them suitable for thermal conversion processes. All physical, chemical and biological properties are taken into account and almost always the biomass needs to undergo pretreatment or preprocessing [7]. Physical properties basically deal with geometric and gravimetric characteristics such as shape and size, surface area, density and volume, porosity, etc. of biological materials [8]. The most important physical properties include particle and bulk density, particle size and particle size distribution. In terms of thermal processes, the proximate and ultimate analyses, and the heating values are most significant. For biomass with high ash content such as switchgrass, the fusion temperature or the eutectic point is an essential factor related to slagging and fouling problems in biomass thermal conversion equipment. For biological or biochemical conversion, the amount of lignin, carbohydrates and extractives are important factors.

Particle and bulk density: Particle density is the measure of the biomass particle mass per unit volume (kg/m^3 or lb/ft^3) occupied by that particle. It includes the volume of all closed pores with the exception of externally connected pores [9]. The measure of bulk density however, includes the void spaces occupied by the biomass. Depending on the species and form, woody biomass has a wide range of density. For example, hardwood (oak) chips has a bulk density of roughly 200 kg/m^3 [3] while dry wood shavings' bulk density is about $80\text{-}100 \text{ kg/m}^3$ [7].

Particle size and particle size distribution: Almost all types of biomass materials need to be size-reduced after being harvested before they can be used in any conversion process. Particle

size of solid fuels largely influences the residence time and the reactions taking place during gasification [10]. In general, biomass materials are ground to less than 10 mm in size for various conversion processes and their particle size distribution is measured using standard sieves [7].

Heating value analysis: It is one of the most important characteristics of biomass which basically gives its energy content. By using a calorimeter, the biomass is combusted in pure oxygen and the energy released during that process is measured. This value is highly dependent on the presence of moisture in biomass. It is recommended to report the heating value of feedstock on dry basis (excludes moisture).

Proximate analysis: It includes the measurement of moisture content, volatile matter, fixed carbon and ash. Moisture is very critical for biomass transportation as well as for any conversion process. In most cases, drying is a pre-requisite since moisture content can be as high as 99% for some aquatic biomass such as algae. Volatiles lead to more combustible gases during thermal conversion. Ash is an inorganic constituent of biomass which contributes to adverse effects such as fouling, agglomeration and slagging in reactors, furnaces and other equipment. Table 1.2 shows the proximate analysis and higher heating value of selected biomass feedstocks.

Table 1.2 Proximate analysis of common biomass (w.b.%) [11]

Biomass	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed Carbon (%)	HHV (MJ/kg)
Corn stover	9.9	5.7	70.7	13.7	15.6
Softwood chips	10	0.3	78.5	11.2	19.4
Switchgrass	9.3	3.6	76.3	10.7	19.8
Cotton gin trash	10.6	6.9	66.7	15.7	17.9
Coconut shells	11.2	0.8	72.7	15.3	20.6

Ultimate analysis: It refers to elements in biomass such as carbon (C), hydrogen (H), nitrogen (N) and sulfur (S). The oxygen (O) content is a calculated value and is the difference between

100% and the sum of the previous elements. Ultimate analysis of common biomass is shown in Table 1.3.

Table 1.3 Elemental analysis of common biomass (as received) [11, 12]

Biomass	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)
Alabama oak	49.5	5.7	0.2	0.0	41.3	3.3
Softwood chips	46.1	6.6	0.2	0.1	46.6	0.4
Switchgrass	42	6.1	0.4	0.1	57.4	4.0
Pine bark	52.3	5.8	0.2	0.0	38.8	2.9
Coconut shells	46.9	6.1	0.3	0.2	45.7	0.9

1.4 Goals and Objectives

The overall goal of this research was to evaluate the effect of different biomass types in gasification, and validate the commercial software - Comprehensive Simulator for Fluidized and Moving Bed Equipment (CeSFaMB), for simulation of a gasification process.

1.4.1 Specific Objectives

- To study the effect of different biomass types and form on syngas composition and contaminants;
- To evaluate the effect of biomass blends having different ash contents on syngas composition and contaminants;
- To simulate the gasification process of different biomass feedstocks using CeSFaMB and compare the model results with experimental; and
- To identify the effect of key parameters such as equivalence ratio, biomass feed rate and moisture content on the model.

1.4.2 Structure of Thesis

The thesis has been organized into chapters in order of the studies that were carried out. A brief description of the remaining chapters is as follows:

- Chapter two comprises the literature review carried out beforehand in order to develop fundamental understanding of the processes that will be applied in this study. It also includes the present scenario in the field of gasification along with description and results from some of the most important studies performed.
- Chapter three covers the experimental study of gasification performed using different biomass feedstocks in a downdraft gasifier. It includes results and analyses from characterization of biomass, composition, heating value and contaminants of syngas, and mass and energy balances.
- Chapter four encompasses the experimental study of gasification using blended biomass feedstock. The methodology and analyses carried out were the same as in chapter three.
- Chapter five incorporates the application of CeSFaMB, the software to simulate the gasification process using the feedstocks discussed in chapter three.
- Appendices include sample calculations, tabulated data for figures and additional information from the downdraft gasification process.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Two phrases synonymous with the world's present energy scenario are energy conservation and environmental impact. Driven by industrial growth in the developing countries, the world energy consumption is expected to increase by 56% over the next three decades [1]. It was highlighted in the International Energy Outlook 2013 report [1] that renewable energy and nuclear power are the world's fastest-growing energy sources, both increasing by 2.5 % every year. However, fossil fuels would continue to supply almost 80 percent of the world energy use through 2040.

Depletion of conventional fossil fuels, which have proved to be hazardous to the environment, has led to much research on finding better alternatives. There have been some vivid changes in the energy market over the last decade. After the oil prices skyrocketed in 2008, there was a lot of speculation of renewable energy sources taking over a larger share of the energy consumption. However, by the end of the same year, the oil prices plummeted and the exponential growth of renewable energy was not actually realized. Even so, the growth of the renewable energy sector has been slow yet steady. Research and development efforts have been focused on different renewable resources owing to dwindling fossil fuels, need of energy security and environmental concerns [2].

Biomass refers to a variety of living species, from grasses to trees, from insects to animal wastes and the products derived from these [3]. Primary sources include forest- and agriculture-derived

biomass, such as logging residues, biomass from forest thinnings, crop residues, and perennially grown grasses and trees. They are known to have the greatest potential to supply large and sustainable quantities of biomass [2]. Biomass, if converted into energy through a pathway that is economical and efficient, has shown promising future. It could help in promoting energy independence, economic growth and reducing the negative impact to the environment. The health impact of air pollution is a significant problem in the developing countries, where fuel wood is burnt inefficiently in open fires for domestic cooking and space heating [4].

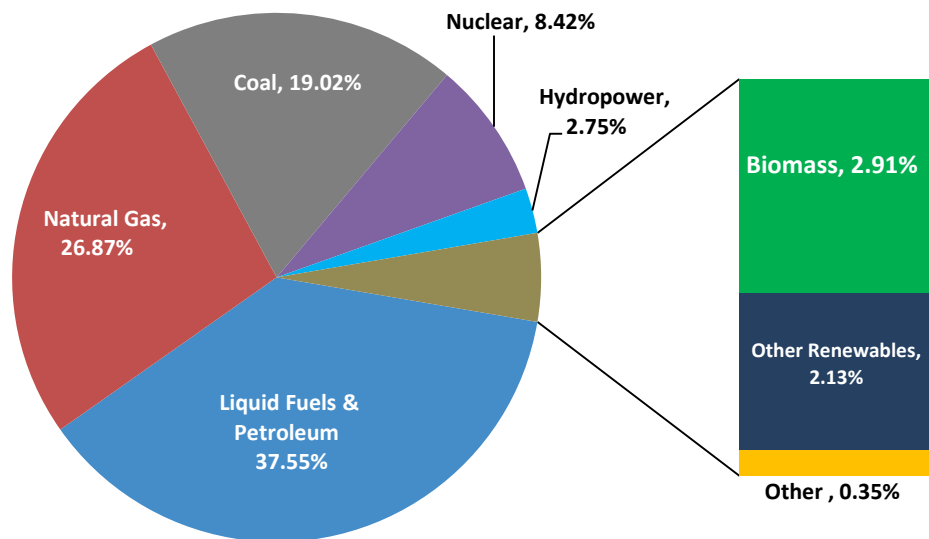


Figure 2.1 Energy consumption scenario in the United States, 2013 [1]

The use of biomass for power supply has been extensive in the developing countries, especially in remote areas untouched by the grid. For renewable energy utilization and solving partially the environmental issues, biomass energy has been marked as an economical and efficient alternative to conventional fuel sources [5]. As shown in Figure 2.1, biomass currently accounts for approximately 3% of the total energy consumption in the United States. Moreover, the supply of biofuels is projected to rise from 1 million barrels/day in 2010 to 3.4 million barrels/day in

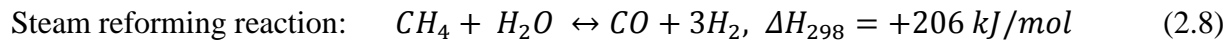
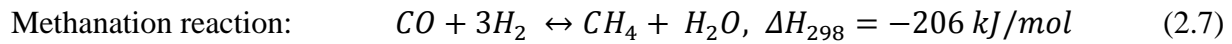
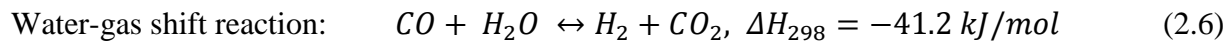
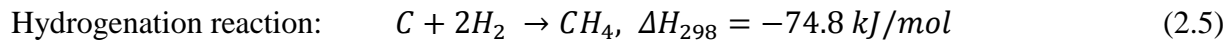
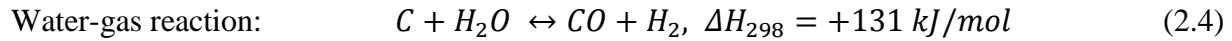
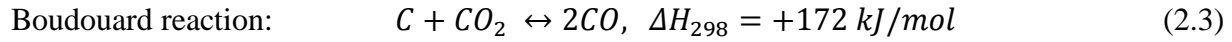
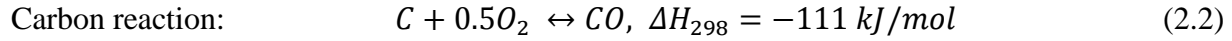
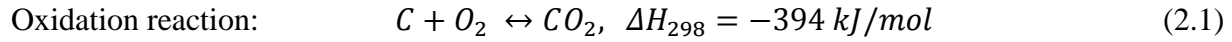
2035, meeting 37% of road transport demand in Brazil, 19% in the US and 16% in the European Union [6]. Efforts to produce more ethanol from nonfood resources (lignocellulosic materials) are being made so as not to hamper the food supply in any way [3].

2.2 Biomass Energy Conversion: Gasification

Basically, there are four biomass conversion technologies: direct combustion, thermochemical process, biochemical process and chemical conversion process. Among them, the thermochemical conversion process which includes gasification and pyrolysis has been extensively studied and proven to have a promising future. Biomass gasification has been studied to show higher efficiencies among the thermochemical processes and is attracting a lot of research interest [7]. Gasification is a partial combustion process which converts solid carbonaceous fuel into a mixture of combustible gas, primarily carbon monoxide, hydrogen, methane, carbon dioxide and nitrogen. This gas mixture, known as syngas (or producer gas), can be used for fuel or power production [8]. One of the major advantages of syngas is that it burns more efficiently, with fewer emissions, thus giving it an edge over direct combustion of biomass. It also means that syngas can be run directly into engines or turbines for transportation or power generation.

The process of gasification comprises of a series of high temperature conversions of the carbonaceous material, some of which are presented in Equations 2.1-2.8. The major difference between gasification and combustion is that the former packs energy into chemical bonds in the product gas while the latter breaks those bonds to release the energy. A typical gasification process follows the sequence of dehydration or drying, thermal decomposition or pyrolysis, partial combustion and finally reduction of decomposition products [3]. The process requires a

gasifying medium like air, steam or oxygen to convert the solid feed into gases or liquids, at the same time adding hydrogen to the product.



Exothermic reactions (2.1) and (2.2) are allowed in the gasifier to provide the required heat for drying and pyrolysis. But the extent of these reactions depends on temperature [3]. The processes that occur during gasification are described in detail as follows:

2.2.1 Drying

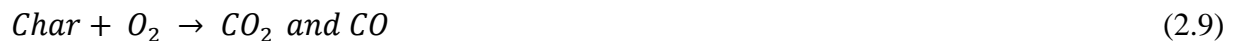
Pre-drying of biomass is necessary to remove as much moisture from the biomass as possible to obtain a fuel gas with high heating value [9]. The feed is dried completely as it enters the gasifier where it receives heat at 100°C from the hot zone downstream. As the temperature rises, the low molecular weight extractives start volatilizing until the temperature of approximately 150-200°C is reached.

2.2.2 Pyrolysis

It occurs between 200 and 700°C depending upon the amount of oxygen present in the gasifier. Larger hydrocarbon molecules in the biomass feed are thermally broken down into smaller gas molecules (H₂, CH₄ and tars) and solid carbon residue (char) [10]. Tar is basically a sticky liquid formed through condensation of condensable vapor produced during the process. Cracking or reforming of tar is an important aspect alongside this process since it creates a nuisance in industrial applications of the end use products. To some extent, the volatiles and char react with oxygen to form carbon dioxide and release heat which is required to sustain the pyrolysis process and cause subsequent thermochemical reactions.

2.2.3 Char Gasification/Combustion

The oxygen or gasifying medium supplied to the gasifier allows further chemical reactions among the hydrocarbons in the fuel as well as the gases formed during pyrolysis. Among them, char-oxidation is considered to be the most significant for gasification. Biomass char contains a certain amount of hydrocarbon and is generally more porous and reactive than coke. Gasification of char involves several reactions, some of which are mentioned as follows [3]:



2.3 Types of Gasifiers

Developing appropriate gasifiers that can process variety of biomass feedstocks to produce high quality syngas is crucial for meeting industrial demand. In the late 1970s, Payne et al. [11] discussed three types of gasifiers – updraft, downdraft and cross-draft, based on the agricultural

applications at the time. Broadly, gasification systems can be classified into three categories: moving bed, fluidized bed, and entrained flow [12]. Moving bed, sometimes also referred to as fixed bed, gasification is the oldest and simplest of all gasification technologies and is generally more suitable for heat applications (<10 MWt) and small-scale energy generation (<1 MWe) [13]. Among the types of available gasifiers, studies have shown that downdraft, updraft, bubbling bed, circulating fluidized bed and entrained flow gasifiers are the most common ones [14]. Furthermore, fluidized bed gasifiers can be classified into bubbling bed and circulating fluidized bed gasifier. Table 2.1 shows the syngas composition from different types of gasifiers found in literature. Sheng [15] introduced the properties of biomass gasifier and the gasifying reaction processes. Unusable or low-value wastes, such as sawdust, wood chips, corn cobs, nut shells, rice hulls, etc., can be used in a biomass gasifier to produce syngas. It was concluded that the gas produced by downdraft gasifiers is tar-free and could be used directly to drive most of the internal combustion engines.

Table 2.1 Syngas composition from different gasifiers

Type of gasifier	Biomass used	Syngas concentration (%)				References
		H ₂	CO	CO ₂	CH ₄	
Updraft	Furniture wood chips	15.4	29	6.8	1.6	Kurkela et al [16]
Downdraft	Commercial wood pellets	11.9	25.7	9.9	2.6	Erlich and Fransson [17]
Downdraft	Pine bark	5.3	9.55	15.7	0.24	Perez et al [18]
Bubbling fluidized bed	Woody biomass	14.5	13.8	16	4	Kim et al [19]

2.3.1 Updraft Gasifier

In updraft gasifiers, the feedstock is fed from the top while the gasifying medium (air) enters from the bottom. The product gas rises through a bed of descending fuel in the chamber and leaves from the top as shown in Figure 2.2. As air moves upward, it meets hot ash and unconverted chars descending from the top. High temperature in the bottom layer allows rapid

combustion, consuming most of the oxygen. As the available oxygen is reduced further up, the combustion reaction changes into partial combustion, thus releasing CO and a moderate amount of heat. Thus, it effectively utilizes combustion heat and achieves high cold gas efficiency. It is more suitable for direct firing where the gas is burnt in a furnace or boiler with no cleaning or cooling required. These gasifiers can handle high ash (up to 25%) and high moisture (up to 60%) biomass [13].

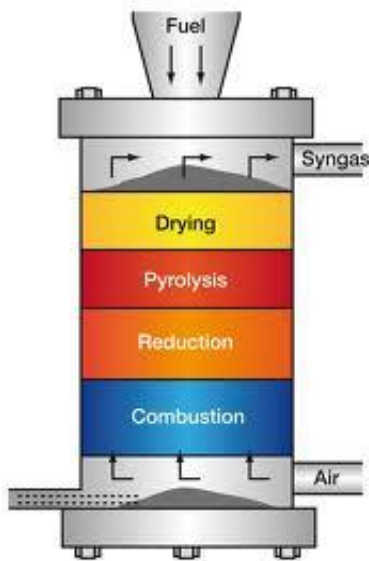


Figure 2.2 Updraft gasifier [20]

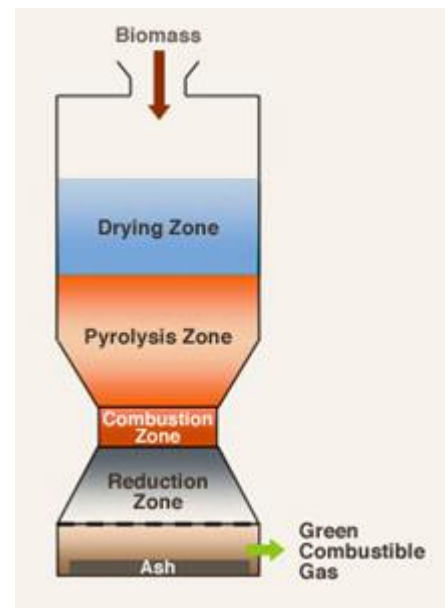


Figure 2.3 Downdraft gasifier [21]

2.3.2 Downdraft Gasifier

In downdraft gasifiers, the gasifying medium is injected from the top of the chamber along with the biomass, and the syngas is pulled out from the bottom portion. Pyrolysis and combustion products flow downward, where the hot gas reacts with the remaining char resulting in gasification. Figure 2.3 shows a throated downdraft gasifier which forces all the pyrolysis gas to pass through the narrow combustion zone. The high temperature zone of hot ash near the bottom

provides favorable conditions for tar cracking, resulting in lower tar production as compared to other gasifiers. Stratified throatless or open top gasifiers have vertical walls throughout the reactor, without any constriction in the vessel. Downdraft gasifiers are preferred for small scale power generation. The moisture content of fuel needs to be lower than 25%. Although the quality of produced syngas is quite high, the heating value is lower as compared to that from an updraft gasifiers.

2.3.3 Fluidized Bed Gasifier

Fluidized bed gasifiers generally contain bed materials made of granular solids that are fluidized with a gasifying medium at certain velocities. These gasifiers are known for excellent mixing and temperature uniformity throughout the reactor [22]. There are basically two types of fluidized bed gasifiers: bubbling and circulating.

In a bubbling fluidized bed gasifier, the fuel is fed from either the top or the sides and the bed material like sand/silica is fluidized with gasifying medium. As seen in Figure 2.4, the air is introduced through the grate at the bottom of the vessel. The biomass is pyrolyzed in the hot bed to form char with gaseous compounds and high tar cracking is fairly achieved [9]. It allows higher rates of throughput which results in good mixing and heat transfer. It is also known to have higher carbon conversion rate and the syngas is rich in particulates [3].

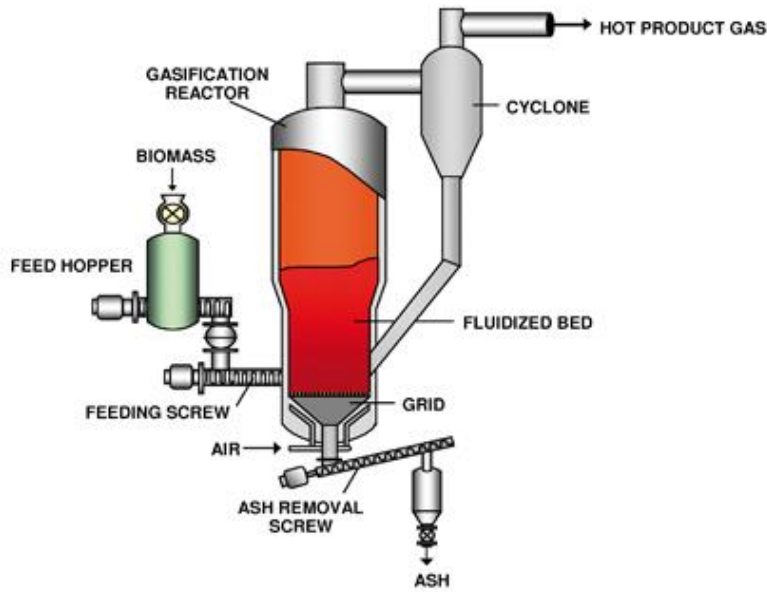


Figure 2.4 Bubbling fluidized bed gasifier [23]

Circulating fluidized bed gasifiers provide long gas residence time, which is suitable for fuels with high volatiles. Cyclones and other separators are employed in CFBs to capture and recycle solids to extend their residence time [24]. The fluidization velocity in CFB is much higher (3.5-5.5 m/s) than that in a bubbling bed (0.5-1.0 m/s). The bed material is circulated between the reaction vessel and a cyclone separator, where the ash is removed as shown in Figure 2.5, and the bed material and char returned to the reaction vessel. Owing to advantages in terms of mass conversion efficiency and higher quality syngas, many commercial gasifiers of this type have been installed in the paper industry for gasification of bark and other forest residues around the world [22, 9].

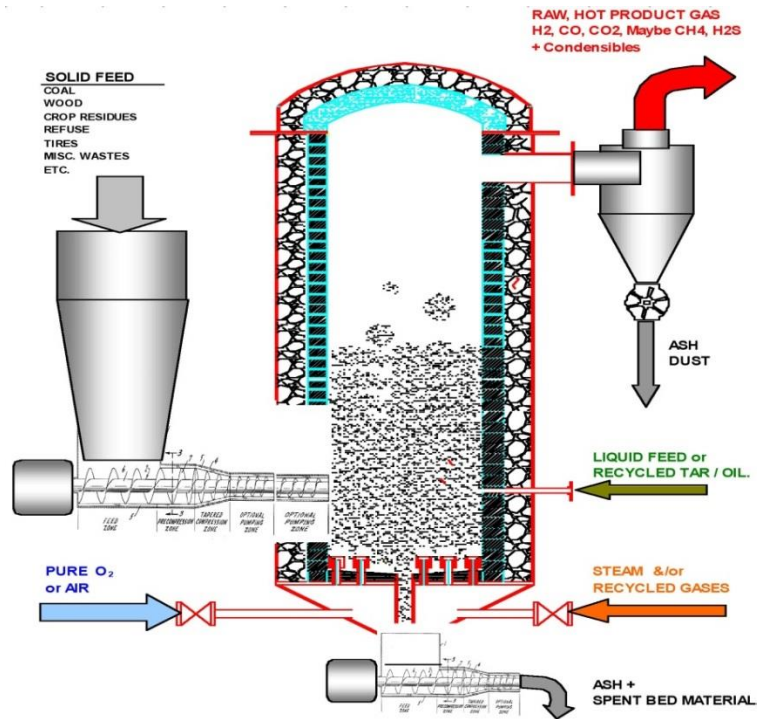


Figure 2.5 Circulating fluidized bed gasifier [25]

2.4 Syngas Quality Considerations

For any biomass gasification system, syngas composition varies with different operating conditions, gasifier type, feedstock and gasifying medium [26]. Other output parameters that are affected by operating conditions include carbon conversion, tar formation and reduction, and energy efficiency. Zainal et al. [5] reported the average gas composition of syngas as: 14% H₂, 24% CO, 15% CO₂, 2% CH₄ and 44% N₂ from downdraft gasification of wood chips. The effect of various parameters affecting the syngas quality and the gasification process are discussed in the sections below:

2.4.1 Biomass Feedstock

Physicochemical properties of biomass such as shape, size, porosity, and chemical compounds contained largely affect the gasifier's performance. The feedstock that have too small size, low porosity may cause some problems such as feedstock bridging, lumping, collapsing or clogging

inside the reaction chambers of fixed-bed downdraft gasifiers during gasification. Fluidized bed gasifiers have higher throughput capacity but they only allow use of feedstock with less than 0.15 mm particle size [22]. Chopped switchgrass has similar ash content and elemental composition as most of the crop residues [27]. But its low bulk density poses major challenge to ensure proper material flow in the reactor and the hopper. Patil et al. [28] used agitators to facilitate the material flow in the biomass hopper and the gasification reactor. Lucas et al. [29] carried out gasification of wood pellets using preheated air and vapor as gasifying agents. It was observed that as temperature increased, the performance and the lower heating value of the produced dry combustible gas also increased.

Updraft gasifiers can handle feedstock with wide variation in particle size [13]. No significant differences in composition, heating value, tar and particle concentrations were observed in syngas produced from gasification of hardwood chips, softwood chips, and switchgrass pellets with a pilot scale (15 kW) fixed-bed downdraft gasifier [10]. Gasification of hardwood chips mixed with 20% of liquid crude glycerol in a downdraft gasifier produced syngas with significant higher CH₄ content, low heating value and tar concentration than those of regular hardwood chips [30]. Moutsoglou [31] used a bubbling fluidized bed gasifier for gasification of cordgrass and switchgrass, the latter showing greater concentration of hydrogen and carbon monoxide.

2.4.2 Moisture Content

High moisture content is known to be detrimental to gasification process but drying prior to gasification increases overall gasification efficiency. Zainal et al. [32] used an equilibrium model for gasification of wood chips and predicted an increase in hydrogen percentage from 20 to 25% for increase in moisture content from 0 to 40%. At the same time, CO reduced from about 28%

to 15% for the same variation of moisture content. Owing to water-gas shift reaction, higher moisture content leads to increase in CO₂ concentration as well as H₂ concentration. Moreover, a consequent decrease in temperature improves the water-gas shift reaction and forms more CO₂. The small gain in H₂ (as well as CH₄) is not sufficient to compensate the loss of significant amount of CO. As a result, the calorific value and exergy of the gas decreases almost linearly with increase of moisture in biomass [33, 34]. The constraint of moisture content of feedstock depends on gasifier types, with updraft gasifiers allowing biomass with higher moisture content. But the acceptable upper limit for downdraft gasifiers is around 40% (d.b.) [35].

2.4.3 Temperature

Operating temperature has a significant impact on the output of syngas and biomass gasification on the whole. Li et al. [36] observed an approximately 10% increase in HHV of syngas for an increase in operating temperature from 700 to 800°C. Amount of CO increases with increase in temperature because endothermic reactions like the Boudouard reaction are more favored at higher temperatures [37]. Increase in temperature reduces the tar content as well as decreases char inside the gasifier, which eventually leads to increase in gas yield due to higher tar cracking. Depending upon the type of gasifier, tar cracking temperatures are usually around 1000-1100 °C [38]. Hernandez et al. [39] reported that the decrease in tar production in the case steam gasification was non-linear and much more notable when increasing the temperature from 750 to 1050°C than an increase from 1050 to 1200°C. However, for gasification with air/steam mixture, the reduction of tar was significant only at temperatures higher than 1050°C.

Temperature of the reactor is basically an output variable which depends on factors like moisture content of feedstock, air flow, amount of steam added, and heat loss from the system [40]. It has

been well observed that the gasification process can benefit from better thermal insulation and preheating of air or gasifying medium.

2.4.4 Equivalence Ratio

Equivalence ratio (ER) is the ratio of the actual amount of air used during gasification process to the total amount of air required for complete combustion. An ER plays a critical role in accelerating pyrolysis and fast heat transfer, thus affecting the biomass consumption rate [8]. Due to the amount of oxygen and ash elementally present in the biomass, the optimum ER varies for different types of biomass. Gautam et al. [41] reported that an increase in ER increases the temperature inside the gasifier while decrease in ER increases char formation. Zainal et al. [5] suggested an optimal equivalence ratio of 0.38 after variation of the calorific value of syngas was observed around that peak value. Sharma et al. [42] reported gas composition of H₂ (9.3±0.8 %) and CO (16.5±1.1 %) at optimum ER of 0.32 from gasification of switchgrass in a fluidized bed gasifier. However, a low ER of 0.2 was reported to be optimum by both Skoulou et al. [43] and Sheth et al. [8] for downdraft gasification of olive kernels and tree cuttings and furniture wood, respectively.

2.4.5 Particle Size

Arising questions on the effects of biomass particle size on the combustion behavior have led to much research work on assessing the optimum pellet size from technical and economic point of view [44]. Pinewood fuel is easy to prepare and can be preprocessed into different sizes and shapes and is a good simulation of pelletized biomass fuels. Erlich et al. [45] carried out pyrolysis and gasification of wood and sugarcane bagasse pellets of different shapes and sizes. They concluded that the rate of gasification is slower for bigger pellets, while the size has little impact on pyrolysis. It was also found that bagasse was less reactive than wood. Horttanainen et

al. [46] experimented with pellets and mixtures of woodchips and sawdust and showed that the range of usable airflow rates increased when the density and size of particles increased. They also found that the mixture between small and large particles was advantageous for combustion.

2.5 Syngas Contaminants

Biomass feedstock contains inorganic impurities like sulfur, nitrogen, chlorine and ash which eventually find their way into syngas and interfere with downstream applications. Moreover, undesirable organic compounds (tar) and particulate char are also found in raw syngas in cases of incomplete gasification [47].

2.5.1 Sulfur

Hydrogen sulfide (H_2S) is the most commonly occurring sulfur contaminant in syngas, followed by carbonyl sulfide (COS) in somewhat lesser amounts. Biomass has significantly less sulfur than coal, containing only 0.1-0.5 g/kg compared to as much as 50 g/kg for some coal-derived syngas [48]. In some biomass, especially few grasses, the sulfur content can exceed 1 g/kg [49, 50]. The primary concern with sulfur contaminants is corrosion of metal surfaces, which basically means the electrochemical oxidation of metals. It also causes catalyst poisoning, and pollution when oxidized to sulfur dioxide (SO_2) [51]. Sharma et al. [42] reported sulfur concentration of less than 0.3% (d.b.) in switchgrass. Sulfur removal to parts per billion levels is often required since even small amounts can poison catalysts used to produce liquid fuels from syngas [51].

2.5.2 Nitrogen

Nitrogen contaminants in syngas usually occur as ammonia (NH_3) with trace amounts of hydrogen cyanide (HCN) [47]. Protein structures or aromatic compounds in the feedstock release

nitrogen in the pyrolysis stage of gasification and combustion [52]. Intrinsic properties such as nitrogen content and particle size of fuel as well as operating conditions determine the amount of NH_3 and HCN released. Although the nitrogen content of many biomass feedstocks can produce ammonia concentrations of several weight percent, up to two thirds of this ammonia decomposes to molecular nitrogen at typical gasification temperatures [47]. Thus, the concentration of ammonia is no more than several hundred to a few thousand parts per million. Even these low concentrations can be detrimental in applications like gas turbines, which demand ammonia concentrations less than 500 ppm [53]. Gautam et al. [41] reported high nitrogen content of 3.39% (d.b.) for poultry pellets while that for sawdust and peanut hull pellets ranged from 0.34-0.82%.

2.5.3 Chlorine

Chlorine in biomass occurs as alkali metal salts, which readily vaporize in high temperature environment of gasifiers and react with water vapor to form HCl [54]. Chlorine levels as low as $0.024 \mu\text{L L}^{-1}$ can create serious problems like hot corrosion of gas turbine blades [55]. Reactions occurring between HCl and other contaminant species create compounds such as NH_4Cl and NaCl , which can cause fouling and create deposits when they condense in cooler downstream piping and equipment.

2.5.4 Particulate Matter

Inorganic compounds and residual solid carbon from the gasification of biomass constitutes the bulk of the particulate matter. The inorganic content includes alkali metals (K, Na), alkaline earth metals (Ca), silica and other metals such as iron and magnesium. Many syngas applications require greater than 99% particulate removal [47]. Common issues with particulate matter are fouling, corrosion and erosion, which can cause efficiency and safety concerns [56]. Fouling in

gasification usually occurs when small amounts of inorganic components and volatile species are condensed and deposited on refractory or heat transfer surfaces. Fouling deposits are formed mainly in the convective parts of the reactor [57]. Erosion is a direct result of the gradual layer-by-layer destruction of metallic surface due to corrosion.

2.5.5 Tar

Tars are condensable organic compounds (with molecular weight larger than benzene) which vary from primary oxygenated products to heavier deoxygenated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) [48]. Among several contaminants of syngas, tars are the main technical hurdle for commercial implementation of biomass gasification [58]. Tar condensation causes plugging and fouling problems in engines while tar polymerization at high temperatures produces polycyclic compounds and soot [59].

Thermochemical conversion creates a large number of tar species in response to the operating parameters, which can be differentiated as shown in Table 2.2. Mostly, tars of class 1, 4 and 5 are responsible for severe fouling and clogging in gasification systems because they readily condense even at high temperatures [60]. Particularly, the most important operating parameters are feedstock composition and processing conditions, especially temperature, pressure, type and amount of oxidant and feedstock residence time. Furthermore, a downdraft gasifier is known to yield lesser amount of tar as compared to an updraft gasifier. The compounds are grouped into primary, secondary and tertiary tars. Primary tars are organic compounds released from devolatilizing feedstock. Higher temperatures and longer residence times result in secondary tars, including phenolics and olefins. Further increase in reaction time and temperature leads to formation of tertiary tars, such as PAHs [49].

Table 2.2 Classification of tar compounds [61]

Class	Description	Properties	Representative compounds
1	GC-undetectable	Very heavy tars	Determined by subtracting the GC-detectable tars from the total gravimetric tar
2	Heterocyclic aromatics	Tars containing hetero atoms, highly water soluble	Pyridine, phenol, quinolone, dibenzophenol cresols
3	Light aromatic (1 ring)	Light hydrocarbons, no problem regarding condensation or solubility	BTEX compounds like toluene, ethylbenzene, xylenes, styrene
4	Light PAH compounds (2-3 rings)	Condense at low temperatures even with low concentrations	Indene, naphthalene, biphenyl, fluorine, phenanthrene, anthracene
5	Heavy PAH compounds (4-7 rings)	Condensation at high temperatures even with low concentrations	Fluoranthene, pyrene, chrysene, perylene

Tar analysis

Many institutes around the world have been developing on-line and off-line methods for the sampling and analysis of tars for a few decades. The most common methods of analysis are gas chromatography (GC) and gravimetric analysis (which involves weighing of collected tars, after careful evaporation of the solvent and condensed water). The sampling part is based on trapping the tar by condensation on cold surfaces or filters, by absorption in a cold organic solvent or by adsorption on suitable sorbents. The European tar protocol has been widely accepted as the “tar standard” to provide technical specifications for sampling and analysis of tars. This guideline was designed to provide a consistent basis of tar measurement globally among researchers [62, 63]

European tar protocol

Given the diversity of methods and definitions for organic contaminants and their resulting problems, the members of the Gasification Task of the IEA Bioenergy Agreement, the US DoE and DGXVII of the European Commission jointly came up with two sampling and analysis protocols; one to be used for small scale, fixed bed, engine-based systems and the other for larger utility scale plants. Known as the Wurzburg Protocols (discussed in the 10th European Biomass Conference in Wurzburg), they were further developed and standardized into one ‘Tar Protocol’ by the EU fifth framework project [64, 65]. The guideline provides a set of procedures for the measurement of organic contaminants and particles in producer gases from biomass gasifiers. These procedures are designed to cover different gasifier types such as updraft and downdraft fixed bed, and fluidized bed gasifiers and operating conditions and concentration ranges.

2.6 Comprehensive Simulator of Fluidized and Moving Bed Equipment (CeSFaMB)

2.6.1 Background

Operations of gasifiers or any other similar equipment dealing with combustion or gasification phenomena involve a number of simultaneous processes, such as heat, mass and momentum transfers; chemical kinetics of several homogeneous and heterogeneous reactions; drying, pyrolysis, etc. Several mathematical models have been built for such equipment and they continue to provide excellent reproductions and predictions of industrial scale operational conditions. The present comprehensive mathematical model and simulation program is an optimum compromise in simulation accuracy, computational resources and processing time [66]. The first successful version of CeSFaMB (previous acronym CSFB) came out in 1987 which was capable of reproducing operational conditions of Babcock and Wilcox boiler unit in USA as well operations of National Coal Board (UK) boilers [67]. Since then the software’s mathematical

model and respective simulation program has improved constantly and been applied to various classes of equipment consuming a wide range of fuels [68, 69, 70]. De Souza-Santos [71] carried out simulation tests with a gasification unit at University of California at Davis and reported that the concentration of species in the produced gas and temperature profiles within the bed were simulated within acceptable deviations.

Enden and Lora [70] applied the CSFB code for the design of a 250 kW thermal output laboratory gasifier for sugarcane bagasse and explained the relation between the performance and the operational and design parameters. The simulator also evaluated other values assumed or calculated in the preliminary sizing, such as the pressure drop in the bed, composition of producer gas, bubble diameters and gas velocities in the bed. Yang et al. [72] studied the combustion process of wood chips in packed beds through experimentation and modeling. They also reported the effect of de-volatilization kinetics, fuel moisture content, primary air rate, fuel heating value, fuel size and density, and bed void fraction on the biomass combustion process.

2.6.2 Working Principle

The model assumes all variable changes occurring in the vertical direction. The one-dimensional approach is followed in almost all modeling of gas-solid packed systems [66, 73]. It is believed to provide the highest cost-benefit ratio among all possible levels of modeling. It has been successfully adopted by many, especially for moving bed gasifiers or combustors [73, 74]. Though it may seem simple initially, the first order model assumption for such reactors may involve up to five physical phases, chemical reactions in all phases, dynamics of each phase, heat and mass transfers among all phases, and heat transfer between phases and the internal (tubes and walls) parts of the reactor [66]. For gasifiers, one-dimensional steady state model seems to be the optimum choice. Zero-dimensional (0D-S) model does not allow description or evaluation

of temperature, velocity or concentration profiles inside the equipment. Also, two-dimensional steady state model seems unnecessary since the variation in concentration and temperature in the radial direction is negligible compared to that in the axial direction.

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CHAPTER THREE

GASIFICATION OF DIFFERENT BIOMASS FEEDSTOCKS

3.1 Abstract

A study was conducted to determine syngas composition and contaminants from gasification of different biomass feedstocks (viz. hardwood or oak, loblolly pine, switchgrass, southern yellow pine and torrefied pine pellets, pine chips and bark). A mobile downdraft gasifier developed by the Community Power Corporation and stationed at Auburn University Center for Bioenergy and Bioproducts was used to conduct the experiments. Switchgrass had the highest ash content of 4.66% (d.b.) followed by pine bark (1.59% d.b.) while other feedstocks had lower ash content. Carbon content ranged from 47 to 56% (d.b.), hydrogen from 6.50 to 7.50% (d.b.) and sulfur from 0.32 to 0.40% (d.b.) for all the feedstocks. The higher heating values (HHVs) ranged from 19 MJ/kg (switchgrass) to 23 MJ/kg (torrefied pine). The alkali index (AI) and Bed Agglomeration Index (BAI) were calculated using inorganic ash composition but only AI could accurately predict that fouling/slagging would occur during switchgrass gasification. Syngas obtained from yellow pine showed the highest hydrogen (17.35%) and carbon monoxide (25.05%) fraction, and the highest HHV (6 MJ/Nm³), while switchgrass and loblolly pine had significantly lower concentration of H₂ and CO as well as lower HHV. Loblolly pine showed the highest total tar concentration (2.54 g/m³) along with higher concentration of condensable tar compound, indene (>0.1 g/m³). The hydrogen sulfide concentration was found to be 70 ppmv or greater in syngas from all the feedstocks; the highest being from hardwood (84 ppmv) and torrefied pine (83 ppmv).

Keywords: syngas, downdraft gasifier, higher heating value, carbon balance, exergy, tar, hydrogen sulfide

3.2 Introduction

The process of gasification has been used for over a hundred years to produce energy. Biomass gasification is a thermo-chemical process which converts biomass into combustible gases through a number of chemical reactions [1]. One of the advantages of biomass gasification process is its carbon neutrality under sustainable conditions. It means that all CO₂ emitted during the process is only what was absorbed during the growth of the biomass. Hence, the use of biomass for efficient energy production is on the rise in the developed countries [1].

Depleting fossil fuels, their rising cost and environmental concerns are some of the major factors driving interests in gasification of different types of available biomass. Other major considerations in using syngas for energy purposes are its heating value, composition and contamination level. The composition and quality of syngas depends on various factors such as biomass properties, operating conditions and gasification approach [2]. The occurrence of gasification reactions depends on temperatures in the reactor and the oxidant: air, steam or pure oxygen used. Mainly, the LHV and syngas composition are affected by the type of gasifying agent. Gasification with pure O₂ has been found to give syngas with greater mixture of CO and H₂ and the LHV could range from 10 to 20 MJ/ Nm³ [3].

Most downdraft gasification studies are focused on the use of wood as fuel, influence of pressure drop in the system on the gas flow rate and the increased hydrogen yield from air to steam gasification in comparison to pure air gasification [4]. Sheth and Babu [5] studied the effect of moisture content in waste wood from carpentry and equivalence ratio on the reaction zone temperature during downdraft gasification. Skoulou et al. [6] reported an optimum equivalence

ratio of 0.42 while using olive tree kernels and olive tree cuttings in a downdraft gasifier as well as studied the impact of temperature on syngas quality.

This chapter includes the results obtained from gasification of seven different biomass feedstocks in a downdraft gasifier. The composition and heating value of syngas from different experiments as well as the results from carbon (mass), energy and exergy balance analyses are reported here. Also, the concentrations of hydrogen sulfide and tars from different biomass are included in this chapter.

3.3 Experimental Setup

Gasification of different biomass was conducted with a mobile downdraft gasifier developed by the Community Power Corporation (Littleton, CO). Figure 3.1 shows the gasifier/reactor unit, which is housed inside a truck. The total height and inside diameter of the reactor are 1200 mm and 350 mm, respectively. The interface between the controls and the gasifier was created using LABVIEW. A seven-inch thick layer of fiber glass is used to insulate the reactor from outside. A hopper and screw feeder was used to inject biomass into the gasifier, and the feeding rate was controlled based on a specified level of biomass in the gasifier. Primary air was supplied from the open top of the gasifier while secondary air injection nozzles were located at five different levels of the gasifier. Secondary air was supplied to improve combustion reactions and maintain uniform temperatures. The air injection rate was controlled and adjusted by the computer software according to the temperature inside the gasifier. The grate at the bottom of the gasifier was shaken at regular interval to remove ash formed during the gasification runs as well as to facilitate smooth flow of biomass and prevent bridging. Biomass was fed only when temperature at any three locations inside the gasifier reaches 800°C, which indicated the steady state of the system. It took approximately 30 minutes to an hour to attain steady state. After reaching the

steady state, the differential pressure in the heat exchanger and syngas exit temperature from the heat exchanger were the significant parameters to be considered during gasification runs.

At the beginning of each experiment, a pre-run checklist was followed. It included checking leaks, hose connections, motors and electrical devices, charcoal level inside the gasifier, flare, etc. After preheating the heat exchangers and filters to 40°C, the igniter inside the gasifier was turned on. The charcoal was thus heated to avoid condensation and the temperature inside the gasifier increased. Five pairs of K-type thermocouples were used to measure the temperature distribution inside the gasifier which was automatically logged at 15 second intervals. A heat exchanger was used to cool the hot syngas coming out of the gasifier from 500-700 °C to about 100 °C. The cooled gas was then passed through parallel bag filters to remove fine char and particulates. After passing through the filters, the syngas was sampled with a gas analyzer (California Analytical Instruments, NDIR) system as shown in Figure 3.2.



Figure 3.1 BioMax downdraft gasifier



Figure 3.2 CAI gas analyzer

Seven types of biomass feedstocks were selected for gasification viz. hardwood (oak), loblolly pine, switchgrass, yellow pine and torrefied pine pellets, pine chips and pine bark. Figure 3.3

shows the images of the feedstocks which were obtained from the southeast region, mainly Alabama, Georgia, Mississippi and Tennessee. Approximately 200 lb_m of biomass feedstock was used for each experiment. Most experiments with pellets were carried out for three to three and half hours while those with pine chips and bark were performed for at least four hours. Three replications for each feedstock were performed consecutively and not randomized since it was not practical to clean out the reactor at the end of each experiment.

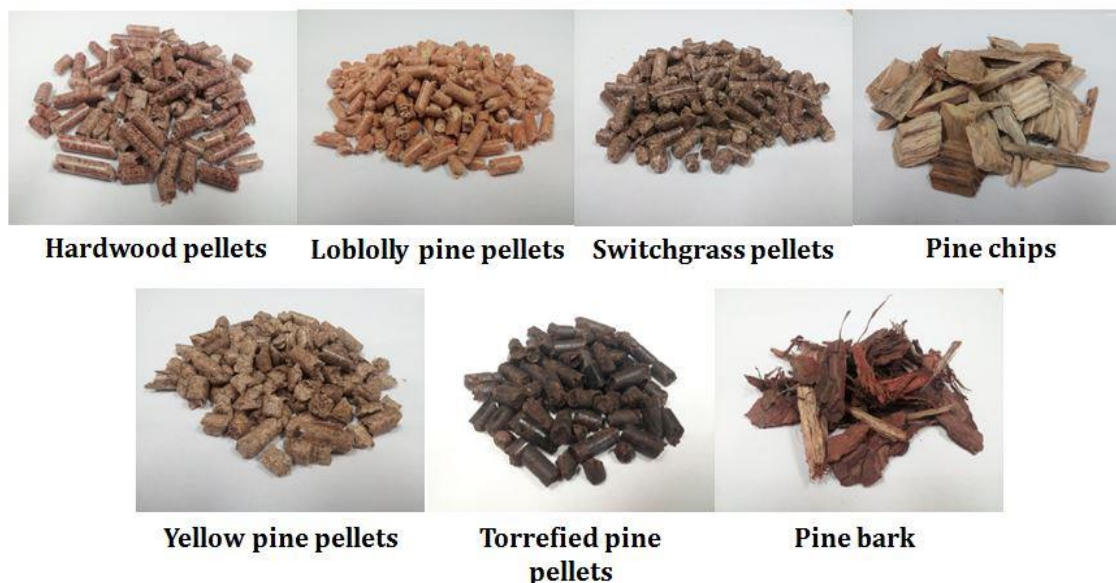


Figure 3.3 Biomass feedstocks used for gasification

3.4 Data Collection

Properties of the different biomass feedstocks were determined through various characterization processes. Results for syngas composition, higher heating value, carbon, energy and exergy analyses, and contaminants' concentration were obtained from the gasification experiments. The description of the methodology applied for all the analyses are described in this section.

3.4.1 Characterization of Biomass

Proximate and ultimate analyses were carried out for each biomass feedstock. Moisture content was measured on the day of the test following ASTM standard E871-82. A known amount

(approximately 10 g) of sample was weighed and heated for over 16 hours at 105°C [7]. The loss in mass of the sample was used to estimate the moisture content. Ash content was measured as per the ASTM standard E 1755-01 which involved heating of biomass sample (0.5 – 1 g) in a muffle furnace to $575 \pm 25^\circ\text{C}$ for three hours and determining the amount left in the container [8]. Volatile matter was measured according to ASTM standard E872 [9]. Dry biomass sample was placed in a platinum crucible with a close fitting cover and placed in a tube furnace at a temperature setting of $\sim 950^\circ\text{C}$ (as per standard). The material was cooled and the loss in mass of the sample was used to determine the volatile matter. Higher heating value (HHV) of the biomass sample was measured using an oxygen bomb calorimeter (Model C200, IKA Works Inc., Wilmington, NC). A CHNS analyzer (Perkin Elmer, model CHNS/O 2400) was used to determine the ultimate analysis of the biomass samples.

Bulk density was determined by using a bulk density measuring apparatus (Burrows Co., Evanston, IL). The sample was poured into a container (volume of 1137 mm³) and weighed. The bulk density was calculated as the mass of the sample divided by the volume of the container. Particle density was also measured using a gas pycnometer (Model AccuPyc II 1340, Micromeritics Instrument Corp., Norcross, GA). Mass of sample (that filled $\frac{3}{4}$ of the mass/volume sample cup) was measured and the volume obtained from the pycnometer was recorded. An average particle density was determined from triplicate measurements. The average diameter of the pellets was 6-7 mm while the length varied from 10 mm to 20 mm. Particle size distribution and sphericity was measured using a digital image analysis system (Model Camsizer, Retsch Technology, Haan, Germany). Each sample (~ 50 g) was placed in a holder funnel of the analyzer. The camsizer recorded the average size and average specific surface area and a plot of particle size distribution for each sample was obtained.

3.4.2 Syngas Composition

Syngas composition was measured using California Analytical Instruments' gas analyzer (CAI ZRE NDIR) which is shown in Figure 3.2. The analyzer is based on the infrared absorption characteristics of gases and uses non-dispersive infrared (NDIR) detector for CO, CO₂ and CH₄. Before the start of experiments, the analyzer was calibrated at least two hours or a day earlier using calibration syngas. The readings for CO, CO₂, CH₄ and H₂ were zeroed with air and spanned with calibration gas, while that for O₂ was zeroed with calibration gas and spanned with air. Once the gasifier reached a steady state temperature, syngas constituents' data i.e. molar concentration of CO, CO₂, H₂, CH₄ and O₂ were recorded in a computer at 15 second interval via the gas analyzer's data logging software. Nitrogen was assumed to be the remainder of the volumetric proportion of syngas. Air flow rate was calculated assuming that the source of nitrogen was air alone. As shown in Equation 3.1, the overall higher heating value of syngas was calculated by adding up the products of the volumetric fraction of syngas constituents (Y_i) and their respective higher heating values (HHV_i). The HHV of H₂, CO and CH₄ are 12.76 MJ/m³, 12.6 MJ/m³ and 39.8 MJ/m³, respectively [10].

$$HHV_{syngas} = HHV_{H_2} Y_{H_2} + HHV_{CO} Y_{CO} + HHV_{CH_4} Y_{CH_4} \quad (3.1)$$

3.4.3 Carbon, Energy and Exergy Analyses

Mass (carbon), energy and exergy balance analyses were performed for all gasification runs. The input stream consisted of biomass feed, dry air and moisture in fuel while the output stream comprised of dry syngas and water present in the gas. It was assumed that the charcoal residues inside the gasifier after each run amounted to the same.

$$Carbon\ in = \frac{\% \text{ of carbon in biomass} \times \text{biomass feed rate} \left(\frac{kg}{h} \right)}{100} \quad (3.2)$$

$$\text{Carbon out} = \frac{\left(\frac{\Sigma(CO+CO_2+CH_4)}{100}\right) \times \text{mol density} \left(\frac{\text{kg}\cdot\text{mol}}{\text{Nm}^3}\right) \times \text{mol wt. of C} \left(\frac{\text{kg}}{\text{kg}\cdot\text{mol}}\right) \times \text{flow rate} \left(\frac{\text{Nm}^3}{\text{h}}\right)}{1000 \left(\frac{\text{mol}}{\text{kg}\cdot\text{mol}}\right)} \quad (3.3)$$

The temperature and pressure of the dead and standard states were assumed to be 25°C and 1 atm, respectively since the gasifier was operated at atmospheric pressure and the pressure drop across the gasifier was not significant. Gases can be treated as ideal at low pressure and high temperature. In the dead state, materials are in thermal, mechanical and chemical equilibrium with the surroundings and incapable of performing any work while the standard state refers to pure chemical species being able to perform work [11].

Applying the first law of thermodynamics to the gasification process can be illustrated as

$$\Sigma(E_{in}) = \Sigma(E_{out}) \quad (3.4)$$

where, $\Sigma(E_{in})$ = energy of biomass feedstock given by its heating value obtained from characterization

$$\Sigma(E_{out}) = \text{energy of syngas constituents} = \Sigma(E_i) \quad (3.5)$$

The energy content of the syngas produced is determined at two locations - the exit of the gasifier ($E_{out, hot}$) at approximately 800°C and the exit of the heat exchanger ($E_{out, cold}$) after the gas is cooled to ambient temperature (25°C). The efficiencies thus calculated are the hot gas efficiency (η_{hot}) and cold gas efficiency (η_{cold}), respectively [11]. Mathematically,

$$\eta_{hot} = \frac{E_{out,hot}}{E_{in}} = \frac{E_{total}+E_{hot}}{E_{in}} \quad (3.6)$$

$$\eta_{cold} = \frac{E_{out,cold}}{E_{in}} = \frac{E_{total}}{E_{in}} \quad (3.7)$$

where E_{total} is the enthalpy of the syngas at ambient temperature and E_{hot} is the enthalpy of gases at higher temperature.

$$E_{total} = \Sigma_i E_i \quad (3.8)$$

where, $E_i = m_i \times HHV$ is the enthalpy of each component of syngas

$$m_i = \% \text{ of } \frac{\text{component}}{100} \times \text{density of component } (\rho_i) \left(\frac{\text{kg}}{\text{Nm}^3} \right) \times \text{flow rate } \left(\frac{\text{Nm}^3}{\text{h}} \right) \quad (3.9)$$

HHV = Higher heating value of the components of syngas obtained from reference [10].

$$E_{hot} = \frac{\sum_i C_{p_i}(T-298) \times m_i}{1000} \quad (3.10)$$

where C_p is the specific heat in kJ/kg K at constant pressure and is expressed by the following equation

$$C_p = c_0 + c_1\theta + c_2\theta^2 + c_3\theta^3 \quad (3.11)$$

Here, c_0, c_1, c_2, c_3 are the coefficients of specific heat capacity and the values for these coefficients are listed in Table 3.1.

Table 3.1 Empirical coefficients of gases [31]

Gases	Empirical coefficients			
	c_0	c_1	c_2	c_3
CO	1.1	-0.46	1	-0.454
CO ₂	0.45	1.67	-1.27	0.39
CH ₄	1.2	3.25	0.75	-0.71
N ₂	1.11	-0.48	0.96	-0.42
O ₂	0.88	-0.0001	0.54	-0.33
H ₂	13.46	4.6	-6.85	3.79

Exergy is generally defined as the measure of a system's potential to perform useful work. It considers irreversible increase in entropy to analyze energy conversion processes [12]. From the second law of thermodynamics, qualitative expression of the law of conservation and conversion of energy to the gasification process gives the entropy balance.

Exergy of dry biomass is given by the following equation:

$$Ex_{in} = \beta \cdot (LHV_{biomass}) \cdot m_{dry} \quad (3.12)$$

$$\text{where } \beta = \frac{\{1.044+0.016\left(\frac{H}{C}\right)-\frac{0.3493}{C}\left[1+0.0531\left(\frac{H}{C}\right)\right]+0.0493\left(\frac{N}{C}\right)\}}{\left[1-0.4124\left(\frac{O}{C}\right)\right]} \quad (3.13)$$

β is the ratio of chemical exergy of the biomass to the lower heating value of the organic fraction of biomass (LHV_{biomass}).

$$LHV_{\text{biomass}} = \frac{HHV-22604 H}{1000} \quad (3.14)$$

where, LHV_{biomass} is in MJ/kg, HHV is in kJ/kg and H is the fraction by weight of hydrogen in the biomass.

The exergy of the individual gases in syngas is given by

$$Ex_i = Ex_{\text{chi}} + \int_{T_d}^T \left[C_p \left(1 - \frac{T_d}{T} \right) \right] dT \quad (3.15)$$

where Ex_i is the exergy of the gas in MJ/kg at temperature T (K), Ex_{chi} is the chemical exergy of the gases at reference or dead state (298 K). The values of Ex_{chi} are given in Table 3.2, taken from the corresponding reference [11].

Table 3.2 Properties of syngas constituents

Gases	Gas constant, R (kJ/kg-K)	Density at STP, ρ (kg/m³)	Heating value (kJ/kg)	Chemical Exergy (Ex_{chi})
N ₂	0.297	1.249	0.000	0
CO	0.297	1.250	10.081	9.9
CO ₂	0.189	1.964	0.000	0
CH ₄	0.518	0.716	55.470	39.8
H ₂	4.124	0.090	141.824	68.9

Now,

$$Ex_{\text{gas}} = \text{exergy of syngas constituents} = \sum(Ex_i) \quad (3.16)$$

The exergetic efficiency is thus given by

$$\eta_x = \frac{Ex_{gas}}{Ex_{in}} \quad (3.17)$$

3.4.4 Ash Composition Analysis

At high reaction temperatures, the inorganic components in biomass feedstocks tend to melt and cause slagging, fouling, bed agglomeration and corrosion [13]. Vamvuka and Zografos [14] evaluated the slagging and fouling potential of biomass residues using alkali index (AI), base-to-acid ratio ($R_{b/a}$), and the bed agglomeration index (BAI). The alkali index (AI) gives the quantity of alkali oxide in the fuel per unit of fuel energy (kg/GJ) and is computed as:

$$AI = \frac{(K_2O + Na_2O) \text{ kg}}{HHV \text{ GJ}} \quad (3.18)$$

Condition for slagging or fouling:

AI = 0.17-0.34 kg/GJ; may or may not occur

AI > 0.34; certain to occur

Bed agglomeration index (BAI) is used to relate agglomeration to ash composition in fluidized bed reactors [15], and given by:

$$BAI = \frac{(Fe_2O_3)\%}{(K_2O + Na_2O)\%} \quad (3.19)$$

Condition for bed agglomeration to occur: BAI < 0.15 [14].

3.4.5 Syngas Contaminants

Tar Analysis

Collection of moisture and tar is performed in a series of six impinger bottles (as shown in Fig 3.4) referred to as “Peterson column”. Moisture and tar are condensed from the process gas by absorption in isopropanol in the first bottle. After that, the gas is passed through a series of four

impingers with solvent and one final bottle which is empty. Analysis of tar is carried out using a gas chromatograph apparatus fitted with a capillary column, a flame ionization detector and a data processing system. The recommended dimensions for the capillary column are an internal diameter of 0.25-0.32 mm and a length of 30-60 m.



Figure 3.4 Tar collection set up



Figure 3.5 Agilent GC FID

Tar was collected from gasification of different biomass feedstock using the process described in the European protocol. As shown in Figure 3.4, syngas was sampled from the port immediately after the downdraft gasifier and passed through a series of six impinger bottles. Each of the first five bottles contained 50 mL of isopropyl alcohol while the last one is empty. Bottles 1, 2 and 4 were kept at ambient conditions while the remaining ones were kept in ice-baths. The tar present in the syngas coming out of the heat exchanger condensed under these conditions in the impinger bottles. The sampled syngas was then passed through Drierite water absorber and activated carbon to remove any remaining moisture and alcohol present in the gas. A flow-meter placed at the end measured the current as well as total syngas flow rate which was used later on to calculate the tar concentration per unit volume.

The tar components were analyzed with an Agilent 7890 (Santa Clara, CA) GC FID (Flame Ionization Detector) using DB-1701 column (30 m, 0.25 mm, 0.25 μ m) shown in Figure 3.5.

The front inlet temperature of the GC was maintained at 250°C, and the oven was programmed with the following temperature regime: hold at 40°C for 2 min, heat to 250°C at 5°C/min, and hold at 250°C for 8 min. A split ratio of 50:1 was set for injection, and He (99.999 pure) was used as the carrier gas at a flow rate of 1.25 mL/min. Compounds were identified using the National Institute of Standards and Technology (NIST) mass spectral library and were quantified based on their consistency of appearance. Quantification was done by injecting calibration standards initially and the slope of the calibration line was taken as the quantification factor in calculation. Analyses were carried out in triplicates and the average values are reported. BTEX compounds (benzene, toluene and ethyl benzene), PAHs (Indene, Naphthalene) and hetero-aromatic compounds (phenol) were few of the compounds that were selected for quantification.

Hydrogen Sulfide Analysis

Syngas coming out of the gasifier was pressurized up to 500 psi and collected in bottles using a compressor and booster system during the course of experiments. For each experiment, the samples of syngas were collected at three different times: half an hour into the test, one and half hour and finally at two and half hours. The bottles were taken to the chemical lab to get the samples analyzed before the next test. H₂S was analyzed with Agilent GC FPD (Santa Clara, CA) using CP-Sil 8 CB column. The front inlet temperature was kept at 250°C, and the oven at 35°C. A split ratio of 20:1 was set for injection and He was used as the carrier gas at a flow rate of 1.1 mL/min.



Figure 3.6 Syngas collection setup for H₂S

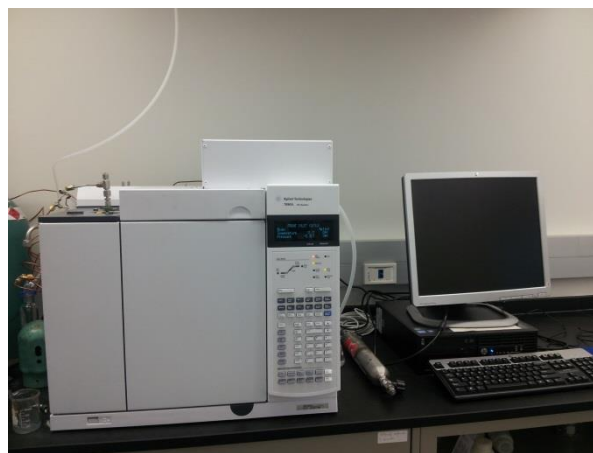


Figure 3.7 Agilent GC FPD

3.4.6 Experimental Design and Statistical Analysis

Different biomass feedstocks were the predictors while the results from characterization of biomass, syngas composition, its higher heating value and concentration of contaminants were the response variables. All the experiments were carried out in triplicates. Statistical significance test ($\alpha = 0.05$) was performed using Proc GLM procedure in the statistical software SAS 9.3 (SAS Institute Inc., Cary, NC). Tukey test was also used to compare the means of the values obtained from different biomass analyses, and composition, higher heating value and contaminants' concentration of syngas.

3.5 Results and Discussion

3.5.1 Analyses of Feedstock

A summary of the proximate analysis is presented in Table 3.3. Switchgrass showed the highest ash content (4.66% d.b.) among the feedstocks. Sharma et al. [28] reported similar ash content (4.62% d.b.) for chopped Kanlow switchgrass. Torrefied pine and pine bark had significantly higher ash content compared to hardwood, loblolly pine, yellow pine pellets and pine chips but significantly lower than switchgrass. Pine chips had the lowest ash content (0.25% d.b.), which made it a suitable feedstock from the point of smooth operation of the gasifier. Hardwood and

yellow pine showed significantly higher volatile matter while torrefied pine had the least amount of it. Pine bark had significantly higher while torrefied pine pellets had the lowest moisture content during the experiments.

Table 3.3 Proximate analysis of biomass (d.b.%)

Biomass	Ash content	Volatile matter	Moisture	Fixed carbon
Hardwood pellets	0.41 ± 0.06 (c)	89.50 ± 0.08 (a)	5.58 ± 1.11 (cd)	10.09 ± 0.09
Loblolly pine pellets	0.44 ± 0.15 (c)	78.19 ± 0.29 (c)	7.69 ± 1.62 (cbd)	21.37 ± 0.18
Switchgrass pellets	4.66 ± 0.06 (a)	72.76 ± 0.34 (d)	9.93 ± 2.03 (bc)	22.58 ± 0.4
Pine chips	0.25 ± 0.11 (c)	81.19 ± 0.26 (bc)	10.49 ± 2.61 (b)	18.56 ± 0.38
Yellow pine pellets	0.53 ± 0.21 (c)	84.94 ± 3.16 (ab)	11.26 ± 0.10 (b)	14.53 ± 3.03
Torrefied pine pellets	1.09 ± 0.11 (b)	66.40 ± 0.38 (e)	4.64 ± 0.44 (d)	32.51 ± 0.31
Pine bark	1.59 ± 0.16 (b)	72.02 ± 2.27 (d)	16.62 ± 3.38 (a)	26.34 ± 2.25

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-e) are not significantly different ($\alpha = 0.05$).

The results from ultimate analysis are shown in Table 3.4. Carbon content ranged from 47 to 56% (d.b.), hydrogen from 6.50 to 7.50% (d.b.) and sulfur from 0.32 to 0.40% (d.b.) for all the feedstocks. Torrefied pine pellets and pine bark had significantly higher carbon content compared to the rest of the feedstocks. Switchgrass had significantly the least carbon fraction among all the feedstocks. Gautam et al. [29] reported similar ultimate analysis for wood chips with slightly lower hydrogen content.

Table 3.4 Elemental (ultimate) analysis of biomass (ash free d.b.%)

Biomass*	C	H	N	S	O
HP	49.65 ± 0.04 (c)	7.02 ± 0.14 (abc)	0.09 ± 0.02 (c)	0.40 ± 0.04 (a)	42.84 ± 0.12 (b)
LP	51.32 ± 0.01 (b)	7.46 ± 0.08 (a)	0.05 ± 0.01 (c)	0.36 ± 0.0 (ab)	40.81 ± 0.08 (c)
SP	47.03 ± 0.02 (d)	6.70 ± 0.02 (bc)	0.74 ± 0.03 (a)	0.36 ± 0.01 (ab)	45.16 ± 0.02 (a)
PC	50.85 ± 0.12 (bc)	7.15 ± 0.12 (ab)	0.04 ± 0.01 (c)	0.33 ± 0.00 (b)	41.63 ± 0.01 (bc)
YP	51.13 ± 0.03 (bc)	7.15 ± 0.02 (ab)	0.04 ± 0.02 (c)	0.32 ± 0.01 (b)	41.36 ± 0.06 (bc)
TP	56.15 ± 0.98 (a)	6.52 ± 0.03 (c)	0.10 ± 0.01 (c)	0.33 ± 0.01 (b)	36.90 ± 0.98 (d)
PB	55.21 ± 0.46 (a)	7.07 ± 0.29 (ab)	0.23 ± 0.02 (b)	0.32 ± 0.01(b)	37.18 ± 0.73 (d)

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-d) are not significantly different ($\alpha = 0.05$).

**Abbreviations for the biomass used: HP – Hardwood pellets, LP – Loblolly pine pellets, SP – Switchgrass pellets, PC – Pine chips, YP – Yellow pine pellets, TP – Torrefied pine pellets and PB – Pine bark*

Table 3.5 shows the physical properties and higher heating value of biomass. The HHV of all the feedstocks were found to be significantly different than each other. The effect of torrefaction can be clearly seen in the high HHV of torrefied pine pellets. Switchgrass had the lowest HHV among other biomass types. The pellets show comparable bulk densities in the range of 610-690 kg/m³, while that for pine chips and bark are quite lower as expected. Similarly, the particle densities of pellets are also similar but much higher than pine chips and bark.

Table 3.5 Higher heating value (d.b.) and density of biomass

Biomass	Higher Heating Value (MJ/kg)	Bulk density (kg/m³)	Particle density (kg/m³)
Hardwood pellets	19.73 ± 0.14 (a)	667.51 ± 5.75	1462.83 ± 3.2
Loblolly pine pellets	20.85 ± 0.14 (b)	684.35 ± 5.37	1456.07 ± 2.4
Switchgrass pellets	18.96 ± 0.03 (c)	635.46 ± 3.52	1476.20 ± 3.2
Pine chips	19.56 ± 0.19 (d)	225.33 ± 4.54	1350.12 ± 1.87
Yellow pine pellets	20.17 ± 0.02 (e)	611.15 ± 3.87	1434.47 ± 0.89
Torrefied pine pellets	22.54 ± 0.14 (f)	685.39 ± 3.08	1424.47 ± 1.66
Pine bark	21.48 ± 0.06 (g)	153.17 ± 3.52	1079.47 ± 0.06

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-g) are not significantly different ($\alpha = 0.05$).

Table 3.6 shows the inorganic composition of biomass as obtained from ash composition analysis conducted at University of Tennessee, Knoxville. The data were used to compute the Alkali Index (AI) and the Bed Agglomeration Index (BAI) for predicting the slagging/fouling and agglomeration behavior of the biomass. As seen in Table 3.7, the AI for switchgrass was 0.85 (>0.34), which meant fouling/slagging certainly occurs. The AI being less than 0.17 for the

rest of the feedstocks showed that phenomenon would not occur. BAI was determined to be lower than 0.15 for hardwood, loblolly pine, switchgrass and pine chips showing that agglomeration would occur. However, ash agglomeration was actually seen only during switchgrass gasification.

Table 3.6 Major inorganic composition (mg/kg biomass)

Biomass	Fe	Ca	Mg	K	Na	Ti	Al
HP	67.18±1.3	1017.39±21.6	51.71±2.5	777.15±29.3	15.72±1.3	0.74±0.01	0.00
LP	14.33±0.6	801.62±26.9	277.95±10.0	901.14±35.1	23.29±0.9	0.00	17.95±1.8
SP	315.74±5.7	2747.25±42.9	1305.74±19.7	6497.26±0.21	166.14±1.0	35.28±0.4	292.93±8.3
PC	32.69±1.5	481.07±11.2	169.32±4.4	419.99±16.5	0.00	0.75±0.0	23.93±2.6
YP	575.11±23.1	768.57±10.8	281.25±6.5	654.29±3.4	40.17±1.9	1.184±0.0	23.70±0.9
TP	341.09±14.5	1556.44±0.9	273.84±0.4	509.27±3.1	168.95±1.1	2.88± 0.2	55.64±2.2
PB	916.38±9.1	1373.28±40.4	436.71±9.7	938.99±18.2	23.19±0.9	20.33±1.8	612.98±8.1

Note: The values after the ± sign denote the standard deviation.

Table 3.7 Determination of alkali index (AI) and bed agglomeration index (BAI)

Biomass	AI (kg/GJ)	BAI
Hardwood	0.09	0.10
Loblolly pine	0.11	0.02
Switchgrass	0.85	0.06
Pine chips	0.05	0.09
Yellow pine	0.09	0.98
Torrefied pine	0.08	0.58
Pine bark	0.13	1.13

3.5.2 Gasification Results

The values of moisture content and mass flow rate of biomass, and the equivalence ratio (E.R.) obtained for the gasification experiments are shown in Table 3.8. Pine bark had the highest moisture content (17%) while torrefied pine (5%) was the driest among all. The average dry biomass flow rate was 23-26 kg/hr for all feedstocks except pine bark which had a low mass

flow rate of approximately 19 kg/hr. The E.R. for the experiments ranged from 0.26 for yellow pine to 0.35 for pine bark gasification.

Table 3.8 Experimental conditions for different feedstocks

Biomass	Moisture (d.b.%)	Dry biomass flowrate (kg/hr)	Equivalence ratio (ER)
Hardwood pellets	5.58 ± 1.11	25.88 ± 0.58	0.28
Switchgrass pellets	9.93 ± 2.03	25.31 ± 0.45	0.34
Loblolly pine pellets	7.69 ± 1.62	24.11 ± 0.69	0.30
Pinewood chips	10.49 ± 2.61	23.59 ± 0.00	0.32
Yellow Pine pellets	11.26 ± 0.10	24.46 ± 1.58	0.26
Torrefied Pine pellets	4.64 ± 0.44	23.01 ± 0.21	0.28
Pine Bark	16.62 ± 3.38	18.75 ± 0.08	0.35

Note: The values after the ± sign denote the standard deviation.

The average composition and higher heating value (HHV) of syngas from gasification of different biomass feedstock is reported in Table 3.9. The gas composition data for one of the torrefied pine gasification experiments generated by the gas analyzer over time and the temperature profile inside the reactor during the same experiment are shown in Appendix A.1 and A.2. Yellow pine which had the lowest E.R. (0.26) during gasification showed the highest fraction of CO as well as H₂. It suggests that there was lesser oxygen available for the oxidation reactions which ultimately produce more CO₂ and H₂O. Higher carbon fraction in yellow and torrefied pine, pine bark and chips also contributed to the syngas being rich in carbon monoxide. Wan et al. [30] performed gasification in a similar model of Bio-Max 25 downdraft gasifier using oak wood chips and reported syngas composition as 18% H₂, 21% CO, 10% CO₂, 2% CH₄ and 48% N₂. Gautam et al. [29] reported the concentration of 20% H₂ and 21% CO from gasification of pine wood chips. Sharma et al. [28] used switchgrass in a lab-scale fluidized bed gasifier and reported slightly lower concentration of H₂ (9%) and CO (16%).

The sample calculation for determination of HHV is given in Appendix B.1. The values for all the feedstock ranged from 4.81-6 MJ/Nm³. Syngas from switchgrass, which had the highest ash content and lowest carbon content, showed the least HHV among others. There was no direct correlation between the higher heating values of the solid fuel, properties such as particle and bulk density to the HHV of syngas. Gautam et al. [29] reported a similar syngas HHV of 5.7 MJ/Nm³ from wood chips but Sharma et al. [28] achieved higher syngas HHV of 6.6 MJ/Nm³ from gasification of switchgrass in a fluidized bed gasifier.

Table 3.9 Composition and higher heating value of syngas from different feedstocks

Biomass	Syngas composition (Molar %)				Higher heating value (MJ/Nm ³)
	H ₂	CO	CO ₂	CH ₄	
HP	16.77 ± 0.25 (ac)	21.13 ± 0.60 (ab)	11.60 ± 2.12 (bcd)	1.94 ± 0.72 (c)	5.57 ± 0.05 (acd)
SP	14.97 ± 0.74 (a)	18.50 ± 0.52 (b)	12.00 ± 1.23 (bc)	1.43 ± 0.61 (bc)	4.81 ± 0.13 (b)
LP	14.33 ± 0.08 (b)	18.40 ± 0.78 (b)	10.54 ± 1.85 (bcd)	1.94 ± 0.78 (c)	4.92 ± 0.07 (b)
PC	15.74 ± 0.62 (abc)	20.10 ± 1.65 (ab)	11.05 ± 1.71 (bcd)	1.57 ± 0.51 (bc)	5.16 ± 0.03 (bc)
YP	17.35 ± 1.67 (c)	25.05 ± 1.67 (c)	9.59 ± 2.24 (ad)	1.56 ± 0.58 (bc)	5.99 ± 0.48 (ad)
TP	15.13 ± 0.25 (a)	24.51 ± 0.62 (c)	7.88 ± 1.33 (a)	1.49 ± 0.54 (b)	5.61 ± 0.06 (acd)
PB	15.19 ± 0.51 (a)	22.95 ± 1.77 (ac)	10.85 ± 1.23 (bcd)	0.94 ± 0.26 (a)	5.20 ± 0.19 (bc)

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-d) are not significantly different ($\alpha = 0.05$).

The effect of equivalence ratio (E.R.) on the higher heating value of dry syngas produced from different biomass is presented in Figure 3.8. It was observed that syngas produced at higher E.R. had lower HHV. Gasification of switchgrass and loblolly pine pellets, pine chips and pine bark were carried out at E.R. ranging from 0.30 to 0.35 and the HHV of syngas from those feedstocks ranged from 4.81 to 5.20 MJ/Nm³. These values were significantly lower than the HHV of syngas from yellow pine (6 MJ/Nm³), the E.R. being 0.26. Figure 3.9 shows the correlation of ash content in biomass to the HHV of syngas produced from it. Although there is no clear trend in HHV for ash content 0.25-0.53%, it can be seen that the HHV decreases gradually for ash

content 0.53 to 4.66%. It should also be noted that there was no significant difference in the ash content values 0.25-0.53 among the feedstocks, as discussed in Table 3.3.

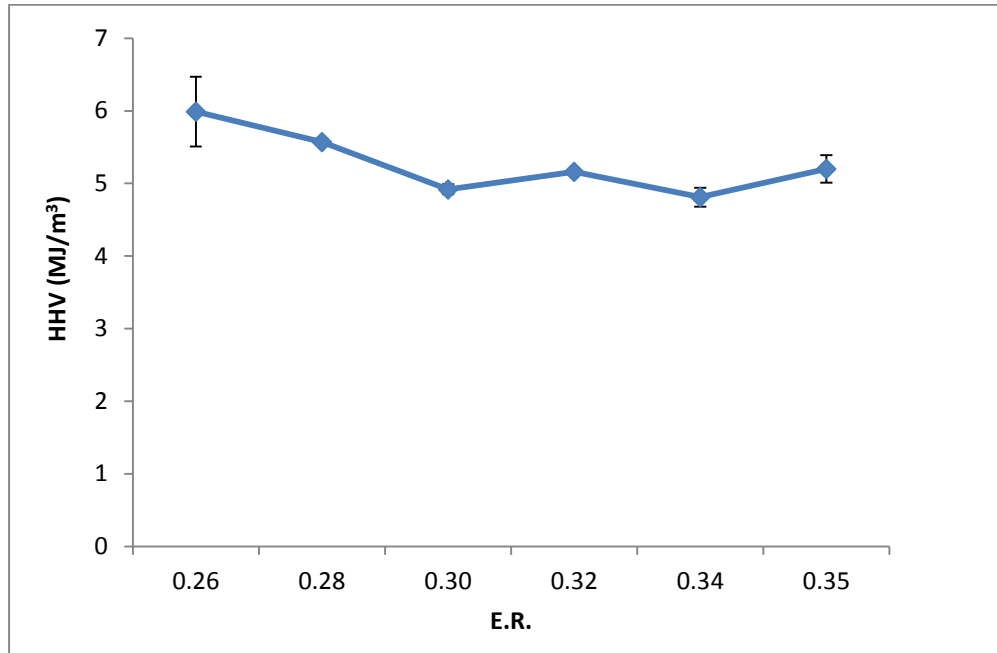


Figure 3.8 Effect of E.R. on higher heating value of syngas

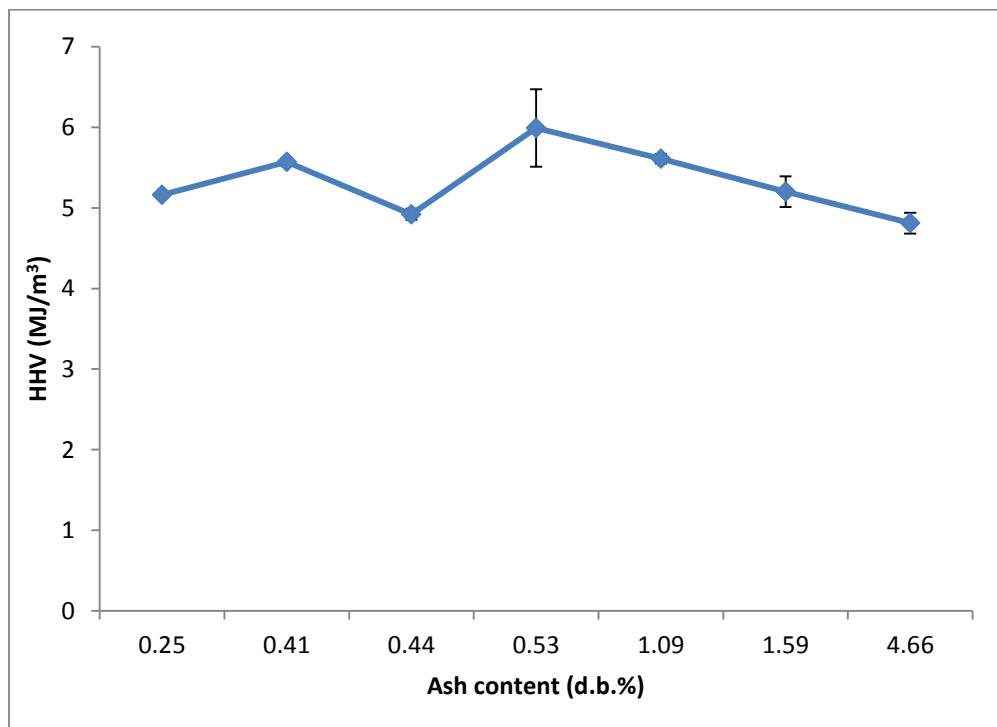


Figure 3.9 Effect of ash content of biomass on higher heating value of syngas

3.6.2 Carbon, Energy and Exergy Analyses

Charcoal was used to start up the experiment and was refilled to the same level before every other run. Hence, the residues inside the gasifier were considered to be the same after each run. The ash and tars trapped inside the gasification system were neglected when doing these analyses. Table 3.10 shows the results from the three experiments carried out for each biomass feedstock. The sample calculations for these analyses are given in Appendix B.2. Carbon conversion of approximately 0.77-0.98 was achieved for different feedstocks, with pine bark showing the highest carbon conversion of 0.98. Operational difficulties due to the size of the system were a factor in not having very accurate carbon conversion values. Gautam et al. [31] reported a carbon closure greater than 0.89 with gasification of wood chips in the same downdraft gasifier as used in this experiment. Wan et al. [32] also used a BioMax 25 system for gasification of oak wood chips and calculated a carbon conversion rate of approximately 0.92. Zainal et al. [33] used furniture wood and wood chips in a downdraft gasifier and reported maximum carbon closure of 0.98 at an ER of 0.27. The hot and cold gas efficiency and exergy for loblolly pine and switchgrass pellets was found to be lower than other feedstocks due to lower concentration of carbon monoxide in syngas. Similarly, loblolly pine showed the lowest and pine bark had the highest exergy ratio.

Table 3.10 Carbon, energy and exergy analyses of different biomass (%)

Biomass	Carbon closure	Hot gas efficiency	Cold gas efficiency	Exergy ratio
Hardwood pellets	0.80 ± 0.01	0.75 ± 0.04	0.62 ± 0.03	0.50 ± 0.01
Loblolly pine pellets	0.77 ± 0.01	0.71 ± 0.01	0.57 ± 0.01	0.46 ± 0.01
Switchgrass pellets	0.82 ± 0.03	0.71 ± 0.02	0.57 ± 0.02	0.47 ± 0.02
Pine chips	0.83 ± 0.01	0.78 ± 0.01	0.66 ± 0.02	0.53 ± 0.01
Yellow pine pellets	0.86 ± 0.02	0.87 ± 0.01	0.80 ± 0.02	0.61 ± 0.01
Torrefied pine pellets	0.79 ± 0.01	0.77 ± 0.01	0.66 ± 0.01	0.55 ± 0.01
Pine bark	0.98 ± 0.05	0.97 ± 0.04	0.82 ± 0.03	0.71 ± 0.03

Note: The values after the \pm sign denote the standard deviation.

3.6.3 Tar Concentration

Loblolly pine pellets showed the highest total concentration of 2.54 g/m^3 of tar compounds among the used biomass feedstock, while pine bark and pine chips had lower concentrations (0.91 and 1.36 g/m^3 respectively) as compared to pellets. This can be attributed to the higher bulk density of pellets than pine chips and bark. Benzene, toluene and 3-methyl phenol were the most commonly occurring non-condensable compounds in all of the samples collected from different biomass as seen in Figure 3.10. However, the concentration of indene (light, condensable PAH) was found to be higher than 0.1 g/m^3 in loblolly pine, which can be a cause of concern in syngas applications. Phuphuakrat et al. [34] reported a maximum tar concentration of 3.3 g/m^3 produced from gasification of dried sewage sludge in a downdraft gasifier. However, the major components in that case were light, non-condensable aromatic hydrocarbon tar such as benzene, toluene, xylene, styrene, indene and naphthalene, which are not harmful to engines. The retention times for the detected compounds are included in Appendix C.

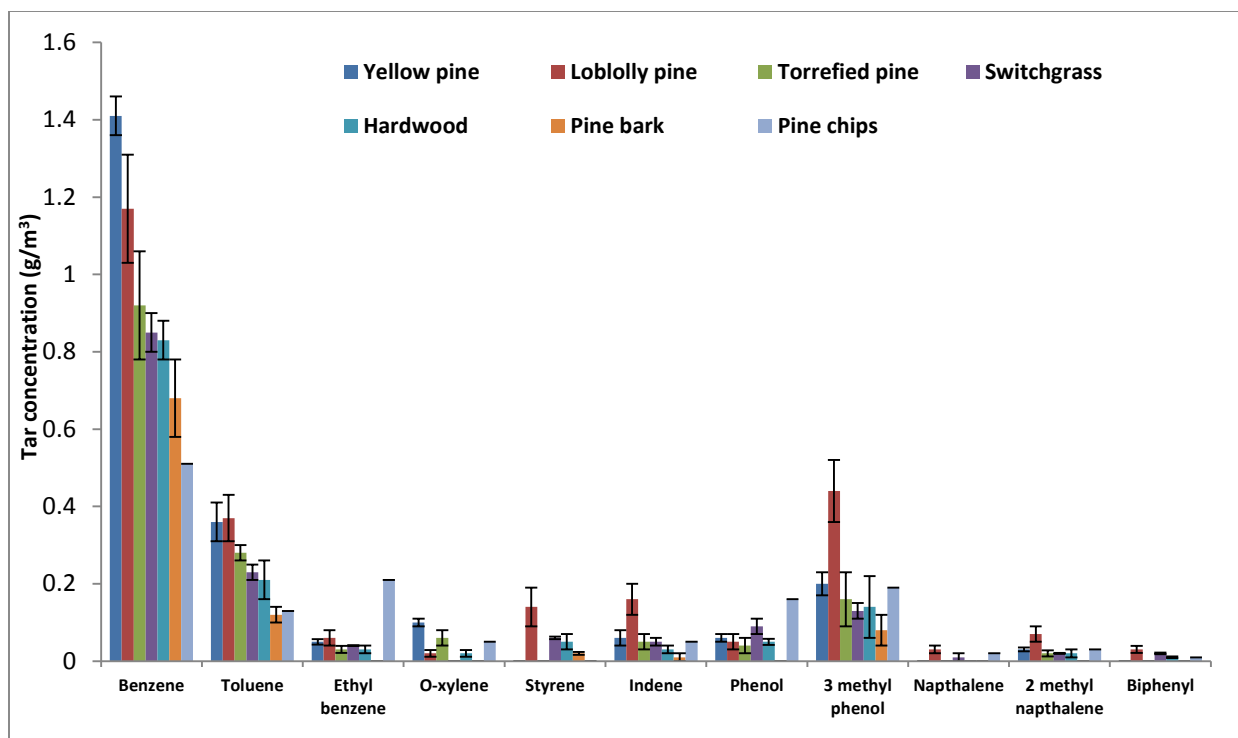


Figure 3.10 Tar concentration in syngas from gasification of feedstocks

Hernandez et al. [35] reported that in air gasification, the most abundant compounds at 750°C were benzene, xylenes and phenol, while PAHs were the least abundant compounds (less than 0.3 g/m³) regardless of the operating temperature. Passen and Kiel [36] studied the impact of feedstock properties and gasifier operating conditions on tar formation in a fluidized bed gasifier. The gasifier temperature was reported to have the largest influence on tar composition. Class 2 tars almost decomposed at 850°C while class 4 and 5 (heavy) tars continuously increased with increasing temperature.

3.6.4 Hydrogen Sulfide Concentration

As shown in Figure 3.11, syngas from hardwood pellets had the highest concentration of H₂S (83.71 ppmv), followed by torrefied pine pellets (82.92 ppmv). It was expected since the hardwood pellets had the highest sulfur content (0.4%) as seen in Table 3.4. Syngas samples from all the biomass runs had higher concentration of H₂S than the maximum limit for different

applications such as gas turbines (< 20 ppmv) and Fischer-Trope synthesis ($< 10^{-8}$ ppmv). Gupta et al. [37] reported an approximate H_2S concentration of 28000 ppmv in syngas from gasification of black liquor produced by the pulp and paper industry. Unfortunately, the H_2S data for loblolly pine and pine chips could not be collected because the GC FPD was under maintenance during the gasification of these biomass feedstocks.

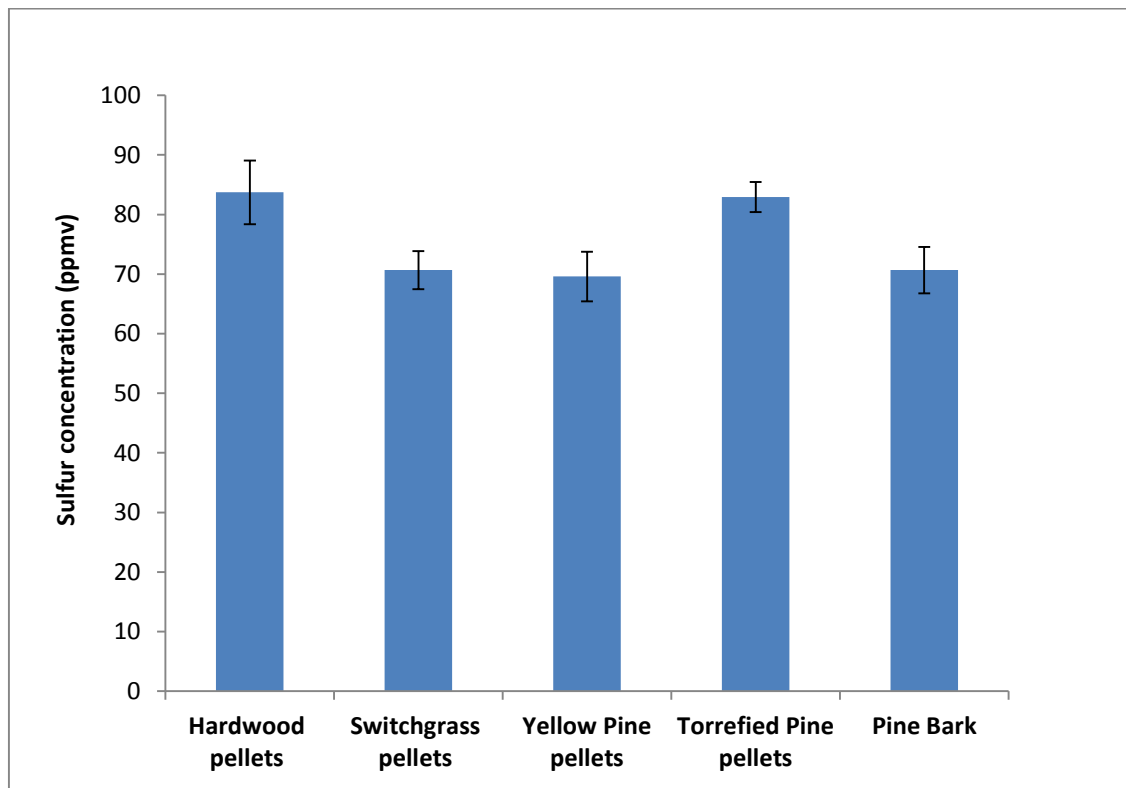


Figure 3.11 H_2S concentration in syngas from different biomass feedstock

3.7 Conclusions and Remarks

Seven biomass feedstocks were selected and characterized for gasification experiments in the CPC mobile downdraft gasifier. Syngas produced from the experiments was analyzed in terms of composition and contaminants. Analyses for carbon closure, hot and cold gas efficiency, and exergy were performed. The following conclusions were drawn from this study:

- Among the biomass feedstock used in the experiments, yellow pine pellets showed the most potential in terms of producing syngas with higher H₂ and CO content, and thus higher HHV.
- Switchgrass due to its low carbon content and high ash content produces syngas with relatively lower heating value. Although the switchgrass pellets showed good flow characteristics in the reactor, there was frequent ash build up in the grate of the gasifier.
- Loblolly pine pellets had the highest total tar concentration along with higher than acceptable limit of condensable compound indene (light PAH). Most commonly occurring compounds were non-condensable, water soluble compounds such as benzene, toluene and phenol.
- Hydrogen sulfide concentration was higher than 70 ppmv for all the feedstocks, which means that the syngas is unsuitable for direct use in many applications.

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CHAPTER FOUR

GASIFICATION OF BLENDED BIOMASS FEEDSTOCKS

4.1 Abstract

A study was conducted to evaluate the effect of blending a biomass that has higher ash content with a biomass that has lower ash content. Switchgrass was blended with yellow pine pellets and pine bark with pine chips in two different ratios of 25:75 and 50:50. A mobile downdraft gasifier developed by the Community Power Corporation and stationed at Auburn University Center for Bioenergy and Bioproducts was used to conduct the experiments. Ash content for the yellow pine/switchgrass blends was reduced to 1.6% for 75:25 and 2.6% for 50:50, while for pine chips/bark blends it was down to 0.6% for 75:25 and 0.9% for 50:50 blends. No ash agglomeration was experienced during gasification of the yellow pine/switchgrass blends. The hydrogen and carbon monoxide concentrations in syngas obtained from yellow pine/switchgrass blends were higher compared to switchgrass alone, while those from pine chips/bark blends were not significantly different from individual runs. The 75:25 and 50:50 blends of yellow pine and switchgrass showed a total tar concentration of 1.97 g/m³ and 1.86 g/m³, respectively, while the concentrations for the 75:25 and 50:50 blends of pine chips and bark were 1.66 g/m³ and 1.57 g/m³, respectively. The hydrogen sulfide concentration was found to be above 65 ppmv for both the yellow pine/switchgrass and pine chips/bark blends.

Keywords: ash content, biomass blends, yellow pine, switchgrass, pine chips, pine bark

4.2 Introduction

Biomass has certain advantages over fossil fuels in terms of renewability and abundance. Agricultural biomass resources have proven to be viable feedstocks in thermal conversion facilities for heat and electrical power production [1]. However, there are challenges in the usage of biomass residues due to high ash content of certain biomass. In case of direct combustion, the inorganic constituents (K, Cl, S and Ca) of biomass can cause fouling on reactors, furnaces, heat exchangers, turbines and other downstream equipment [2]. The inorganic components of biomass cause problems such as slagging, bed agglomeration and corrosion [3]. Deposit formation on heat transfer surfaces is one of the biggest problems for solid fuel fired boilers, especially in biomass combustion [4].

Ash agglomeration is a major issue in gasification when using a biomass feedstock with particularly high ash content. Among the previously selected feedstocks, switchgrass pellets and pine bark were found to have higher ash content as compared to oak, pine pellets and pine chips. Sharma et al. [5] reported high ash content of 4.62% (d.b.) for chopped switchgrass as feedstock for fluidized bed gasification. Liu and Bi [2] found the ash content of switchgrass to vary from 4.31% for 0.95 mm to 10.53% for 0.15 mm particle size. They reported that the finer fractions of ground switchgrass contained substantially higher ash content than the coarser fractions. Similarly, the ash content for pine bark varied from 2.38% to 4.93% for the same particle size distribution. Another major advantage of using blended biomass for gasification is that different biomass available within a certain geographic area can be used and dependency on a particular feedstock can be reduced.

The results from blending of switchgrass with yellow pine pellets, and pine bark with pine chips for use in gasification are reported in this chapter. Composition, heating value and contaminants'

concentration of syngas from the different blends are compared with results from individual feedstock gasification reported in the previous chapter. Similarly, carbon closure, hot and cold gas efficiency and exergy analysis are also included.

4.3 Experimental Setup

The experimental setup was the same as reported in the previous chapter except for the fact that blended biomass was used for gasification. The total amount of biomass used for each experiment was 200 lb. Pellets of yellow pine and switchgrass were blended using a concrete mixer in the mass ratio of 75:25 and 50:50. Pine chips and bark were blended in the same manner. The pellets were fed into the gasifier using an external hopper while the mixture of pine chips and bark was fed using the on-board hopper.



Figure 4.1 Concrete mixer for blending biomass

4.4 Data Collection

Characterization of biomass was performed in the same way described in the previous chapter for different biomass feedstocks. Three replicates of each blend's gasification were performed. One-way ANOVA ($\alpha = 0.05$) was carried out to check for significant differences in

concentrations of syngas constituent gases and higher heating value among the blends and their respective pure feedstocks.

4.5 Results and Discussion

4.5.1 Analyses of Feedstock

Table 4.1 shows a summary of the proximate analysis of different blends of biomass. Switchgrass pellets which had high ash content (4.66% d.b.) were blended with yellow pine pellets (0.53% d.b. ash) in two different ratios of 75:25 and 50:50, respectively. The ash content of the blends was found to be significantly lower than pure switchgrass. Also, pine bark (1.59% d.b. ash) was blended with pine chips (0.25% d.b. ash) and similar results were obtained. During gasification, the moisture content of the yellow pine and switchgrass pellets' blends was similar to that of their individual run.

Table 4.1 Proximate analysis of biomass blends (d.b.%)

Biomass blend*	Ash content	Volatile matter	Moisture	Fixed carbon
YP	0.53 ± 0.21 (a)	84.94 ± 3.16 (a)	11.26 ± 0.10 (a)	14.53 ± 3.03
YP/SG 75:25	1.56 ± 0.15 (b)	81.89 ± 2.45 (ab)	8.49 ± 1.14 (a)	16.55 ± 2.37
YP/SG 50:50	2.59 ± 0.09 (c)	78.85 ± 1.74 (b)	9.42 ± 1.20 (a)	18.56 ± 1.7
SG	4.66 ± 0.06 (d)	72.76 ± 0.34 (c)	9.93 ± 2.03 (a)	22.58 ± 0.4
PC	0.25 ± 0.11 (c)	81.19 ± 0.26 (a)	10.49 ± 2.61 (b)	18.56 ± 0.38
PC/PB 75:25	0.59 ± 0.12 (bc)	78.91 ± 0.67 (ab)	12.36 ± 1.18 (ab)	20.50 ± 0.62
PC/PB 50:50	0.92 ± 0.13 (b)	76.63 ± 1.20 (b)	15.65 ± 2.95 (ab)	22.44 ± 1.24
PB	1.59 ± 0.16 (a)	72.02 ± 2.27 (c)	16.62 ± 3.38 (a)	26.34 ± 2.25

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-d) are not significantly different ($\alpha = 0.05$).

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

The results from ultimate analysis of the blends are shown in Table 4.2. Yellow pine/switchgrass blends had significantly higher carbon and hydrogen content than switchgrass. Pine chips/bark

blends were found to have significantly higher carbon content than pine bark while the hydrogen content was similar.

Table 4.2 Ultimate analysis of biomass blends (ash free d.b.%)

Biomass blends	C	H	N	S	O
YP	51.13 ± 0.03 (a)	7.15 ± 0.02 (a)	0.04 ± 0.02 (a)	0.32 ± 0.01 (a)	41.36 ± 0.06 (a)
YP/SG 75:25	50.10 ± 0.02 (b)	7.04 ± 0.02 (b)	0.22 ± 0.01 (b)	0.33 ± 0.02 (a)	42.31 ± 0.04 (b)
YP/SG 50:50	49.08 ± 0.01 (c)	6.93 ± 0.02 (c)	0.39 ± 0.02 (c)	0.34 ± 0.01 (a)	43.26 ± 0.05 (c)
SG	47.03 ± 0.02 (d)	6.70 ± 0.02 (d)	0.74 ± 0.03 (d)	0.36 ± 0.01 (b)	45.16 ± 0.02 (d)
PC	50.85 ± 0.12 (a)	7.15 ± 0.12 (a)	0.04 ± 0.01 (a)	0.33 ± 0.00 (a)	41.63 ± 0.01 (a)
PC/PB 75:25	51.94 ± 0.031 (b)	7.13 ± 0.16 (a)	0.09±0.01 (ab)	0.33 ± 0.01 (a)	40.51 ± 0.18 (ab)
PC/PB 50:50	53.03 ± 0.17 (c)	7.11 ± 0.20 (a)	0.13±0.02 (b)	0.32 ± 0.01 (a)	39.40 ± 0.36 (b)
PB	55.21 ± 0.46 (d)	7.07 ± 0.29 (a)	0.23 ± 0.02 (c)	0.32 ± 0.01 (a)	37.18 ± 0.73 (c)

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-d) are not significantly different ($\alpha = 0.05$).

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

Table 4.3 shows the physical properties and higher heating value of the biomass blends. The blends for yellow pine and switchgrass pellets had significantly lower HHV than yellow pine but significantly higher HHV than switchgrass. Pine chips/bark blends showed significantly lower HHV compared to pine bark alone.

Table 4.3 Higher heating values (d.b.) and densities of feedstock

Biomass blends	HHV (MJ/kg)	Bulk density (kg/m³)	Particle density (kg/m³)
YP	20.17 ± 0.02 (a)	611.15 ± 3.87	1434.47 ± 0.89
YP/SG 75:25	19.86 ± 0.06 (b)	617.23 ± 3.78	1444.90 ± 1.46
YP/SG 50:50	19.56 ± 0.10 (c)	623.31 ± 3.69	1455.33 ± 2.04
SG	18.96 ± 0.03 (d)	635.46 ± 3.52	1476.20 ± 3.2
PC	19.56 ± 0.19 (c)	225.33 ± 4.54	1350.12 ± 1.87
PC/PB 75:25	20.04 ± 0.14 (bc)	207.29 ± 4.28	1289.13 ± 2.85
PC/PB 50:50	20.52 ± 0.08 (b)	189.25± 4.03	1228.12 ± 4.85
PB	21.48 ± 0.06 (a)	153.17 ± 3.52	1079.47 ± 0.06

Note: The values after the \pm sign denote the standard deviation and those with the same alphabet (a-d) are not significantly different ($\alpha = 0.05$).

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

4.5.2 Gasification of Biomass Blends

Moisture content, mass flow rate of biomass and the equivalence ratio (E.R) observed during gasification of the biomass blends are shown in Table 4.4. It can be seen that the E.R. for both the blends was similar (0.30 - 0.31) and so was the biomass flow rate.

Table 4.4 Experimental conditions for different feedstocks

Biomass blends	Moisture (d.b.%)	Dry biomass flow rate (kg/m³)	Equivalence Ratio (E.R.)
YP/SG 75:25	8.49 \pm 1.14	21.02 \pm 0.00	0.30
YP/SG 50:50	9.42 \pm 1.2	20.55 \pm 0.00	0.31
PC/PB 75:25	12.36 \pm 1.18	19.08 \pm 0.17	0.31
PC/PB 50:50	15.65 \pm 2.95	19.03 \pm 0.10	0.30

Note: The values after the \pm sign denote the standard deviation.

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

As shown in Table 4.5, the hydrogen concentrations of the yellow pine/switchgrass as well as the pine chips/bark blends were not significantly different from their respective pure feedstock. But the carbon monoxide concentration for the yellow pine/switchgrass blends was significantly higher than that from switchgrass. As reported in the previous chapter, H₂, CO and CO₂ concentrations were significantly different (at $\alpha = 0.05$) between switchgrass and yellow pine, while pine chips and bark significantly differed only in CH₄ concentration. Concentrations of CO from both the 75:25 and 50:50 blends of yellow pine and switchgrass were significantly higher than that from pure switchgrass gasification. However, no significant difference was found in syngas constituents among the pine chips and bark blends.

Table 4.5 Composition of syngas from different biomass blends

Biomass type	Syngas composition from different biomass			
	Volume (%)			
	H ₂	CO	CO ₂	CH ₄
YP	17.35 ± 1.67 (a)	25.05 ± 1.67 (a)	9.59 ± 2.24 (a)	1.56 ± 0.58 (a)
YP/SG 75:25	15.27 ± 0.25 (ab)	25.24 ± 1.21 (a)	11.02 ± 0.35 (ab)	1.65 ± 0.20 (a)
YP/SG 50:50	16.14 ± 0.64 (ab)	21.97 ± 1.28 (a)	11.19 ± 0.07 (ab)	1.54 ± 0.13 (a)
SG	14.97 ± 0.74 (b)	18.50 ± 0.52 (b)	12.00 ± 1.23 (b)	1.43 ± 0.61 (a)
PC	15.74 ± 0.62 (c)	20.10 ± 1.65 (c)	11.05 ± 1.71 (c)	1.57 ± 0.51 (c)
PC/PB 75:25	17.02 ± 0.07 (c)	19.91 ± 0.63 (c)	11.22 ± 0.59 (c)	1.48 ± 0.13 (c)
PC/PB 50:50	16.07 ± 0.76 (c)	21.28 ± 0.90 (c)	10.69 ± 0.56 (c)	1.26 ± 0.12 (cd)
PB	15.19 ± 0.51 (c)	22.95 ± 1.77 (c)	10.85 ± 1.23 (c)	0.94 ± 0.26 (d)

Note: The values after the ± sign denote the standard deviation and those with the same alphabet (a-d) are not significantly different ($\alpha = 0.05$).

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

Figure 4.2 shows the comparison of the higher heating value of syngas achieved from yellow pine and switchgrass pellets with their blends. It clearly shows that the 75:25 (YP: SG) blend has higher HHV than the 50:50 (YP: SG) blend since the HHV of syngas from yellow pine itself is greater than that from switchgrass. However, the HHVs of syngas from pine chips and bark were not significantly different with each other and hence their blends were not different either, as seen in Figure 4.3.

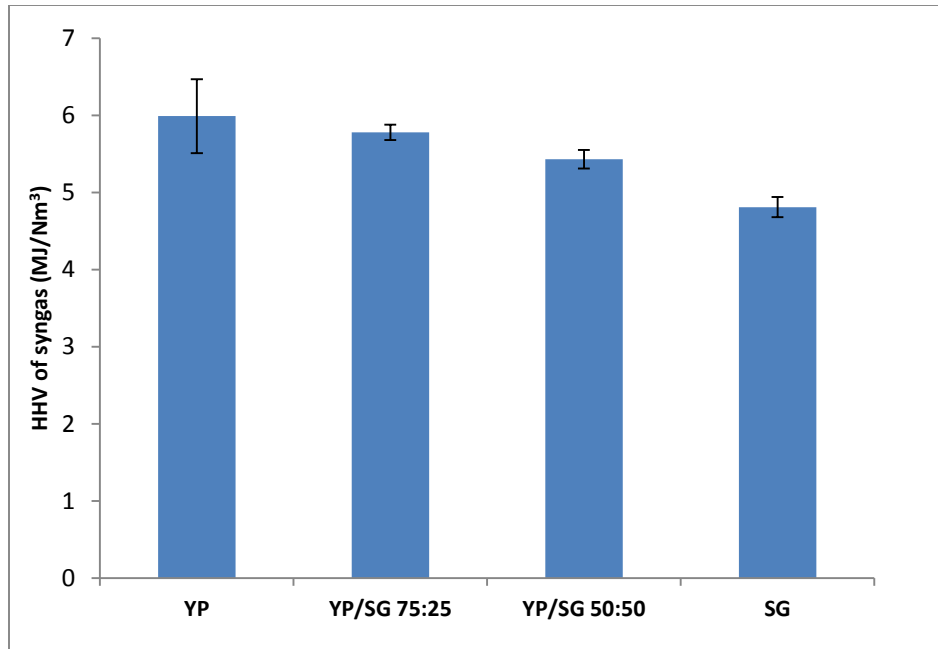


Figure 4.2 HHV of syngas from blends of yellow pine and switchgrass

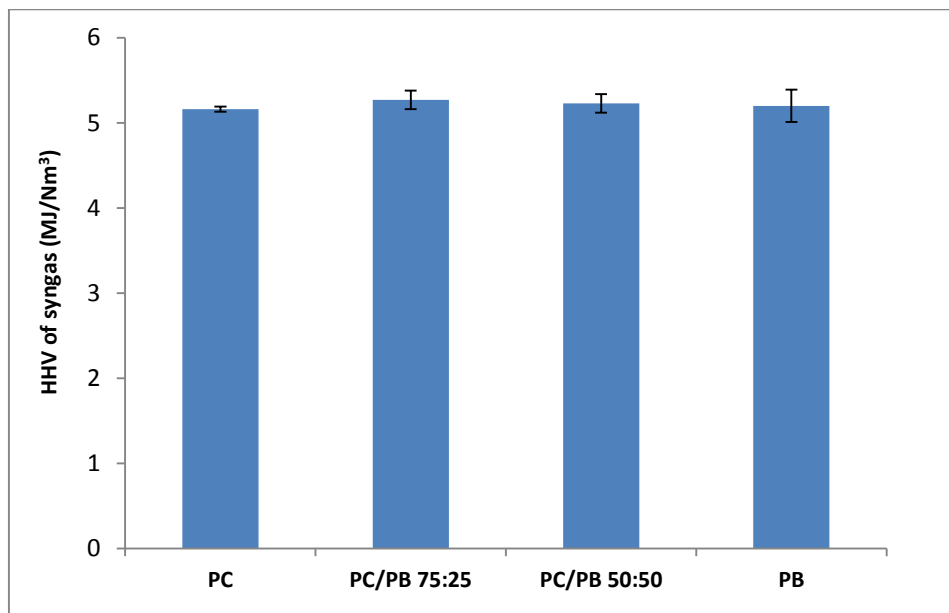


Figure 4.3 HHV of syngas from blends of pine chips and bark

The ash agglomeration that was seen during gasification of switchgrass alone was not an issue anymore with either of the two blends of switchgrass and yellow pine. As observed in the proximate analysis, the ash content of the blends was significantly reduced and as a result, the

gasification run was smooth and uninterrupted. Also, unlike the gasification runs of pine pellets, there was no clogging of filter bags during the blended material runs.

4.5.3 Carbon, Energy and Exergy Analyses

High carbon closure values of above 0.95 were achieved for both the yellow pine and switchgrass pellets' blends as seen in Table 4.6. Although carbon closure is ideally supposed to be unity, it was found to be greater than one for the 75:25 yellow pine and switchgrass blend. This might be due to some technical errors and also the fact that there was some residual biomass inside the reactor which could not be accounted for due to operational difficulties. The hot and cold gas efficiency for the blends was also quite high, ranging from 0.92-0.95 and 0.76-0.79 respectively. Exergy ratio for the blends was found to be ~0.62-0.67.

Table 4.6 Carbon, energy and exergy analyses

Biomass blends	Carbon closure	Hot gas efficiency	Cold gas efficiency	Exergy ratio
YP/SG 75:25	1.02 ± 0.10	0.94 ± 0.01	0.79 ± 0.01	0.66 ± 0.01
YP/SG 50:50	0.99 ± 0.03	0.92 ± 0.01	0.76 ± 0.02	0.62 ± 0.01
PC/PB 75:25	0.95 ± 0.10	0.94 ± 0.02	0.77 ± 0.02	0.63 ± 0.01
PC/PB 50:50	0.96 ± 0.10	0.93 ± 0.01	0.76 ± 0.02	0.65 ± 0.01

Note: The values after the ± sign denote the standard deviation.

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

4.5.4 Tar Concentration

Tar content of syngas was analyzed by the GC-FID and the results for yellow pine/switchgrass and pine chips/bark blends are shown in Figures 4.5 and 4.6, respectively. There was a substantial presence of BTX compounds, mainly benzene and toluene in all the blends. Some tertiary condensed tar products were also observed due to thermal cracking inside the gasifier. The 75:25 and 50:50 blends of yellow pine and switchgrass showed a total concentration of 1.97

g/m³ and 1.86 g/m³, respectively. As expected, these values were lower compared to yellow pine alone (2.27 g/m³) but higher than switchgrass (1.5 g/m³), which are reported in the previous chapter. However, blends of pine chips and bark showed higher concentrations (1.66 g/m³ in 75:25 and 1.57 g/m³ in 50:50) as compared to pine chips (1.36 g/m³) and pine bark (0.91 g/m³).

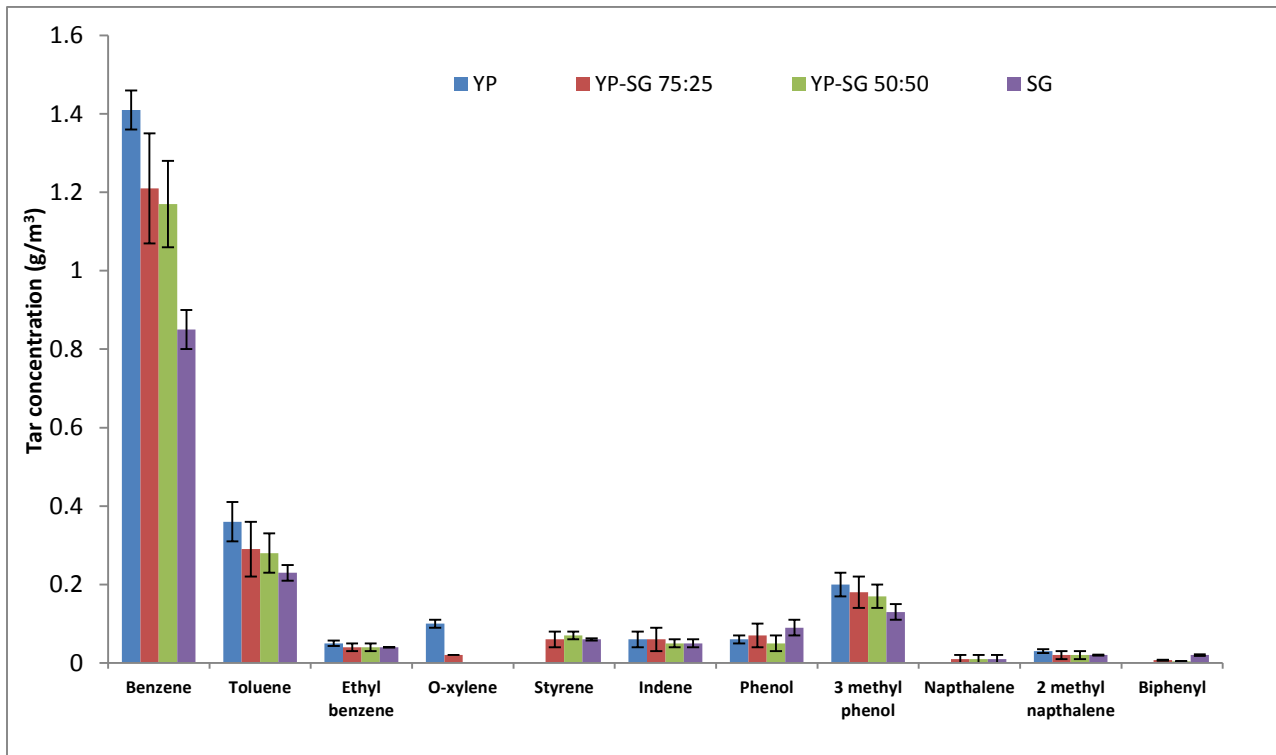


Figure 4.4 Tar concentration in syngas from yellow pine/switchgrass blends

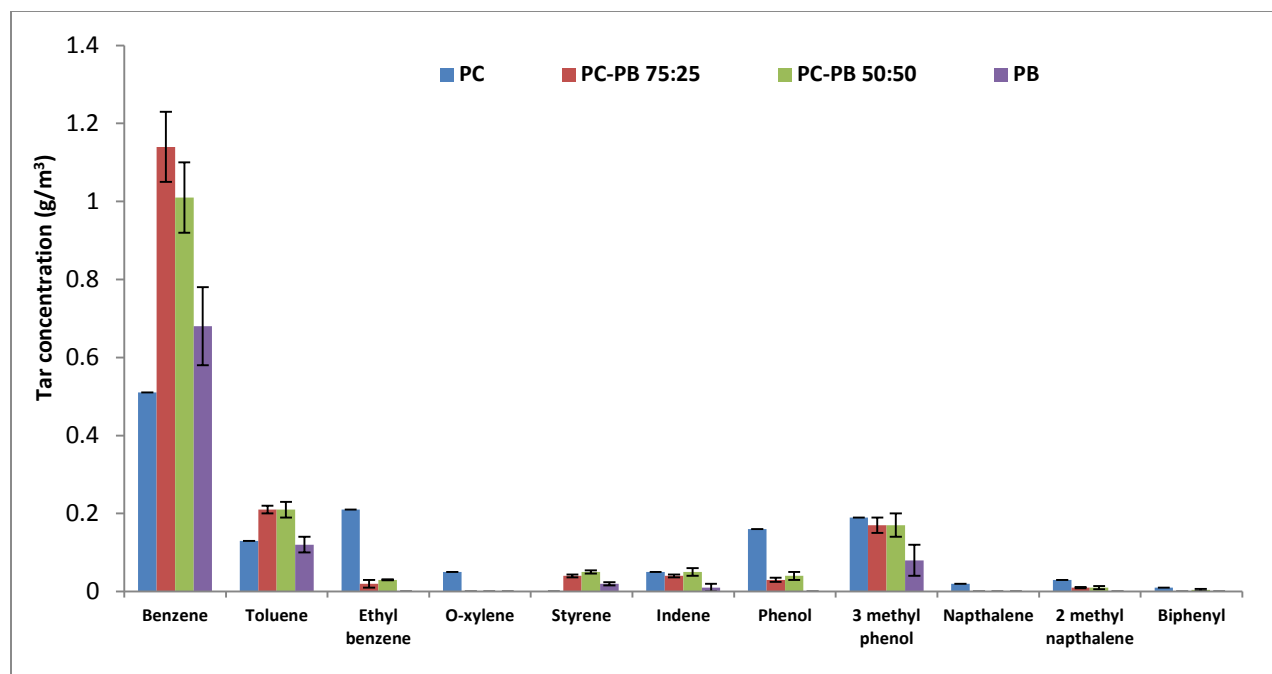


Figure 4.5 Tar concentration in syngas from pine chips/bark blends

**Abbreviations used for the biomass: YP – yellow pine, SG – switchgrass, PC – pine chips and PB – pine bark*

4.5.5 Hydrogen Sulfide Concentration

Figure 4.6 shows that the hydrogen sulfide concentration is reduced as the percentage of yellow pine comes down in the pine/switchgrass blend. This was expected since the H₂S concentration was lower in syngas from yellow pine as compared to that from switchgrass. However, the reduction was not statistically significant at $\alpha = 0.05$ level. An increase in H₂S concentration was observed in the 50:50 blends of pine chips and bark than in the 75:25 blends, as shown in Figure 4.8. Again, this increment was not significant at $\alpha = 0.05$ level. Although the datum for pine chips was not available, it can be derived from this trend that the H₂S concentration in syngas from pine chips would be lower than that from pine bark.

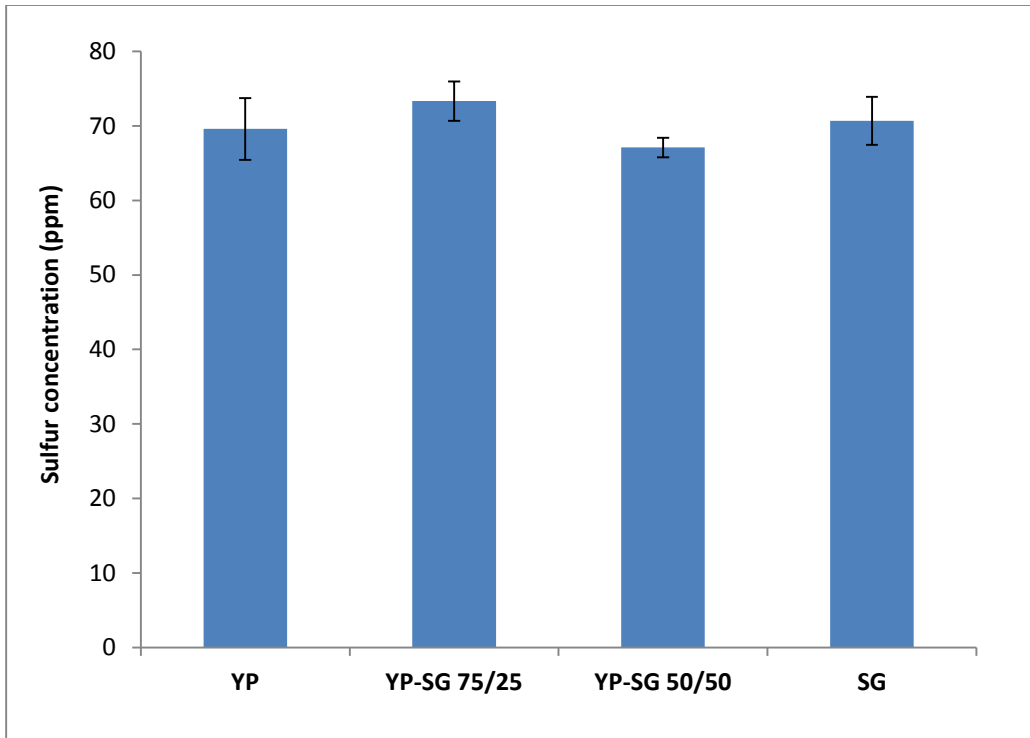


Figure 4.6 H₂S concentration in syngas from yellow pine and switchgrass blends

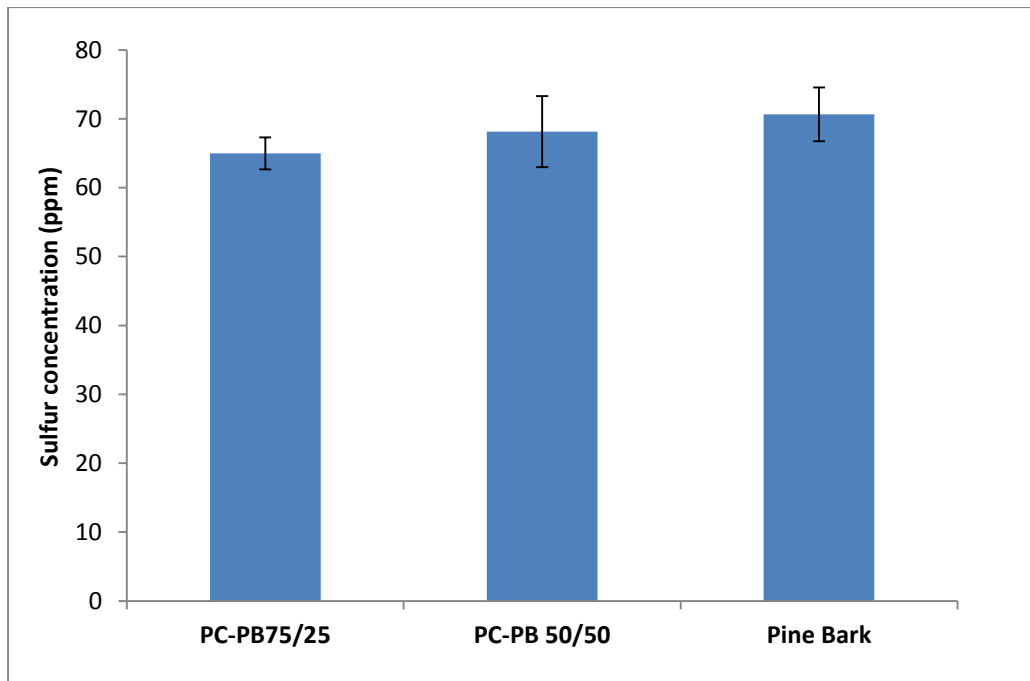


Figure 4.7 H₂S concentration in syngas from pine chips and bark blends

4.6 Conclusions and Remarks

Yellow pine and switchgrass pellets, and pine chips and bark were blended in the ratio 75:25 and 50:50 to study the effects of blending biomass for gasification, especially to cope with problems related to ash agglomeration. Syngas produced from the experiments was analyzed in terms of composition and contaminants. Analyses for carbon closure, hot and cold gas efficiency, and exergy were performed. The following conclusions were drawn from this study:

- Both the blends for pellets showed higher hydrogen and carbon monoxide concentration compared to switchgrass alone but lower compared to yellow pine alone.
- Both the blends for chips and bark showed higher hydrogen concentration compared to both the individual runs of pine chips and bark.
- The HHVs of syngas from the blends of pine chips and bark were not significantly different from each other as well as from the individual runs of pine chips and bark.
- Both the blends of pine chips and bark showed higher tar concentration than their individual runs.
- The ash agglomeration seen in the gasifier grate during switchgrass gasification was not experienced during any of the blended runs of yellow pine and switchgrass.

4.7 References

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CHAPTER FIVE

COMPREHENSIVE SIMULATOR APPLIED TO DOWNDRAFT GASIFICATION

5.1 Abstract

Comprehensive Simulator of Fluidized and Moving Bed Equipment (CeSFaMB), a simulation program, has been used to predict the effect of operational conditions on syngas composition and validate experimental tests conducted in a mobile downdraft gasifier using a number of biomass feedstock. Accuracy in determining the composition of major constituents of syngas viz. hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4) serves as the yardstick for usefulness of the model. Experiments were carried out at atmospheric pressure and air was used as the gasifying agent. The model was calibrated according to the nature of feeding fuel before its application, using results from gasification of loblolly pine pellets. After calibration, deviations between the experimental and simulation results for the composition of hydrogen, carbon monoxide and carbon dioxide were within 5-10% but greater than that for methane in all the cases. Effects of equivalence ratio (E.R.), moisture content and flow rate of biomass were also studied by means of a parametric analysis in the model. The concentration of H_2 , CO and CH_4 decreased while CO_2 increased with increasing E.R.; H_2 and CO_2 increased while CO and CH_4 decreased with increasing moisture content; and H_2 , CO and CH_4 increased while CO_2 decreased with increasing biomass flow rate as well as increasing carbon and hydrogen content in biomass.

Keywords: simulation, CeSFaMB, equivalence ratio, parametric analysis

5.2 Introduction

Producing quality syngas faces many challenges due to the diverse nature of different types of biomass and various operating parameters which need to be optimally met. With interest being generated in the development of an economical and efficient gasifier, mathematical models that predict the performance of such reactors and feeding fuels have gained popularity. Such theoretical models reveal detailed structure of the burning process inside a solid bed, such as reaction zone thickness, combustion staging, gas emission and char burning characteristics, thus contributing to better understanding and controlling of the process [1]. The application of mathematical simulation helps save useful time and financial resources otherwise required in error-prone experimental search for favorable conditions.

Since its early version, which was named CSFB, the program was used to predict the behavior of bubbling fluidized beds [2]. It has recently been classified as comprehensive because it includes all sub-models related to combustion and gasification of solid fuels and allows detailed simulation of boilers and gasifiers [121, 122, 123]. It has also been improved and expanded in order to simulate a wider range of operations, such as those taking place in circulating fluidized beds and moving bed equipment [1, 6, 7]. Development of the basic model took place as part of a PhD thesis at the University of Sheffield (UK). Later, the first successful version of the model was developed in 1987 which was capable of reproducing operational conditions of Babcock and Wilcox boiler unit in USA as well as those of National Coal Board (UK) boilers [4]. The new improved version (CeSFaMB) is said to be more reliable and flexible regarding feeding fuels. It is also said to be more robust in terms of convergence [8].

The model assumes all variable changes occurring in the vertical direction. The one-dimensional approach is followed in almost all modeling of gas-solid packed systems [1, 9]. It is believed to

provide the highest cost-benefit ratio among all possible levels of modeling. It has been successfully adopted by many, especially for moving bed gasifiers or combustors [9, 10, 11]. Though it may seem simple initially, the first order model assumption for such reactors may involve up to five physical phases, chemical reactions in all phases, dynamics of each phase, heat and mass transfers among all phases, and heat transfer between phases and the internal (tubes and walls) parts of the reactor [1]. For gasifiers, one-dimensional steady state model seems to be the optimum choice. Zero-dimensional (0D-S) model does not allow description or evaluation of temperature, velocity or concentration profiles inside the equipment. Also, two-dimensional steady state model seems unnecessary since the variation in concentration and temperature in the radial direction is negligible compared to that in the axial direction.

The present comprehensive mathematical model and simulation program is an optimum compromise in simulation accuracy, computational resources and processing time. It calculates the steady state performance using point-by-point energy and mass differential balances, kinetics of chemical reactions, fluidization dynamics and an auxiliary data bank for computations of physical–chemical properties. The model considers around a hundred possible chemical reactions, including processes such as de-volatilization and drying of carbonaceous solid fuels. Concentration and mass profiles of 18 gas components, composition, circulation rates and particle size distributions of solid species, temperature profiles of gases, etc. are only some of the plethora of information that can be derived from this model.

The objective of this chapter was to apply the software CeSFaMB to determine the syngas composition from gasification for biomass feedstocks that are of regional interest for power and fuels production. The model will be used as the guide to selection of operational parameters when a new biomass is being considered for gasification. Results from actual experiments were

compared with the simulation output to validate the accuracy of the program. Moreover, a parametric study was conducted to identify the effect of key operating parameters viz. equivalence ratio, moisture content and mass flow rate of biomass on the output of the program as well as the gasification process.

5.3 Methodology

5.3.1 Model Assumptions for a Downdraft Gasifier [129, 130]

- a.) ***Steady state operation:*** For reactors that operate for long periods with almost no interruptions, a steady state operation can be assumed. However, the assumption does not include the starting-up and shutting-down periods. For the downdraft gasifier, the rates of biomass feeding and withdrawal of syngas were relatively constant (with low fluctuations).
- b.) ***Plug-flow regime of gas and solid particles:*** Due to absence of rotational velocity and all variables being uniformly distributed, angular components can be neglected. Only axial velocity component is present in the solid phase as the radial flow is zero. The overall combination of gas streams being forced to pass through small corridors or channels between particles mimic a plug-flow. Assuming the gas velocity to be even throughout the bed cross-section, the temperature and concentration profiles can also be modeled as flat profiles. Hence, the rates of gas-solid reactions do not vary much in the radial or horizontal direction.
- c.) ***Negligible momentum transfer between solid and gas phase:*** Velocity profile of one phase is not affected by the flow of the other phase. Since the velocities in moving bed gasifiers are found to be very small for both solid and gas phase, the momentum transfer between them can be neglected.

- d.) ***Inviscid flow:*** The layers of gases between solid particles are thin enough to assume that there is no turbulent flow. Also, there are no shear stresses between layers if plug-flow regimes are assumed.
- e.) ***Flat temperature and concentration profiles:*** Given the thin layers of solid particles in the gasifier, it can be assumed that the heat transfer within each particle is fast enough to equalize the temperature throughout its volume. Thus, the difference between the temperatures of gas and solid phase can be neglected. Also, if the total mass flow in the vertical (main) direction is much higher than the flow exchanged between phases, the flat temperature and concentration profiles can be assumed.
- f.) ***No heat transfer by radiation:*** Since the gas layers between particles are small, heat transfer by radiation inside each phase and between phases can be neglected.

5.3.2 Program Input

The present mathematical model is an approximation of reality. The objective of simulation results is to reproduce existing real operation variables with small deviations. The degree of deviation between real operational data and simulation results depends strongly on the accuracy of entered data as well as that of the model. The better the accuracy, the better are the chances of applying CeSFaMB to simulate existing operating unit or help designing future installation. The program requires reliable and detailed description of reactor geometry as well as information regarding rates and characteristics of injected gas streams and particulate solids fed into the gasifier. The most significant input and output parameters are listed in detail in Appendix D.

The information regarding the geometry of the gasifier and operating conditions are given in Table 5.1. Primary air was delivered from the open top of the gasifier at atmospheric temperature and pressure. Secondary air was injected through five different ports at 0.4 m, 0.53 m, 0.66 m,

0.79 m and 0.92 m along the height of the gasifier. Biomass was fed into the gasifier at a rate of 25-30 kg per hour depending upon the type of feedstock. The gasifier was insulated on the outside with fiberglass. The properties of the different biomass feedstock are given in Table 5.2.

Table 5.1 Gasifier data

Detail	Input values
Class description	
Operating mode	Gasification
Equipment type	Downdraft moving bed
Basic geometry	
Shape of bed cross section	Circular
Hydraulic internal diameter (m)	0.35
Bed depth (m)	1.2
Position of fuel feeding (m)	1.2
Average operational pressure (kPa)	101.3
Thermal insulation of reactor	
Thickness (m)	0.18
Average thermal conductivity (W/mK) [14]	0.04
Average emissivity	0.75

The targeted syngas outflow was 65 m³/hr in the actual experiments. However, due to presence of certain amount of base air flow in the system, the actual value varied between 52-57 m³/hr. The actual value was easily obtained from generated lab-view data of the system and thus applied. The inlet air flow for different experiments is listed in Table 5.2. The feeding rate of biomass was adjusted according to the type of biomass and whilst maintaining the syngas flow rate. Pine bark has the lowest flowability among the biomass feedstock used in these experiments, as shown by its low flow rate in Table 5.2. Sphericity for the biomass was measured using the RETSCH Camsizer, which was also used to determine the particle size distribution given in Tables 5.3 and 5.4.

Table 5.2 Characteristics of feeding fuel

Details	Biomass*						
	LP	HP	SP	PC	YP	TP	PB
Proximate analysis (w.b. %)							
Moisture	7.13	5.28	9.01	9.46	9.09	4.55	14.41
Volatile	84.96	88.00	78.59	84.17	86.95	74.85	78.16
Fixed carbon	7.47	6.32	7.95	6.12	3.44	19.51	5.86
Ash	0.44	0.41	4.45	0.25	0.53	1.09	1.57
Ultimate analysis (d.b. %)							
C	50.85	50.02	46.79	51.80	50.98	57.40	53.33
H	7.25	6.97	7.33	7.32	7.15	6.14	6.66
N	0.08	0.11	0.74	0.10	0.09	0.15	0.40
O	41.26	42.38	40.33	40.44	40.86	34.91	37.66
S	0.12	0.12	0.15	0.09	0.40	0.30	0.36
Ash	0.44	0.41	4.66	0.25	0.53	1.10	1.59
Physical properties							
HHV (MJ/kg)	20.85	19.73	18.96	19.56	18.55	21.54	18.59
Inlet mass flow rate (kg/s) x 10 ²	0.72	0.76	0.77	0.72	0.76	0.67	0.61
Bulk density (kg/m ³)	684.35	667.51	635.46	225.33	611.15	685.00	154.00
Particle density (kg/m ³)	1456.00	1462.83	1476	1416.50	1434	1424	1079
Sphericity	0.75	0.69	0.78	0.53	0.68	0.75	0.51
Operational condition							
Primary air mass flow (kg/s) x 10 ²	0.85	0.67	0.81	0.77	0.60	0.73	0.65
Intermediate air flow (kg/s) x 10 ²	0.52	0.52	0.52	0.52	0.52	0.52	0.52

**Abbreviations for the biomass used: LP – Loblolly pine pellets, HP – Hardwood pellets, SP – Switchgrass pellets, PC – Pine chips, YP – Yellow pine pellets, TP – Torrefied pine pellets and PB – Pine bark. (Note: The properties of biomass are shown as used in the model. Their respective standard deviations are informed in the previous chapter.)*

Table 5.3 Particle size distributions of loblolly, hardwood and switchgrass pellets

Biomass	Particle size distribution	
	Sieve opening (mm)	Retained mass (%)
Loblolly pine pellets	6.36	94.50
	5.05	3.70
	4.01	1.40
	3.18	0.40
Hardwood pellets	8.01	98.50
	6.36	1.20
	5.05	0.20
	0.25	0.10
Switchgrass pellets	10.09	0.70
	8.01	88.60
	6.36	9.40
	5.05	1.10
	4.01	0.20

Table 5.4 Particle size distributions of yellow and torrefied pine pellets, and pine chips and bark

Biomass	Particle size distribution		Biomass	Particle size distribution	
	Sieve opening (mm)	Retained mass (%)		Sieve opening (mm)	Retained mass (%)
Pine chips	1000.00	17.70	Torrefied pine pellets	10.50	2.20
	16.00	12.80		10.00	0.10
	12.70	16.50		8.50	0.90
	10.09	27.10		8.25	13.90
	8.01	11.20		8.00	39.70
	6.36	10.70		7.75	27.60
	5.05	2.20		7.50	8.20
	4.01	1.30		7.25	1.80
	3.18	0.40		7.00	2.50
	2.01	0.10		6.50	1.10
Yellow pine pellets	10.50	0.30		6.25	0.40
	10.00	0.20		6.00	0.30
	9.75	0.50		5.75	0.50
	9.50	0.50		5.50	0.30
	9.25	4.40		5.25	0.20
	9.00	23.10		5.00	0.30
	8.50	13.30	Pine bark	22.50	3.90
	8.25	12.60		20.00	3.00
	8.00	6.80		17.00	14.70
	7.75	3.20		15.00	8.90
	7.50	3.20		13.00	16.50
	7.25	3.40		11.20	15.60
	7.00	7.20		9.50	12.00
	6.50	2.80		8.00	9.50
	6.25	2.10		6.70	2.70
	6.00	2.40		6.30	4.10
	5.75	2.40		5.60	2.90
	5.50	2.70		4.75	2.80
	5.25	2.30		4.00	1.40
	5.00	3.00		3.35	1.00
	4.50	1.30		2.80	0.40
	4.25	0.80		2.36	0.20
	4.00	0.60		2.00	0.10
	3.75	0.30		1.70	0.10
	3.50	0.40	1.00	0.10	
	3.00	0.20	0.21	0.10	

5.4 Results and Discussion

Initially, the program was not able to reproduce the results from gasification of pine pellets in the mobile downdraft gasifier, mainly due to the difference in reactivity of feeding fuel as well as limitations of the simulator. It can also be due to the fact that many fuels contain components that even at very low concentrations tend to act as catalysts or poisons to various reactions [12]. Different kinetic parameters can be found in literature even for a single reaction. If specific kinetics of key reactions is not available for a given fuel, the alternative is to calibrate the simulator based on data from one experimental test [13]. Similar approach was adopted by de Souza-Santos [13] while simulating results for experiments carried out using coal in a bubbling fluidized bed gasifier at the National University of Colombia (UNC). The usefulness of the simulator would be assured if it is capable of reproducing other tests consuming fuels with similar composition.

The effect of reactivity on the model can be seen illustrated in Table 5.4. Gasification of loblolly pine pellets was carried out using the CPC mobile downdraft gasifier. The simulation results related to the composition of produced syngas are shown in Table 5.5. Large deviations in concentrations of syngas components, especially carbon monoxide and hydrogen can be seen between the simulation and experimental outputs. It shows that the reactivity of loblolly pine was considerably different from bituminous coals that were used as standards by the program [2, 14]. Using the syngas data obtained from the runs, the values of kinetic coefficients were set accordingly to simulate the experimental results more accurately.

Table 5.5 Syngas composition (molar d.b. %) produced from loblolly pine pellets obtained during gasification and respective simulation results obtained without calibration

Gases	Syngas Composition (molar %)	
	Experimental	Simulation
H ₂	14.3	5.9
CO	18.4	10.9
CO ₂	10.5	17.6
CH ₄	1.9	11.5
N ₂	54.8	53.8
H ₂ S	n.d.	280 ppm
NH ₃	n.d.	340 ppm
NO	n.d.	260 ppm
SO ₂	n.d.	70 ppm
HCN	n.d.	210 ppm
C ₂ H ₄	n.d.	480 ppm
C ₃ H ₆	n.d.	20 ppm

n.d.: not determined

5.4.1 Calibration of Reaction Kinetics

The reactivity of different chemical reactions occurring in the gasifier varies according to carbonaceous fuel used. In some cases, the difference in reactivity of fuels is so significant that it is almost impossible to set a completely general bank of kinetic coefficients [4]. There is an extensive data bank of kinetic coefficients which is automatically applied once the type of fuel is entered as input. In addition, the model allows the user to enter specifically laboratory-determined kinetic coefficients to calibrate the simulation for special cases where the fuel or absorbent might present different kinetics.

The reactions that were found to have a significant impact on our gasification process and the program are shown in Table 5.6.

Table 5.6 Kinetic parameters of reactions

Reaction number	Reaction	Kinetic coefficient (<i>k</i>) from reference	Value of <i>k</i> used in the model	Unit of <i>k</i>
R. 41	$CO + H_2O \leftrightarrow CO_2 + H_2$	2.778×10^3	2.778×10^5	$\text{kmol}^{-1} \text{m}^3 \text{s}^{-1}$
R. 42	$2CO + O_2 \leftrightarrow 2CO_2$	1.3×10^{11}	1.3×10^9	$\text{kmol}^{-0.75} \text{m}^{2.25} \text{s}^{-1}$
R. 50	$Tar \rightarrow Gases$	4.0×10^4	4.0×10^5	s^{-1}
R. 71	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	3.0×10^{-9}	8.0×10^{-7}	$\text{kmol}^{-1} \text{m}^3 \text{s}^{-1}$

Using the simulation trial setting from Table 5.6, noticeable decreases in deviations between simulation and experimental results were achieved, as presented in Table 5.7. The program predicts the concentration of H₂, CO and CO₂ to a satisfactory level of accuracy, indicated by the fact that the simulated values fall in the range of the standard deviations seen in the experiments. However, the simulation shows the CH₄ concentration to be 5.26% while that achieved from experiment was only 1.94%.

Table 5.7 Syngas composition (molar d.b.%) produced from loblolly pine pellets obtained during gasification and respective simulation results obtained after calibration

Gases	Syngas Composition (%)	
	Experimental	Simulation
H ₂	14.3 (2.8)	14.9
CO	18.4 (3.2)	20.1
CO ₂	10.5 (2.3)	10.5
CH ₄	1.9 (0.9)	5.3
N ₂	54.8	49.1
H ₂ S	n.d.	140 ppm
NH ₃	n.d.	80 ppm
NO	n.d.	550 ppm
SO ₂	n.d.	170 ppm
HCN	n.d.	100 ppm
C ₂ H ₄	n.d.	370 ppm
C ₃ H ₆	n.d.	10 ppm

Figure 5.1 shows a steady level of CO in the upper half of the reactor and then a slight decrease in the lower half. Logarithmic representation of the concentration in Figure 5.2 shows small surges of oxygen at the intermediate air injection positions of the reactor. The concentration of CO₂ remains more or less constant throughout the reactor. This trend can also be substantiated by Figure 5.4 where the rate of shift-reaction (R. 41) seems to slightly increase in the middle of the reactor. The concentration of H₂ increases up to one third of the reactor height and stabilizes for the most part, as seen in Figure 5.3. In the same figure, the concentration of CH₄ is dropping throughout the reactor. Steam reforming reaction (R.71) is shown to be prevalent in Figure 5.5. It shows a steady decline in methane throughout the reactor, thus leading to formation of more carbon monoxide and hydrogen.

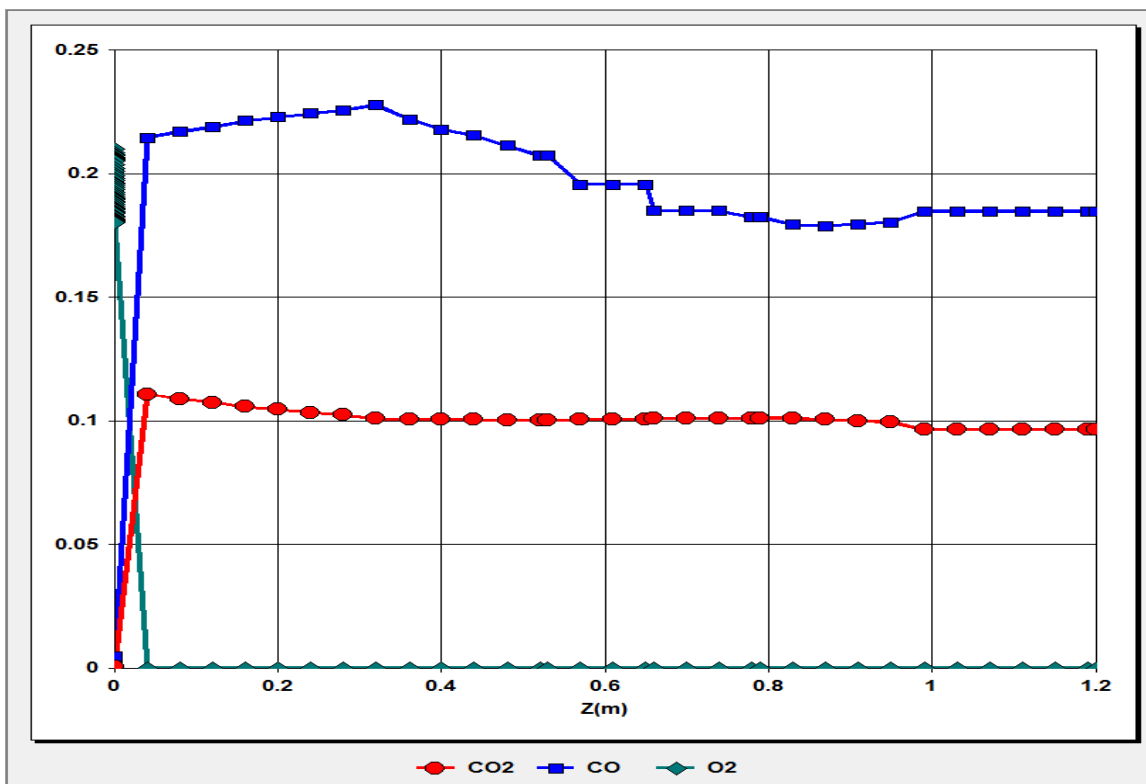


Figure 5.1 Molar fraction profiles of CO, CO₂ and O₂ throughout the reactor

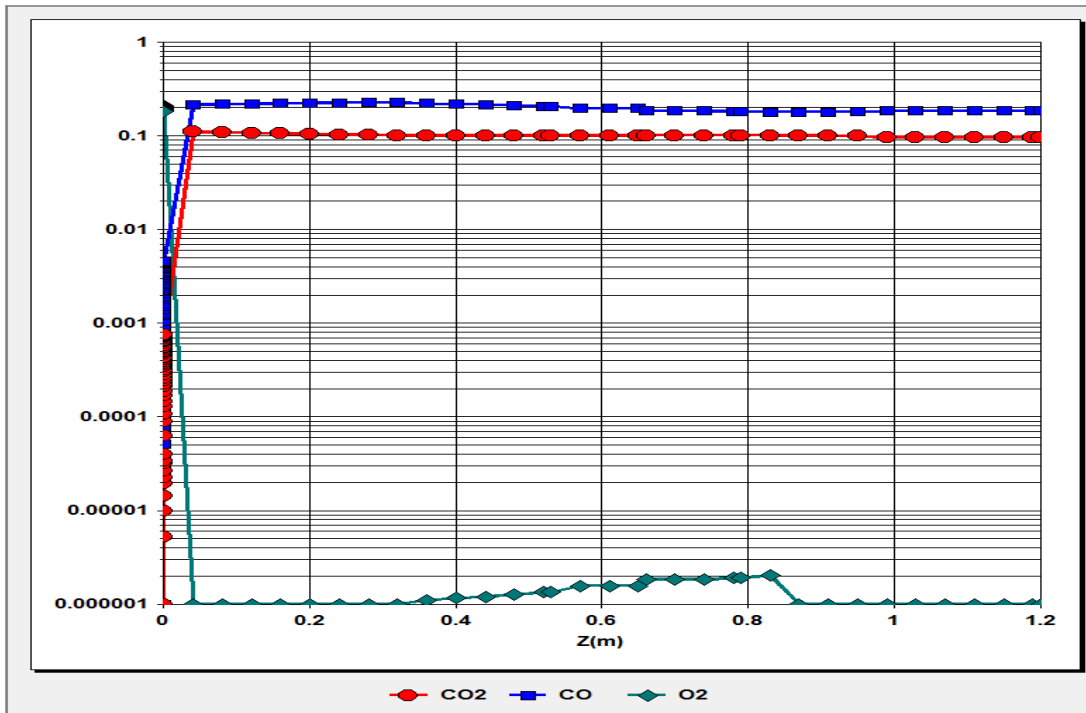


Figure 5.2 Molar fraction profiles of CO, CO₂ and O₂ (Y-logarithmic)

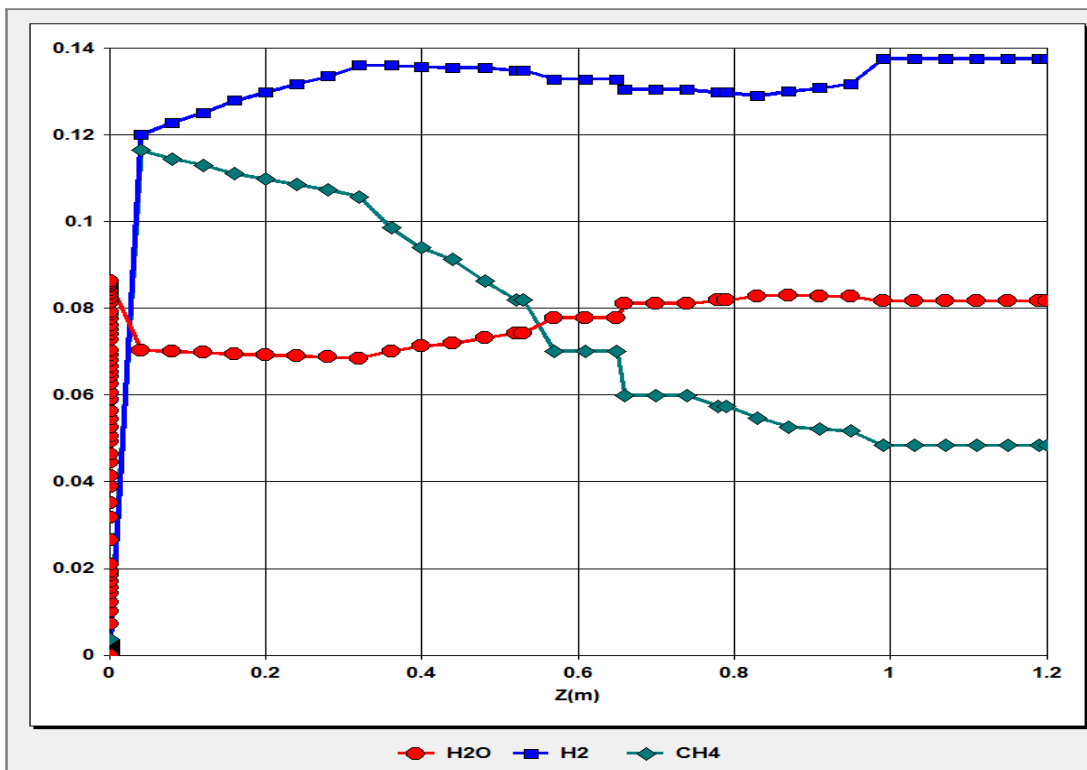


Figure 5.3 Molar fraction profiles of H₂O, H₂ and CH₄ throughout the reactor

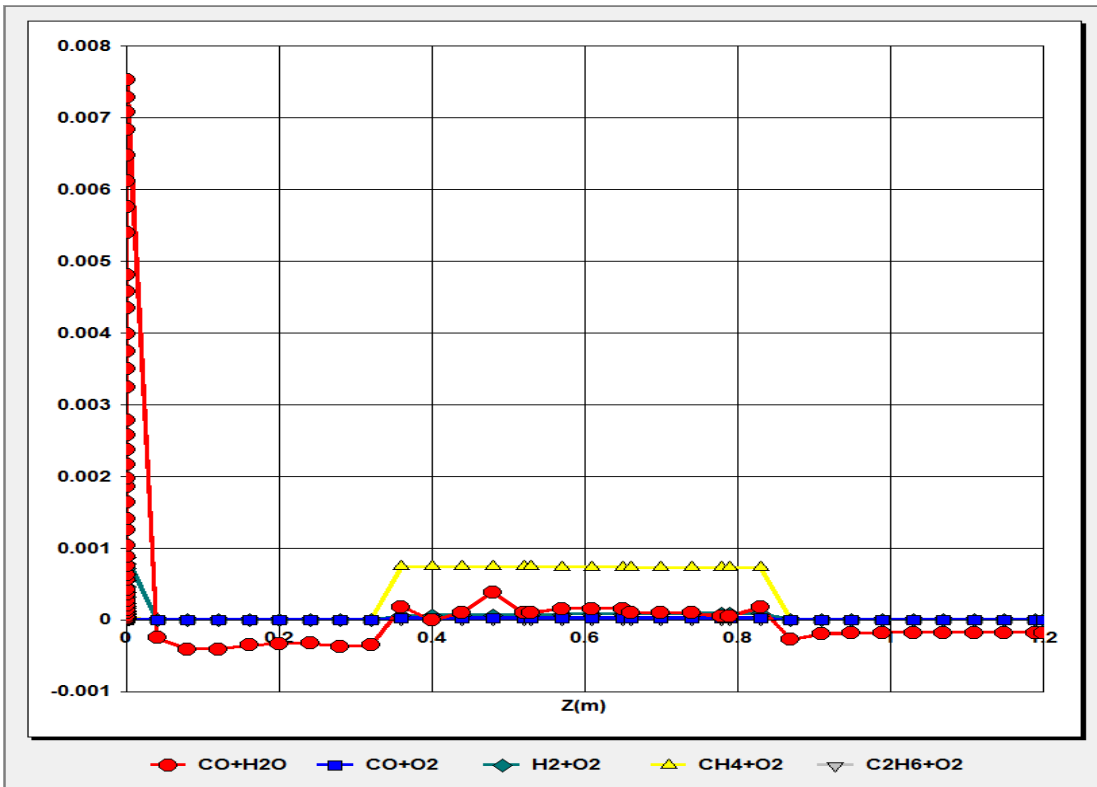


Figure 5.4 Reaction rates of homogeneous reactions throughout the reactor

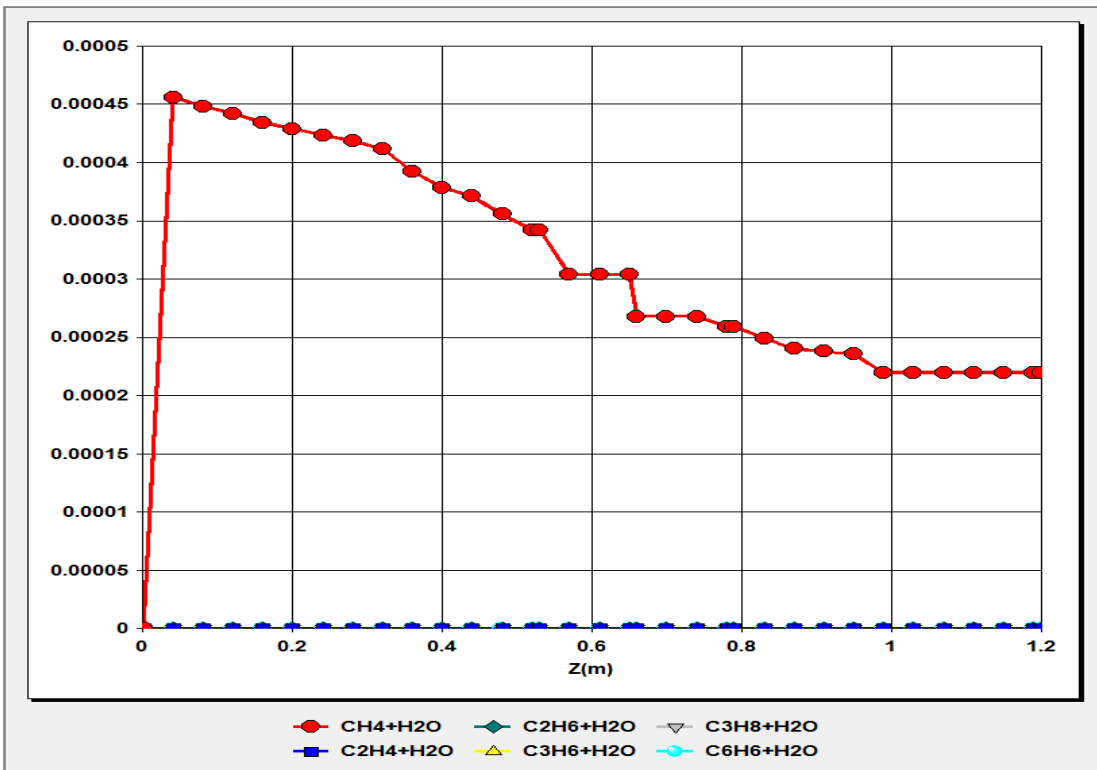


Figure 5.5 Reaction rates of reactions throughout the reactor

5.4.2 Application of Calibrated Program to Other Feeding Fuels

The percent mole fractions of major syngas constituents (H_2 , CO , CO_2 and CH_4) obtained from simulation of experiments conducted with different biomass (hardwood, switchgrass, yellow pine and torrefied pine pellets and pine chips and bark) are shown in comparison with the actual results in Figures 5.6-5.11. The H_2 , CO and CO_2 concentration is seen to be predicted more or less accurately (5-10% deviation) in almost all the cases, while the CH_4 concentration is higher than the actual value in most cases. Switchgrass is predicted to have greater H_2 concentration than loblolly pine even though the hydrogen content in biomass is almost the same.

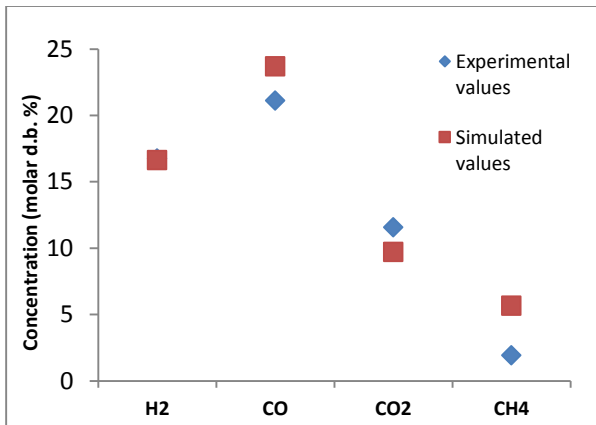


Figure 5.6 Syngas composition: hardwood

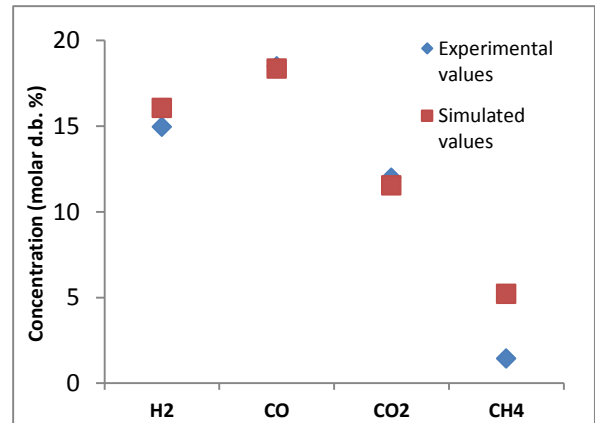


Figure 5.7 Syngas composition: switchgrass

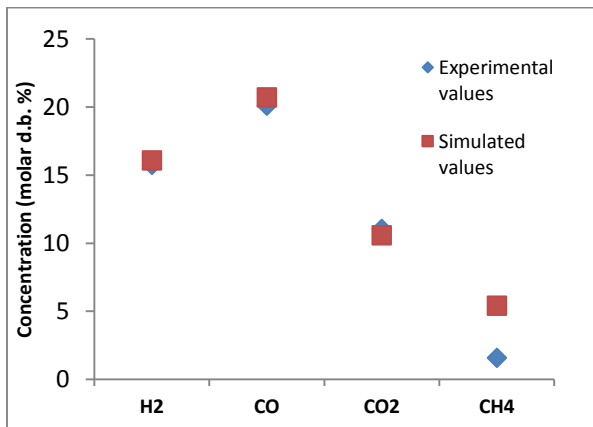


Figure 5.8 Syngas composition: pine chips

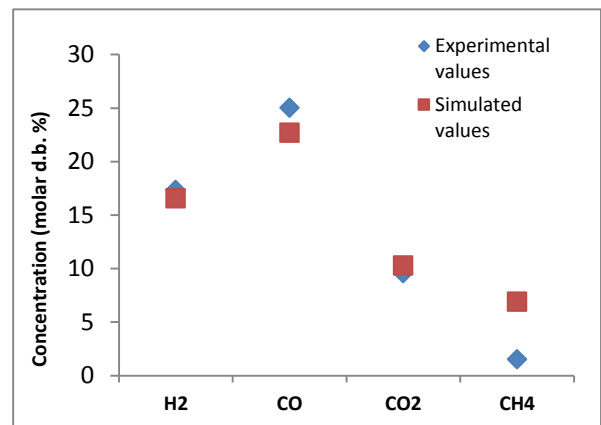


Figure 5.9 Syngas composition: yellow pine

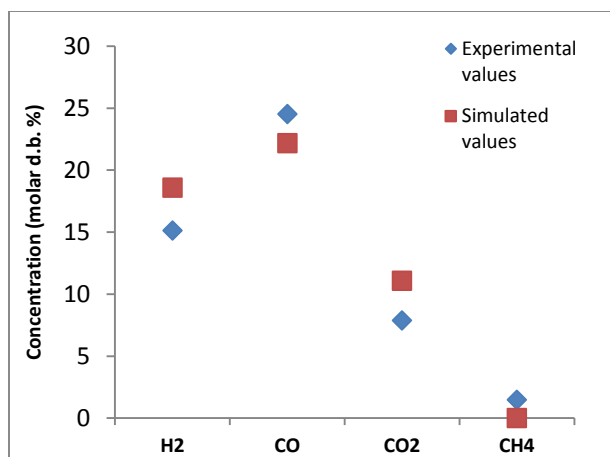


Figure 5.10 Syngas composition: torrefied pine

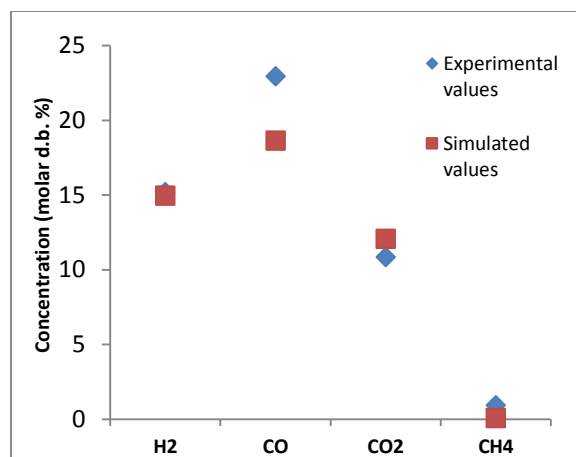


Figure 5.11 Syngas composition: pine bark

5.5 Parametric Study

Performance parameters need to be studied effectively when it comes to designing a reactor. Different operating parameters such as equivalence ratio (E.R.), moisture content and mass flow rate of feeding fuel were varied in the CeSFaMB program in order to optimize the gasification process for maximum gasifier efficiency and gas heating value. Loblolly pine pellets was selected as the biomass feedstock to perform the parametric study and obtain simulated results for syngas composition under varying operating conditions.

5.5.1 Equivalence Ratio (E.R.)

The effect of equivalence ratio on the concentration of syngas constituent gases was studied by varying the parameter ‘Inlet gas flow’ in the program. All the other input parameters were kept the same as used during simulation of actual experimental conditions. Secondary or intermediate air injection was maintained at 40% of the total air input (based on experimental condition). The actual experiment was carried out an E.R. of 0.31 and it was varied from 0.20 to 0.40 for the purpose of this study. H₂, CO and CH₄ concentrations were found to decrease with increasing E.R. while CO₂ shows an increasing trend, as seen in Figure 5.12. This trend can be attributed to

the oxidation reactions (Equations 5.1-5.4) which give carbon dioxide in the presence of excess oxygen.

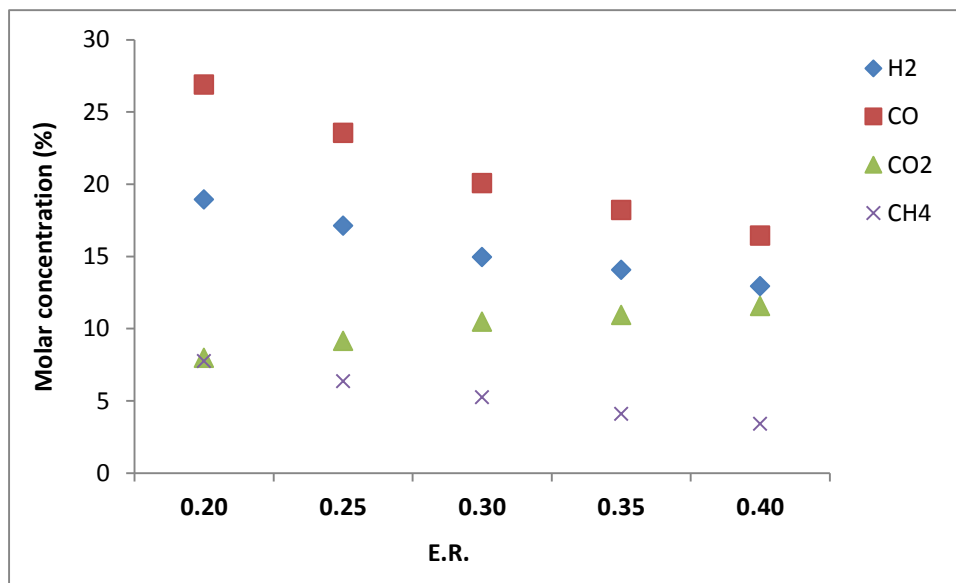
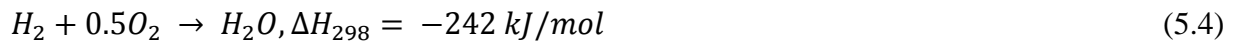
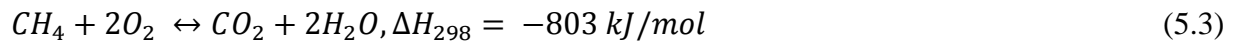
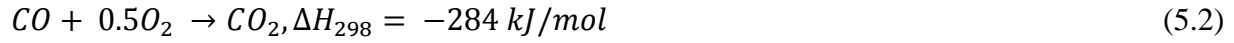


Figure 5.12 Effect of equivalence ratio on the concentration of syngas constituents

5.5.2 Moisture Content

Figure 5.13 shows the effect of moisture content on the concentration of syngas species. Moisture content of loblolly pine pellets was found to be 7.13% during experiments. CO concentration showed significant reduction while H₂ and CO₂ had a slight increasing trend with increasing moisture content in biomass. This phenomenon can also be justified by considering the water gas shift reaction in which carbon monoxide reacts with water to give carbon dioxide

and hydrogen. Reduction in methane can be related to the methane reforming reaction in which methane reacts with water to give carbon monoxide and hydrogen.

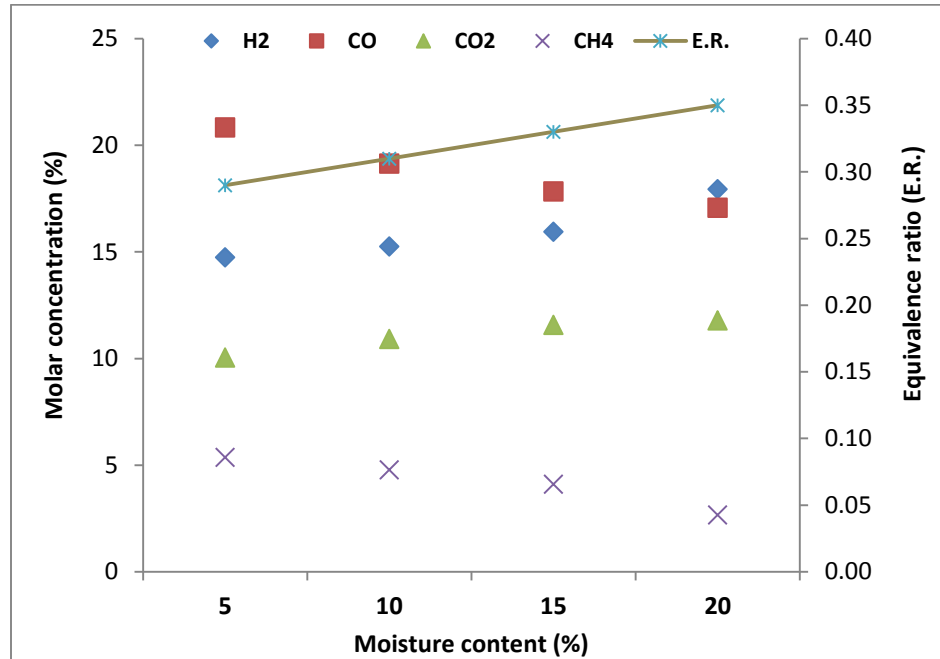


Figure 5.13 Effect of moisture content of biomass on the concentration of syngas constituents

5.5.3 Biomass Feed Rate

The actual feeding rate of the loblolly pine pellets during experiments was 26 kg/hr and the equivalence ratio (E.R.) was observed to be 0.30. As seen in Figure 5.14, the concentration of H₂, CO and CH₄ increased gradually as the biomass feed rate was varied from 15 to 35 kg/hr, while CO₂ concentration showed a slight decrease. The equivalence ratio (E.R.) was found to be decreasing from 0.51 to 0.21 with increasing biomass flow rate since the air required for complete combustion kept increasing but the inlet air flow rate was kept constant in the program.

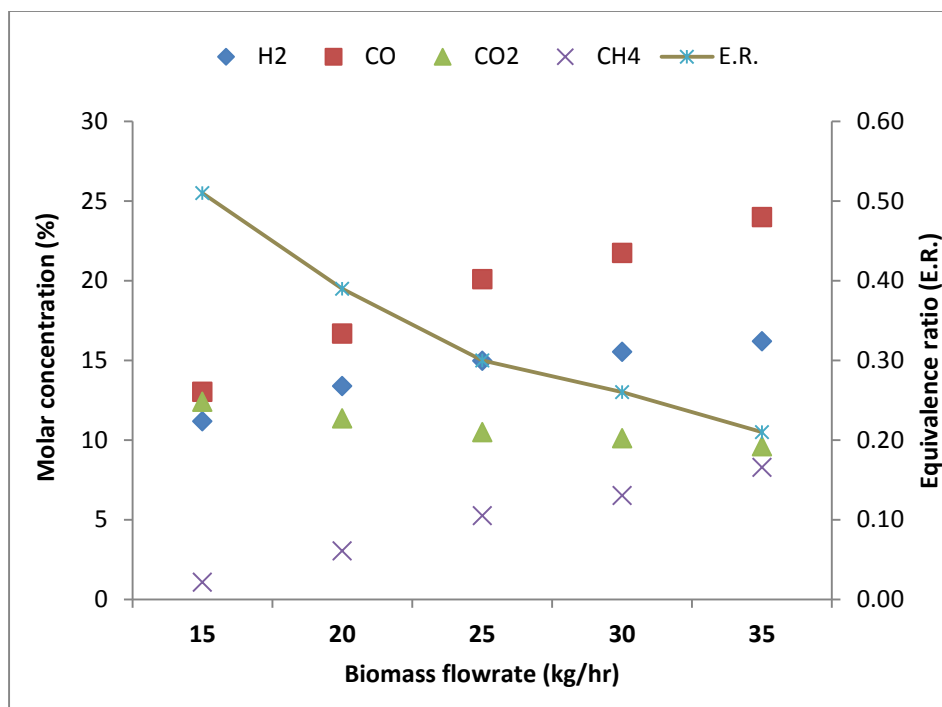


Figure 5.14 Effect of biomass flow rate on the concentration of syngas constituents

5.5.4 Properties of Biomass: Proximate and Ultimate Analyses

Tables 5.8 and 5.9 show the proximate and ultimate analyses, respectively of five switchgrass samples conducted by Biosystems Engineering Research Laboratory at Auburn University. Similar moisture content was observed for the samples while the ash content and volatile matter ranged from 1 to 4% and 81 to 83%, respectively. The sample SG 1 showed the least carbon fraction (~ 45%) while sample SG 5 had the highest carbon content (47.5%). The hydrogen content was found to be 6.2 – 7.3% for all the samples. These data were used in the model to evaluate the effect of properties such as ash content, volatile matter and elemental composition on syngas concentration obtained from the program. Sulfur concentrations for samples SG 3, 4 and 5 could not be accurately determined and were entered as zero in the program.

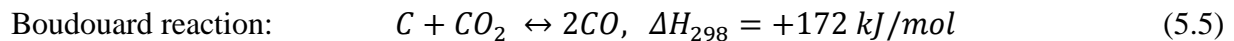
Table 5.8 Proximate analysis (w.b.%) of switchgrass samples

Sample	Moisture	Ash	Volatile matter	Fixed carbon
SG 1	7.67	2.55	81.77	8.01
SG 2	7.14	2.54	83.05	7.27
SG 3	6.16	1.84	82.29	9.71
SG 4	6.94	3.64	81.64	7.78
SG 5	6.62	2.29	81.97	9.12

Table 5.9 Ultimate analysis (ash free d.b.%) of switchgrass samples

Sample	C	H	N	S	O
SG 1	44.98	6.35	0.47	0.07	48.13
SG 2	45.35	6.20	0.56	0.12	47.77
SG 3	45.94	6.42	0.46	0.00	47.18
SG 4	46.75	7.21	0.73	0.00	45.31
SG 5	47.45	7.33	0.61	0.00	44.61

Figure 5.15 shows the syngas composition from five switchgrass samples as obtained from the program. The concentrations of H₂ and CO showed an increasing trend for samples SG 1 to SG 5, which are in order of increasing carbon content. On the contrary, CO₂ concentrations were found to be decreasing for that order. This trend can be attributed to Boudouard and Water-gas reactions as given by Equations 5.5 and 5.6, respectively, which show that presence of more carbon produces more CO and H₂. The increase in CH₄ can also be justified by the Hydrogenation reaction given by Equation 5.7. Sample SG 1 which had lower hydrogen content as compared to SG 3, was found to have higher H₂ concentration than SG 3. It was also observed that SG 1 had the highest moisture content (7.67%) which caused a spike in the H₂ concentration.



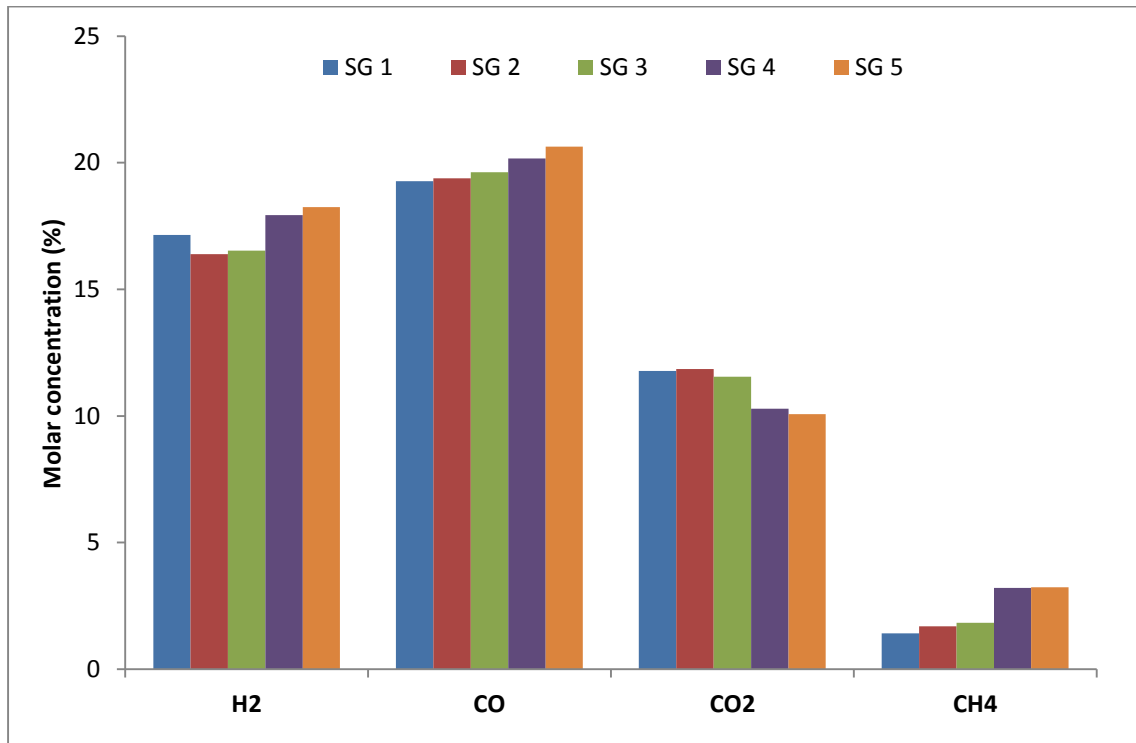
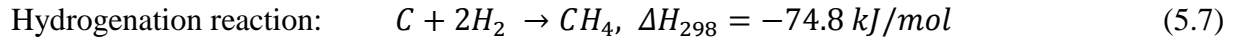
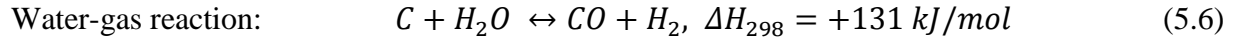


Figure 5.15 Simulation of syngas composition from switchgrass samples

5.6 Conclusions

Syngas composition from gasification of various feedstocks obtained through simulation was compared to the experimental results. The program was unable to reproduce experimental results initially and calibration was needed to adjust the model to the properties of feeding fuel. After calibration of reaction kinetics, it was capable of providing reasonable reproduction of experimental tests after calibration of reaction kinetics. However, the concentration of methane was significantly higher than the actual experimental value.

The parametric study concluded that the model is most sensitive to inlet air or gas flow, moisture content, mass flow rate and elemental composition of feeding fuel. Higher concentration of hydrogen and carbon monoxide was achieved in the model output at lower equivalence ratio and higher biomass flow rate. In order to produce syngas with greater higher heating value, these parameters need to be controlled accordingly.

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CHAPTER SIX

SUMMARY AND FUTURE WORK

6.1 Concluding Remarks

The thesis was able to establish the effect of different biomass feedstocks on the quality of syngas produced from downdraft gasification in terms of the composition of major gases and contaminants. Among the seven types of biomass feedstocks, yellow pine pellets produced syngas with the highest HHV. Although the tar content was relatively high, the syngas from yellow pine showed lower hydrogen sulfide concentration. Gasification of switchgrass was not promising due to frequent ash agglomeration in the reactor. Switchgrass and pine bark both of which have high ash content were blended with yellow pine pellets and pine chips to inhibit the problem of ash fusion. Gasification of the blended biomass showed no ash agglomeration at all and the operation of the gasifier was smooth as usual.

The CeSFaMB program was calibrated with new kinetic coefficient parameters to reproduce experimental results for syngas composition from different feedstocks. However, the output for the temperature profile inside the reactor was not as accurate as compared to the actual measured values in experiments. The inlet air flow, moisture content, mass flow rate and elemental composition of feeding fuel were the most sensitive factors in the model. Low equivalence ratio, high biomass flow rate and high carbon content showed to yield syngas with high concentration of hydrogen and carbon monoxide.

6.2 Limitations and Recommendations for Future Work

The mobile downdraft gasifier system is operated in such a way that it allows us to control only the temperatures inside the reactor and the output flow rate of syngas coming out of the gasifier. These two factors then determine other parameters such as inlet air flow rate and biomass flow rate. Thus, the effect of equivalence ratio (E.R.) on the downdraft gasification process could not be studied in detail due to limitations imposed by this control system. It is suggested that the configuration should be modified to accommodate control of important parameters such as the inlet air flow rate and fuel feed rate.

Before the start of the actual experiments, charcoal was used as the feed until the temperatures inside the reactor reached steady state. The biomass feedstock was then fed up to the top of the gasifier to start the experiment. At the end of the experiment, some amount of biomass would remain inside the gasifier to be used to start up the next run, thus practically nullifying the mass balance. This practice caused some inconsistencies in the determination of carbon conversion from the process. Moreover, the effect of the remaining char inside the gasifier on syngas composition could not be studied due to impracticality of obtaining the char after every other run.

One of the major issues faced was ash build up at the bottom of the reactor during switchgrass gasification. The gasifier operates at very high temperatures (800-1000°C) and ash agglomeration can occur since the ash fusion temperature of switchgrass is ~1016°C. Hence, gasification of biomass having high ash content such as switchgrass would cause agglomeration and slagging/fouling problems. As concluded in Chapter Four, agglomeration was not experienced with the switchgrass/yellow pine blends' gasification due to decreased ash content

in the feedstock. Thus, it is recommended that switchgrass or any other high ash content biomass should be blended with a biomass that has lower ash content for use in the gasifier.

The CeSFaMB model should be able to incorporate diverse types of feeding fuels without the need of calibration of the program. Kinetic coefficients of different reactions involving various fuels are not always available for use. Keeping this in mind, proper laboratorial work to obtain major gasification kinetics as well as pyrolysis parameters should be conducted in order to feed the simulator data bank and achieve better reproductions.

APPENDIX A

SUPPLEMENTAL (LABVIEW) DATA FROM GASIFIER

A.1 Syngas composition data generated by CAI gas analyzer (torrefied pine pellets)

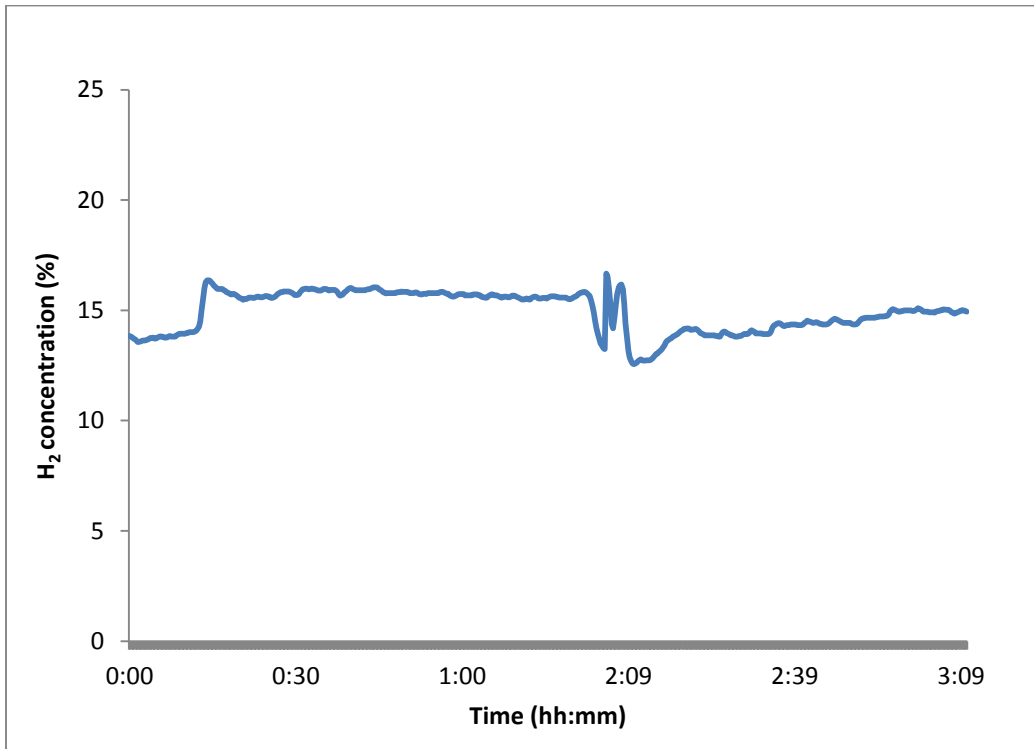


Figure A.1 Hydrogen concentration over time

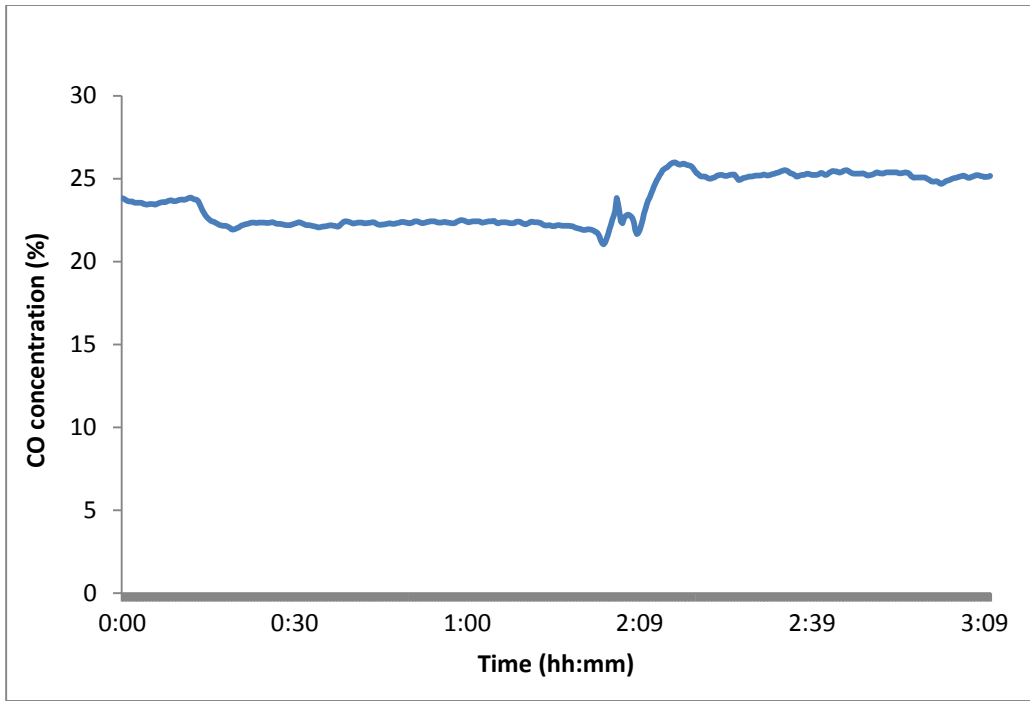


Figure A.2 Carbon monoxide concentration over time

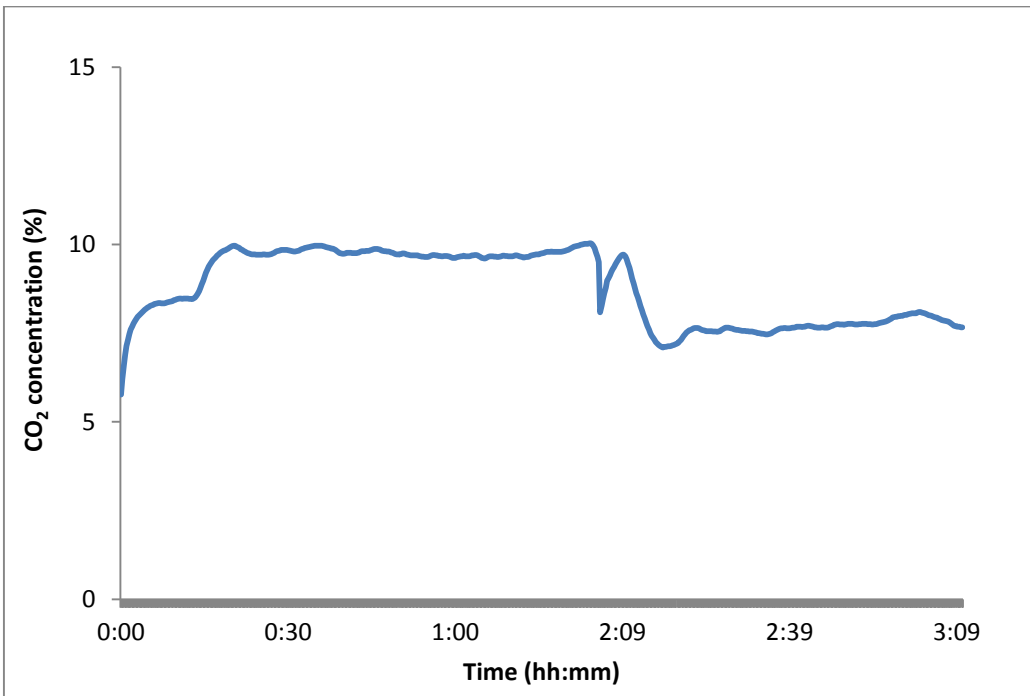


Figure A.3 Carbon dioxide concentration over time

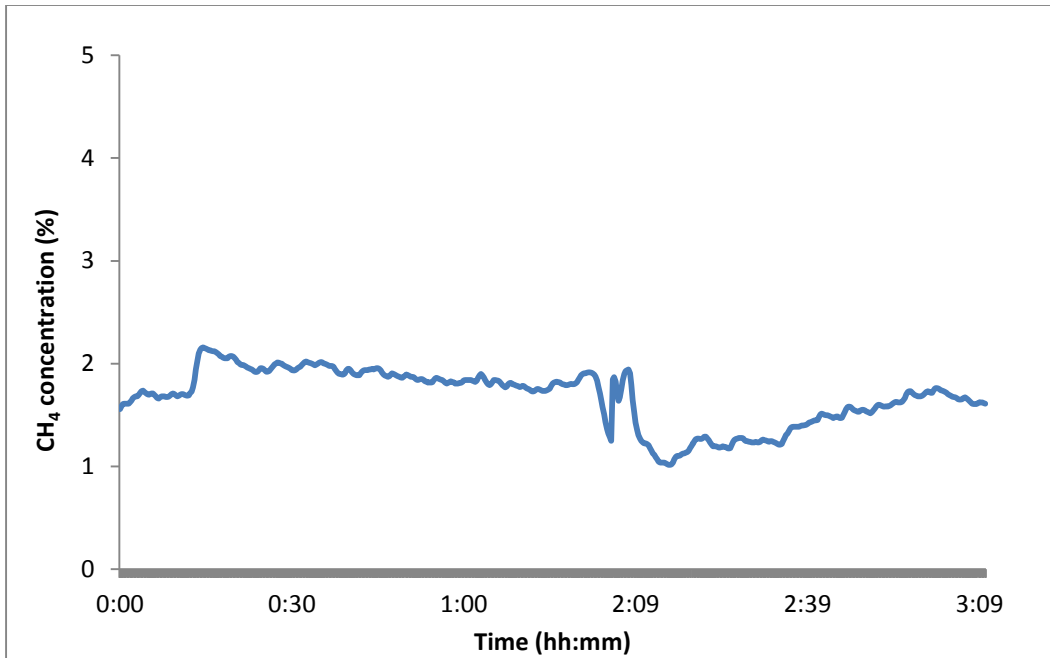


Figure A.4 Methane concentration over time

A.2 Temperature profile inside the reactor (torrefied pine pellets gasification)

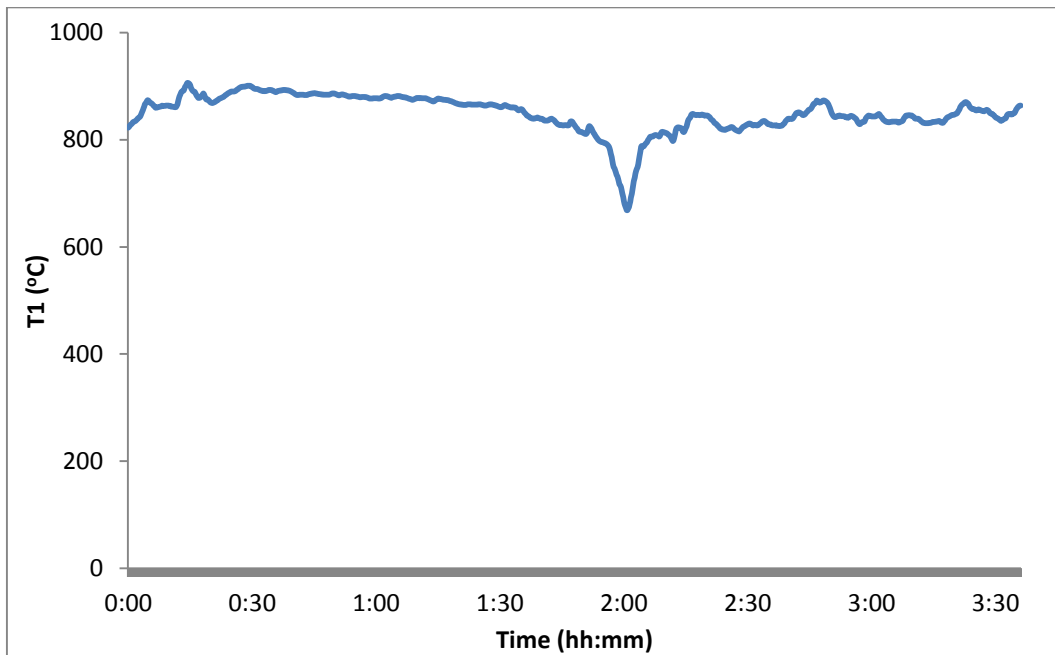


Figure A.5 Temperature profile recorded by thermocouple T1 (at z = 0.4 m)

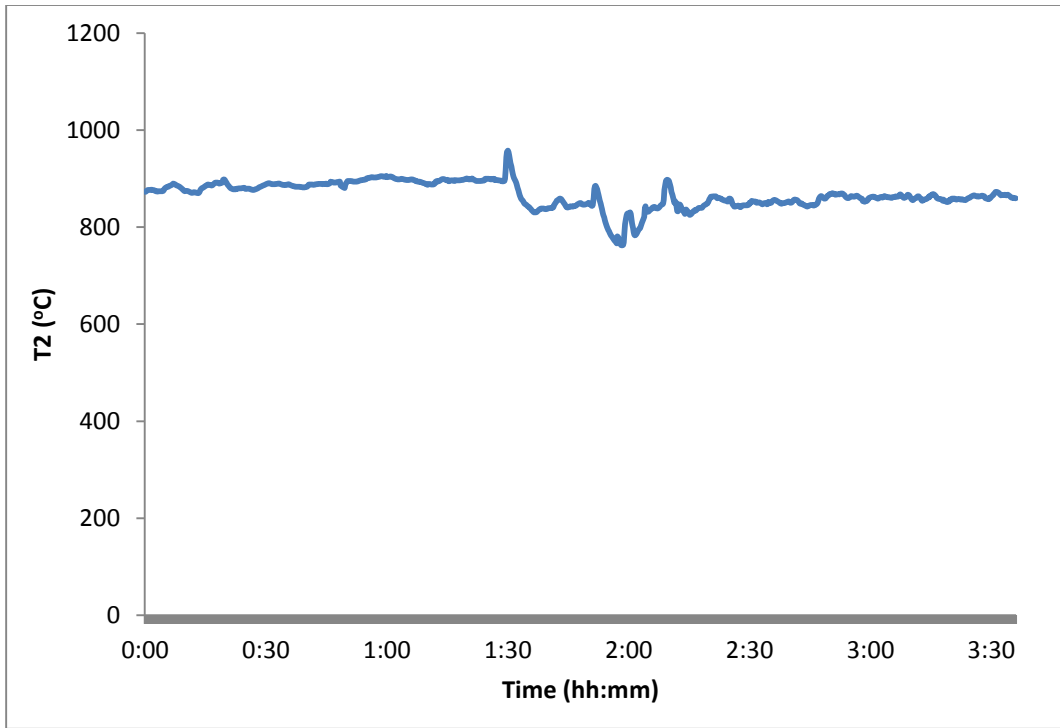


Figure A.6 Temperature profile recorded by thermocouple T2 (at $z = 0.53$ m)

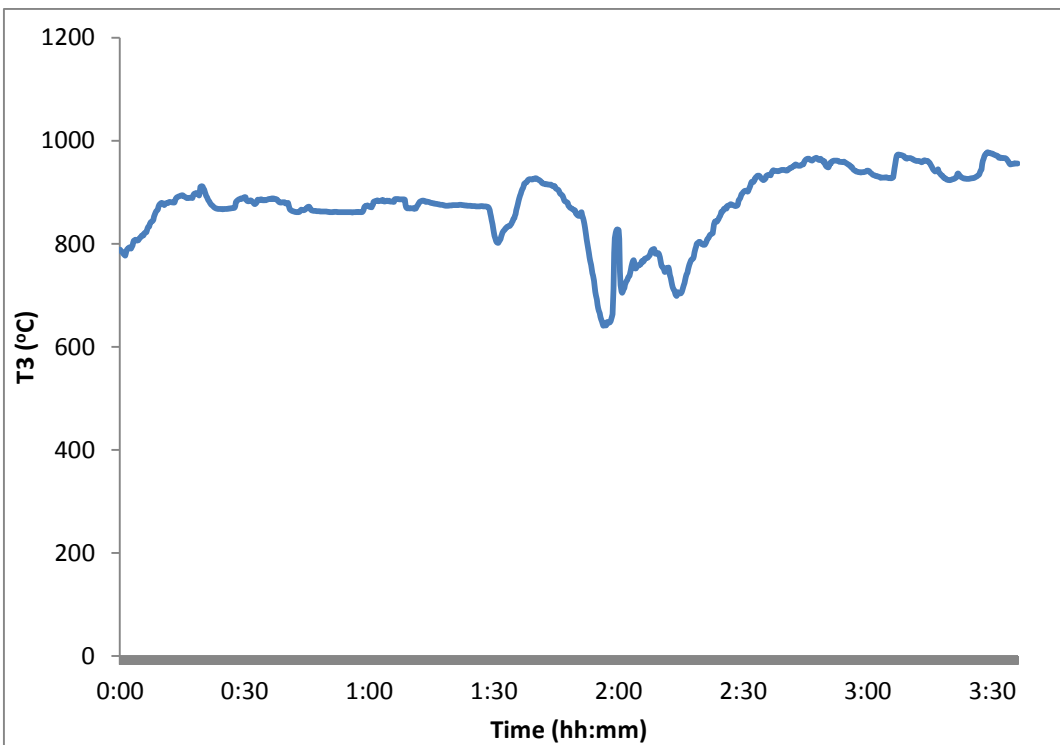


Figure A.7 Temperature profile recorded by thermocouple T3 (at $z = 0.66$ m)

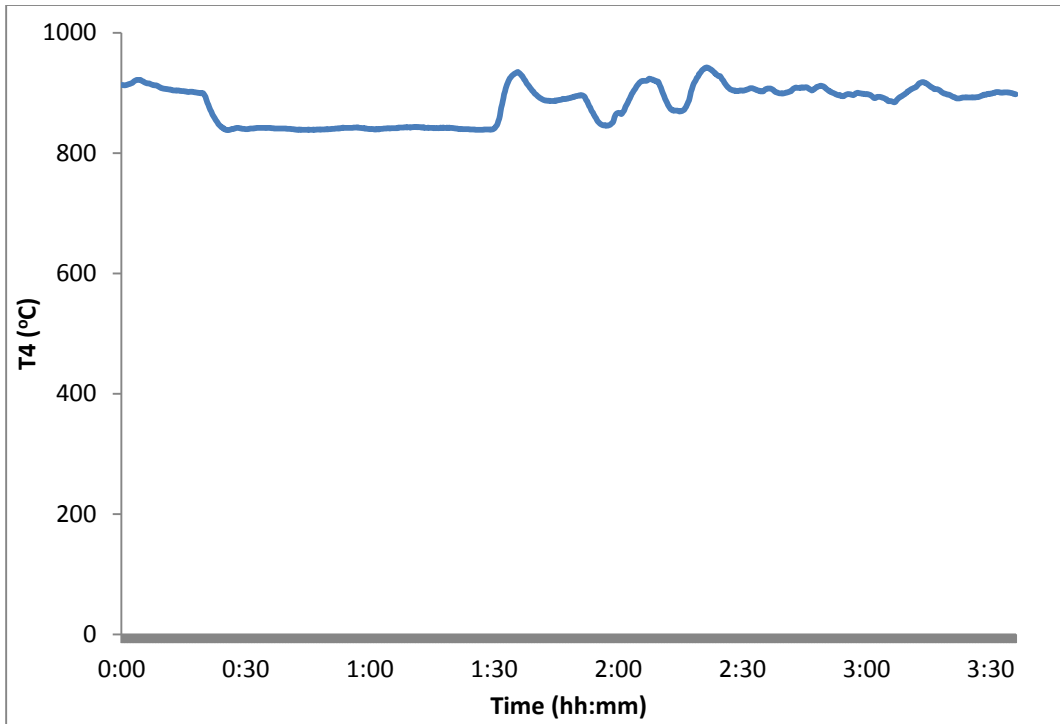


Figure A.8 Temperature profile recorded by thermocouple T4 (at $z = 0.79$ m)

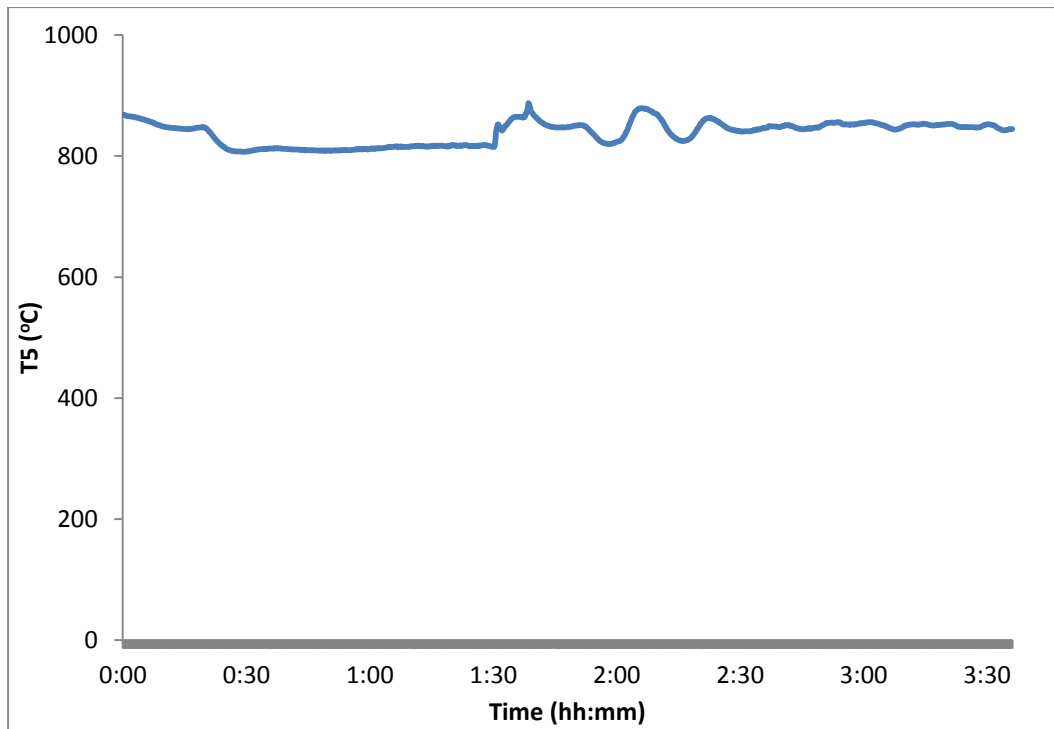


Figure A.9 Temperature profile recorded by thermocouple T5 (at $z = 0.92$ m)

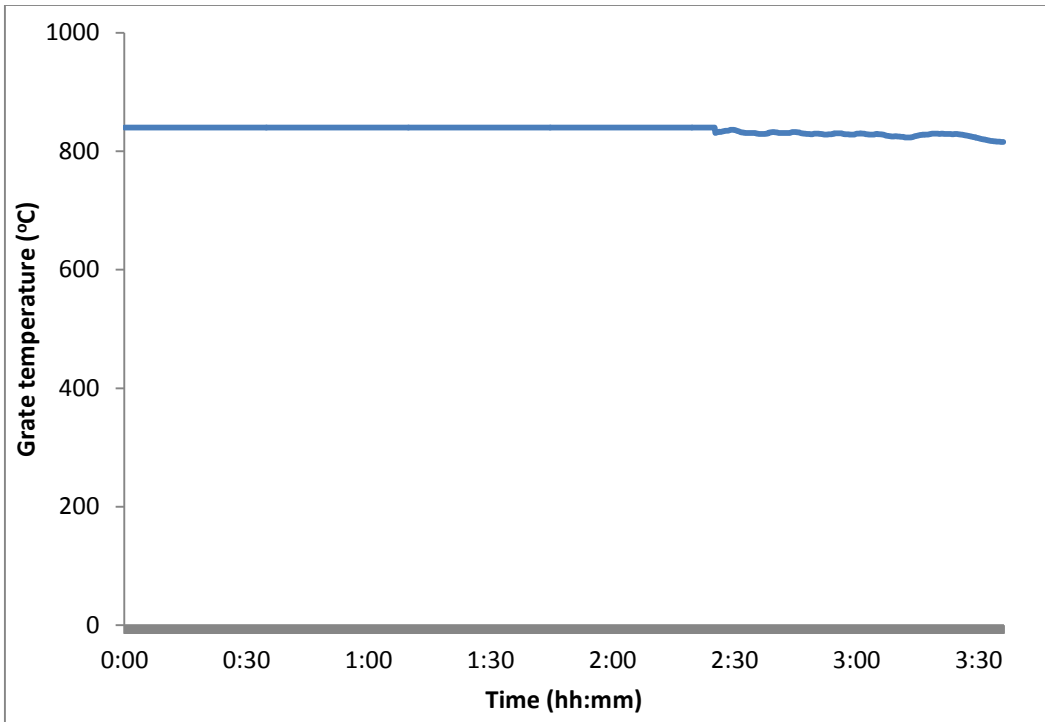


Figure A.10 Temperature profile recorded at grate

APPENDIX B
SAMPLE CALCULATIONS

B.1 Higher Heating Value (HHV) of Syngas

As shown in Eq. B.1, the overall higher heating value of syngas was calculated by adding up the products of the volumetric fraction of syngas constituents (Y_i) and their respective higher heating values (HHV_i).

$$HHV_{syngas} = HHV_{H_2} Y_{H_2} + HHV_{CO} Y_{CO} + HHV_{CH_4} Y_{CH_4} \quad (B.1)$$

The HHV of H_2 , CO and CH_4 are 12.76 MJ/m^3 , 12.6 MJ/m^3 and 39.8 MJ/m^3 respectively [1].

$$\text{So, } HHV_{syngas} = 12.76 \times 0.175 + 12.6 \times 0.256 + 39.8 \times 0.015 = 6.05 \text{ MJ/m}^3$$

B.2 Carbon, Energy and Exergy Analyses

Table B.1 shows the syngas composition obtained from a gasification run of yellow pine pellets, at a certain point of time midway through the test. The table also presents the biomass flow rate, carbon and moisture content, grate temperature and the actual syngas flow rate observed in the experiment.

Table B.1 Syngas composition (yellow pine) midway through the test

Carbon content (% d.b.)	Biomass flow rate, m_{wet} (kg/hr)	Moisture, m.c. (%)	Syngas constituents (molar %, d.b.)				Actual syngas flowrate (m^3/hr)
			H_2	CO	CO_2	CH_4	
51.13	27.85	10.12	17.5	25.6	9.76	1.48	55*

Note*: Although the syngas flow rate was set to be 65 m³/hr for each experiment, the actual flow was found to be lower (55 m³/hr in this run) due to presence of certain base flow in the system. This base flow is determined from the LABVIEW data extracted from the onboard computer and subtracted from the set flow rate.

B.2.1 Carbon Conversion

Dry biomass flow rate (m_{dry}) was calculated simply by subtracting the amount of moisture (%) present in the biomass:

$$m_{dry} = m_{wet} - m.c. = 27.85 - \left(\frac{10.12}{100}\right) \times 27.85 = 25.03 \text{ kg/hr}$$

Total amount of carbon in the feedstock (C_{in}) is given by multiplying the dry biomass flow rate with its carbon content (%):

$$C_{in} = 25.03 \times \left(\frac{51.13}{100}\right) = 12.79 \text{ kg/hr}$$

Equation (B.2) gives the total carbon coming out with syngas:

$$C_{out} = (Y_{CO} + Y_{CO_2} + Y_{CH_4}) \cdot \rho_{mol} \cdot M_C \cdot AF \quad (B.2)$$

where, $Y_{CO}, Y_{CO_2}, Y_{CH_4}$: molar fractions of CO, CO₂ and CH₄

ρ_{mol} : molar density of ideal gas = 44.615 mol/m³ at STP

M_C : molecular weight of carbon, kg/mol

AF: Actual syngas flow rate, m³/hr

Thus,

$$C_{out} = (0.256 + 0.098 + 0.015) \times 44.615 \times \frac{12}{1000} \times 55 = 10.87 \text{ kg/hr}$$

Carbon closure is given by the ratio of C_{out} to C_{in}

$$C_C = \frac{C_{out}}{C_{in}} = \frac{10.87}{12.79} = 0.85$$

B.2.2 Hot and Cold Gas Efficiency

Energy content in biomass was found as follows:

$$E_{in} = HHV_{biomass} \times m_{dry} = 18.55 \times 25.03 = 464.31 \text{ MJ/hr}$$

The mass flow rates (m_i) of syngas constituent gases are shown in Table B.2. A sample calculation for CO is given here:

$$m_{CO} = Y_{CO} \times \rho_{CO} \times AF = 0.26 \times 1.25 \times 55 = 17.60 \text{ kg/hr}$$

Enthalpy of syngas constituent gases is given by:

$$E_i = m_i \times HHV_i \tag{B.3}$$

where, HHV_i for each gas is obtained from reference and mentioned in Table A.2. For CO,

$$E_{CO} = 17.6 \times 10.08 = 177.41 \text{ MJ/hr}$$

Total enthalpy of syngas at ambient temperature is presented in Table A.2 to be

$$E_{total} = \sum_i E_i = 332.44 \text{ MJ/hr}$$

The specific heat capacity (C_p) for given temperature was calculated using Eq. (B.4):

$$C_p = c_0 + c_1\theta + c_2\theta^2 + c_3\theta^3 \tag{B.4}$$

The values of empirical coefficients are given in Table B.3. For this experiment, the average grate temperature was $T = 784^\circ\text{C}$

$$\text{So, } \theta = \frac{T+274}{1000} = 1.06$$

For CO,

$$C_p = 1.1 + (-0.46) \times 1.06 + 1 \times 1.06^2 + (-0.45) \times 1.06^3 = 1.19$$

Enthalpy of gases at higher temperature (sensible heat) is given by Eq. (B.5)

$$E_{hot} = \frac{\sum_i C_{p_i}(T-25) \times m_i}{1000} \tag{B.5}$$

For CO,

$$E_{hot,CO} = \frac{1.19 \times (1058 - 298) \times 17.6}{1000} = 15.96 \text{ MJ/hr}$$

Total sensible heat was calculated as the sum of individual sensible heats and is presented in Table B.2 to be

$$E_{hot} = 66.09 \text{ MJ/hr}$$

The energy content of the syngas produced is determined at two locations - the exit of the gasifier ($E_{out, hot}$) and the exit of the heat exchanger ($E_{out, cold}$) after the gas is cooled to ambient temperature. The efficiencies thus calculated are the hot gas efficiency (η_{hot}) and cold gas efficiency (η_{cold}).

$$\eta_{hot} = \frac{E_{out,hot}}{E_{in}} = \frac{E_{total} + E_{hot}}{E_{in}} = \frac{332.44 + 66.09}{464.31} = 0.86$$

$$\eta_{cold} = \frac{E_{out,cold}}{E_{in}} = \frac{E_{total}}{E_{in}} = \frac{332.44}{464.31} = 0.72$$

Table B.2 Properties of syngas constituents

Gases	ρ at STP (kg/m ³)	Gas fraction (Y _i)	C _p (MJ/kgK)	Mass flow rate, m _i (kg/hr)	HHV _i of gas (MJ/kg)	E _{total (i)} (MJ/hr)	E _{hot (i)} (MJ/hr)
CO	1.25	0.26	1.20	17.60	10.08	177.41	15.96
CO ₂	1.96	0.10	1.26	10.54	0.00	0.00	10.06
CH ₄	0.72	0.01	4.64	0.58	55.47	32.32	2.05
H ₂	0.09	0.18	15.15	0.87	141.82	122.72	9.95
N ₂	1.25	0.46	1.18	31.37	0.00	0.00	28.08
Σ						332.44	66.10

Table B.3 Empirical coefficients of gases

Gases	Empirical coefficients			
	c_0	c_1	c_2	c_3
CO	1.1	-0.46	1	-0.454
CO ₂	0.45	1.67	-1.27	0.39
CH ₄	1.2	3.25	0.75	-0.71
N ₂	1.11	-0.48	0.96	-0.42
O ₂	0.88	-0.0001	0.54	-0.33
H ₂	13.46	4.6	-6.85	3.79

B.2.3 Exergy

Chemical exergy of dry biomass is given by Eq. (B.6).

$$Ex_{in} = \beta \cdot (LHV_{biomass}) \cdot m_{dry} \quad (B.6)$$

$$\beta = \frac{\{1.044 + 0.016 \left(\frac{H}{C}\right) - \frac{0.3493}{C} [1 + 0.0531 \left(\frac{H}{C}\right)] + 0.0493 \left(\frac{N}{C}\right)\}}{[1 - 0.4124 \left(\frac{O}{C}\right)]} \quad (B.7)$$

$$LHV_{biomass} = \frac{HHV - 22604 H}{1000} \quad (B.8)$$

H, C, O and N represent the fraction of hydrogen, carbon, oxygen and nitrogen present in the biomass respectively, and are obtained from the ultimate analysis. For yellow pine, the values were 50.98% C, 7.15% H, 0.09% N and 41.38% O.

Substituting these values in Eq. (B.7) and (B.8), we get:

$$\beta = 1.15$$

$$LHV_{biomass} = 16.93 \text{ MJ/kg}$$

Thus,

$$Ex_{in} = 1.15 \times 16.93 \times 25.03 = 485.63 \text{ MJ/hr}$$

Table B.4 Properties of constituent gases

Gases	Ex_{chi} (MJ/kg)	Ex_i (MJ/kg)	Ex_{out} (MJ/hr)
CO	9.90	10.36	182.24
CO ₂	0.00	0.48	5.06
CH ₄	39.80	41.57	24.22
H ₂	68.90	74.68	64.62
N ₂	0.00	0.45	14.12
Σ			290.26

The exergy of the individual gases in syngas is given by

$$Ex_i = Ex_{chi} + \int_{T_d}^T \left[C_p \left(1 - \frac{T_d}{T} \right) \right] dT \quad (B.9)$$

where Ex_i is the exergy of the gas in MJ/kg at grate temperature $T = 1058$ K, Ex_{chi} is the chemical exergy of the gases at reference or dead state ($T_d = 298$ K). The values of Ex_{chi} are given in Table B.4 and other values for calculation are taken from Table B.3.

For CO,

$$Ex_{CO} = 9.9 + \int_{298}^{1058} \left[1.2 \times \left(1 - \frac{298}{T} \right) \right] dT = 10.36 \text{ MJ/kg}$$

$$Ex_{out,CO} = Ex_{CO} \cdot m_{CO} = 10.36 \times 17.6 = 182.24 \text{ MJ/hr}$$

Total exergy out from syngas was calculated as the sum of individual exergies of gases (Ex_{out}) and is shown in Table B.4 to be

$$Ex_{ratio} = \frac{Ex_{out}}{Ex_{in}} = \frac{290.26}{485.63} = 0.60$$

APPENDIX C

TAR COMPOUNDS

Table C.1 Retention time of tar compounds

Tar compound	Retention time (s)
Benzene	2.53
Toluene	4.33
Ethyl benzene	7.71
O-xylene	8.75
Styrene	9.03
Indene	14.63
Phenol	17.64
3-methyl phenol	19.15
Napthalene	19.39
2-methyl napthalene	22.38
Biphenyl	24.61

APPENDIX D

CESFAMB MODEL PARAMETERS

D.1 Input Parameters

The simulator input list includes various equipment geometry and operational characteristics which allow proper description of the unit. The list is organized according to groups of data as follows:

- **Equipment geometry data**

Along with the shape of the cross section of bed, hydraulic diameter according to the height of the equipment can be entered. Also, positions of the bed top, freeboard top, solid particle and gas injections, position of tube banks (if used) in the bed or freeboard along with their aspects are available. Moreover, material quality and thickness of vessel walls, water or gas-jacket geometries (if used), insulations, thickness and quality (thermal conductivity and emissivity), cyclone system design, etc. are some of the geometry input data in the program.

- **Feeding fuels characterization**

Flow rates and characteristics of feeding of carbonaceous particles have a significant impact on the output results of the program. Type of fuel, proximate and ultimate analysis, higher heating value, bulk and particle densities, shape and sphericity, particle size distribution and water fraction in slurry (if any) are used to characterize the fuel. In addition, if any absorbents (limestone, dolomite, etc.) or inert particles (sand, aluminum,

etc.) are used in the process, similar information as for carbonaceous fuel can be provided.

- **Stream characterization**

The mass flow rates and characteristics of primary injected gas/steam streams with any composition and within a wide range of temperature and pressure can be entered into the program. Liquid streams are also allowed. Moreover, the flow rates and characteristics of eventually injected intermediate gas streams and intermediate gas withdrawals can also be informed along with the position of injections and withdrawals respectively.

- **Special kinetic parameters related to fuels**

For each fuel, the values of reaction pre-exponential parameter and the exponential one can be entered which will eventually replace the default values internally set in the model. It allows user to interfere in the rate of up to ten different reactions in order to calibrate the program according to a particular carbonaceous fuel or sulfur absorbents.

D.2 Output Parameters

- **Equipment performance parameters:** Overall aspects of the unit operation such as: flow rates of gases and solids leaving the equipment, carbon conversion, residence time of solid species, flow rates of tar or oil leaving with gases, etc.
- **Devolatilization parameters:** Rates, composition of released gases and average time for complete pyrolysis
- Composition, flow rates and thermodynamic properties of gas streams
- Composition, particle size distribution and flow rates of solids or liquids at each point inside the equipment as well as those streams leaving the equipment.
- Overall elemental mass balance verification

- Temperature profiles of each gas and solid throughout the entire equipment
- Rate profiles of reactions at each phase throughout the equipment
- Overall exergy analysis of the unit operation
- General warnings to the user related to possible operational problems