



EFFECT OF GASIFICATION OPERATING PARAMETERS ON QUALITY OF
SYNGAS PRODUCED USING SAWDUST FEEDSTOCK

BY

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SYNGAS PRODUCED USING SAWDUST FEEDSTOCK

BY

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MARCH, 2016

Declaration

I Muhammad Bello MUHAMMAD, hereby declare that this dissertation entitled “EFFECT OF GASIFICATION OPERATING PARAMETERS ON QUALITY OF SYNGAS PRODUCED USING SAWDUST FEEDSTOCK” has been carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. To the best of my knowledge no part of this project was previously presented for the award of degree or diploma at this or any other institution.

Muhammad Bello Muhammad

Name of Student

Signature

Date

Certification

This is to certify that this dissertation entitled “EFFECT OF GASIFICATION OPERATING PARAMETERS ON QUALITY OF SYNGAS PRODUCED USING SAWDUST FEEDSTOCK” by Muhammad Bello MUHAMMAD with registration number MSc/ENG/38701/2012-2013 meets the regulations governing the award of Master of Science (M.Sc.) degree in Chemical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literacy presentation.

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Dedication

To my Parents

Acknowledgement

All praises are due to Allah (SWT), most beneficent, most merciful and most kind. May peace and blessings of Allah (SWT) be upon His final prophet, Muhammad (SAW), his companions and those that follow the right path to the last day.

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Abstract

This research work investigates the effect of gasification operating parameters, namely: equivalence ratio (ER), gasification agent, reaction zone temperature, and residence time on quality of syngas produced using sawdust. The research experiments were conducted using a pilot scale downdraft gasifier with constricted throat and a rotating grate. Temperatures at reaction zone of the gasifier were monitored directly using a digital thermometer whereas an online gas analyzer capable of detecting percentage composition and calorific value was employed to monitor quality of the syngas. Two sets of experiments were carried out separately; one using air and the other using oxygen-enriched air as gasifying agents. With air, flow rates at 6.4, 1.9 and 0.7 litre per minute (LPM) were used for the study. The results obtained shows that the higher air flow level favours better quality of syngas. Air flow rate at 0.64LPM generated the best quality of syngas containing 13.55 and 2.59% of CO and H₂, respectively. Syngas maximum caloric value of nearly 3MJ/Nm³ at a temperature of 550°C was observed. Using oxygen enriched-air on the other hand, flow rate was maintained at 10LPM while varying the percentage oxygen at 21, 30, 40, 50, 60 and 80%. It was found that 40% oxygen enrichment generated the best quality of syngas containing 29.57 and 14.29% of CO and H₂ respectively. Syngas calorific value was observed to rise consistently from 2.08 to a maximum of 6.69MJ/Nm³ as percentage oxygen in the gasifying agent was increased from 21 to 40%. Gasification performance shows that both cold gas efficiency (CGE) and carbon conversion efficiency (CCE) reaches peak value of 46.81 and 82.04% respectively at ER value of 0.2953 which also corresponds to the 40% oxygen level in gasifying agent.

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CHAPTER ONE

INTRODUCTION

1.1 Background

The alarming rate of global warming as a result of harmful gases released into the atmosphere combined with continual depletion of fossil fuel resources at unprecedented rate led researchers to devote effort in developing alternative energy technologies from agricultural wastes like sawdust, rice husk and sugar cane bagasse to meet up future energy demand (Christus *et al.*, 2014).

Although it is not known how much fossil fuel is still available, it is generally accepted that it is being depleted and is non-renewable. With these challenging circumstances, search for other alternative renewable forms of energy sources becomes imperative. Other consequences associated with fossil fuel use include the release of the trapped carbon in the fossil fuels to the atmosphere in the form of carbon dioxide which has led to increased concerns about global warming. Also, fossil fuel resources are not distributed evenly around the globe which makes many countries heavily dependent on imports (Ajay *et al.*, 2009). Evidence suggests that conventional oil production has a limited capacity to meet growing demand, and most additional demand will have to be met by unconventional sources. Since the globe is turning towards the sustainable development, renewable energy technologies are getting more attention all over the world (Bergerson and Keith, 2006).

The combustion of biomass of different varieties has gained dramatic applications ranging from woodstove for domestic usage to industrial power generation. However more extensive applications lie ahead from effective technology for conversion of the biomass

into valuable gaseous and liquid resources which can be processed further to fuel or commodity chemicals (Reed and Das, 1988).

Biomass according to the United Nations Framework Convention on Climate Change (UNFCCC, 2005) can be defined as non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. The term also applies to products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes. Biomass has high but variable moisture content and is made up of carbon, hydrogen, oxygen, nitrogen, sulphur and inorganic elements.

Gasification refers to the partial conversion of biomass resulting in production of combustible gases consisting of carbon monoxide (CO), hydrogen (H₂) and traces of methane (CH₄). This mixture is called producer gas which can be used to run reciprocating internal combustion engines, can be used as substitute for furnace oil in direct heat applications and can be used to produce, in an economically viable way, methanol – an extremely attractive chemical which is useful both as fuel for heat engines as well as chemical feedstock for industries (Reed *et al.*, 1982).

Previously, extensive researches have been carried out either experimentally or using model to evaluate gasification performance. Mendiburu *et al.*, (2014) carried out a work on Parametric study on gasification process using non-equilibrium model. It was found that increment in equivalent ratio ER enhance carbon conversion efficiency. However above a value of 0.3 ER, LHV of producer gas decreases. Lahijani *et al.*, (2013) conducted a work on air gasification of oil palm waste over dolomite in a fluidized bed. It was concluded that high temperature favors the quality of producer gas, however agglomeration was observed

at temperature above 850°C. Pratik et al., (2009) lead an experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier. It was reported that Increase in the moisture content decreases biomass consumption rate while increase in the air flow rate increases biomass consumption rate.

1.2 Problem Statement

Sawdust commonly generated as waste in Nigerian sawmills attracts limited economical utilization rather constitutes damaging environmental problems as a result of indiscriminate disposal. Moreover, research on gasification operating parameters using locally available biomass material for syngas production has not been fully established.

1.3 Aim and Objectives

The aim of this research work is to investigate the effect of various gasification operating parameters, namely; equivalence ratio, reaction zone temperature, gasifying agents, residence time on quality of syngas produced using sawdust as feedstock and a downdraft gasifier.

Specific objectives of the research work are:

1. To collect sawdust sample from sawmill at timber market (*Kasuwan Katako*) Zaria in Sabon Gari Local Government Area of Kaduna State, Nigeria.
2. To characterize the sawdust sample using proximate and ultimate analysis.
3. To carry out gasification of the sawdust sample using air and oxygen enriched-air as gasifying agents.
4. To carry out qualitative and quantitative analysis of gasification products, namely; CO, CO₂, CH₄, H₂ and O₂ using online gas analyzer.

5. To carryout MATLAB simulationof thermodynamic equilibrium modelusing proximate and ultimate analyses data and to compare results obtained with experimental data.

1.4 Justification

In situations where price of petroleum fuels are high or where supplies are unreliable, biomass gasification has been identified as one promising technology for converting carbonaceous materials into a clean, renewable and sustainable energy carrier gas known as producer gas which is also called syngas. Moreover utilization of sawdust as gasification feedstock does not impose direct impact on food security. In addition, indiscriminate sawdust disposal commonly practiced in Nigeria constitutes a major health and environmental hazard.

1.5 Scope

This research work was limited to carrying out gasification experiments in a downdraft gasifier using sawdust sample collected from the sawmills at timber market (*Kasuwan Kartako*), Sabon Gari Local Government Area of Kaduna State, Nigeria, whereas air and oxygen enriched air were used as gasifying agents.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

There are two main routes of converting biomass into biofuels, namely biochemical and thermochemical conversion processes. Biochemical process operates at lower temperatures and employs microbial activities on wet biomass such as molasses, starch, animal dung etc. Biomass with moisture content less than 50% can be converted to combustible gas fuel using thermal process operated at higher temperatures.

The term gasification refers to a process of conversion of any solid or liquid carbon-based material (feedstock) into gaseous fuel through partial oxidation with air, oxygen, water vapour or their mixtures. In practice gasification process converts only 60 – 90 % of energy originally stored in the biomass into energy contained in gaseous or liquid fuel(Reed and Das, 1988).

2.2 Historical Development of Gasification

Historical records dated the earliest gasification back to 1659 as illustrated in Figure 2.1 when “carbureted hydrogen” popularly known as methane was discovered by Thomas Shirley from coal mine(Basu, 2010). The need for lighting streets became the primary motivation behind the discovery of coal-gas also known as town gas. In 1792 William Murdoch was the first to exploit the flammability of coal-gas for practical application for lighting. In 1798 Murdoch lit up the main building of the Soho Foundry (steam engine works) where he works. In 1808 Murdoch made a striking paper presentation to the Royal Society where he demonstrated the application of coal-gas for lighting. One of the major economic implications of gas lighting was the extension of working hours during the

industrial revolution. Factories operated even at night especially during the winter months when nights are significantly longer. Later around 1920, town gas lighting technology crosses over the Atlantic Ocean and became widespread in the United States (Singer, 1958; Kaupp, 1984).

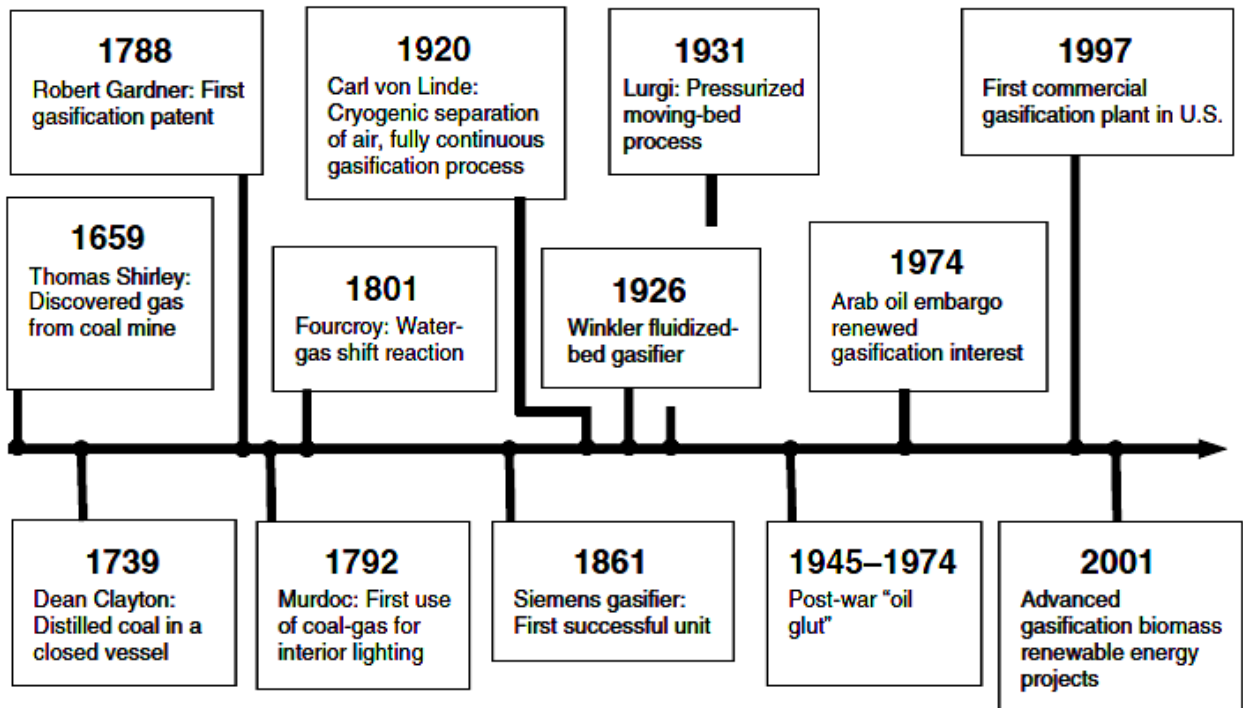


Figure 2.1: Historical Timeline of Gasification Development(Basu, 2010).

The period 1940–1975 saw gasification enter two fields of application of synthetic fuels as internal combustion and chemical synthesis into oil and other process chemicals. During the second world war, allied bombing of Nazi oil refineries and oil supply routes greatly diminished the crude oil supply that fueled Germany’s massive war machinery. This forced Germany to synthesize oil from coal-gas using the Fischer-Tropsch and Bergius processes. Other chemicals and aviation fuels were also synthesized from coal.

Development of gasification technology witnessed a major drawback at the end of second world war in 1946 as inexpensive gasoline from Middle East became available during the oil glut. However this technology experiences dramatic renaissance as oil supplies to the western world cuts off during the Arab oil embargo in 1973 which was triggered by the Yom Kippur War. On October 15, 1973, Arab members of the Organization of Petroleum Exporting Countries (OPEC) banned oil exports to the United States and other western countries, which were at that time heavily reliant on oil from the Middle East. This shocked the western economy and gave a strong impetus to the development of alternative technologies like gasification in order to reduce dependence on imported oil. Global warming and political instability in some oil-producing countries gave a fresh momentum to gasification at the millennium.

Gasification came out as a natural choice for conversion of renewable carbon-neutral biomass into gas. The quest for energy independence and the rapid increase in crude oil prices prompted some countries to recognize the need for development of integrated gasification combine cycle (IGCC) plants. The attractiveness of gasification for extraction of valuable feedstock from refinery residue was rediscovered, leading to the development of some major gasification plants in oil refineries. In fact, chemical feedstock preparation took a larger share of the gasification market than energy production (Basu, 2010).

2.3 Biomass Reserve in Nigeria

Biomass resources in Nigeria include agricultural crops, wood, charcoal, grasses and shrubs, residues and wastes (agricultural, forestry, municipal and industrial), as well as aquatic biomass. Obioh and Fagbenle, (2009) reported an estimate of Nigerian land use

allocation as shown in Figure 2.2. Nigeria has a total area of 923, 768 km² (comprising 910, 768 km² of land and 13,000 km² of water). Out of this, approximately 33 % (300,550 km²) is arable, 3.1 % (28,235 km²) is under permanent crop, 44 % is under permanent pasture, 12 % is under forest and woodland and approximately 0.3 % (2,820 km²) is under irrigation.

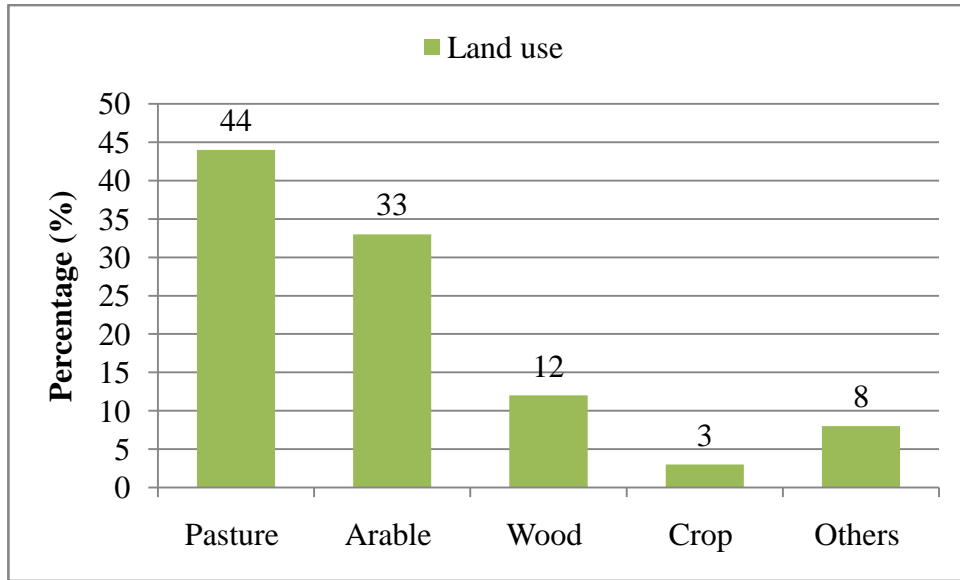


Figure 2.2: Land use Estimate in Nigeria (Obioh and Fagbenle, 2009)

Fuel wood is the most widely used domestic renewable energy resource in rural areas of Nigeria and especially by low income earners in the urban areas. Fuel wood and charcoal constituted 32% and 40 % of the total primary energy consumption with 39 million tons estimate in national demand in 2000. Table 2.1 presents estimated quantities of fuel wood and some other waste resources generated in Nigeria. Fuel wood forms the largest percentage of the non-commercial energy (about 37.4 % of the total energy demand) and will continue to dominate the non-electricity energy needs for the majority of people in the country so long as other options are left unexploited (Sambo, 2009).

Table 2.1: Biomass Resources and Estimated Quantities in Nigeria

Biomass	Quantity (1000,000 kg)	Energy value(1000 MJ)
Fuel wood	39100.0	531.0000
Agro-waste	11244.4	147.7000
Sawdust	1800.0	31.4333

(Sambo, 2009)

About $80 \times 10^6 \text{ m}^3$, equivalent to $43.4 \times 10^6 \text{ kg}$ of fuel wood with an average daily consumption ranging from 0.5 - 1.0kg of dry fuel wood per person is being consumed in the country annually for cooking and domestic purposes (Ohunakin, 2010). The energy content of the fuel wood that is being used is $6.0 \times 10^9 \text{ MJ}$ out of which only between 5-12% is gainfully utilized for cooking and other domestic uses (Sambo, 2009).

Badejo, (2005) reported that the quantity of wood waste generated in the saw mills is estimated at about $3.87 \times 10^6 \text{ m}^3$ of which sawdust accounts for about 20%. According to the report, the number of sawmills in Nigeria rose from over 500 in 1975 to 1200 in 1981. These mills are estimated to produce well over $1.7 \times 10^6 \text{ m}^3$ of wood waste annually. Sawdust in its original form attracts no commercial value rather it constitutes disposal problems to millers (who expend money for transportation to disposal sites), fire hazard as a result of its burning and pollution of the environment. According to Ohunakin (2010), about $42 \times 10^3 \text{ kg}$ of sawdust is generated from every $100 \times 10^3 \text{ kg}$ of timber produced with an average of about $4.39 \times 10^6 \text{ m}^3$ of log split and plywood processed annually in Nigeria. The potential for sawdust generated can therefore be estimated as $1.8 \times 10^9 \text{ kg}$ annually. Figure 2.3 shows the different forms of biomass that can be utilized as feedstock for gasification.



Figure 2.3: Assorted Biomass Materials(www.biomasspelletplant.com)

2.4 Biomass Material

Since earliest existence of mankind, tree branches, twigs, bark, peat, grasses, plant and animal waste, leaves, moss, and various other forms of biomass were a source of energy to provide heat and light. The role of biomass in more recent history has been expanded to uses in the production of charcoal, paper, steam, weapons, tools and building materials. Biomass as renewable source of materials and energy has experienced a sharp decline in its utilization due to the discovery and development of worldwide fossil and mineral resources. However, concerns about the finite, and decreasing amount of fossil and mineral resources in addition to the health and climate impacts of fossil resource use have caused a growth in interest and innovative methods for converting renewable biomass resources into

products that fit our modern lifestyle. Utilization of biomass and waste materials has the potential to make a significant contribution to domestic energy supply (Daniel, 2012).

The term biomass refers to material of biological origin, derived from living or recently dead organisms. The chemical energy lodged in bonds of biomass fuel can be used directly via combustion to produce heat or indirectly by conversion technology to various forms of biofuel. Wood remains the largest pool of biomass energy source around the world. Biomass includes agricultural and forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips, municipal solid waste, sludge waste etc. Forest residues include wood residue or wastes from logging and wood-processing activities. Logging residues are the unused portions of trees cut during logging operations and left in the woods. These include stumps, branches, leaves, off-cuts, and sawdust. Wood processing residues, or primary mill residues, are composed of wood materials (such as discarded logs, bark, sawdust and shavings) generated at manufacturing plants – sawmill, veneer mill, plywood mill, or pulp mill- when round-wood are processed into primary wood products. Forest residues can be used to generate heat, electricity, liquid fuels and solid fuels (compressed wood such as pellets, briquettes, or charcoal briquettes (Milbrant, 2009).

2.5 Components of Biomass

Biomass constitutes of three major components namely; Cellulose, hemicellulose and lignin.

2.5.1 Cellulose

Cellulose is a linear chain polymer of anhydrous of glucose units with a higher degree of polymerization (~10000). It is represented by the generic formula $(C_6H_{10}O_5)_n$. This

structure gives it high strength, permitting it to provide the skeletal structure of most terrestrial biomass (Klass, 1998).

2.5.2 Hemicellulose

Hemicellulose is a group of carbohydrates with a branched chain structure and a lower degree of polymerization (~100–200), and may be represented by the generic formula $(C_5H_8O_4)_n$ (Klass, 1998).

2.5.3 Lignin

Lignin is a complex highly branched polymer of phenyl-propane and is an integral part of the secondary cell walls of plants (Diebold and Bridgwater, 1997). Lignin forms the cementing agent of cellulose fibers holding adjacent cells together. The dominant monomeric units in the polymers are benzene rings. Figure 2.3 presents a schematic diagram illustration of the components making up a biomass fiber structure (Basu, 2010).

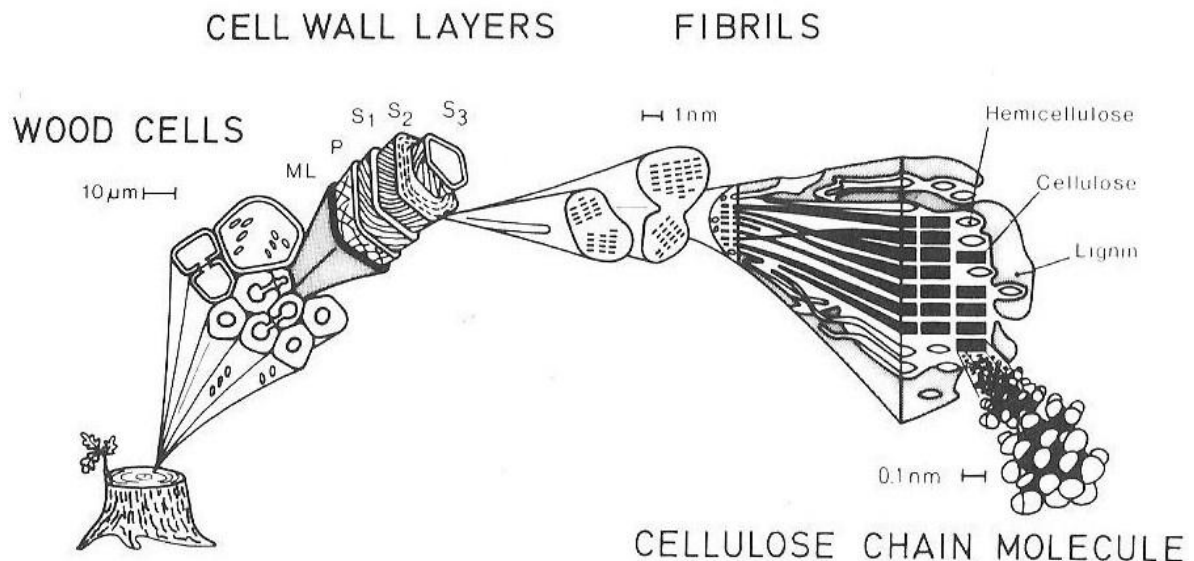


Figure 2.4: Components of Biomass Cellwall Structure (Basu, 2010).

These three polymers form an interpenetrating fiber network that varies across the cell wall. Raveendran *et al.*, (1995) reported typical composition of different biomass materials as shown in Table 2.2. Woody plant species are typically characterized by slow growth and are composed of tightly bound fibers responsible for the hard external surface, whereas herbaceous plants have more loosely bound fibers indicating a lower proportion of lignin which binds together the cellulosic fibers.

Table 2.2: Typical Composition of Different Biomass Materials

Plant	Lignin	Cellulose	Hemicellulose
Wheat straw	16.4	30.5	28.9
Bagasse	18.3	41.3	22.6
Corn cob	16.6	40.3	28.7
Groundnut shell	30.2	35.7	18.7
Coconut shell	28.7	36.3	25.1
Millet husk	14.0	33.3	26.9
Rice husk	14.3	31.3	24.3

(Raveendran *et al.*, 1995)

2.6 Biomass Characterization

Proximate and Ultimate analysis of biomass feedstock enables physical properties and chemical compositions data to be established.

2.6.1 Proximate analysis

Proximate analysis determines moisture content (M), volatile matter (VM), ash content (A) and fixed carbon content (C) of fuel using standard of the American Society of Testing Material (ASTM). Moisture content of biomass sample is analyzed by weight loss observed at about 110°C. Subjecting dried biomass further to a temperature of about 950°C

drives off volatile content leaving behind the fixed carbon. Properties of biomass vary with its source or type therefore it is a common practice to make analysis on the dry basis and sometimes on Moisture-Ash-Free (MAF)(Anjireddy and Sastry, 2011). Table 2.3 presents proximate analysis data of different biomass materials on weight percentage basis (Chiang *et al.*, 2012).

Table 2.3: Proximate Analysis of Selected Biomass Feedstock

Material	Moisture content (wt.%)	Volatile matter (wt. %)	Fixed carbon (wt. %)	Ash (wt. %)
Sawdust	11.30	71.99	16.03	0.68
Willow	11.86	73.69	13.86	0.59
Rice husk	9.68	62.43	15.93	11.96
Rice straw	10.71	64.22	15.61	9.46
Bamboo trimmings	11.11	70.19	15.56	3.14
Banana trimmings	11.74	62.46	19.46	6.34

(Chiang *et al.*, 2012)

2.6.2 Ultimate analysis

Ultimate analysis determines the chemical composition and higher heating value (HHV) of fuels. Elemental composition of dry fuel on weight percentage basis is analyzed. Typically, hydrogen, oxygen, carbon, nitrogen, sulphur and Ash content are determined. Table 2.4 shows ultimate analysis of selected biomass materials reported by Reed and Das, (1988).

Heating value can be determined by exposing a sample of biomass feedstock to react with oxygen in a bomb calorimeter and then measuring the amount of heat released relative its

moisture content driven off in form of water vapor. Results from the procedure represent the maximum energy obtainable from combustion reaction of the fuel and it is a useful parameter in calculating gasification efficiency.

Table 2.4: Ultimate Analysis of Data for Selected Biomass Materials

Material		Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Ash	Heating Value (MJ/kg)
Municipal waste	solid	47.6	6.0	1.2	0.3	32.9	12.0	19.83
Animal waste		42.7	5.5	2.4	0.3	31.3	17.8	17.1
Paper		43.4	5.8	0.3	0.2	44.3	6.0	17.57
Sawdust pellet		47.2	6.5	0.0	0.0	45.4	1.0	20.45
Sawdust chips		50.91	6.13	0.23	0.0	42.14	0.59	20.1
Rice straw		39.2	5.1	0.6	0.1	35.8	19.2	15.8
Rice hulls		38.5	5.7	0.5	0.0	39.8	15.5	15.3
Maple		50.6	6.0	0.3	0.0	41.7	1.4	19.9
Poplar		51.6	6.3	0.0	0.0	41.5	0.6	20.7
Redwood		53.5	5.9	0.1	0.0	40.3	0.2	21.0
Beech		51.6	6.3	0.0	0.0	41.5	0.6	20.3
Pine bark		52.3	5.8	0.2	0.0	38.8	2.9	20.4

2.7 Biomass Heating Value

Heating is the energy release when a material undergoes complete combustion with oxygen under standard condition. This value can be express in two ways; either as higher or lower value.

2.7.1 Higher heating value

Higher heating value (HHV) which is also called gross calorific value (GCV) is defined as the amount of heat released by the unit mass or volume of fuel (initially at 25 °C) once it is combusted and the products have returned to a temperature of 25 °C. It includes the latent heat of vaporization of water. HHV can be measured in a bomb calorimeter using ASTM E 711-82 (2013).

2.7.2 Lower heating value

The lower heating value (LHV), also known as the net calorific value (NCV), is defined as the amount of heat released by fully combusting a specified quantity of material, less the heat of vaporization of the water in the combusted material. In real practice flue gases produced from combustion are rarely cooled to the initial temperature of the fuel, which is generally below the condensation temperature of steam. So the water vapor in the flue gas does not condense, and therefore the latent heat of vaporization of this component is not recovered. The effective heat available for use is a lower amount, which is less than the chemical energy stored in the fuel. The relationship between HHV and LHV can be expressed as follows: (Basu, 2010).

$$\text{LHV}_{\text{fuel}} = \text{HHV} - \frac{\lambda}{100} (9H + M) \quad (2.1)$$

where, H and M stands for percentage hydrogen and moisture respectively in the fuel. λ , is the latent heat of steam approximately 2260 kJ/kg.

2.7.3 Estimation of biomass heating values

Experimental methods are the most reliable means of determining the heating value of biomass. If these are not possible, empirical correlations like the Dulong-Berthelot Equation, originally developed for coal with modified coefficients for biomass, may be used. Channiwala and Parikh (2002) developed the following unified correlation for HHV based on 15 existing correlations and 50 fuels, including biomass, liquid, gas, and coal.

$$\text{HHV} = 349.1C + 1178.3H + 100.5S - 103.4O - 15.1N - 21.1\text{ASH} \text{ kJ/kg} \quad (2.2)$$

Where C, H, S, O, N, and ASH; are percentages of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash as determined by ultimate analysis on a dry basis. This correlation is valid within the range:

$$0 < C < 92\%; 0.43 < H < 25\%$$

$$0 < O < 50\%; 0 < N < 5.6\%$$

$$0 < \text{ASH} < 71\%; 4745 < \text{HHV} < 55,345 \text{ kJ/kg}$$

2.8 Biomass Beneficiation

Upstream processing of biomass makes it suitable for gasification operations. Size reduction is needed to obtain appropriate particle sizes. Drying is needed to achieve appropriate moisture so that the process can work efficiently. Densification also may be required where biomass material has substantially low density (Ajayet *al.*, 2009).

2.8.1 Size reduction

Smaller particles have larger surface areas per unit mass and larger pore sizes which facilitate faster rates of heat transfer and gasification (Kirubakaran *et al.*, 2009). Smaller

particles resulted in formation of more CH₄, CO, C₂H₄ and less CO₂ which led to higher gas yields, gas energy content (LHV) and carbon conversion efficiency (Lv *et al.*, 2004). It was observed that particle size reduction from 1.2 mm to 0.075 mm shows a significant increase in H₂ and CO contents as well as carbon conversion efficiencies whereas the CO₂ content decreases (Luo *et al.*, 2009). It can be implied that higher gas yields and energy efficiencies were attributes of the increased heat transfer in smaller size particles as a result of larger surface area (Akay *et al.*, 2009).

2.8.2 Pre-drying

Drying constitutes an important biomass fuel pretreatment in that moisture content affects the quality of gas produced. To vaporize water off about 2300 kJ of heat energy is required and 1500 kJ will be consumed to raise gasification temperature up to 700°C during pyrolysis and gasification processes. For direct combustion, heat expense for drying comes from total heat budget amounting to reduction in performance of the process in terms of tar formation, low gas efficiency and low throughput. Biomass with moisture content up to 25% requires drying often accomplished by radiant energy from the sun or using hot air driers for high grade application. At high temperatures, higher rate of drying is experienced. Surfaces of biomass fuel material dried up completely and began to undergo pyrolysis leaving significant moisture buried deep at the center. (Reed, 1988) reported that 20 minutes residence time accomplished moisture content reduction from 50 to 5% operated with 90% recycle of hot air (Reed and Das, 2000).

2.9 Biomass Conversion Process

There are two main route of converting biomass feedstock into biofuels namely; biochemical conversion and thermochemical conversion processes as depicted in Figure 2.5(Basu, 2010).

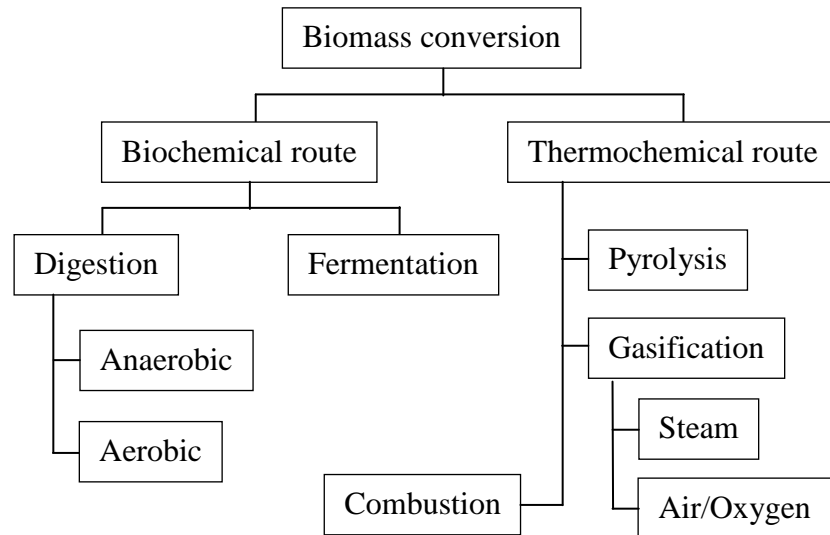


Figure 2.5: Schematic Diagram of Biomass Conversion Routes

2.9.1 Thermochemical conversion

Thermochemical conversion processes utilize heat as the dominant mechanism to convert biomass into constituent chemical components. Alternatives to combustion principally; drying, pyrolysis and gasification are distinguished by the extent to which the chemical reactions involved are allowed to proceed mainly dictated by amount of oxygen supply and conversion temperature.

Combustion requires high temperature operation condition around $700 - 1400^{\circ}\text{C}$ to convert biomass in excess air into carbon dioxide and steam. Gasification on the other hand involves a chemical reaction taking place at moderate temperatures around $500 - 1300^{\circ}\text{C}$ in an oxygen-deficient environment. Benefits of gasification process include; increase in the

heating value of the fuel, reduction in greenhouse gas (GHG) emission and reduction in carbon-to-hydrogen (C/H) mass ratio of the fuel.

Pyrolysis takes place at a relatively low temperature around 280 – 430°C in the total absence of oxygen. The rate at which pyrolysis take place determines the type of product obtained. Fast pyrolysis produces mainly liquid fuel, known as bio-oil; slow pyrolysis produces some gases and solid charcoal (Basu, 2010).

Thermochemical conversion technology has certain advantages and disadvantages over biochemical conversion technology. The main advantages are that the feedstock for thermochemical conversion can be any type of biomass ranging from agricultural residues to municipal wastes. Product gases obtain through this process can be converted to a variety of fuels (H₂, diesels, synthetic gasoline) and chemicals (methanol, urea) as substitutes for petroleum-based chemicals. The major disadvantages are the high cost associated with cleaning the product gas from tar and undesirable contaminants like alkali compounds as well as inefficiency due to the high temperatures required (Akay *et al.*, 2009).

2.9.2 Biochemical conversion

Biochemical conversion makes use of the enzymes produced by bacteria and other microorganisms to break down biomass. In most cases, microorganisms are used to perform the conversion process through anaerobic digestion, fermentation or decomposition. Biochemical methods are generally selective in terms of feedstock. Starch or sugar rich feedstock can be processed effectively to desired products. However limitations are often encountered when handling lignocellulose materials. Despite highly

developed technology in biochemical conversion route operation is often carried out in batch process making it time consuming.

2.10 Gasification Process

Gasification is a thermochemical process carried out under limited oxygen condition to convert carbonaceous feedstock to synthesis gas which is a valuable gaseous fuel primarily comprising hydrogen (H_2), carbon monoxide (CO), methane (CH_4) and carbon dioxide (CO_2). Reducing atmosphere of the gasification means that only 20% to 40% of stoichiometric amount of oxygen (O_2) related to a complete combustion enters the reaction. Elevated temperature condition up to $700^\circ C$ in an oxygen starved environment is required to convert the carbonaceous feedstock to synthesis gas. Gasification takes place in four different stages as shown in Figure 2.6, namely: drying, pyrolysis, combustion and reduction. Although, there is a considerable overlap of these stages, each can be assumed to occupy a separate zone where fundamentally different chemical and thermal reactions take place.

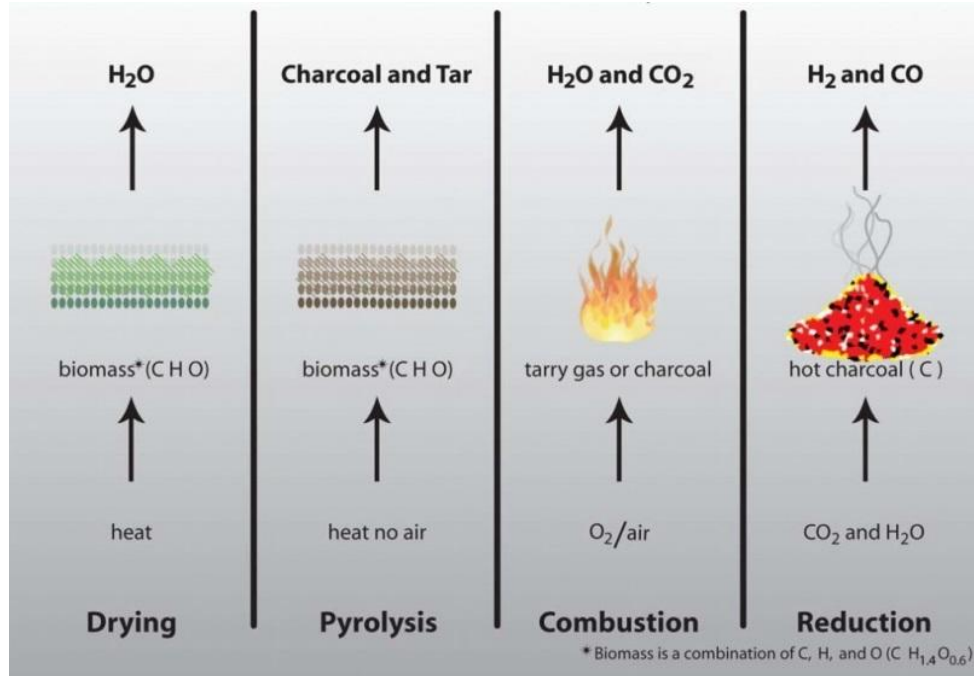


Figure 2.6: Stages of Biomass Gasification

2.10.1 Drying

The drying process involves driving off the moisture content which occurs rapidly as the fuel particle is introduced into the high-temperature environment. Low moisture content (MC) fuel is desirable because latent heat of vaporization requires relatively large amounts of energy at the expense of the principal endothermic reactions. Typically the resulting steam is mixed into the gas flow and may take part in subsequent chemical reactions, notably the water-gas reaction if the temperature is sufficiently raised high enough.

2.10.2 Pyrolysis

Pyrolysis process includes the heating of biomass at temperatures 500 – 900°C in a closed chamber or reactor in the absence of oxygen. It is an irreversible chemical change, which is due to heat supplied in the absence of oxygen. This process yield solid (char), liquid (tar) and gaseous products. In the absence of oxygen the heat energy in the reactor splits the

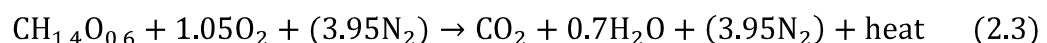
chemical bonds thereby releasing tremendous energy stored in biomass. As the temperature rises the cellulose and lignin break down to simpler substances which are driven off leaving a char residue behind(Shrivastava, 2012).

Tar is a condensable vapor of complex hydrocarbon mixture approximately represented by atomic formula $CH_{1.2}O_5$. During pyrolysis, volatiles component of biomass fuel are released and char is produced resulting to about 70% weight losses. The process is dependent on the properties of the carbonaceous material and determines the structure and composition of the char which is a solid residue mainly containing carbon and non-combustible ash. Composition of the gaseous product depends on operation temperature, pressure, and the type of oxidizing agent used.

2.10.3 Combustion

After biomass fuel material undergoes pyrolysis, portion of the volatile gases and char react with the oxidant in a series of exothermic reactions. This process is critical for gasification as it provides the heat required to drive the endothermic gasification reactions. In the case of steam gasification, the water-gas shift reaction is utilized to produce increased amounts of hydrogen.

The endothermic reactions that are driven by the reactive conditions in the gasifier yield combustible gases including hydrogen, carbon monoxide and methane. Combustion reaction can be represented generally by the following reaction:



Where $\text{CH}_{1.4}\text{O}_{0.6}$ represent an average formula for biomass feedstock. Nitrogen present comes in when air is used as oxidant, however remains inert and does not partake in the reaction. Where pure oxygen or steam is used, nitrogen disappears completely. Char reacts with oxygen to form primarily carbon dioxide and small amount of carbon-monoxide. The total oxidation reaction is exothermic and thus provides enough heat to maintain subsequent endothermic reactions.

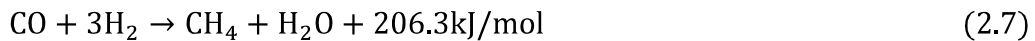
Partial oxidation reaction:



Total oxidation reaction:



Methane reformation reaction:



2.10.4 Reduction

Reduction also called gasification in some literature occurs when char represented as carbon reacts with steam to form carbon monoxide and hydrogen gas (synthesis gas).

Here CO_2 and H_2O produced from oxidation zone are reduced to form carbon monoxide (CO) and hydrogen (H_2) by absorbing heat from the oxidation zone. Oxidation zone raise the temperature of reduction zone to promote the steam gasification reaction which has higher activation energy. This reaction requires temperature of 900°C and above. Over 90% of CO_2 is reduced to CO at higher temperatures.

Gas-shift reaction:



Boudouard reaction:



Hydrogenation reaction:



In addition the reversible gas phase water gas shift reaction reaches equilibrium very fast at gasifier temperature. This balances the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen.

Reverse water-gas shift reaction:



2.11 Gasifier Design

Various designs of biomass gasifier have been developed over the years and each of them suits a particular form of biomass fuel to handle and also the end application of producer gas. However a number of gasifiers are designed with ingenuity and versatility to handle a range of biomass fuel. Basically there are two common classifications of biomass gasifiers based on bed type, namely fixed bed and fluidized bed. Figure 2.7 shows application of different gasification technology base scale of power production. Fixed bed technology is suitable for small applications with output power requirement <100 kW. On the other hand fluidized bed technology applies for higher power output.

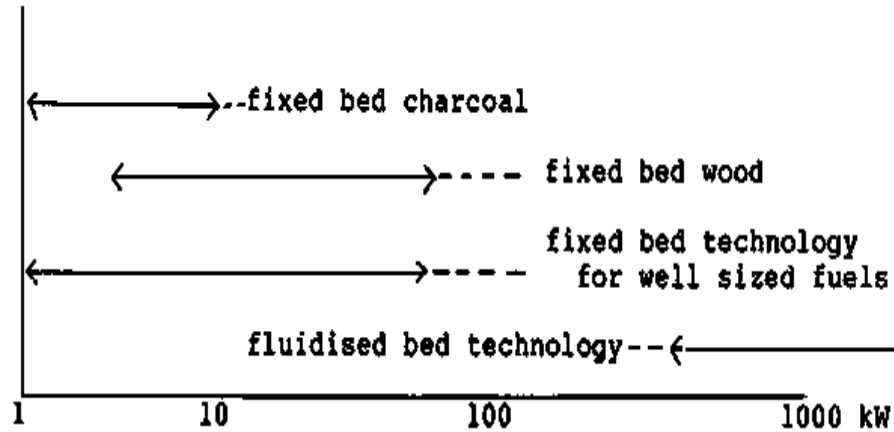


Figure 2.7: Application of Various Gasifier Design for Power Generation

2.11.1 Fixed bed design

Fixed bed uses bed of solid fuel particles through which air and produced gases flows either in upward or downward direction. Where the gasification agent usually air flows upward and producer gas exit at the top, the reactor configuration is called updraft. Inversely where air flows downward and producer gases exit through outlet at the bottom, reactor is called downdraft. Where both the gasifying agent and producer gas flows across the biomass bed, it is called cross draft. For the present research purpose, priority will be centered toward downdraft reactor design because of its suitability in small scale applications.

2.11.1.1 Updraft gasifier

Configuration of the updraft gasifier is depicted on Figure 2.8. Biomass feedstock goes in from the top while air supplies enters below the combustion zone through grate and flows upward through bed. The grate is mounted at the base of gasifier where air and steam reacts with charcoal from biomass to produce very hot CO_2 and H_2O . These gases undergo endothermic reaction with char to form CO and H_2 . The ascending hot reducing gases decompose biomass above combustion zone through pyrolysis. The producer gas has no

ash but contains tar and water vapor because of passing of gas through fresh biomass fuel. About 5% to 20% of tars and oils are produced at temperature too low for significant cracking and are carried out in the gas stream. The remaining heat dries the wet biomass so that none of the energy is lost as sensible heat in the gas. The advantage of updraft gasifier over other gasifier is its high conversion efficiency up to 80% but it produces tar with producer gas which is the major feedback of updraft gasifier. Tar content producer gas cannot be used in engine application because it has the potential to corrode the engine parts like piston, valve and fuel line(Shrivastava, 2012).

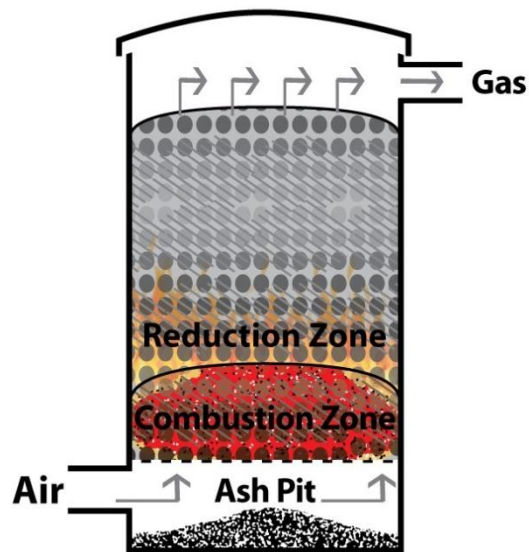


Figure 2.8:Schematic Diagram of Updraft Gasifier

2.11.1.2 Downdraft gasifier

In the downdraft gasifier, the upper cylindrical part of gasifier acts as a collection device for wood chips or other biomass fuel. The geometry of the downdraft gasifier is shown in Figure 2.9. Below this cylindrical part of gasifier, there is a radially directed air nozzle that permits air to be drawn in to chips as they move down to be gasified. This nozzle

constitutes combustion and reduction zone as shown in Figure 2.9. Air contacts the biomass undergoing pyrolysis before it contacts with char and support a flame. The limited air supply in the gasifier is rapidly consumed, so that the flame gets richer as pyrolysis proceeds. At the end of pyrolysis zone, the gases consist mostly of CO_2 , H_2O , CO and H_2 . The throat ensures that the gaseous products pass through the hottest zone where most of the tar cracked into gaseous hydrocarbon. Thus produces relatively clean gas. Product gas application for internal combustion (IC) engine, downdraft gasifier is more suitable as it produces very less tar(Shrivastava, 2012).

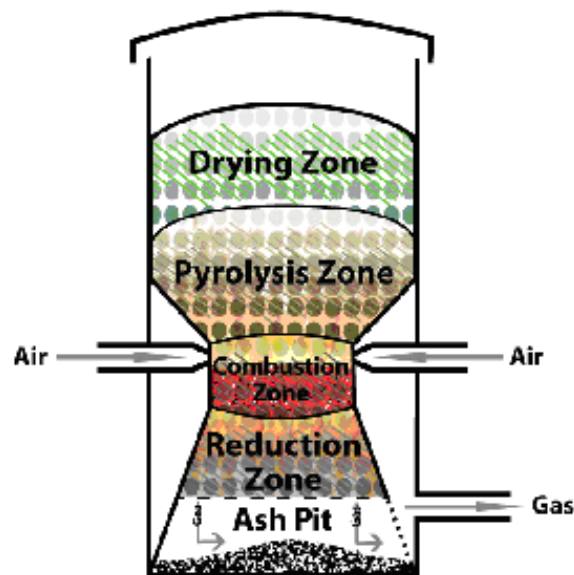


Figure 2.9: Schematic Diagram of Downdraft Gasifier

Downdraft gasification technology has an increased interest among researchers worldwide due to the possibility to produce mechanical and electrical power from biomass in small-scale to an affordable price. There exist mainly two designs for downdraft gasifiers: the Imbert gasifier (Throated or closed top gasifier) and the stratified gasifier (Throatless or open core gasifier). These gasifiers have been used for gasification of bark, wood blocks,

chips and pellets, straw, maize cobs, refuse derived fuel (RDF), and waste pellets with various gasifying media like air, oxygen, Steam (Anjireddy and Sastry, 2011).

(a) Imbert Downdraft Gasifiers

The Imbert downdraft gasifiers are suitable to handle biomass fuel having ash and moisture content less than 5% and 20% respectively (Pathak *et al.*, 2008). This gasifier features a concurrent flow of gases and solids through a descending packed bed, which is supported across a constriction or throat. The biomass fuel enters through the hopper and flows down, gets dried and pyrolysed before being partially combusted by the gasifying media entering at the nozzles. The throat allows maximum mixing of gases in high temperature region, which aids tar cracking. Below the constriction or throat the combustion gases along with tar pass through the hot char and are reduced to primarily CO and H₂. The imbert downdraft gasifier is generally used for gasification of woody biomass of uniform sizes and shapes as they flow smoothly through the constricted hearth. The producer gas from downdraft gasifier has lesser tar-oils (<1 %), higher temperature (around 700°C) and more particulate matter than that from an updraft gasifier. The gasifier has lower overall efficiency since a high amount of heat content is carried over by the hot gas (Clarke, 1981; Reed *et al.*, 1999). The physical limitations of biomass particle size limit the capacity of the imbert downdraft gasifiers to 500 kW.

(b) Stratified Downdraft Gasifiers

Stratified or throatless downdraft gasifier was developed to overcome the problem of bridging and channeling associated with throated downdraft gasifiers. The open top ensures uniform access of air and permits fuel to be fed easily and uniformly, which keeps the local temperatures in control (Panwar *et al.*, 2009). The hot producer gas generated is

drawn below the grate and up through the annulus of the reactor, where a part of the heat of the gas is transferred to the cold fuel entering the reactor, improving the thermal efficiency of the system. The pyrolysis components are cracked in the oxidation zone, as gas traverses a long uniformly arranged bed of hot char without any low temperature zones, therefore the tar generated is low 0.05 kg tar/kg gas. The open top throatless gasifier is suitable for small sized biomass having high ash content up to 20 % (Stassen and Knoef, 1995; Sims, 2003; Tiwari *et al.*, 2006).

2.11.1.3 Cross draft gasifier

Schematic diagram of a crossdraft gasifier is shown in Figure 2.10. Air enters at high velocity through a water cooled nozzle mounted on one side of the firebox, induces substantial circulation and flows across the bed of fuel and char. The gas is produced in the horizontal direction in front of the nozzle and passes through a vertical grate into the hot gas port on the opposite side. This produces very high temperature in a very small volume and results the production of minimum or tar free gas (Shrivastava, 2012).

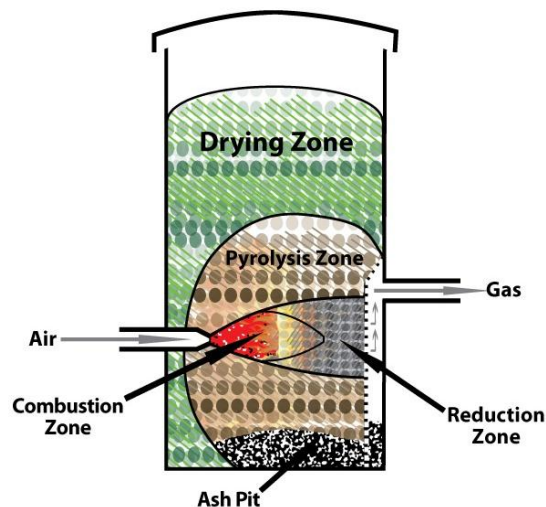


Figure 2.10: Schematic Diagram of Crossdraft Gasifier

2.11.2 Fluidize bed gasifier

Fluidized bed gasification system is used for the fuel which has high ash contents and the ash has low melting point. In fluidized bed gasifiers the air is blown upwards through the biomass bed. The bed under such conditions behaves like boiling fluid and has excellent temperature uniformity and provides efficient contact between gaseous and solid phase. Figure 2.11 depicts a schematic diagram of a fluidize bed Gasifier.

Generally the heat is transferred initially by hot bed of sand. Normally the operation temperature of the bed is maintained within the range of 750-950°C, so that the ash zones do not get heated to its initial deformation temperature and this prevents clinkering and slagging. The major advantage of fluidized bed gasifier over downdraft is its flexibility with regard to feed rate and rate of consumption but it produces more dust and tars as compared to downdraft gasifier (Maniatis and Buekens, 1982).

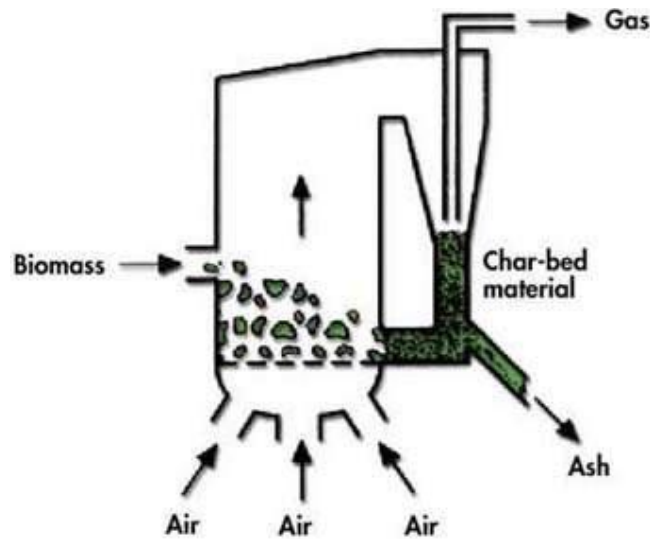


Figure 2.11: Schematic Diagram of a Fluidize Bed Gasifier

2.12 Gasification Operating Parameters

2.12.1 Equivalence ratio

The equivalence ratio (ER) expressed by equation (2.12) is an important operating parameter in gasification process. Where ER equals unity then stoichiometric oxidation or complete combustion is said to occur (Mevissen *et al.*, 2009).

$$ER = \frac{(\text{air/biomass})_{\text{actual}}}{(\text{air/biomass})_{\text{theoretical}}} \quad (2.12)$$

Equivalence ratio strongly influences the type of gasification products. This is very crucial because a high ER value results in a lower concentration of H₂ and CO as well as in a higher CO₂ content in the product gas. Thus, a higher ER decreases the heating value of the syngas. Increasing the ER also has a beneficial effect on reducing tar formation given the greater availability of oxygen to react with volatiles. This phenomenon is more significant at higher temperatures. On the other hand, an increase in the steam/biomass ratio is expected to produce a higher hydrogen fraction as a result of the water gas shift reaction. In addition, excess steam often drives the cracking of higher hydrocarbons and reforming reactions (Narvaez *et al.*, 1996). Lv *et al.*, (2004) divided biomass gasification into two stages based on the ER. In the first stage, the ER varied from 0.19 to 0.23. At this ER value, the gas yield increased from 2.13 to 2.37 Nm³/ kg biomass and the lower heating value (LHV) of the gas was augmented from 8817 to 8839 kJ/Nm³. In the second stage, the ER ranged from 0.23 to 0.27 and the heating value decreased as the ER increased. When the ER range was between 0.59 and 0.73; this had a slight effect on the hydrocarbon content. However, according to (Zhou *et al.*, 2000), ER does not significantly influence the concentration of nitrogen-containing products in biomass gasification. A slight increase in NH₃ was observed when the ER was increased from 0.25 to 0.37 at 800 °C in sawdust

gasification. Nevertheless, the steam/biomass ratio provides an upper limit set by gasification stoichiometry. Exceeding this limit yields excess steam and H₂O in the product gas. The energy associated with excess steam and the enthalpy losses resulting from the unnecessary production of this steam need to be considered in the system energy balances. Such issues demonstrate the importance of selecting an optimal steam/biomass ratio in biomass steam gasification for achieving high process efficiency. Figure 2.12 illustrates the effect of ER on Gasification temperatures. It can be seen that pyrolysis at temperature below 1000°C with zero ER value meaning no air is required. Gasification occurs typical between 0.2 - 0.4 ER, and according to a number of studies, ER is one of the most important variables in the gasification process in fixed bed reactors (Dogru *et al.*, 2002) which affect the quality of syngas produced. García-Bacaicoa *et al.*, 2008 reported that the amount of air fed into downdraft moving bed gasifiers controls the biomass consumption rate. The stoichiometric air/fuel ratio in cubic meters (at normal conditions) per kg of biomass can be expressed in terms of the chemical composition of the fuel and its typical value is between 5 and 6 Nm³/kg when firewood is used. (Sheth *et al.*, 2010) reported in his studies that Molar fractions of N₂ and CO₂ decrease up to an equivalence ratio of 0.21. For larger values of ER ranging from 0.21 to 0.41, there is an increase in N₂ and CO₂ fractions. This is opposite to the trend observed for H₂ and CO molar fractions. The temperature of oxidation zone varies from 900°C to 1150°C and that of pyrolysis zone varies between 150°C and 400°C. At an equivalence ratio of 0.21, the oxidation zone temperature passes through maxima. The trend of calorific value, producer gas production rate and cold gas efficiency variation is similar to that of variation of CO and H₂ fractions with an increase

in equivalence ratio. With an increase in the equivalence ratio, calorific value, producer gas production rate and the calorific value have maxima at an equivalence ratio of 0.21.

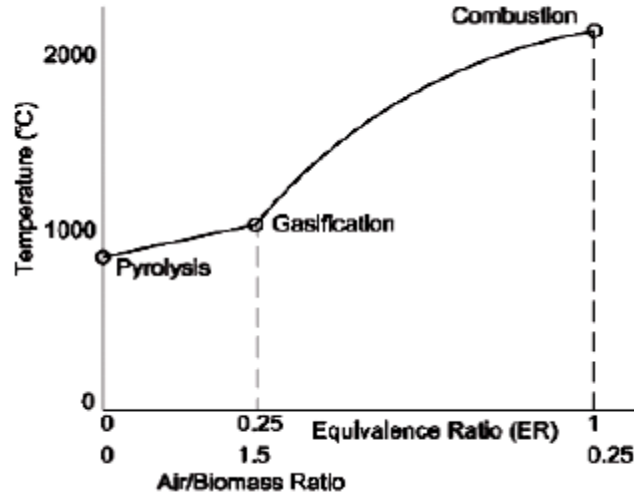


Figure 2.12: Effect of ER on Gasification Temperatures

2.12.2 Temperature

Researchers have conducted extensive studies reviewing the influence of temperature on tar production during biomass gasification (Skoulou *et al.*, 2009). To achieve a high carbon conversion of the biomass and a low tar content, a high operating temperature ($>800^{\circ}\text{C}$) in the gasifier is recommended. With the increase in temperature, combustible gas content, gas yield, hydrogen, and heating value all increased significantly, while the tar content decreased sharply (Hanping *et al.*, 2008). Although this trend shows that higher temperatures are favorable for biomass gasification, from an overall process perspective, very high temperature may cause agglomeration of ash (Luo *et al.*, 2009; Gao *et al.*, 2009). In practice, this may limit gasification temperatures up to 750°C (Salaices *et al.*, 2010). Moreover (Mahishi and Goswami, 2007) reported that the hydrogen at chemical equilibrium initially increased with temperature, reached a maximum, and then gradually

decreased at the highest temperatures. Temperature affects not only the amount of tar formed but also the composition of tar by influencing the chemical reactions involved in the gasification network (Wolfesberger *et al.*, 2009). To produce a relatively clean gas by increasing temperature, several operational strategies are reported in the literature. Fagbemi *et al.*, (2001) showed that tar yields were augmented first while temperature rose up to 600 °C and then dropped after this temperature was surpassed. Subramanian *et al.*, (2009) identified two temperature ranges above and below 500°C. Generally temperatures above 500°C are chosen for reduction of carbon dioxide by carbon to carbon monoxide. Therefore, pyrolysis of biomass is carried out at temperature less than 500°C for the maximum yield of char with inert medium flowing complete gasification is achieved at temperature above 500°C with air flowing. Mae *et al.*, (2009) conducted experiments for treatment of biomass in nitrogen and air at 240-340°C in order to examine the low-temperature region in a downdraft gasifier by analyzing the treated precursors and product distribution. Gas-treated precursors were then pyrolyzed in flash mode at 764°C for further analysis. Overall, the tar yield decreased from approximately 50 wt. % to less than 20 wt. % upon oxidation of the sample at a very low heating rate to 260-300°C in air. Moreover, tar evolution was almost completely suppressed during the subsequent flash pyrolysis. This indicates that the structure of the treated precursors was gradually changed to suppress tar release through cross-linking reactions and partial oxidation.

From elemental analysis of the precursors treated with air, it was also estimated that dehydration and partial oxidation proceeded simultaneously. The results indicate that the release of tar products such as dimers can be partially suppressed by air treatment at low temperature. Therefore, several factors including tar content, gas composition determining

gas heating value, and char conversion should all be taken into consideration and weighted carefully in the selection of the gasifier operating temperature (Anjireddy and Sastry, 2011).

2.12.3 Gasification medium

Gasification under different atmospheres such as air, steam, oxygen, and carbon dioxide has been reported in the literature. In general, the gasifier atmosphere determines the calorific value of the syngas produced. When one uses air as the gasifying agent, a syngas with low heating value is obtained. This is mainly due to the syngas dilution by the nitrogen contained in air (Gil *et al.*, 1999; Mathieu & Dubuisson, 2002). However, if one uses steam or a combination of steam and oxygen, a syngas with a medium calorific value is produced (Zhang *et al.*, 2004). In addition, the combined use of steam and air gives much higher H₂ yields than with air alone. This also helps to reduce the energy required for the process, which is normally provided by combusting a fraction of the biomass.

2.12.4 Moisture content

Moisture in biomass fuel is an important parameter in gasification as it drains much of the deliverable energy in the process of drying. This important input design parameter must be known for assessment of the cost of or energy penalty in drying the biomass. The moisture in biomass can remain in two forms: (i) free or external and (ii) inherent or equilibrium. Free moisture is that above the equilibrium moisture content. It generally resides outside the cell walls. Inherent moisture, on the other hand, is absorbed within the cell walls. When the walls are completely saturated the biomass is said to have reached the fiber saturation point, or equilibrium moisture. Equilibrium moisture is a strong function of the relative humidity and weak function of air temperature. For example, the equilibrium moisture of

wood increases from 3 to 27% when the relative humidity increases from 10 to 80%. It is found that with an increase in the moisture content, the biomass consumption rate decreases. For higher moisture content of biomass, the energy requirement for drying increases and reduces the biomass pyrolysis. The biomass moisture content greatly effects both the operation of the gasifier and the quality of the product gas. The constraint of moisture content for gasifier fuels are dependent on type of gasifier used (Anjireddy and Sastry, 2011). Higher values of moisture content could be used in updraft systems but the upper acceptable limit for a downdraft gasifier is around 25% (Basu, 2010).

2.12.5 Superficial velocity

A superficial velocity (SV) is defined as a ratio of the syngas production rate at normal conditions and the narrowest cross sectional area of the gasifier. A number of authors have indicated that SV influences the gas production rate, the gas energy content, the fuel consumption rate, the power output and char and tar production rates (Anjireddy and Sastry, 2011).

Better performance of the gasifier was observed when low tar content in producer gas and high efficiency were obtained for SV values of about 0.4 Nm/s. Low values of SV result in a relatively slow pyrolysis process with high yields of char and significant quantities of unburned tars. On the contrary, high values of SV cause a very fast pyrolysis process, formation of a reduced amount of char and very hot gases in the flaming zone. However, such high SV values may significantly decrease the gas residence time in the gasifier, resulting in lower efficiencies in the tar cracking processes. The lowest gravimetric tar yield of 0.7% was obtained at 0.4 m/s SV, and the highest was obtained at 0.7 m/s. High

tar yields at high SV are attributed to short residence time and channeling (Yamazaki *et al.*, 2005).

2.13 Product Gas Treatment

Despite numerous credits attributed to syngas produced from biomass gasification, the technology still faces huge challenges due to the presence of impurities such as tars and particulate matters which invariably affects downstream application of the gas (Asadullah, 2014). Consequently, rigorous clean up procedure must be implemented to ensure acceptable limit of impurities depending on specification of application (Paethanomet *et al.*, 2012). Concentration of impurities in the product gas depends on many factors however feedstock type and gasification conditions are two major factors that control the gas quality.

2.13.1 Tar removal

Tar is a complex mixture constituted primarily of aromatic hydrocarbons with molecular weight higher than benzene which are condensable at ambient temperature. Its formation occurs during pyrolysis stage of gasification precisely at a relatively low temperature of around 200°C and gets completed at about 500°C. In this temperature range the cellulose, hemicellulose, and lignin components of biomass break down into primary tar also known as wood oil or wood syrup. Above 500 °C the primary tar components start reforming into smaller, lighter non-condensable gases and a series of heavier molecules (Milne *et al.*, 1998).

Tar remains in vapor along the carrier gas stream until cools below the dew point of around 300°C forming either a liquid phase or fine aerosol drops (<1 micron). This characteristic

makes the tarry product gas unsuitable for use in gas internal combustion(IC)engines which has very low tolerance limit (Basu, 2010).It is reported that the maximum tar yield can go up to 6g/Nm³ for air blown fixed downdraft reactor while 10 – 150g/Nm³ updraft reactor.(Graham & Bain, 1993). However, the maximum allowable limit of tar in synthesis gas application is 0.02g/Nm³ and 0.1g/Nm³ for particulate matter (Milne *et al.*, 1998).

There are three major basic reactions responsible for tar destruction namely steam reforming, thermal cracking and steam cracking (Delgado *et al.*, 1996). Both steam and dry reforming are catalytic reactions involving the use of additives such as dolomite, char and olivine among others to facilitate reaction rate. In this way tar reduction becomes easier to reach at relatively lower operation temperature of around 800°C.

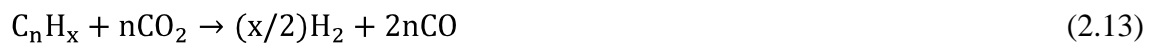
(a) Steam reforming

Steam reforming takes place in the presence of steam which breaks the tar into simpler gaseous molecules as represented by equation (2.12)



(b) Dry reforming

Dry reforming reaction takes place in the presence of CO₂ as the gasifying medium to effect cleavage on the giant tar cleavage as represented by equation (2.13)



(c) Thermal cracking

Thermal cracking in contrast does not require the use of catalyst for tar decomposition rather exclusively by mean of high temperature effect typically raised around 1100°C.

This option may not be attractive in small scale application because of its associated energy implication where external heating may be required to achieve operation condition.

2.13.2 Particulate removal

Particulates matter mainly consists of unconverted biomass material (ash and char) and a portion of finely divided bed material. Ash materials are the mineral components of the biomass; char is the unconverted portion of the biomass which is less reactive, resulting in decreased carbon conversion efficiency, and the fines from the bed material also are entrained with the gas stream (Ajay *et al.*, 2009). These particulates can cause abrasion to downstream equipment or present environmental emission hazard. Therefore, it will be mandatory to remove the particulates before using the gas in any downstream process. (Laurence and Ashenaf, 2012)

When the product gas is used for internal combustion engine, the particles deposit in the nozzle and causes blockage of the system. For turbine application the particles adversely affect the turbine blade due to abrasion effect. The particles also affect the anode of the solid oxide fuel cell and deactivate the catalyst for the Fischer Tropsch synthesis. The Internal Combustion (IC) engine can satisfactorily accept the particle concentration $<50 \text{ mg/Nm}^3$ with size $<10 \text{ }\mu\text{m}$, while it is $<30 \text{ mg/Nm}^3$ for gas turbine. Fischer Tropsch synthesis requires complete separation of particulate matter for production of methanol and other hydrocarbon fuel (Hasler and Nussbaumer, 1999).

There are many different technologies for removal of particulates matter from gases that can be applied to both syngas and product gas. To remove particulates from the synthesis

gas the following systems can be used: cyclones, barrier filters, electrostatic filters (ESP), and solvent scrubbers (Boerrigter and Rauch, 2006).

2.13.3 Gas conditioning

Gas conditioning comprises all gas treatment steps to adjust the main gas composition of the syngas (or product gas) to meet the specifications of the gas application. The main issues in gas conditioning are adjustment of the H₂/CO ratio and CO₂ removal. Typically, processes for the manufacturing of syngas from hydrocarbon feedstock produce mixtures of hydrogen, carbon dioxide, methane, and varying amounts of carbon monoxide. For the majority of industrial processes, the carbon monoxide content is higher than that required for synthesis. The presence of CO₂ is undesired in most processes and this compound should be removed(Boerrigter & Rauch, 2006).

2.14 Synthesis Gas Application

Syngas basically refers to a mixture of two gases specifically hydrogen and Carbon monoxide. These gases are conventionally produced through gasification of fossil fuels such as coal and coke more so from biomass feedstock in a corresponding manner. Based on the general composition and the typical applications, two main types of gasification gas can be distinguished, i.e. 'biosyngas' or simply syngas and 'product gas'(Boerrigter & Rauch, 2006).

(a) Product gas

Product gas is produced from low temperature gasification (below 1000°C) and contains CO, H₂, CH₄, CO₂, H₂O, C_xH_y in addition tars and other higher hydrocarbons (aromatics).

(b) Syngas

Syngas is produced from high temperature (above 1200°C) or catalytic gasification. Under these conditions the biomass is completely converted into H₂ and CO as the dominant gases. Syngas can also be made from product gas by thermal cracking or catalytic reforming. Typically syngas contain about 50% of the energy in the product gas, while the remainder is contained in CH₄ and higher hydrocarbons.

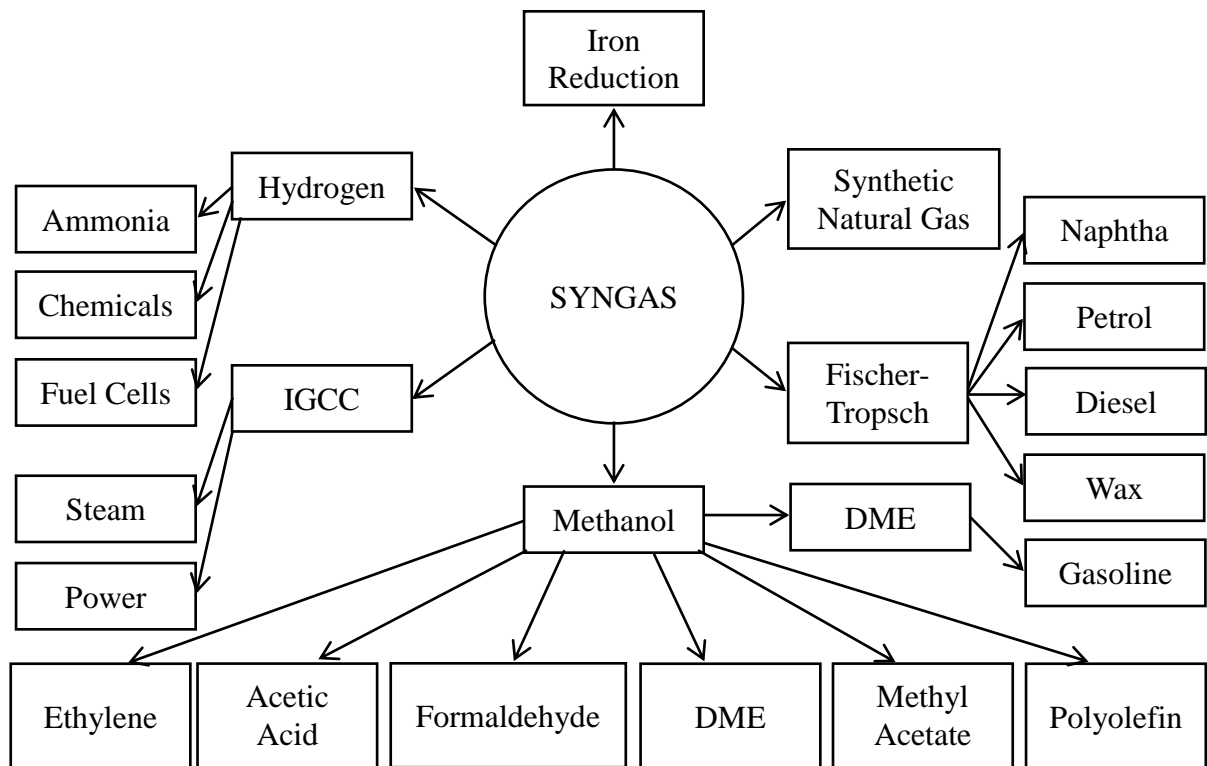


Figure 2.13: Application of Syngas

2.14.1 Thermal energy

For heat production by direct firing of the gas there are in principle no technical specifications for the main gas composition and the impurities (for corrosion reasons the chloride content should not be too high, which for biomass is hardly ever an issue). The product gas must be combustible, i.e. a lower heating value of >5 MJ/m³. Limitations for

the dust content of the gas may apply depending on the type of boiler and the burner. Emission limits can be met with standard and commercially available flue gas cleaning. Gasification gives the advantage of separating the noxious substances from the fuel gas prior to combustion therefore alternatively product gas cleaning might be applied. The choice of either approach will be made case-specific and in most cases based on economic considerations(Boerrigter & Rauch, 2006).

2.14.2 Power generation

Syngas is a combustible gas and can be used for the production of electricity in all prime movers from steam cycles, to gas engines, turbines (combined cycle), as well as fuel cells. For this purpose, syngas must be free from dust, volatiles and condensable hydrocarbon content. Pressure requirement is also an important criterion for power generation. Where gasification under atmospheric pressure is considered, syngas compression can be applied to achieve desired pressure.

2.14.3 Transportation fuels

In the future, syngas will become increasingly important for the production of ultra-clean designer fuels from GTL processes, with the main examples being Fischer-Tropsch diesel and methanol/DME.

2.14.4 Methanol production

Methanol can be produced by means of the catalytic reaction of carbon monoxide and some carbon dioxide with hydrogen. The presence of a certain amount of carbon dioxide in the percentage range is necessary to optimize the reaction. Both reactions are exothermic

and proceed with volume contraction; a low temperature and high pressure consequently favours them (Boerrigter & Rauch, 2006).



2.15 Gasification Safety Consideration

2.15.1 Gas toxic hazard

Carbon monoxide(CO) being a deadly poisonous gas constitutes a principal component of product gas. Exposure of carbon monoxide causes hemoglobin saturation with severe suffocation effect due to limited oxygen supplies to body tissues.CO exposure up to 20 - 30% blood saturation lead to manifestation of severe health conditions such as increase pulse, headache, nausea and dizziness. Further exposure up to 40% blood saturation may lead to loss of consciousness and possible failure of the respiratory system. Carbon dioxide threshold limit value (TLV) is 50 ppm for 8 hours per day while exposure up to 400 ppm is considered a short time exposure limit (STEL) in a work environment. Strenuous activity involving poisoned victim poses more threat to health condition in that absorption of carbon monoxide into blood stream becomes faster inherently causing adverse effect to become pronounced within shortest time(Reed and Das, 1988).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials and Equipment

List of materials and Equipments used in the present gasification experiment are provided as follows:(See Appendix B for equipments specifications).

1. Portable infrared gas analyzer
2. Gas conditioning system
3. Digital thermometer
4. Air blower
5. Mass flow meter
6. Thermocouple probe
7. Air/oxygen cylinder
8. Silicone sealer
9. Matches sticks

3.2 Sawdust Characterization

Sawdust sample was collected in plastic bags from Sawmills at Timber Market (*Kasuwan Katako*), Zaria in Sabon Gari Local Government Area of Kaduna State, Nigeria. Prior to characterization, the collected sample was sorted and spread in open air for about 2 weeks to reduce significant amount of its initial moisture content.

Ultimate and proximate analysis procedure published by the American Society for Testing and Material (ASTM) E870-82(2013) was used in characterization of the sawdust sample. In this analysis moisture content (M), volatile matter (VM), ash content (A), sulfur

(S) content and nitrogen (N) content of the sawdust sample were determined. However, correlation developed by Shen *et al.*, (2010) was used to estimate percentage composition of hydrogen (H), oxygen (O) and carbon (C) in the sawdust sample using proximate analysis data as input variables (see equation 3.1 – 3.3). Moisture content was determined using ASTM E871-82 designated for particulate wood analysis. In this method, 50 grams of sawdust sample was weighed and heated in an air oven at 103°C for about 30 minutes. The sample was then removed from the oven and weighed again after cooling. To ensure complete drying of the sample, the process was repeated until the sample weight remains unchanged. The difference in weight between the dry and the fresh sample gives the moisture content. Feedstock sample further subjected to higher temperature of about 950°C drives off volatile content leaving behind the fixed carbon. Table 3.1 provides summary of ASTM specification used in characterization of the sawdust sample.

Table 3.1 ASTM for Proximate and Ultimate Analysis

Proximate Analysis	
Moisture content	E871 – 82.
Volatile Matter	E 872 – 82.
Ash	E1755 – 01.
Ultimate Analysis	
Sulphur	E 775 – 87.
Nitrogen	E 778 – 87.

$$C = 0.635FC + 0.460VM + 0.095ASH(\text{wt. \%}) \quad (3.1)$$

$$H = 0.059FC + 0.060VM + 0.010ASH(\text{wt. \%}) \quad (3.2)$$

$$O = 0.340FC + 0.469VM + 0.023ASH(\text{wt. \%}) \quad (3.3)$$

3.3 Experimental Setup

The gasification experiment was conducted using a pilot scale downdraft gasifier, designed and fabricated at the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. Figures 3.1(a) and (b) depicts a schematic diagram of experimental setup used consisting of nine separate parts: (1) Gasifier (reactor), (2) Cyclone, (3) Filter, (4) Tar collector, (5) Flare, (6) Gas analyzer (7) Thermometer (8) and (9) Air/Oxygen Cylinder. See Appendix A for detail description of the experimental setup.

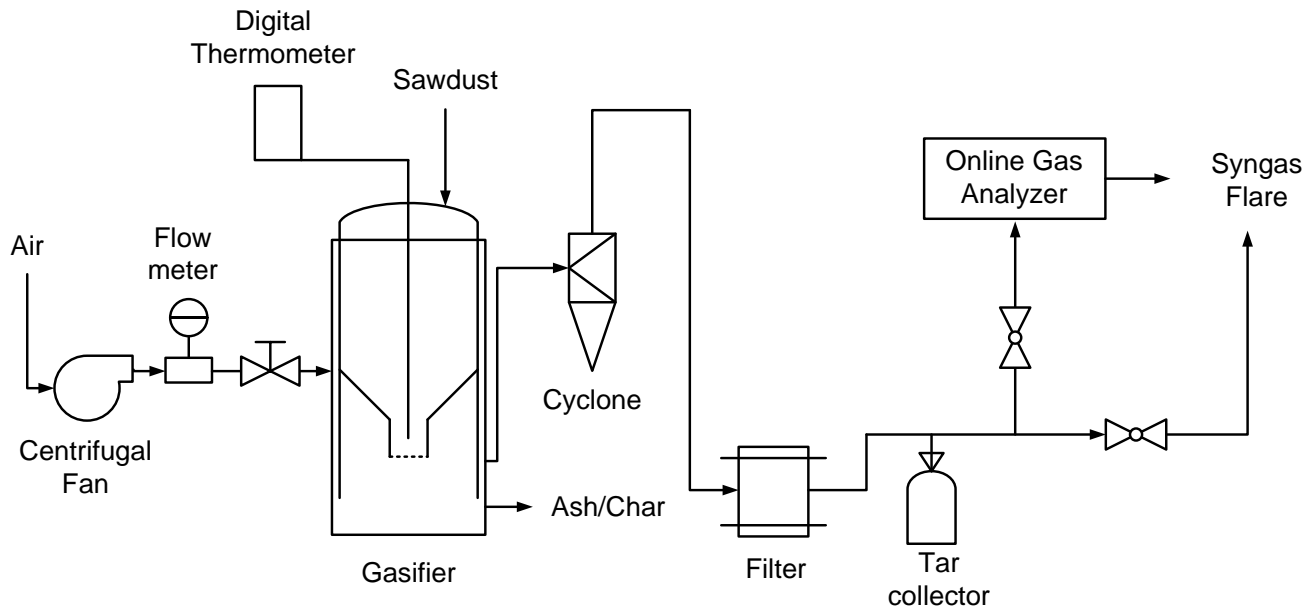


Figure 3.1 (a): Experimental Setup for Air Gasification

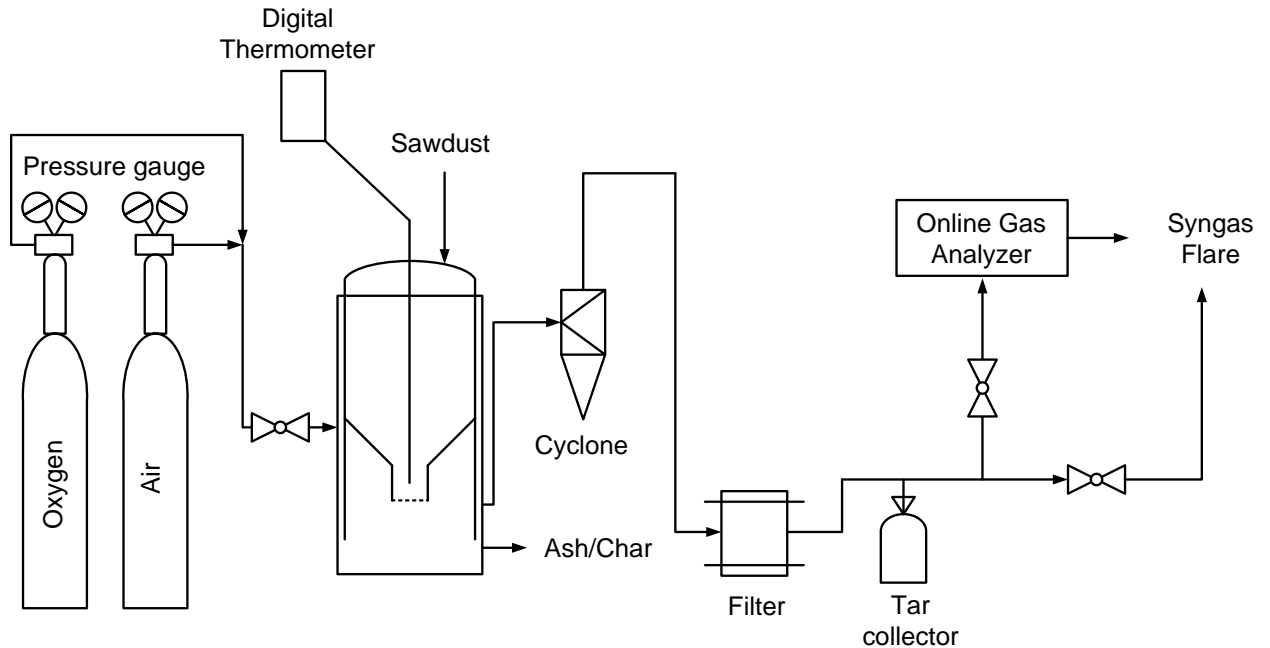


Figure 3.1 (b): Experimental Setup for Oxygen Enriched Air Gasification

3.4 Experimental Measurement

After successful startup procedure, the reactor was allowed to run for about 5 minutes to attend auto-ignition conditions so as to sustain the thermal process. A flow meter positioned ahead of the blower monitors the rates at which air flows while a ball valve positioned between them controls the flow rate by way of manual setting. Reactor temperature was measured using K-type thermocouple with readings displayed on digital screen. A thermocouple sensor inserted through an aperture on the reactor outer shell extends to reach the oxidation zone. Typically axial and radial temperature distributions are trends observed in gasifiers reactors however within the context of the current study only the oxidation zones were prioritized. The oxidation zone is located exactly at the constriction or throat of the gasifier where the maximum operating temperature is expected.

Gas composition in percentage volume bases was determined using online digital gas analyzer after removal of particulate matter and the tarry component of the product gas. Additional gas washing unit with three treatment integrated parts was used to double check gas quality. In this way the analyzer sensor is carefully protected to effectively avoid potential damage by trace of contaminant in the product gas. The compositions of the gases; CO, H₂, CO₂ and CH₄ were recorded by direct reading from the display screen in addition to the calorific value of the combine gases.

Flow rates of air at 6.4, 1.9 and 0.7 LPM were used separately to investigate the effect of equivalent ratio (ER) on composition of product gas and gasification temperature while moisture content of sawdust constant was kept constant.

3.5 Gasification Performance Evaluation

The overall performance of gasification experiment carried out in a downdraft gasifier was evaluated based on the lower heating value (LHV) of producer gas, cold gas efficiency (CGE) and carbon conversion efficiency (CCE) of the conversion process (see equation 3.4 – 3.7). These parameters significantly depend on properties of the feedstock determined by the proximate analysis (Zainal *et al.*, 2002; Jayah *et al.*, 2003).

$$\text{LHV}_{\text{gas}} = 107.98\text{H}_2 + 126.36\text{CO} + 358.18\text{CH}_4 \quad (3.4)$$

$$\text{CGE} = \frac{[\text{LHV}_{\text{gas}}] \times V_g}{[\text{LHV}_{\text{fuel}}]} \times 100\% \quad (3.5)$$

$$\text{CCE} = \frac{12(\text{CO}_2 + \text{CO} + \text{CH}_4) \times V_g}{22.4 \times C} \quad (3.6)$$

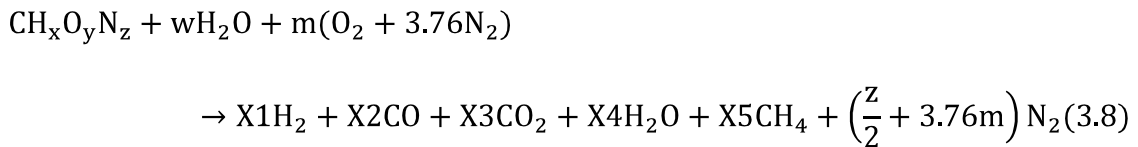
$$V_g = \frac{Q_a \times N_{2o}}{N_{2g}} \quad (3.7)$$

where C is the mass fraction of carbon in fuel feedstock and V_g is the amount of product gas (Nm^3/kg) at standard state. Where Q_a is the amount of gasifying agent supplied in (m^3) per the amount of sawdust feedstock in (kg). Ratio of nitrogen in oxidizing medium (N_{2o}) to nitrogen trace in producer gas (N_{2g}) was used as the producer gas quantitative indicator.

3.6 Thermodynamic Equilibrium Model

In this research, thermodynamic equilibrium model developed by Jarunthammachote and Dutta, (2007) was used to predict product gas composition, gasification temperature and equivalence ratio by way of specifying the feedstock properties and selected input variables. The model takes into consideration basic phenomena that occur during gasification process notably mass transfer and energy transfer. The following equations describe each of the principle in addition to the concept of chemical equilibrium.

1. The global gasification equation:



Where x, y, and z represents the number of atoms of hydrogen, oxygen, and nitrogen per number of atom of carbon in the feedstock respectively. Similarly, w and m represents the amount of moisture and oxygen per kmol of feedstock respectively. Furthermore $X_1 - X_5$ represents the moles fraction of respective adjacent chemical species.

$$m = \frac{M_{bio}M_c}{18(1 - M_c)} \quad (3.9)$$

Where, M_c is the moisture content of feedstock and M_{bio} is the molecular weight of feedstock.

2. Mass balance equations:

Atomic balance given in Equation (3.8) is used to find the amount of each product gas.

Carbon balance:

$$X_2 + X_3 + X_5 - 1 = 0 \quad (3.10)$$

Hydrogen balance:

$$X_1 + 2X_4 + 4X_5 - x - 2w = 0 \quad (3.11)$$

Oxygen balance:

$$X_2 + 2X_3 + X_4 - w - 2m - y = 0 \quad (3.12)$$

3. Thermodynamic equilibrium:

All gases were assumed to be ideal and all reactions form at pressure 1 atm. Equilibrium constant (K) for hydrogenation reaction and water-gas-shift reactions discussed in chapter two (Equations 2.10 and 2.11) are given by equation (3.13) and (3.14) respectively:

$$K_1 = \frac{X_3 X_1}{X_2 X_4} \quad (3.13)$$

$$K2 = \frac{X5(X_{total})}{X1^2} \quad (3.14)$$

4. Gibbs free energy equation:

$$\ln K = \frac{\Delta G_T^0}{RT} \quad (3.15)$$

$$\Delta G_T^0 = \sum_i v_i \Delta g_{f,T,i}^0 \quad (3.16)$$

$$\Delta g_{f,T}^0 = h_f^0 - aT \ln(T) - bT^2 - \left(\frac{c}{2}\right) T^3 - \left(\frac{d}{3}\right) T^4 + \left(\frac{e}{2T}\right) + f + gT \quad (3.17)$$

5. Energy balance

$$\sum_j h_{f,j} = \sum_i X_i (h_{f,i}^0 + \Delta h_{T,i}^0) \quad (3.18)$$

$$\Delta h_{T,i}^0 = \int_{298}^T C_p(T) dT \quad (3.19)$$

$$C_p = C1 + C2T + C3T^2 + C4T^3 \quad (3.20)$$

$$h_{f,j} = LHV + \sum_k X_k h_{f,k} \quad (3.21)$$

$$LHV = 4.187(81C + 300H - 26(O - S) - 6(9H + m)) \quad (3.22)$$

3.6.1 Model assumptions

The following assumptions were considered in the model formulation for simplicity:

1. All gaseous products are assumed to be ideal gases.
2. All carbon content in biomass is converted into gaseous form and the residence time is high enough to achieve thermodynamic equilibrium.
3. Amount of condensable hydrocarbon (tar) produced is considered negligible.
4. Ash content in feedstock was assumed inert and therefore fusion effect at high temperature is considered negligible.
5. The process is assumed auto-thermal and completely adiabatic so that no external heating is required and no heat losses occur.

3.6.2 MATLAB Simulation Algorithm

The following outline gives summary description of MATLAB simulation algorithm used in predicting gasification temperature, producer gas composition and its lower heating value. See Appendix C for detailed MATLAB coding.

1. Inputting elemental composition, moisture and ash contents of the sawdust sample.
2. Selection of reasonable initial guess values for temperature (500°C), amount of oxygen (21%) and water vapor (5.8%) per the amount of feedstock.
3. Computing the value of equilibrium constants, K_1 and K_2 using equation (3.8) - (3.10).
4. Computing the moles of each species in producer gases (X_i) using five non-linear equations: (3.3) – (3.7).
5. Computing a new value of temperature (T) using equation (3.11) – (3.15).
6. Computing absolute tolerance and checking convergence criteria.
7. If convergence is not attained, iterate step 2 -5 until result converges.

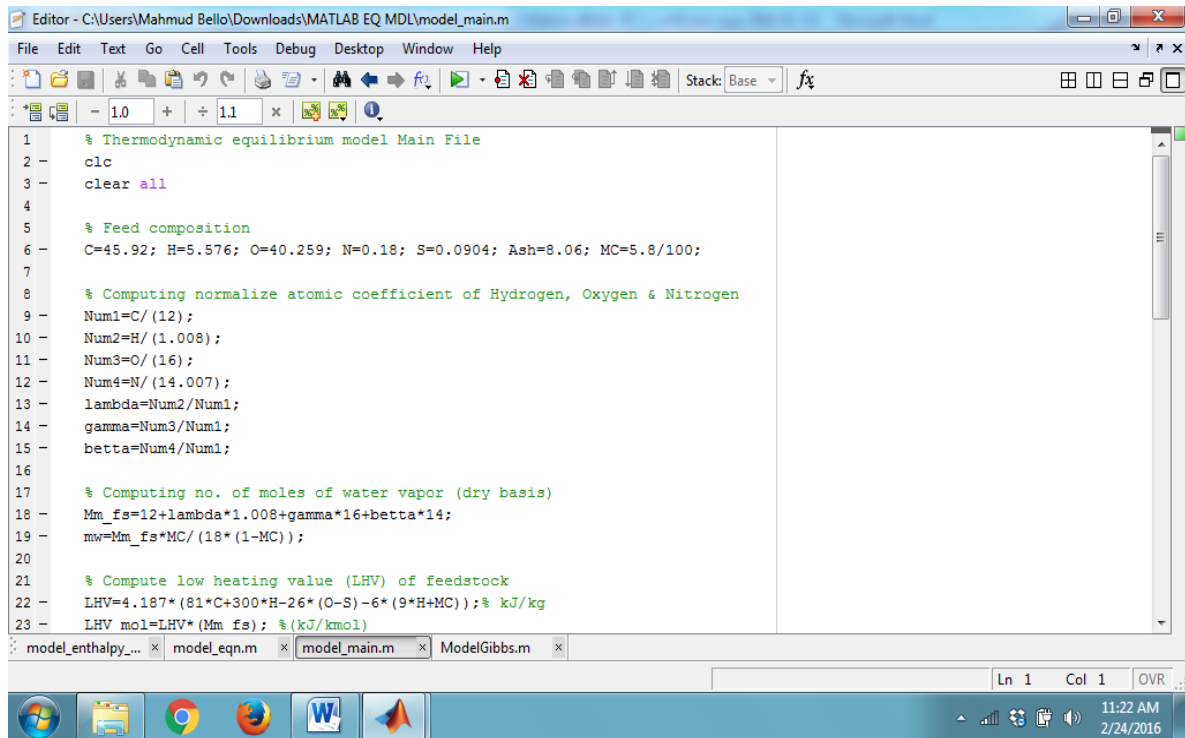


Figure 3.2: Snapshot of MATLAB Window

3.7 Root Mean Square Error

Root mean square error (RMSE) given by equation (3.23) was used to measure the difference between experimental results and its equivalent predicted by the thermodynamic equilibrium model. Hyndman et al, (2006) stated that RMSE serves to aggregate the magnitudes of the errors in predictions for various times into a single measure of predictive power and therefore a good measure of accuracy.

$$\begin{aligned}
 & \text{RMSE} \\
 &= \sqrt{\frac{\sum_i^N (\text{Exp}_i - \text{Mod}_i)^2}{N}} \quad (3.23)
 \end{aligned}$$

Where: Exp_i is the experimental value, Mod_i is the model predicted value and N is the number of corresponding data points.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Proximate Analysis Result

From proximate analysis of the sawdust sample presented in Table 4.1, it can be seen that fixed carbon content, volatile matter and ash content were found be 14.94, 71.2 and 8.06% respectively. Similar result was reported by Jigisha *et al.*, (2004) as 25.00, 72.40 and 2.60% respectively. Kong *et al.*, (2013) in their work observed that FC, VM and M significantly affect the HHV of biomass sample. They demonstrated that HHV improves from 15.86 – 29.49 MJ/kg by pyrolysis at 773K which reduces the VC and MC of the sample used.

Table 4.1: Proximate Analysis of Sawdust Feedstock

Content	Percentage (%)
Moisture Content	5.80
Volatile Matter	71.20
Fixed Carbon	14.94
Ash	8.06
Total	100.00

4.1.2 Ultimate analysis result

Ultimate analysis determines elemental composition of dry fuel on weight percentage basis. Typically hydrogen, oxygen, carbon, nitrogen, sulfur and ash contents are determined. Table 4.2 presents the ultimate analysis results of the sawdust feedstock sample. It can be seen that carbon content of 45.92% indicates significant level typically observed in woody feedstock. Hydrogen and oxygen content of approximately 5.58% and 40.17%

respectively show similar trend as reported by Feiqiang *et al.*, (2014). Low sulfur and nitrogen contents approximately 0.18 and 0.09 respectively is also similar to values reported in the literature for woody raw material, so this indicates added advantage in terms of product gas quality because low NO_x and SO_x emission is expected compared to fossil feedstock where emission may be significantly higher.

Table 4.2: Ultimate Analysis of Sawdust Feedstock

Content	Percentage (%)
Carbon	45.92
Hydrogen	5.58
Nitrogen	0.18
Sulfur	0.09
Oxygen	40.17
Total	91.94

4.2 Gasification Using Air Medium

4.2.1 Effect of air flow rate on equivalence ratio and temperature

Table 4.3 presents the effect of air flow rate on equivalence ratio and reaction zone temperature. Using pure air as gasifying agent, three flow rates; 6.4, 1.9 and 0.7 LPM were selected representing ER values of 0.0972, 0.0289 and 0.0106, respectively. It can be observed clearly that decrease in air flow rate corresponds to decrease in ER values. In a similar way, reaction zone average temperature decreases from 583.82 to 274.10°C as ER decreases from 0.0972 to 0.0106. This implies that more oxygen is supplied into the reactor at higher flow rate which in turn supports the combustion reaction resulting to higher temperature. According to Knoef, (2005) exit-gas temperature of downdraft gasifier

is in the neighborhood of 700°C whereas peak temperature at reaction zone (throat) rises up to 1000°C. Experimental data also reported on Table 4.3 shows peak temperature value falls between gas-exit and reaction zone temperatures for downdraft gasifier implying that gasification temperature was achieved.

Table 4.3: Effect of Air Flow Rate on Equivalence Ratio and Reaction Zone Temperature

Air Flow Rate (LPM)	Equilibrium Ratio (ER)	Average Temperature (°C)	Peak Temperature (°C)
6.4	0.0972	583.82	809.4
1.9	0.0289	468.63	616.0
0.7	0.0106	274.10	507.1

Reaction zone temperature profile at 6.4, 1.9 and 0.7 LPM air flow rates selected for the experiment is presented in Figure 4.1. Observed trend shows that temperature initially rises to a certain peak at around 10 minutes then slightly falls subsequently to nearly steady state condition at about 30 minutes. It can be seen that higher flow rate result to corresponding higher temperature at the reaction zone. This factor-effect response closely similar to trend observed in Figure 4.1, can be ascribe to the amount of oxygen reaching the reaction zone at different air flow rate which is sole responsible for supporting the combustion reaction accompanied by release of heat energy and temperature rise.

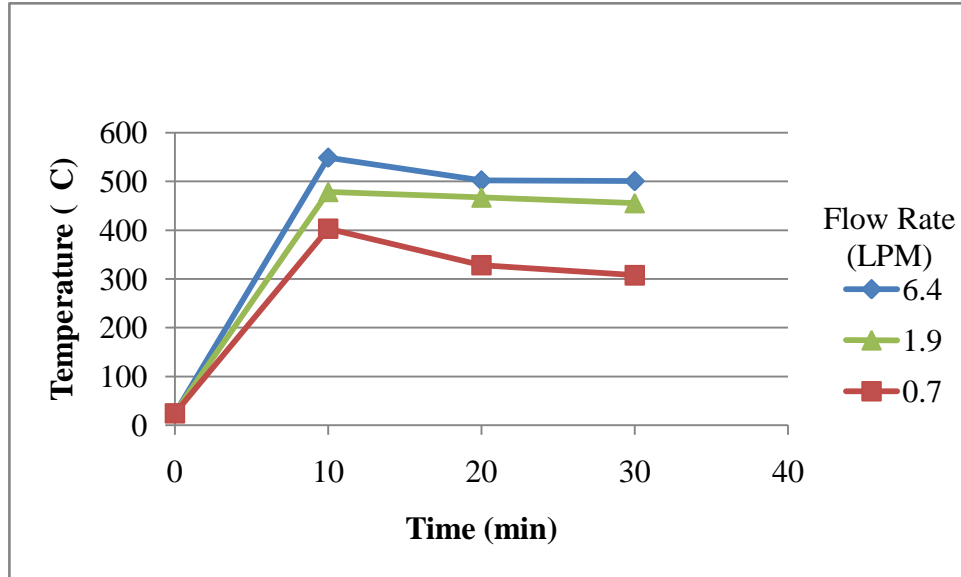


Figure 4.1: Reaction Zone Temperature Profile at Different Air Flow Rates

4.2.2 Effect of air flow rates on product gas composition

Figures 4.2 – 4.4 present the effects of air flow rate on product gas composition. It was observed that with each of the selected air flow rate, producer gas percentage composition increase initially with residence time whereas residual oxygen composition in producer gas decreases. This trend indicates the occurrence of oxidation reactions which consumes the supplied oxygen in the formation of CO and CO₂ as illustrated by equation (2.4) – (2.6). Similarly CH₄ and H₂ percentage compositions are seen to rise gradually indicating the occurrence of methane reformation and gas-shift reactions described by equation (2.7) and (2.8) respectively. Compositions of CO and H₂ in product gas recorded highest levels of 13.55% and 2.59%, respectively at 6.4 LPM air flow rate as shown in Figure 4.2. With increase in residence time however drastic fall in CO percentage composition was observed while CO₂ and H₂ rise slightly. This trend describes water-gas shift reaction as illustrated by equation (2.11) which favors the forming of H₂ and CO₂ at

the expense of moisture present in the sawdust and CO in the producer gas. Similar trend of product gas composition was observed at lower air flow rates of 1.9 and 0.7 LPM as presented in Figures 4.3 and Figure 4.4 respectively. Decreasing air flow rate from 6.4 – 1.9 LPM led to a significant rise in CO₂ peak concentration from 3.45 - 6.16%. However, reduction in CO, H₂ and CH₄ peak concentrations was observed. Methane concentration generally kept a low concentration profile throughout the entire experiment. Gujaret *al.*, (2014); Lahijani et al., (2013) and Fiseha *et al.*, (2014) observed similar trend in their works, which was attributed to the fact that higher oxygen flow rates tend to facilitate combustion reaction responsible for the release of enormous heat.

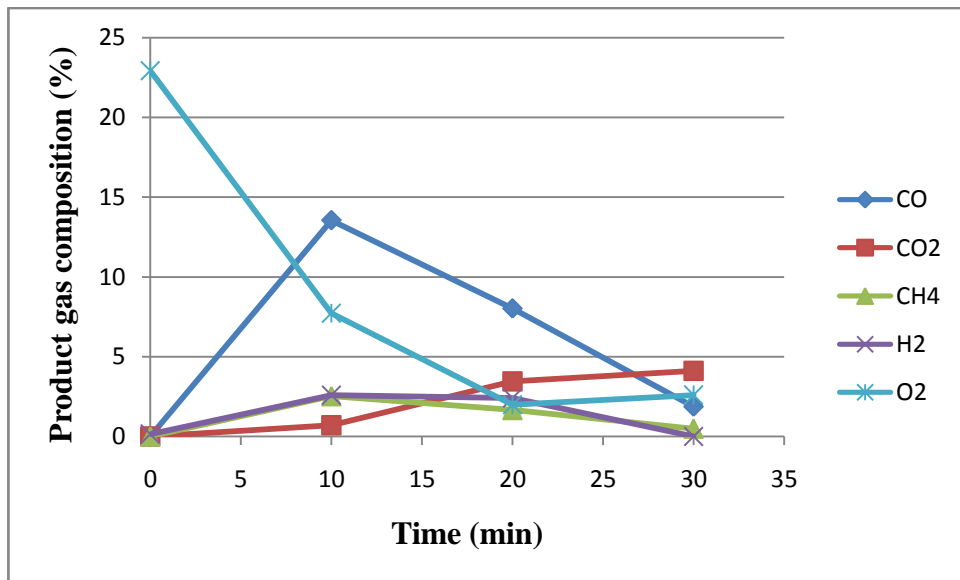


Figure 4.2: Composition Profile of Product Gas at 6.4 LPM Air Flow

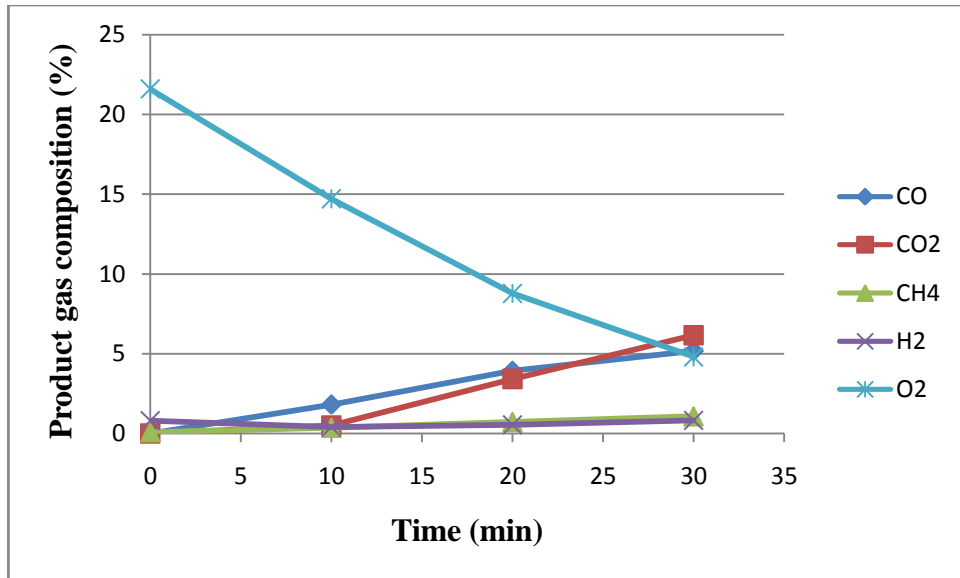


Figure 4.3: Product Gas Composition Profile at 1.9LPM Air Flow

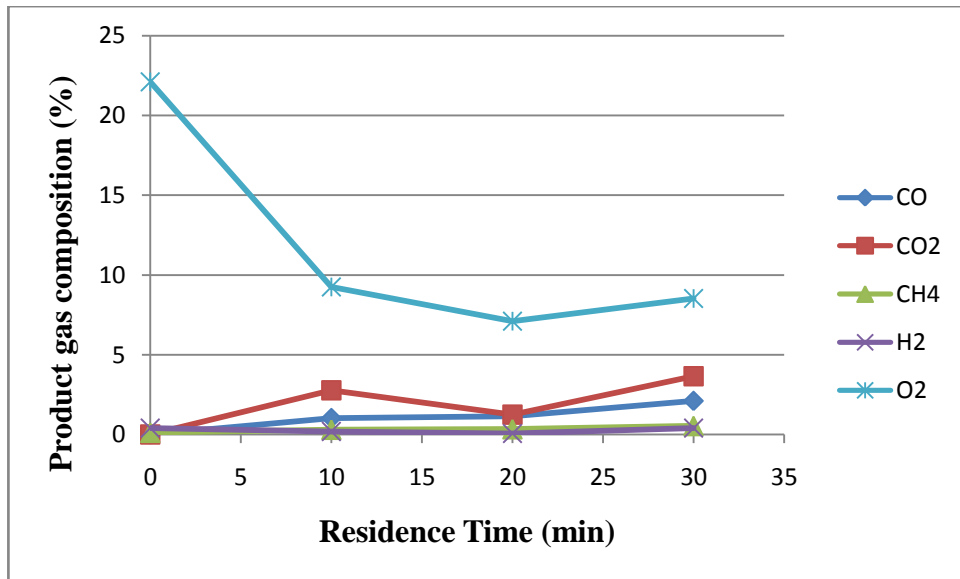


Figure 4.4: Product Gas Composition Profile at 0.7LMP Air Flow

4.3 Gasification Using Oxygen Enriched Air

4.3.1 Effect of oxygen enrichment on equivalence ratio and temperature

Experimental data reported in Table 4.4 shows that increase in percentage oxygen from 21 to 80% led to significant increase in ER from 0.1520 to 0.6226 while average

temperature of reduction zone vary from 381.17°C to 706.4°C. Peak temperatures recorded ranged from 660.9 – 1059°C which matches closely with gasification temperature range (500°C – 1300°C) reported in the literature(Basu, 2010). This is sufficient to facilitate tar cracking in addition to endothermic reactions responsible for the formation of energy carrier product gases. It can be inferred that variation in ER has a direct dependency on percentage oxygen in gasification medium. Principally, increase in ER enhances combustion reactions which in turn release enormous thermal energy sufficient to sustain the process and further raised the operating temperatures.

Table 4.4: Effect of Oxygen Enrichment on Equivalence Ratio and Reaction Zone Temperature

Oxygen (%)	Equivalence Ratio (ER)	Average Temperature (°C)	Peak Temperature (°C)
21	0.1520	381.17	660.9
30	0.2187	448.35	603.2
40	0.2953	454.33	521.7
50	0.3741	564.64	860.7
60	0.4550	651.08	778.5
80	0.6226	706.48	1059

The relevance of temperature in gasification cannot be overemphasized as it dictates key process conditions. At temperature of around 100°C drying takes place thereby driving off moisture content available in the feedstock material. Pyrolysis follows thereafter at around 200°C where volatile compounds are formed including char, product gases and non-condensable mixture of hydrocarbon also known as tar. Further rise in temperature to about 500°C by increasing supply of oxidizing medium leads to cracking of tar to valuable product gases.

4.3.2 Effect of oxygen enrichment on gasification performance parameter

Table 4.5 shows gasification performance parameter evaluated at different percentage oxygen in gasification medium. The Lower Heating Value (LHV), Cold Gas Efficiency (CGE) and Carbon Conversion Efficiency (CCE) were computed using equations(3.4), (3.5) and (3.6),respectively.

Table 4.5:Effect of Oxygen Enrichment on Gasification Performance Parameters

Oxygen (%)	LHV (MJ/Nm ³)	CGE (%)	CCE (%)
21	2.08	8.65	19.10
30	4.24	22.19	48.17
40	6.69	46.81	82.04
50	5.06	25.24	50.34
80	6.50	21.96	45.74

It can be seen in Table 4.5, LHV increases consistently at first from 2.08 – 6.69 MJ/Nm³ as percentage oxygen in air rises from 21–40%. Further increase of percentage oxygen in air from 40–80% resulted to a rise after fall trend which is attributed to percentage composition of combustible gases (CO, H₂ and CH₄) in the producer gas. It can be seen that the maximum LHV value of 6.69 MJ/Nm³ achieved at 40% oxygen in air corresponds to ER value of 0.2953 reported in Table 4.2, which agrees well with typical ER value range (0.2 - 0.4) for gasification (Dogru *et al.*, 2002). Similar trend was observed by (Feiqiang *et al.*, 2014) where product gas attained LHV peak value of about 5.4 MJ/Nm³ at ER value between 0.25 – 0.27. CGE expressed by Equation (3.5) is the ratio of energy in producer gas per kg of biomass to the LHV of the biomass feed used as fuel. CGE depends on the calorific value and the amount of producer gas released at constant LHV of biomass (Sheth and Babu, 2009). Considering Table 4.4 and 4.5 together it can be seen that CGE rises

continuously from lowest value of 8.65% at 0.152 ER to a maximum value of 46.81% at 0.2953 ER. CGE declines by about 53% with further increase in ER to a maximum value of 0.6225.

CCE expressed by Equation (3.6) is defined as the ratio of carbon converted into product gas to the carbon content of fuel feedstock. Reexamining Table 4.4 and 4.5 it can be seen that CCE follows a similar trend as CGE with a maximum value of 82.04% attained at the same 0.2953 ER value. Considering the overall gasification performance evaluation it can be deduced that the optimum operating condition was achieved at 0.2953 ER.

4.3.3 Effect of oxygen enrichment on product gas composition

The amount of oxygen in gasification medium profoundly affects product gas percentage distribution. Figures 4.5, 4.6 and 4.7 depict product gas composition profiles for 30, 40 and 50% oxygen enrichment respectively. It can be noticed that formation of CO and CO₂ dominates over formation of H₂ and CH₄ as O₂ gets depleted progressively. This is evident because the initial combustion reactions expressed by Equations (2.4) – (2.6) require oxygen to convert the carbon in feedstock to CO and CO₂. At a certain point however the percentage composition of CO reaches a maximum beyond which it begins to fall while CO₂ rises higher. This can be ascribed to the slightly endothermic water-gas-shift reaction given by Equation (2.11) which favors formation of CO at the expense of CO₂. Moreover CH₄ percentage composition remains relatively the lowest because its formation given by Equations (2.7) and (2.10) requires H₂ which is also relatively low. Similarly the formation of H₂ expressed by Equation (2.8) and (2.11) requires steam solely derived from the moisture content of the feedstock which is also found to be low around 5.8%. Generally from the experiment results shown here, it can be noticed that product gas

concentration reaches stability roughly around 20 minutes. However peak points for desired syngas (CO and H₂) were achieved earlier approximately in the neighborhood of 15 minutes from start time. For example gasification using 30% oxygen enrichment recorded peak point at 15 minutes with 18.02% CO and 4.46% H₂. Similar trend was observed with 50% oxygen enrichment where peak values were recorded at 12 minutes corresponding to 17.29% CO and 6.08% H₂. The overall best product gas profile was observed at 40% oxygen enrichment where CO continue to increase up to 20 minutes and reaches peak value of 29.57% while H₂ reaches 14.29%.

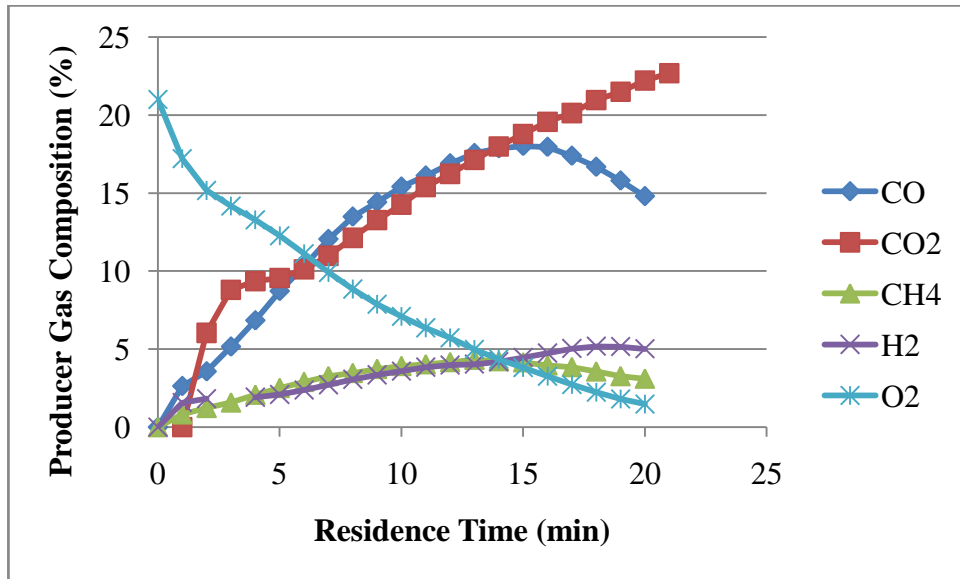


Figure 4.5: Product Gas Composition Profile for 30% Oxygen Enrichment

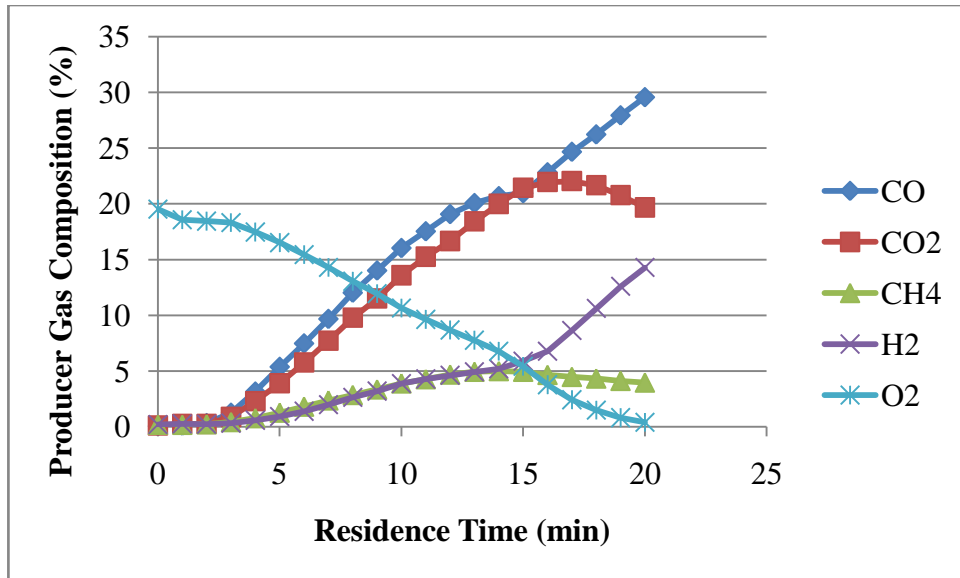


Figure 4.6:Product Gas Composition Profile for 40% Oxygen Enrichment

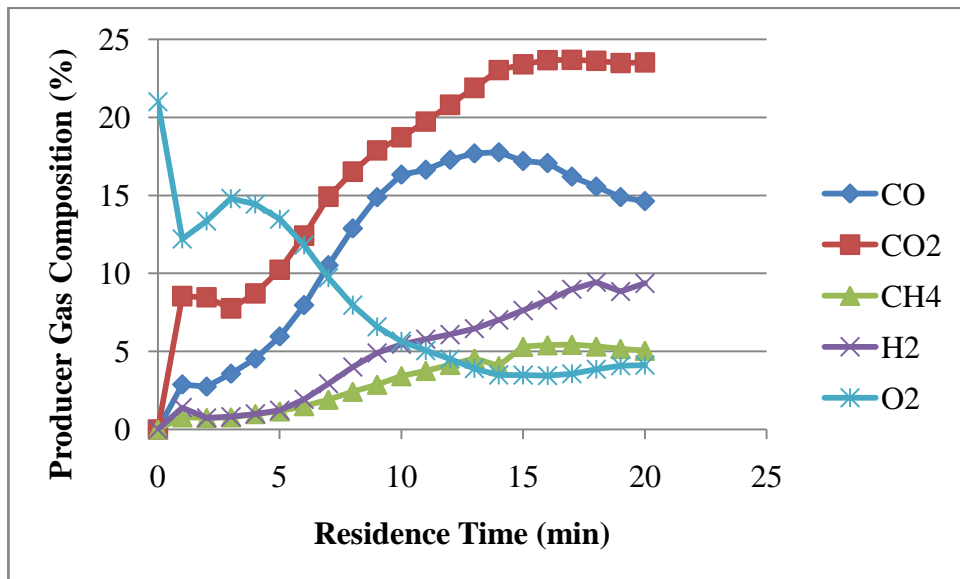


Figure 4.7:Product Gas Composition Profile for 50% Oxygen Enrichment

4.3.4 Effect of oxygen enrichment on H₂/CO and CO/CO₂ratio

Ratio of hydrogen and carbon monoxide in the gasification product gas is a critical parameter in various applications of syngas such as production of gasoline, methanol and methane. In each case, the desired product determines the appropriate H₂/CO ratio required (Basu, 2010).

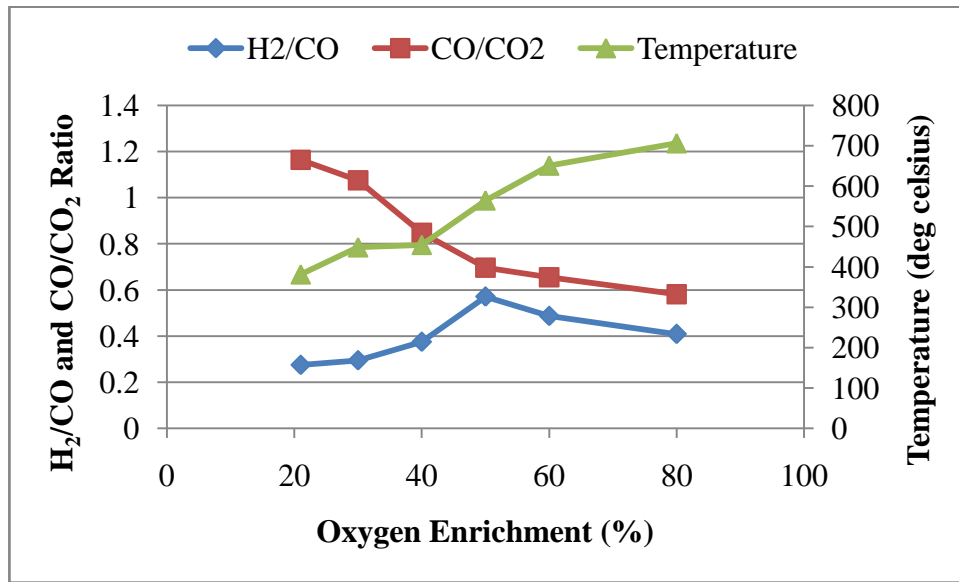


Figure 4.8: Effect of Oxygen Enrichment on H₂/CO and CO/CO₂Ratio

Experimental data presented in Figure 4.8 shows the effect of oxygen enrichment on H₂/CO and CO/CO₂ ratio. It is observed that increase in percentage oxygen in gasification medium (air/oxygen) result to corresponding increase in H₂/CO ratio and decrease in CO/CO₂. However slight change of course manifested at 50% oxygen enrichment corresponding to 564.64 °C temperature condition beyond which decrease in H₂/CO ratio was observed. Moreover low values of H₂/CO ratio appreciably less than 1 indicated dominance of CO over H₂.

Generally, the proportion of each component in product gas can be attributed to kinetics of reactions taking place at different condition. For example reversible water-gas-shift reaction given by Equation (2.11) allows the formation of H_2 at the expense of CO which is favoured at low temperature because of its exothermic nature. At higher temperature however steam gasification reaction and boudouard reaction given by Equation (2.8) and (2.9) respectively dominates and thus favour the formation of more CO over H_2 . These conflicting scenarios explain the initial rise and subsequent fall in H_2/CO ratio. Consistent decrease of CO/CO_2 ratio indicates increasing dominance of total oxidation reactions expressed by Equation (2.4) – (2.6) which are primarily responsible for the formation CO_2 with accompanying release of enormous energy as seen by consistent rise in temperatures shown in Figure 4.8.

4.4 Model Validation

4.4.1 Model validation with literature data

Table 4.4 presents experimental data from three published works compared with model result used in this study. Input variables, precisely temperature and moisture content were preset to $800^\circ C$ and 5.8% respectively. From the data comparison, it can be noted that the model result generally matches with reported work. However error values computed using root mean square (RMSE) formula expressed by Equation (2.23) revealed model result fit more closely with experimental work by Wei *et al.*, (2011) and Jayah *et al.* (2003) than with Son *et al.*, (2011) and values obtained were 1.27, 1.59 and 3.79 for the three respective experimental works. Data points considered for RMSE computation were only the values of four primary constituent of product gas, namely H_2 , CO, CO_2 and CH_4 .

Table 4.6:Data Comparison of the Present Model and other Experimental Works

Parameter	Present Model	Jayah <i>et al.</i> , (2003)	Wei <i>et al.</i> ,(2011)	Son <i>et al.</i> ,(2011)
H ₂ (%)	18.49	17	19.19	16.50
CO (%)	20.23	18.40	19.19	15.90
CO ₂ (%)	9.49	10.6	11.58	15.30
CH ₄ (%)	3.14	1.3	2.41	2.10
T(°C)	800	800	800	800
ER	0.39	0.33	0.293	0.350

Further comparison of present model with model results of other authors as presented in Table 4.6 which shows similar general trend. However absolute percentage error about 24.3% was observed to be more pronounced with H₂ concentration when comparing present model with value reported by Barman *et al.* (2012). In addition for same H₂ concentration, absolute percentage error drops down to about 2.5% when comparing present model with predicted value by Jarungthammachote and Dutta (2007).

Table 4.7:Data Comparison of the Present Model with other Model Works

Parameter	Present Model	Barman <i>et al.</i> (2012)	Jarungthammachote and Dutta (2007)	Mendiburu <i>et al.</i> (2014)
H ₂ (%)	18.49	14	18.03	21.73
CO (%)	20.23	19.95	18.51	23.49
CO ₂ (%)	9.49	10.36	11.47	10.65
CH ₄ (%)	3.14	0.31	0.11	0.00
T (°C)	800	800	800	886.36
ER	0.39	0.39	0.39	0.293

4.4.2 Model validation with present experimental data

Figures 4.9 - 4.14 illustrate comparison of simulation and experimental data obtained both in this study. Model input variables were defined to match experimental operation conditions in a similar way as previous validation. Specifically, temperature was set at 381.17, 448.35, 454.33, 564.64, 651.08 and 706.48°C corresponding to oxygen levels in gasifying agent at 21, 30, 40, 50, 60 and 80% respectively. Ultimate analysis data for sawdust sample used in present experimental research was equally employed as input parameter in the model. Finally, moisture content was preset to 30% for the model as opposed to 5.8% actual value in experimental feedstock. This overrated value itself subjects the model to measurement error. However, it was considered a fairly reasonable option in controlling equivalence ratio to match with experimental value.

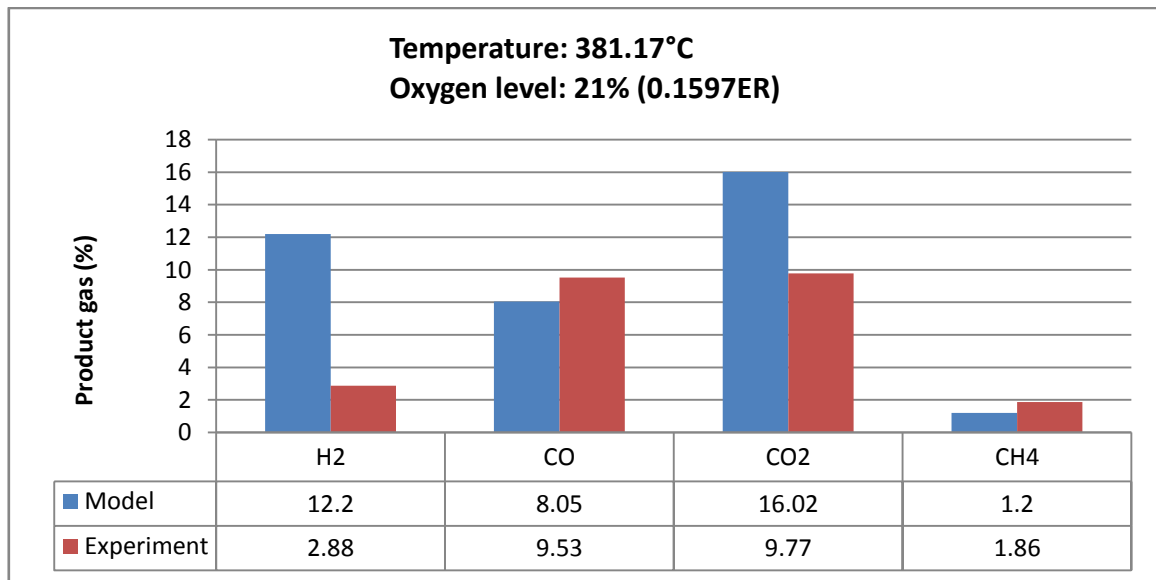


Figure 4.9: Model and Experimental Results at 381.17°C

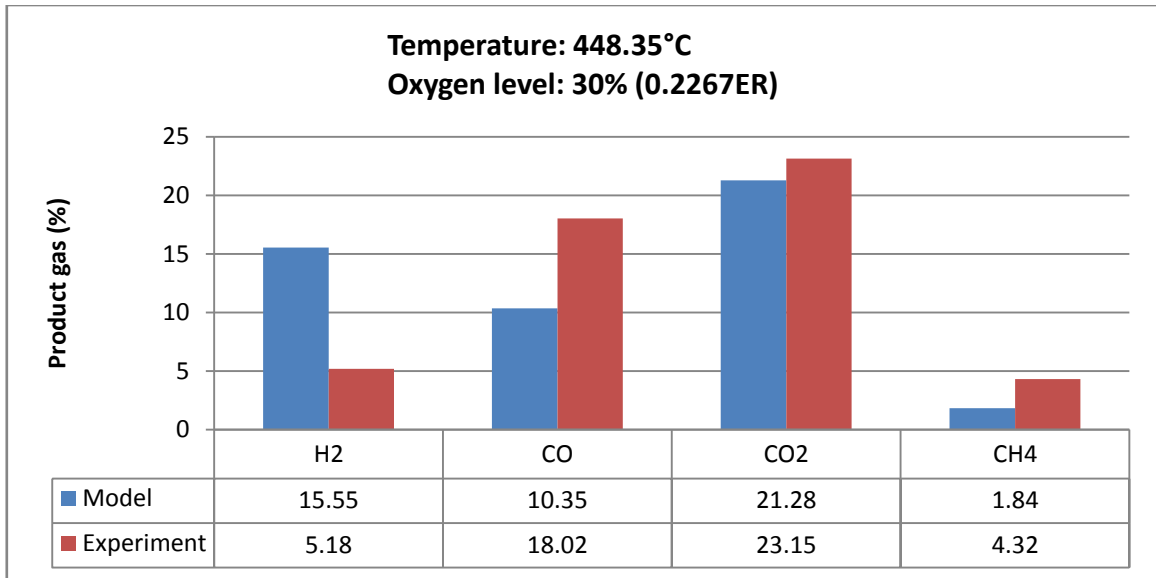


Figure 4.10: Model and Experimental Results at 448.35°C

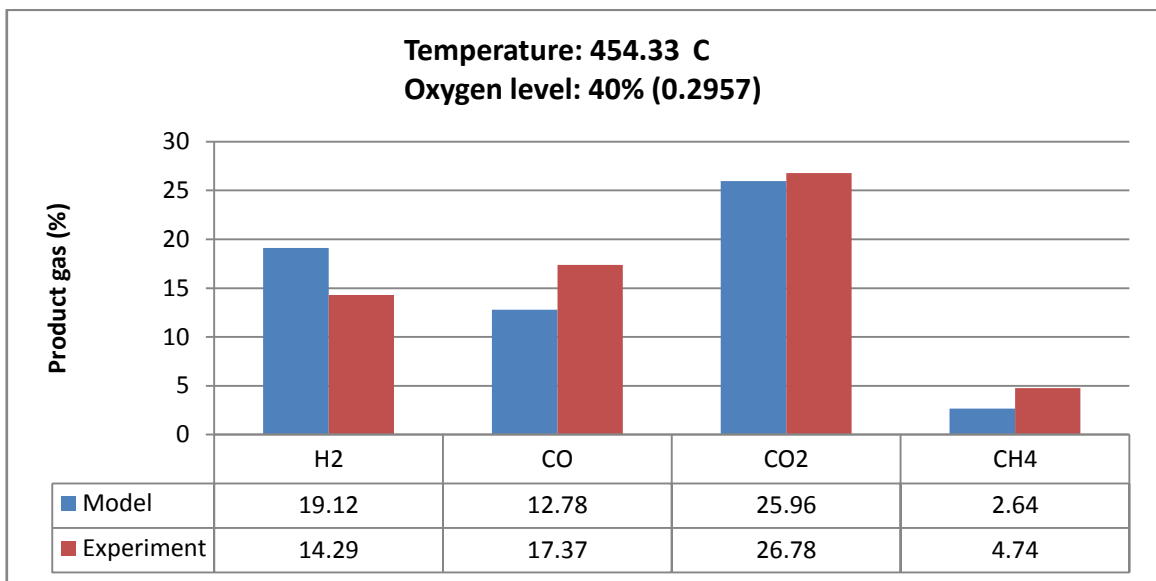


Figure 4.11: Model and Experimental Results at 454.33°C

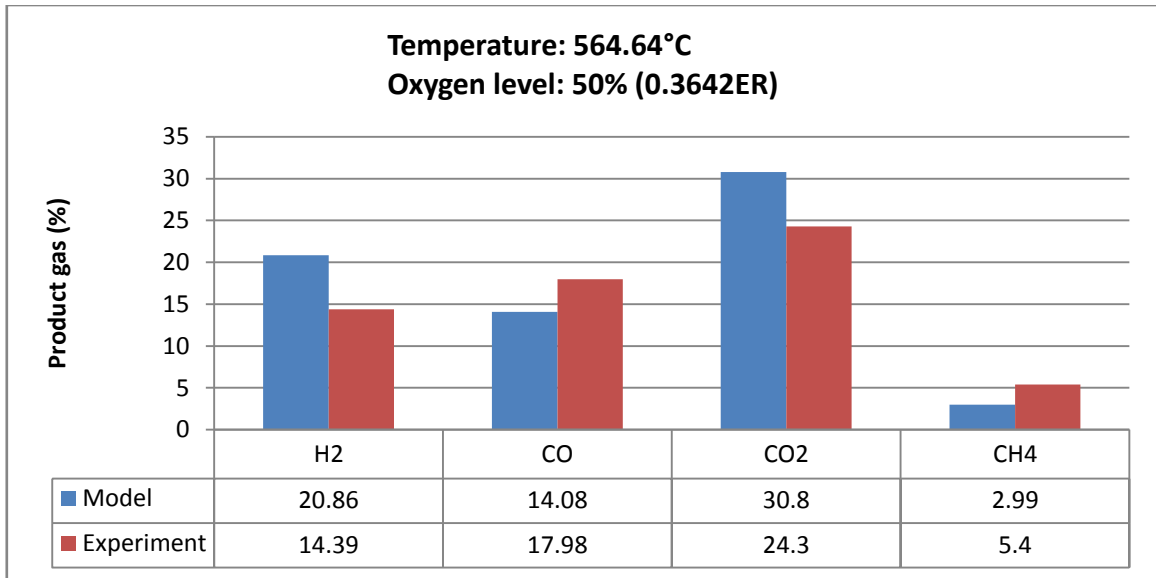


Figure 4.12: Model and Experimental Results at 564.64°C

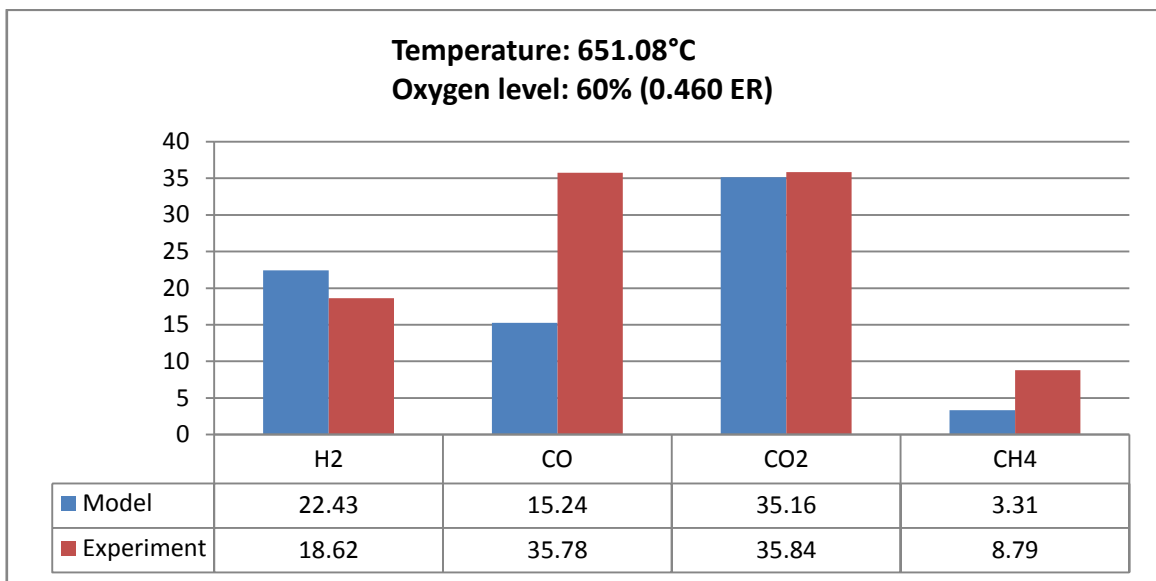


Figure 4.13: Model and Experimental Results at 651.08°C

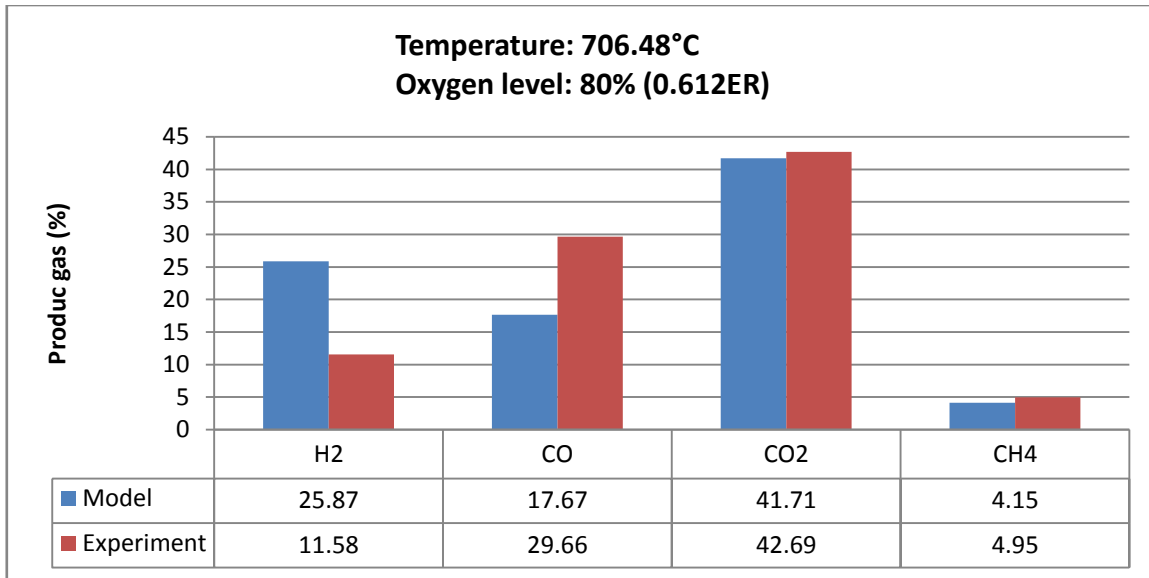


Figure 4.14: Model and Experimental Results at 706.48°C

It was found that predicted CO concentration in product gas of value 8.05% best fit experimental value of 9.53% at the lowest preset temperature of 381.17°C as shown in Figure 4.11. Similarly at same preset temperature CH₄ best fit were 1.2 and 1.86% respectively. Model predicted value of H₂ on the other hand was observed to best fit experimental data at preset temperature 651.08°C with recorded value of 22.43 and 18.62% respectively as shown in Figure 4.15. Similarly at same preset temperature CO₂ best fit were 35.16 and 35.84% for model and experimental values respectively.

RMSE value of model and experimental data comparison for the six presented results were found to be 5.67, 6.63, 3.51, 5.13, 10.80 and 9.35% corresponding to 21, 30, 40, 50, 60 and 80% percentage oxygen in gasifying agent. Consequently model comparison at 40% oxygen level in gasifying agent and 454.33°C average gasification temperature shown in Figure 4.13 represents the overall best data fitting point identified with the lowest RMSE value of 3.51.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this research work, experimental study was carried out to investigate the effect of various gasification operating parameters on quality of syngas produced in a downdraft gasifier using sawdust feedstock. Air and oxygen enriched air were used separately as gasification medium with varying equivalence ratios to determine their respective effect on reduction zone temperature, product gas percentage composition and heating value. Gasification performance was determined using Cold Gas Efficiency (CGE) and Carbon Conversion Efficiency (CCE), which are indicators evaluated at different operating conditions. Within the range of parameters examined in this work, the following conclusions were drawn.

1. Levels of CO and H₂ in product gas recorded peak values of 13.55 and 2.59% respectively using air as gasification medium at a flow rate of 6.4 LPM. Decreasing the flow rate to 1.9 LPM however led to a corresponding drop in CO and H₂ levels to 5.18 and 0.82%, respectively.
2. Increasing the percentage of oxygen in the gasifying medium from 21 – 80% led to a significant increase in the Equivalence Ratio (ER) from 0.152 – 0.622. Similarly, the average temperature of the reduction zone rose from 381.17 – 706.4°C.
3. The overall best product gas profile using oxygen-enriched gasifying medium was observed at 40% oxygen enrichment, where CO continued to increase up to 20 minutes and reached a peak value of 29.57% while H₂ reached 14.29%.

4. Lower Heating Value (LHV) of product gas rises consistently from 2.08 – 6.69MJ/Nm³ as percentage oxygen in gasifying medium rises from 21–40%.
5. Cold Gas Efficiency (CGE) rises continuously from lowest value of 8.65% at 0.152 ER to a maximum value of 46.81% at 0.295 ER. The CGE was observed to decline by about 53% with further increase in ER value of 0.6225.
6. Carbon Conversion Efficiency (CCE) followed similarly trend as CGE with a maximum value of 82.04% attained at same 0.2953 ER. Thus considering overall gasification performance evaluation it can deduce that the optimum operating condition was achieved at ERknee point stated above beyond which performance falls continuously.
7. Model validation with experimental data obtained in this research revealed that CO predicted value of 8.05% best fit experimental value of 9.53% at the lowest preset temperature of 381.17°C.
8. Root Mean Square (RMSE) value of model and experimental data comparison at six preset temperatures were found to be 5.67, 6.63, 3.51, 5.13, 10.80 and 9.35%. Consequently model comparison with lowest RMSE value (3.51%) is considered the overall best data fitting point which is obtained at a preset temperature of 454.33°C.

5.2 Recommendations

The following recommendations were made base on the present research work carried out:

1. In this research work only one point temperature probe was employed and therefore inadequate to monitor temperatures at other points of interest at the same time. In addition inconsistent temperature profile was identified as a major challenge. It is

therefore recommended that additional temperature probe should be considered in further research.

2. The feeder system of gasifier used in this work operates in batch mode and therefore imposes constraint to continuous operation. Moreover the rotating grate system intended to discharge ash and to allow continual flow of fresh feedstock down the reactor end up not working properly by a way of scooping out the entire combustion zone. It is therefore recommended that a continuous feeder system reactor be design and constructed in subsequent research work.
3. Lack of lagging around the gasifier contributes enormously to heat losses to the environment principally by convection and radiation. It is therefore recommended that appropriate lagging material be selected and applied according to design principle to improve stability of operating temperature.
4. Current gasifier used in this work operates under positive pressure displacement and therefore prone to active leakages. For safety reasons and accuracy of findings, it is therefore recommended that negative pressure displacement should be considered in future research.
5. Experimental investigation conducted using compressed air/oxygen mixture experiences significant pressure buildup inside the gasifier and hence subjects the system to potential explosion. It is therefore recommended that appropriate design principle be applied in developing new gasifier with clear specification for ranges of operating condition.

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APPENDIX A

Detail Description of Experimental Setup

The reactor geometry consist of double coaxial cylindrical shells with inner diameter of 30cm and height of 72cm. Carbon steel of 1mm thickness was used as construction material for both internal and external shells of the reactor while galvanized pipe of 1.5 inch (3.81cm) internal diameter connects all the system units together for continuous flow of producer gas.

Fresh feedstock was fed manually through the upper section of the gasifier for every batch operation. An agitator shaft mounted on a suspended grate below the inner shell extended to pass through a small opening on a mild steel circular lid which aids to reduce bridging during feeding process. In a similar manner it serves as a means by which reduced fuel in form of ash and char can be dislodged from the grate.

Air blower mounted at the inlet end of the air nozzle with maximum speed rating of 360 rpm supplies air into the reactor in two stages. At first air reaches a manifold like chamber that goes round the inner reactor shell. At second stage air flows directly across the biomass through perforations around the circumference of the manifold with nearly uniform distribution.

In principle gasification process occur sequentially in four distinct reaction zones notably; drying, pyrolysis, oxidation and reduction. However, in practice, these zones are not completely distinct from one another rather forms overlap. Drying takes place at the uppermost part of the reactor where moisture and volatile component of the biomass are driven off. Pyrolysis zone lies immediately below where tarry gases and charcoal are

produced. The tarry gases then pass downward through the combustion zone where oxidation reactions occur with enormous release of heat available to sustain pyrolysis and drying processes. Cracking of tar occurs during the passage of gases through the high temperature oxidation also refer to as combustion zone. The gas stream flows to the reduction zone at the bottom of the grate where the unconverted carbon reduces to produce more combustible gases by a number of endothermic reactions. Product gas finally leaves the reactor from the bottom through a narrow constriction of diameter 12.50cm.

Gasification Experiment Procedure

Initially a quantity of feedstock sample approximately 8.627kg was charged, filling up the inner shell of the gasifier to its volumetric capacity of 0.0451m³. A metallic rod used in thrusting feedstock was then mounted on and passed through an aperture on a circular mild steel lid to properly close the reactor shell. The aperture was also used as pressure relieve vent in case of excessive pressure buildup. All possible leakages around the reactor were properly sealed up to avoid loss of product gases using a 100% silicone material tagged '*gasket maker*' which has the capacity to withstand temperatures up to 260°C (500°F).

To start ignition firstly an air blower was mounted in negative pressure orientation to drive out air inside the reactor while allowing fresh air to flow into the reactor through the ignition port. In this way the biomass feedstock was ignited and then allowed to attend temperature up to 200°C so as to avoid quenching of the initiated combustion. The ignition port was then closed tightly while the valve leading to the flare was left open. For experiment using pure air as gasifying agent as illustrated in Figure 3.1(a), the air blower orientation was then reversed to positive pressure while for experiment using air/oxygen as gasifying agent as depicted in Figure 3.1(b), the air blower was completely replaced by two

gas cylinders. The metallic rod stuck in the biomass was then moved intermittently in an oscillatory manner to facilitate biomass progression downward. The rotating gratescoops out some amount of char and ashesto create slot for fresh feedstock.



Plate I: Experimental Setup

APPENDIX B

Experimental Equipment

Table B1: Detailed List of Experimental Equipment

S/N	Name	Model	Manufacturer	Specification
1.	Portable NDIR Syngas Analyzer	GASBOARD-3100P	WUHAN CUBIC CO LTD	CO: 0-75% CO ₂ :0-40% CH ₄ :0-75% H ₂ : 0-75% O ₂ : 0-25% CH ₄ :0-10%
2.	Gas Conditioning System	-	WUHAN CUBIC CO LTD	-
3.	Digital Thermometer	UNI-TREND UT321	UNI-TREND Group Limited	-200.0°C - +1372°C
4.	Mass Flow Meter	MF5706 SERIES	SIARGO Limited	0 – 25LPM
5.	Thermocouple probe	K-Type	OMEGA Engineering	Nickel-Alumel



PlateII: Portable NDIR Syngas Analyzer



Plate III: Gas conditioning System



Plate IV: Digital Thermometer



Plate V: Mass Flow Meter



Plate VI: Temperature Probe



Plate VII: Air Blower

APPENDIX C

MATLAB Codes

Main File

```
% Thermodynamic equilibrium model Main File
clc
clear all

% Feed composition
C=45.92; H=5.576; O=40.259; N=0.18; S=0.0904; Ash=8.06; MC=5.8/100;

% Computing normalize atomic coefficient of Hydrogen, Oxygen & Nitrogen
Num1=C/(12);
Num2=H/(1.008);
Num3=O/(16);
Num4=N/(14.007);
lambda=Num2/Num1;
gamma=Num3/Num1;
beta=Num4/Num1;

% Computing no. of moles of water vapor (dry basis)
Mm_fs=12+lambda*1.008+gamma*16+beta*14;
mw=Mm_fs*MC/(18*(1-MC));

% Compute low heating value (LHV) of feedstock
LHV=4.187*(81*C+300*H-26*(O-S)-6*(9*H+MC)); % kJ/kg
LHV_mol=LHV*(Mm_fs); % (kJ/kmol)

% Compute enthalpy of Feedstock in kJ/kmol
HF_H2O_v=-241.818; HF_H2O_l=-285.830; HF_CO2=-393.509; %kJ/mol
HF_fuel=(lambda/2)*1e3*HF_H2O_v + 1e3*HF_CO2 + LHV_mol;

% Compute stoichiometric amount of air to fuel ratio required kg/(kg dry
fuel)
O2=0.21;
stoic=1.293/O2*(1.866*C/100+5.55*H/100+0.7*S/100-0.7*O/100);

% Computed values of equilibrium constants
T = 800+273.15; % Gasification Temperature in kelvin
specie=1:6;
[k1 k2] = ModelGibbs(T);

% Solve equilibrium model equations
x0=[0.1 0.1 0.1 0.1 0.1 0.1];
% x0=input('Enter initial guess >>');
options=optimset('display','iter','MaxFunEvals',642);
x =
fsolve(@model_eqn,x0,options,mw,k1,k2,lambda,gamma,beta,HF_H2O_l,HF_H2O_
v,HF_fuel);
% disp(x);
% Compute percentage product gas composition
x(7) = beta/2+3.76*x(6);
prodsum = x(1)+x(2)+x(3)+x(5)+x(7);
```

```

vol(1) = x(1)/prodsum;
vol(2) = x(2)/prodsum;
vol(3) = x(3)/prodsum;
vol(5) = x(5)/prodsum;
vol(7) = x(7)/prodsum;
vol=[vol(1);vol(2);vol(3);vol(5);vol(7)];
disp(vol);
ER=x(6);
disp(ER);

```

Function File for Model Equation

```

function f =
model_eqn(x,mw,k1,k2,lambda,gamma,betta,HF_H2O_l,HF_H2O_v,HF_fuel)
%Thermodynamic equilibrium model function file
%Variable definition
x1=x(1);
x2=x(2);
x3=x(3);
x4=x(4);
x5=x(5);
xg=x(6);

% mass balance equations
f(1)=x2+x3+x5-1;
f(2)=x1+2*x4+4*x5-2*mw-lambda;
f(3)=x2+2*x3+x4-2*xg-mw-gamma;
f(4)=k1*x2*x4-x3*x1;
f(5)=k2*x1^2-x5*(x1+x2+x3+x4+x5+(betta/2)+3.76*xg);
% Energy balance equation
% 1 = H2
% 2 = CO
% 3 = CO2
% 4 = H2O
% 5 = CH4
% 6 = N2
T = 800+273.15; % Gasification Temperature in kelvin
f(6)=x1*model_enthalpy_change(T,1)+...
      x2*model_enthalpy_change(T,2)+...
      x3*model_enthalpy_change(T,3)+...
      x4*model_enthalpy_change(T,4)+...
      x5*model_enthalpy_change(T,5)+...
      (betta/2+xg*3.76)*model_enthalpy_change(T,6)-...
      HF_fuel-mw*1e3*(HF_H2O_l+HF_H2O_v);

f=f(:);
end

```

M-File for Computing Enthalpy Change

```

function [delH] = model_enthalpy_change(T,product)
% This routine calculates the total enthalpy change of gasification...
% product gases (kJ/kg)

```

```

% 1 = H2
% 2 = CO
% 3 = CO2
% 4 = H2O
% 5 = CH4
% 6 = N2
% other = O2

switch product
case 1
%       M_Wt=2.0;
%       HoF=0;
%       Cp=[29.11 -0.1916e-2 0.4003e-5 -0.8704e-9];
case 2
%       M_Wt=28.0101;
%       HoF=-110.53;
%       Cp=[28.16 0.1675e-2 0.5372e-5 -2.222e-9];
case 3
%       M_Wt=44.0095;
%       HoF=-393.51;
%       Cp=[22.26 5.981e-2 -3.501e-5 -7.469e-9];
case 4
%       M_Wt=18.0153;
%       HoF=-241.83;
%       Cp=[32.24 0.1923e-2 1.055e-5 -3.595e-9];
case 5
%       M_Wt=16.0425;
%       HoF=-74.87;
%       Cp=[19.89 5.204e-2 1.269e-5 -11.01e-9];
case 6
%       M_Wt=28.01348;
%       HoF=0;
%       Cp=[28.90 -0.1571e-2 0.8081e-5 -2.873e-9];
end
% Analytical Integration
a=Cp(1); b=Cp(2); c=Cp(3); d=Cp(4);
delH=(1e3)*HoF + a*(T-298)+b/2*(T^2-298^2)+c/3*(T^3-298^3)+d/4*(T^4-
298^4);
end

```

Function File for Computing Gibbs Energy

```

function [k1 k2] = ModelGibbs(T)
% This routine calculates the equilibrium constants of two rxns...
% Methane formation rxn: C + H2 = CH4
% Water-shift rxn: CO + H2O = CO2 + H2
% 1 = CO
% 2 = CO2
% 3 = H2O
% 4 = CH4
% 5 = H2
% 6 = C
% G = [heat of formation (kJ/mol) and coefficients of gibbs free energy]
delG = zeros(1,6);

```

```

for i = 1:6
%     product = specie(i);
switch i
case 1
    G=[-110.5 5.619e-3 -1.190e-5 6.383e-9 -1.846e-12 -4.891e2 8.684e-
1 -6.131e-2];
case 2
    G=[-393.5 -1.949e-2 3.122e-5 -2.448e-8 6.946e-12 -4.891e2 5.270
-1.207e-1];
case 3
    G=[-241.8 -8.950e-3 -3.672e-6 5.209e-9 -1.478e-12 0.0 2.868 -
1.722e-2];
case 4
    G=[-74.8 -4.620e-2 1.130e-5 1.319e-8 -6.647e-12 -4.891e2 1.411e1
-2.234e-1];
otherwise
    G=zeros(1,8);
end

Hfi = G(1); a =G(2); b = G(3); c = G(4); d = G(5); e = G(6); f = G(7); g
= G(8);

delG(i) =  Hfi - a*T*log(T) - b*T^2 -c/2*T^3 - d/3*T^4 + e/2/T + f + g*T;
end

delta_ws=delG(2)+delG(5)- delG(1)-delG(3);

delta_meth=delG(4)-delG(6)- 2*delG(5);

R=8.314; % universal gas constant(kJ/kmol.K)
k1=exp(-delta_ws/R/T);
k2=exp(-delta_meth/R/T);
end

```