

# **QUANTIFICATION OF TARS AND PARTICULATES FROM A PILOT SCALE, DOWNDRAFT BIOMASS GASIFIER**

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## ABSTRACT

Alternative energy production through biomass gasification produces combustible gases, such as carbon monoxide, hydrogen, and methane. These gases can be used for generation of direct heat, electricity, or liquid fuels through the Fischer Tropsch process. However, a major limitation of the overall process is the purity of the generated synthesis gas. The tars and particulates generated in the gasification process constitute a major impediment to the commercial use of this technology because they may condense on valves, fittings, and therefore, hinder the smooth running of an engine. This research was aimed at developing a gas characterization and testing protocol, and the removal of tars and particulates in the synthesis gas generated from a downdraft biomass gasifier. The tars and particulates sampling and analysis was based on a modified EPA Method 5. The protocol modifications were done to suit the specific characteristics of the gasifier and the generated synthesis gas. This test protocol involves gravimetric analysis of the particulates retained on a high temperature glass-fiber filter and tars dissolved in a series of solvent bottles (with acetone). Baseline studies using woodchips produced tar and particulates concentrations of  $1.63 \text{ g/Nm}^3 \pm 0.46$  and  $3.84 \text{ g/Nm}^3 \pm 1.16$  respectively; while pine pellets produced  $0.85 \text{ g/Nm}^3 \pm 0.16$  and  $4.75 \text{ g/Nm}^3 \pm 0.07$  respectively. Downstream treatment using a catalytic bed of calcined dolomite, albermale proprietary catalyst, and bag filter were designed for cleaning the raw gas. An investigation of the dolomite bed temperature on gas cleaning showed that at temperature above  $750^\circ\text{C}$ , about 90% and 50% of the tar and particulate were respectively removed; while at  $650^\circ\text{C}$  about 60% and 40% of tar and particulate were removed respectively. A combined use of the proprietary catalyst at  $250^\circ\text{C}$  and bag filter reduced the tars and particulate concentration by approximately 90% and 98% respectively. The exiting gas was also characterized for its heating

value and found to be approximately  $3.38 \text{ MJ/Nm}^3 \pm 0.39$  and  $3.67 \text{ MJ/Nm}^3 \pm 0.09$  for woodchips and pine pellets respectively.

## CHAPTER 1: INTRODUCTION

### 1.1 Background

The gasification of carbon-containing materials to produce combustible gas is an established technology. Coal gasification has been the primary focus due to its higher energy density and ease of transportation in comparison to renewable biomass resources (Maxwell *et al.*, 2005). Currently, environmental issues and the need to augment or replace existing power generation facilities have shifted the focus of gasification development from non-renewable fossil fuel sources to renewable fuel sources, mainly biomass. The term “biomass” represents material of biological origin derived from plants as a result of the photosynthetic conversion process excluding materials embedded in geological formations and transformed to fossil (Quake *et al.*, 1999). In principle, biomass is a less damaging and environmentally benign fuel as the carbon dioxide released from the combustion process is captured during the plant growth. One of the most important biomass fuels is wood, however, wood is often too valuable to be used for power generation and the timber industry is able to make better use of trees by processing them into construction materials. Therefore, residues such as bark, sawdust, and odd-sized pieces are frequently used as fuel. Many agricultural residues can, indeed, be used as fuels. They include straw from grains, husks from rice, coconuts or coffee, stalks from maize or cotton, bagasse from sugarcane, and animal manure. In addition to these, dedicated energy crops such as switch grass are being used as fuel sources. Using these biomass residues as fuels may solve the environmental problem of how to dispose of them (Quake *et al.*, 1999).

Biomass gasification is a thermochemical process that produces relatively clean and combustible gases through pyrolytic reaction. The synthesis gas (also known as syngas or producer gas) generated can be an important resource suitable for direct combustion, application in prime movers such as engines and turbines, or for the production of synthetic natural gas (SNG) and transportation fuels (*e.g.* Fischer-Tropsch diesel) (Boerrigter *et al.*, 2004) . Producing high quality

syngas to meet operational requirements of turbines or internal combustion engines is critical to the successful implementation of biomass gasification. Specifically, the efficient and economic removal of tars and particulates from the syngas are the major obstacles to be overcome (Maniatis, 2001). Of the various gasifier types, the downdraft gasifier is attractive for its simple and robust construction, reliable operation, suitability with various biomass, high conversion rate (90-99%), and production of relatively clean syngas containing low tar and particulate concentrations (Warnecke, 2000; Tatsiopoulos and Tolis, 2003).

For energy production, the major concerns about syngas are its heating value, composition, and possible contamination (Wei, 2005). The proportion of the combustible gases hydrogen ( $H_2$ ), methane ( $CH_4$ ), carbon monoxide (CO), and steam in the syngas determines the heating value of the gas. The composition of syngas depends on the biomass properties and gasifier operating conditions. For a particular gasification system, operating conditions play a vital role in all aspects of biomass gasification. These include carbon conversion, syngas composition, tar formation and reduction (Devi *et al.*, 2003). Syngas from biomass gasification contains tar and particulates as impurities which can cause severe operational problems. Tar is undesirable because of various problems associated with condensation, formation of tar aerosols and polymerization to form more complex structures, which can damage internal combustion engines (ICEs), gas turbines, and other machinery (Devi *et al.*, 2005). Therefore, before the syngas can be used in a gas engine or turbine, it must be cleaned of impurities, especially tars, a major impediment to widespread use of biomass gasification technology. Currently, there is no specific method for determining the concentration of tar and particulates from biomass gasification. Developing a simple and effective protocol for quantifying the gravimetric tar and particulate in biomass gasification is an important goal of this study. Gas cleaning and tar reduction have been the subject of research on thermochemical conversion of biomass for the production of energy and chemicals. Catalytic tar destruction for coal

gasification has been studied for several decades and a number of reviews have been written on biomass gasification hot gas cleanup emphasizing the use of dolomites and nickel based catalyst (Stevens, (2001); Sutton *et al.*, (2001); Milne *et al.*, (1998)). Physical treatment of syngas using mechanical methods such as cyclone, scrubber, and particulate filters has also been identified (Devi *et al.* 2003). This study will also look at the effects of temperature on the performance of dolomite and albermale proprietary catalysts for tar removal.

## **1.2 Objectives**

The overall purpose of this research was to investigate a biomass gasification process for the production of high quality syngas for use in an IC engine. The following objectives were identified:

- 1) To develop a protocol to quantify the tars and particulates from biomass gasification.
- 2) To characterize the syngas produced.
- 3) To quantify the tars and particulates removal efficiencies using calcined dolomite, albermale proprietary catalyst, and bag filter.

## **1.3 Justification**

The wide implementation of biomass gasification is hampered by the fact that there was no economic incentive to use biomass e.g. biomass-based energy is more expensive than energy from fossil fuels because fossil fuels are easy to use in machinery. Biomass gasification is also more complex than coal gasification due to variability in feedstock and lower energy content. One of the major issues in biomass gasification is dealing with the tar and particulate formed during the process. Tars are considered to be a complex mixture of the condensable fraction of the organic gasification products and are largely aromatic hydrocarbons. Tars are problematic in integrated biomass gasification systems as they may condense on valves and fittings, hampering the ability of valves to function properly. Particulates are solid particles that also clog engine parts and thus affect the ability of engines to run smoothly. The purpose of this project is to investigate tar and

particulates generated in biomass gasification. To achieve this objective a pilot scale downdraft gasifier was designed and constructed in the Biological and Agricultural Department of the Louisiana State University AgCenter.

After this introduction, Chapter 2 presents an overview of biomass sources, gasifier types, and gasification principles and a review of literature on gas cleaning and quality requirements for IC Engines. Chapter 3 describes a new protocol for tar and particulate characterization. Chapter 4 contains the results obtained from the initial baseline experimental analysis, and details the experimental study on the use of calcined dolomite and albermale proprietary catalysts, and bag filter for syngas cleaning and conditioning. A summary of this research and suggestions for future work are presented in Chapter 5.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 Biomass as a Fuel**

Biomass simply refers to organic materials originated from plants (wood, crops etc.) and animal wastes. Different biomass conversion processes produce heat, electricity and fuels. Among all biomass conversion processes, gasification is one of the most promising (Devi *et al.*, 2003). An assessment of the use of biomass as a fuel requires a basic understanding of their composition, characteristics, and performance. Each type of biomass has specific properties that determine its performance as a fuel in combustion or gasification devices or both (Quaak *et al.*, 1999). The most important properties relating to the thermal conversion of biomass are moisture content, ash content, volatile matter, and energy density. In addition to high temperature gasification, biomass can be used to produce energy via low temperature microbial gasification process where methane is mainly produced anaerobically.

#### **2.1.1 Moisture Content**

This is the amount of water in the material, expressed as a percentage of the material's weight. This weight can be on a wet basis, on a dry basis, and on a dry-and-ash basis. Biomass materials exhibit a wide range of moisture content and since this affects its value as a fuel source, it is important that the basis be stated whenever moisture content is measured (Quaak *et al.*, 1999). If the moisture content is excessive, the combustion process may not be self-sustaining and supplemental fuel must be used, which could defeat the objective of producing energy by biomass combustion for captive use or market (Klass, 1998)

#### **2.1.2 Ash Content**

This refers to the inorganic component in biomass. It is expressed in the same format as the moisture content. This property is especially important under high temperature gasification as melted ash may cause problems in the reactor (Quaak *et al.*, 1999).

### 2.1.3 Elemental Composition

The ash-free organic components of biomass are relatively uniform. The major components are carbon, oxygen, and hydrogen. Most biomass may also contain a small amount of nitrogen (Quaak *et al.*, 1999). Table 2.1 lists the major elemental components in biomass (BTG, 1987).

Table 2.1: Elemental Composition of Typical Biomass as derived from Ultimate Analyses

Element	Symbol	Weight percent (dry and ash-free basis)
Carbon	C	44-51
Hydrogen	H	5.5-6.7
Oxygen	O	41-50
Nitrogen	N	0.12-0.60
Sulfur	S	0-0.2

Source: BTG (1987). Thermo-chemical conversion of biomass to energy, UNIDO, Vienna.

### 2.1.4 Volatile Matter Content

The part of the biomass that is released when the biomass is heated is referred to as the volatile matter. Biomass feedstock contains a very high proportion of volatile organic material, 70 to 90% for wood (Klass, 1998).

### 2.1.5 Energy Density

The energy density refers to the potential energy available per unit volume of the biomass. It is dependent on the feedstock heating value and bulk density. In general, the biomass energy density of biomass is about one-tenth of that of fossil fuels (Quaak *et al.*, 1999). Table 2.2 lists the heating value of some biomass sources and their corresponding moisture and ash contents.

## 2.2 Biomass Gasification Principle

The chemistry of biomass gasification is similar to that of coal gasification in the sense that thermal decomposition of both solids occurs to yield a mixture of essentially the same gases

Table 2.2: Typical Characteristics of Different Biomass Fuel Types

Biomass Type	Lower Heating Value (kJ/kg)	Moisture Content (%)	Ash Content (dry) (%)
Bagasse	7,700-8000	40-60	1.7-3.8
Rice husks	14,000	9	19
Wood	8,400-17,000	10-60	0.25-1.7
Cotton residues			
Gin trash	14,000	9	12
Stalks	16,000	10-20	0.1

Source: Quaak *et al.*, (1999)

(Klass, 1998). However, biomass gasification occurs under much less severe operating conditions than for coal feedstock because its main constituents, the high-oxygen cellulose and hemicellulose, have higher reactivity than the oxygen-deficient, carbonaceous materials in coal (Klass, 1998). The thermo-chemical processes involved in gasification are drying, pyrolysis, oxidation, and reduction.

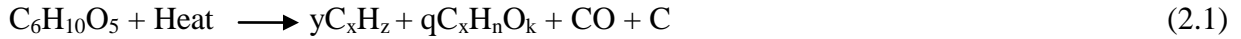
### 2.2.1 Drying

This phase involves evaporation of the moisture contained in the biomass. At temperatures above 100°C, water in the bio-fuel is converted to steam. Part of this vapor may be reduced to hydrogen during gasification and the rest ends up as moisture in the produced syngas.

### 2.2.2 Pyrolysis

The bio-fuels begin to pyrolyze at temperatures above 200°C (Wei, 2005). This is the thermal decomposition of the fuel into volatile gases and char. The proportion of these components is influenced by the chemical compositions of bio-fuels being fed and the operating conditions of the

gasifier (Wei, 2005). The main process of thermal decomposition of biomass can be represented as follows:



### 2.2.3 Oxidation

After pyrolysis, there is an oxidation zone where the pyrolysis products move into the hotter zones of the gasifier. Air is introduced into the oxidation zone under starved oxygen conditions. The oxidation takes place at temperatures ranging from 700-1000°C (Wei, 2005). The principal oxidation reactions are as follows (Wei, 2005):



### 2.2.4 Reduction

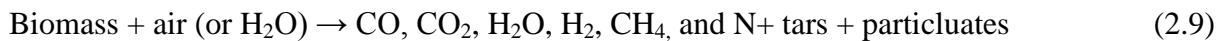
The reaction products of the oxidation zone continually move into the reduction zone where there is insufficient oxygen, leading to reduction reactions between the hot gases and char. The principal reactions are as follows (Wei 2005):



In this zone, the sensible heat of the gases and char is converted into the stored chemical energy in the syngas. Therefore, the temperature of the gases is reduced during this process (Wei, 2005).

## 2.3 Gasification Systems

Gasification is a form of incomplete combustion; heat from the burning solid fuel creates gases which are unable to burn completely, due to insufficient amounts of oxygen from the available supply of air. By weight, syngas from gasification of wood contains approximately 15-21% hydrogen (H<sub>2</sub>), 10-20% carbon monoxide (CO), 11-13% carbon dioxide, and 1-5% of methane, all of which are combustible plus nitrogen (N<sub>2</sub>) (Heesch *et al.*, 1999). The nitrogen is not combustible; however, it does occupy volume and dilutes the syngas as it enters and burns in an engine. A generalized reaction describing biomass gasification is as follows (Dayton, 2002):



The actual biomass syngas composition depends on the gasification process, the gasifying agent, and the feedstock composition [Beenackers and van Swaaij, (1984); Hos and Groeneveld, (1987)]. Various gasification technologies have been under investigation for converting biomass into a gaseous fuel. A characteristic of the various gasifiers is the way in which the fuel is brought into contact at the gasification stage. Four types of reactors exist: updraft or countercurrent gasifiers; downdraft or co-current gasifiers; cross-draft gasifiers; and fluidized-bed gasifiers.

### 2.3.1 Fixed Bed Gasifiers

Fixed bed gasifiers have grates built in to support the feedstock and maintain a stationary reaction bed. They are relatively easy to design and operate but have limited capacity. Therefore, fixed bed gasifiers are preferred for small to medium scale applications with thermal requirements up to 1 MW (Klein, 2002). Fixed bed gasifiers can be classified as either updraft or downdraft depending on the method of air introduction.

#### 2.3.1.1 Updraft or Countercurrent Gasifiers

In this type of reactor, air is taken in at the bottom, and the gas leaves at the top. The biomass moves counter to the gas flow and passes successively through drying, pyrolyzation, reduction, and

hearth zones. In the drying zone, the biomass is dried. In the pyrolyzation zone, it is decomposed into volatile gases and solid char. The heat for pyrolyzation is mainly delivered by the upward-flowing producer gas and partly by radiation from the hearth zone. The advantages of this type of gasifier are its simplicity, relatively low gas-exit temperature, high thermal efficiency and as a result, biomass with high moisture content (up to 60% wb) (Quaak *et al.*, 1999) can be gasified without any pre-drying of the feed. Moreover, size specifications are not very critical for this gasifier (Beenackers and Maniatis, 1996). Major drawbacks are the high amounts of tar produced.

#### **2.3.1.2 Downdraft or Co-current Gasifiers**

In the downdraft gasifier, air is introduced into downward flowing packed bed or solid fuels and gas is drawn off at the bottom. The zones are similar to those in the updraft gasifier; but the order is somewhat different (Quaak *et al.*, 1999). A lower overall efficiency and difficulties in handling higher moisture and ash content are common problems in small downdraft gas producers. In addition to these drawbacks, it is important for downdraft gasifiers to maintain uniform high temperatures over a given cross-sectional area in the reaction chamber. These factors limit the use of downdraft gasifiers to a power range of less than 1 MW (Turare, 1997; FAO, 1986; Warnecke, 2000; and Maniatis, 2001). This gasifier is, however, preferred to updraft gasifier for internal combustion engines because of the low tar content associated with the syngas (Quaak *et al.*, 1999).

#### **2.3.2 Fluidized-Bed Gasifiers**

Fluidized-bed gasification was initially developed to overcome operational problems of fixed-bed gasification of fuels with high ash content, but is suitable for large capacities (more than 10 MW) in general (Quaak *et al.*, 1999). The fuel is fed into a suspended (bubbling fluidized-bed) or circulating (circulating fluidized-bed) hot sand bed. The bed behaves like a fluid and is characterized by high turbulence. Fuel particles mix quickly with the bed material, resulting in rapid pyrolysis and a relatively large amount of gases. Major problems with fluidized bed

gasification are the resulting high tar content (up to 500mg/Nm<sup>3</sup>) (Wei, 2005), incomplete carbon combustion, and poor response to load changes. Problems with feeding, instability of the reaction bed, and fly-ash sintering in the gas channels can occur with some bio-fuels (Van Den Aarsen *et al.*, 1982; FAO, 1986; and Maniatis, 2001). There are two principal types of fluidized bed gasifiers namely, bubbling fluidized bed (BFB) and circulating fluidized bed (CFB). The circulating type separates and recycles fly-ash from the reaction bed while the bubbling type does not. Fluidized bed gasifiers have been the focus of appreciable research and development for large scale generation. Many commercial fluidized bed gasifier applications have been seen in Europe and the U.S. over the last decades; for example, a 15-MW CFB project at McNeil power station at Burlington (Vermont, USA), a 5- MW BFB project at Paia (Hawaii, USA), a 15-MW BFB pilot plant of Enviropower Inc. in Tampere (Finland), a 27-MW CFB power plant at Pöls (Austria), a 10.9-MW CFB “Energy Farm” project at Pisa (Italy), and 100-MW CFB power plant at Rudersdorf (Germany) (Klein, 2002; and Spliethoff, 2001).

## **2.4 Gas Quality Requirements**

The product gas formed from biomass gasification contains both combustible and noncombustible components. The combustible gases include CH<sub>4</sub>, CO, and H<sub>2</sub>. The major noncombustible components are CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>, in addition to organic (tars) and inorganic impurities (Alkali metals, H<sub>2</sub>S, HCl, NH<sub>3</sub>), and particulates (Dayton, 2002). The generation of H<sub>2</sub>S is of little importance in biomass gasification as long as the biomass contains less than 0.5% sulfur content. NH<sub>3</sub> is dependent on the nitrogen content of the biomass and biomass with less than 2% nitrogen is safe for gasification (Turare, 1997).

In gasification, tar is defined as a mixture of organic compounds in the product stream that are condensable in the gasifier or in downstream processing steps or conversion devices (Milne *et al.*, 1998). The gas quality indicates the extent to which the gas is suitable for end use equipment or

process and is represented by several parameters including chemical composition, tar and particulate concentration, and Lower Heating Value (LHV) and is dependent upon the requirements of the end use itself. The gas quality for power generation is tabulated below.

Table 2.3: Typical Characteristics of Fixed-Bed and Fluidized-Bed Gasifiers

Characteristic	Fixed-bed downdraft	Fluidized-bed
Fuel: size (mm)	10-100	0-20
Ash content (% wt)	<6	<25
Operating temperature (°C)	800-1400	750-950
Control	Simple	Average
Turndown ratio	4	3
Capacity (MW)	<2.5	1-50
Tar content (g/m <sup>3</sup> )	<3	<5
LHV (MJ/m <sup>3</sup> )	4.5	5.1

Sources: van Swaay *et al.*, (1994) and BTG (1993).

Table 2.4: Gas Quality Requirements for Power Generators

Parameter	Unit	IC engine	Gas turbine
Particles	mg/Nm <sup>3</sup>	<50	<30
Particle size	µm	<10	<5
Tar	mg/Nm <sup>3</sup>	<100	N/A
Alkali metals	mg/Nm <sup>3</sup>	N/A	0.24

Sources: Stassen (1993) and Milne *et al.*, (1998)

## **2.5 Gas Conditioning**

Before the producer gas can be used in a gas engine or turbine, it must be cooled and cleaned of tars, alkali metals, and dust. Basically, there are two main options for controlling the tar content in gasifier product gas depending on where tar is removed; either in the gasifier itself (primary measures) or outside the gasifier (secondary measures) (Devi *et al.*, 2003).

### **2.5.1 Primary Methods**

This is achieved by optimizing biomass fuel properties and/or gasifier design and operating conditions. An ideal primary method concept eliminates the use of secondary treatments. These methods are not yet fully understood and yet to be commercialized (Devi *et al.*, 2003). The primary measures include: proper selection of the operating conditions, the use of catalysts during gasification, and proper gasifier design.

#### **2.5.1.1 Temperature**

Biomass gasification is carried out at relatively high temperatures (above 800°C) (Devi *et al.*, 2003). Increasing the temperature in the gasification of sawdust in a fixed bed gasifier produces a decrease in the total number of detectable tar species (Kinoshita *et al.*, 1994).

#### **2.5.1.2 Pressure**

Pressurized and atmospheric gasifiers are currently used in advanced biomass gasification designs. Experiments involving gasification of Wisconsin whole tree chips indicated that when pressure was increased to 21.4 bar, the amount of total tar decreased (Knight, 2000).

#### **2.5.1.3 Gasifying Medium**

Air, steam, steam-oxygen mixture and carbon dioxide have been used as gasifying media. Heating value of the producer gas with air as the gasifying is lower because of the high percentage of nitrogen produced. Steam gasification produces a gas with a lower percentage of nitrogen and a

higher percentage of hydrogen. However, steam gasification is endothermic and hence sometimes requires complex design for heat supply in the process (Devi *et al.*, 2003)

#### **2.5.1.4 Equivalence Ratio (ER)**

Equivalence ratio can be defined as the ratio of the actual air fuel ratio to the air fuel ratio needed for complete combustion. This is an important factor in biomass gasification using air as gasifying medium. Tar yield decreases as ER increases because of more availability of oxygen to react with volatiles in the flaming pyrolysis zone (Kinoshita *et al.*, 1994). However, a higher ER value tends to favor high carbon dioxide content in the producer gas at the expense of hydrogen and carbon monoxide, and therefore a lower heating value.

#### **2.5.1.5 Catalysts**

The use of catalysts during biomass gasification affects the producer gas composition and reduces the tar yield. Three group of catalyst materials have been applied in biomass gasification systems-alkali metals, non-metallic oxides, and supported metallic oxides. Alkali metals are considered as primary catalysts. They enhance char formation reactions during thermo-chemical conversion [(Antal and Varhegyi, (1995); Raveendran *et al.*, (1995 & 1996); Richards and Zheng, (1991)].

#### **2.5.1.6 Gasifier Design**

A two-stage gasifier has been studied in the Asian Institute of Technology (AIT), Thailand (see Figure 2.1) (Devi *et al.*, 2003), and it resulted in a gas of tar content about 50 mg/m<sup>3</sup>, about 40 times less than a single-stage reactor under similar operating conditions (Bui *et al.*, 1994). In a two-stage gasifier, tars formed during pyrolysis (first stage) are decomposed in the reduction zone (second stage). The Technical University of Denmark also designed a two-stage gasifier (see Figure 2.2) (Devi *et al.*, 2003) where a combination of pyrolysis of the biomass feed with subsequent partial oxidation of the volatile products in the presence of a charcoal bed was achieved. The

modifications made in the gasifier design should be able to produce a gas of high heating value with low tar content, and it should be economically feasible.

### 2.5.2 Secondary Methods

This is achieved by applying downstream cleaning processes. These methods can be physical or chemical and include the following:

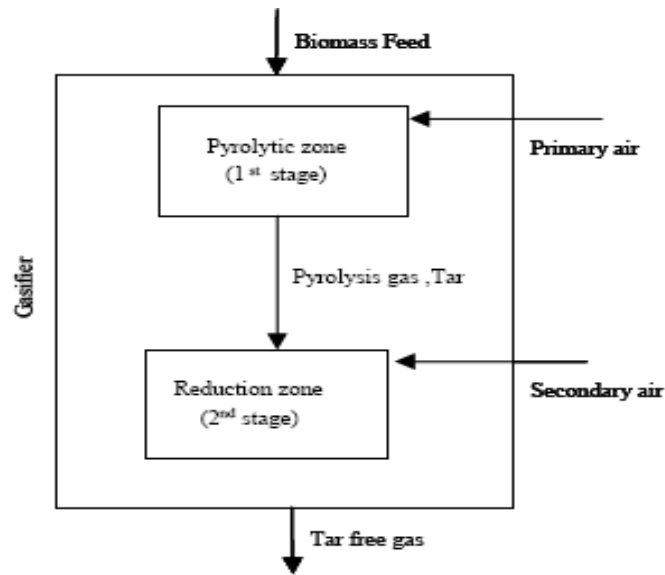


Figure 2.1: Two-stage Gasifier Concept (Devi *et al.*, 2003)

- 1) The use of cyclone, baffle filter, ceramic filter, fabric filter, rotating particle separator, electrostatic filter and/or scrubbers. These are normally placed external to the gasifier.
- 2) Tar cracking downstream the gasifier either thermally or catalytically. Although, these methods are reported to be very effective in tar reduction, in some cases they are not economically viable (Devi *et al.*, 2003). Figure 2.3 illustrates the secondary method of gas cleaning and conditioning.

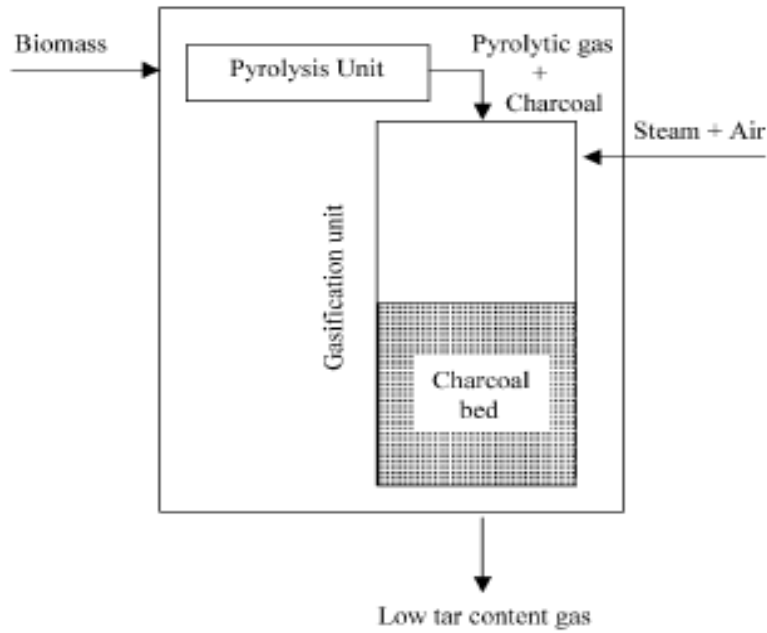


Figure 2.2: Two-stage Gasifier (Devi *et al.*, 2003)

### 2.5.2.1 Cyclone

The Cyclone is the most widely used technique to separate the Syngas from the dust and ash entrained in the gas stream. The basic principle behind cyclone separators is to use centrifugal force to make it possible to separate dust particles from a gas stream. A cone section causes the vortex

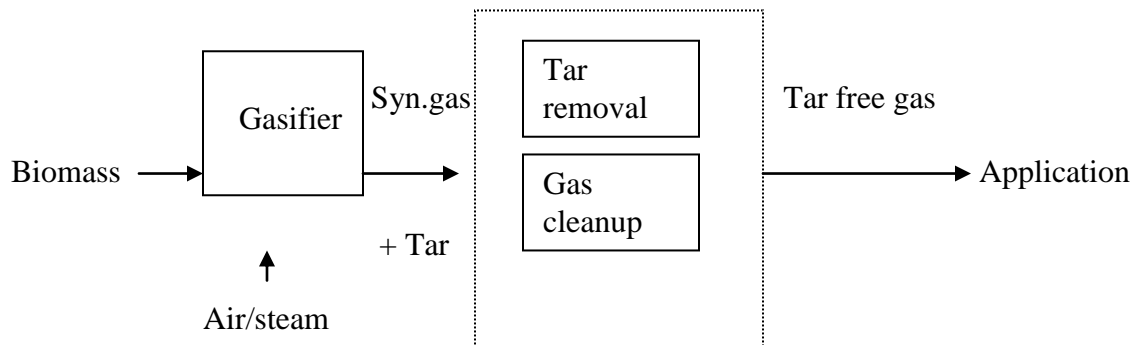


Figure 2.3: Tars Reduction by Secondary Methods (Devi *et al.*, 2003).

diameter to decrease until the gas reverses on itself and spins up the center to the outlet pipe or vortex finder. The shape of the cone induces the stream to spin, creating a vortex. Larger or denser

particles are forced outward to the walls of the cyclone where the drag of the spinning air as well as the force of gravity causes them to fall down the sides of the cone into an outlet (Seinfeld, 1975; Svarovsky, 1984). The separation efficiency of a cyclone is usually expressed as the particle size that will be separated with 50% efficiency (Fredriksson, 1999).

### 2.5.2.2 Particulate Filters

To separate particles from a flowing gas, some type of filter may be used. A filter has two important characteristics: its efficiency and resource consumption. The efficiency is quantified as the fraction of incoming particles which are retained by the filter. The efficiency of a filter depends on many parameters, of which the particle size is often the most important. The resource consumption can be divided into initial costs and costs of operation (*e.g.* pressure drop and use of materials) as well as maintenance costs. The pressure drop often depends on the The resource consumption can be divided into initial costs and costs of operation (*e.g.* pressure drop and use of materials) as well as maintenance costs. The pressure drop often depends on the accumulated amount of particles, and may well define the practical capacity of the filter.

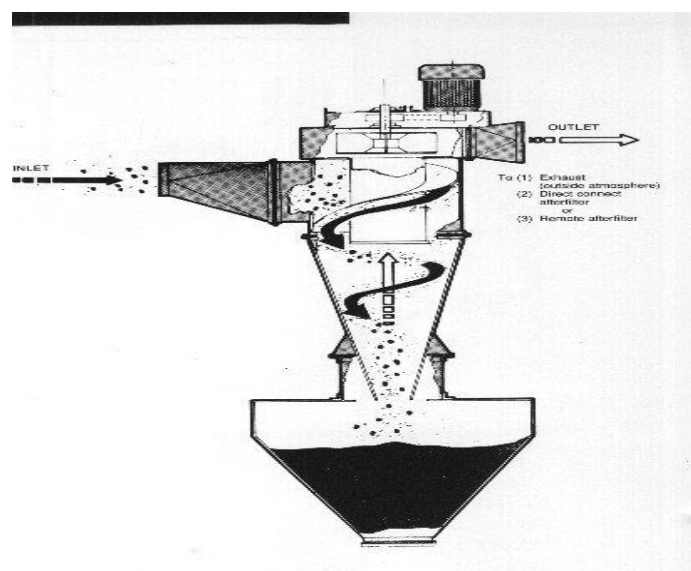


Figure 2.4: Cyclone Separator (Global Air Filtration Systems Inc.)

Filter media are materials which collect particles from a contaminated gas passing through. Bag-filters, cartridge filters and granular filters belong to this category. Filter materials may be of the surface collection type (*e.g.* Gore-TEX and Tetra-TEX membranes) or depth collection type (glass fibers and granular filters) (Hindsgaul, 2000). The particles are collected on the fibers by interception and diffusion. Interception is when a particle hits a fiber due to inertia effects or because the particle is large enough to touch the fiber as it passes. Interception is the most important effect for larger particles ( $>1\mu\text{m}$ ) (Hindsgaul, 2000). Diffusion is when the Brownian motions of the particle bring it in contact with the filter material. Diffusion is the major collection effect for submicron particles ( $<1\mu\text{m}$ ) (Hindsgaul, 2000). Hindsgaul, 2000 identified two common types of filters namely, baghouse and cartridge filters.

**A) Baghouse Filters:** In baghouse collectors, the dust filled air stream passes through fabric bags that filter the dust particles. Bags are made of different material such as woven or felted cotton, synthetic, or glass-fiber and the choice of one over the other may depend on the temperature of the raw gas. Figure 2.5 shows a baghouse filter arrangement. An advantage of this setup is the ability to do maintenance on one filter while in operation.

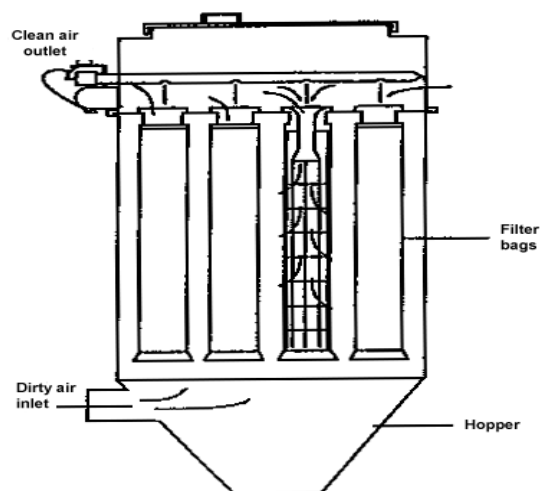


Figure 2.5: Baghouse Filters (Menardi, 2003)

**B) Cartridge Filters:** Cartridge filter can be surface or depth-type filter. Depth-type filters capture particles and contaminant through the total thickness of the medium, while in surface filters (usually made of thin materials like papers, woven wire, and cloths) particles are blocked on the surface of the filter. The membrane and fibrous type of filters have been used for gasification (Hindsgaul, 2000). It can be generally stated that if the size of filter surface is increased, higher flows are possible, the filter last longer, and the dirt holding capacity increases. Cartridge filters are normally designed disposable: this means that they have to be replaced when the filter is clogged.

### **2.5.2.3 Electrostatic Precipitators (ESP)**

Electrostatic precipitators operate by charging and collecting particles in a strong electric field between a central electrode and the wall. Gravity forces the mixture of tar and dust to the bottom of the precipitator where it can be removed. Only wet ESP can be used to remove tar from a biomass gasifier gas, because tar condensation on dry ESPs precipitation electrode would progressively inhibit particle removal. With ESPs, particle removal efficiencies of more than 99% are possible for particles as small as  $0.05\mu\text{m}$  (Milne *et al.*, 1998).

### **2.5.2.4 Rotating Particle Separator (RPS)**

This is a technique used to separate small particles from a gas or liquid. The filter consists of a large number of small parallel channels, which rotate around a common axis. The specific shape of the channels is not important. Centrifugal forces drive the solid or liquid particles towards the walls, where the particles stick as a result of the centrifugal force, Van der Waals force, or surface tension. The particles collected and agglomerated on the channel walls are removed periodically by injecting pressurized air at high velocity in reverse flow direction into the channels. This is done by a nozzle moving over the rotating filter element at periodic intervals without disturbing the

operation of the RPS. The technique is proven for removal of small particles or droplets, down to 0.1 $\mu\text{m}$  from gases at ambient temperature (van Kemenade, 2003).

#### **2.5.2.5 Cooling Towers and Venturi Scrubbers**

Cooling/scrubbing towers are usually used after cyclones as the first wet scrubbing units. All “heavy tar” components condense there. However, tar droplets and gas/liquid mists are entrained by the gas flow, thus rendering the tar removal rather inefficient. Venturi scrubbers are usually the next step (Milne *et al.*, 1998). A venturi scrubber accelerates the waste gas stream to atomize the scrubbing liquid and improve the gas-liquid contact. In a venturi scrubber, a throat section is built into the duct that forces the gas stream to accelerate as the duct narrows and then expands. As the gas enters the venturi throat, both gas velocity and turbulence increase. Depending upon the scrubber design, the scrubbing liquid is sprayed into the gas stream before the gas encounters the venturi throat, or in the throat, or upwards against the gas flow in the throat. The scrubbing liquid is then atomized into small droplets by the turbulence in the throat and droplet-particle interaction is increased. After the throat section, the mixture decelerates, and further impacts occur causing the droplets to agglomerate. Once the particles have been captured by the liquid, the wetted particulate matter and excess liquid droplets are separated from the gas stream by an entrainment section which usually consists of a cyclonic separator or mist eliminator (Corbitt, 1990). The correct selection and dimensioning of wet gas cleaning systems requires information on the particle size distribution in the gas. There are no reliable sets of tar droplet size distributions from biomass producer gases (Corbitt, 1990).

A major issue with using wet gas cleaning systems is the wastewater generated and this economic effect needs to be taken into consideration when recommending such techniques (Milne *et al.*, 1998).

### **2.5.2.6 Thermal Cracking of Tars**

Thermal processes raise the temperature of the producer gas to the levels that “crack” the heavy aromatic tar species into lighter and less problematic species, such as hydrogen, carbon monoxide and methane. For this process, it is suggested that temperatures exceed 1000°C in order to reduce tars effectively (Milne *et al.*, 1998).

### **2.5.2.7 Steam Reforming**

The addition of steam, over and above that formed from the water and oxygen in the feedstock, has been reported to produce fewer refractory tars, enhance phenol formation, reduce the concentration of other oxygenates, have only a small effect on the conversion of aromatics, and produce tars that are easier to reform catalytically (Milne *et al.*, 1998).

### **2.5.2.8 Partial Oxidation**

Oxygen or air added to steam seems to produce more refractory tars but, while enhancing the conversion of primary tars. When oxygen is added selectively to different stages, such as in secondary zones of a pyrolysis-cracker reactor, tars can be preferentially oxidized (Milne *et al.*, 1998).

### **2.5.2.9 Catalytic Cracking of Tars**

The research on catalytic, hot-gas cleanup has involved (a) incorporating or mixing the catalyst with the feed biomass to achieve so-called catalytic gasification or pyrolysis; and (b) treatment of gasifier raw gas in a second bed or beds. Two main classes of catalyst have been studied: non-metallic and metallic oxides. The most widely used non-metallic catalysts are calcined dolomites and magnesites, zeolites, and olivine (Dayton, 2002). Metallic oxides used as catalyst are generally Nickel based catalysts because they have proved to be efficient for tars and ammonia decomposition in laboratory-scale gas purification experiments (Hepola, 1993). Other transition metals such as Cobalt and Molybdenum may be used as well (Milne *et al.*, 1998). Although

dolomite is the most widely used catalyst and has been proven to be a very effective bed additive in terms of tar reduction, it has some critical limitations. Dolomite is softer and thus gets eroded by the silica sand particles. Also, some dolomite particles break during the calcinations and result in a large production of fines leading to increased carryover of solids from the bed. Dolomite is a calcium magnesium ore with the general chemical formula  $\text{CaMg}(\text{CO}_3)_2$  that contains approximately 20% MgO, 30% CaO, and 45%  $\text{CO}_2$  on a weight basis (Dayton, 2002). The use of calcined dolomites in biomass gasification for tar cracking and removal has been the subject of interest in hot gas cleaning. Delgado *et al.* (1996) studied the use of calcined dolomites in biomass gasification with steam. The catalytic decomposition of biomass tars using calcined dolomites was also reported by Devi *et al.* (2005). Calcination of dolomite involves decomposition of the carbonate mineral, eliminating  $\text{CO}_2$  to form MgO-CaO. Complete dolomite calcination occurs at fairly high temperatures and is usually performed at  $800^\circ\text{C}$ - $900^\circ\text{C}$  (Dayton, 2002) and restricts its effective use to these relatively high temperatures. Aznar *et al.* (1997) performed experiments involving a bed of calcined dolomite placed after a biomass fluidized bed gasifier in which gasification was made with steam-oxygen mixtures to clean the raw syngas. The dolomite was calcined for 2 hours at  $900^\circ\text{C}$  in an external oven and weighed before its introduction into the reactor. The temperature of the catalytic bed reactor was measured at both the center and at its wall. Experimental results showed a tar elimination of 90-95% with space time of 0.06-0.15 kg calcined dolomite  $\text{h}^{-1}$  and an increase in the gas yield by 0.15-0.40  $\text{m}^3$  at standard temperature and pressure (STP) per kg dry, ash free (daf) biomass fed (Aznar *et al.*, 1997).

An alternative of dolomite can be naturally occurring particles of olivine which is a mineral containing magnesium, iron oxide and silica. Rapagna *et al.* (2000) have found the tar reforming activity of Olivine comparable to calcined dolomite. Olivine is advantageous in terms of its ability to withstand friction and does not easily break (Devi *et al.*, 2005). However, there is still ambiguity

on the prospective use of olivine as a tar decomposing catalyst. It is not yet well known how tars behave in the presence of olivine and hence more attention should be given to find out whether olivine could produce a clean gas with very low tar content (Devi *et al.*, 2005).

Nickel based catalysts have been found to almost completely remove the tar and are also very effective for NH<sub>3</sub> removal at temperatures above 800°C (Wang *et al.*, 1999). The main limitation of using Nickel based catalysts is severe deactivation of the catalyst. This deactivation occurs mainly when the catalyst is placed right after the gasifier; the high tar concentration has a devastating effect on catalyst activity. More recent work has included dual systems with catalysts such as dolomite serving as a guard bed for highly active catalysts such as Nickel based reforming catalysts. Catalytic processes can operate at much lower temperatures (600-800°C) than thermal processes, alleviating the need for expensive alloys for reactor construction (Zhang *et al.*, 2003). Also, unlike physical processes, catalytic cleaning converts the tar, eliminating waste disposal problems. Potentially, catalytic cracking processes provide the simplest and most effective means of removing tars while retaining the sensible heat required for efficient use of the producer gas in close coupled applications. The use of a catalytic reactor downstream of the gasification reactor has proven to be a more effective approach to tar destruction (Kurkela *et al.*, 1993). In using catalysts as gas cleaning technique, there is almost no difference in the lower heating value of the gas produced as the increase in the hydrogen production is compensated by a decrease in carbon monoxide, and there is hardly any change in methane production (Corella *et al.*, 1999).

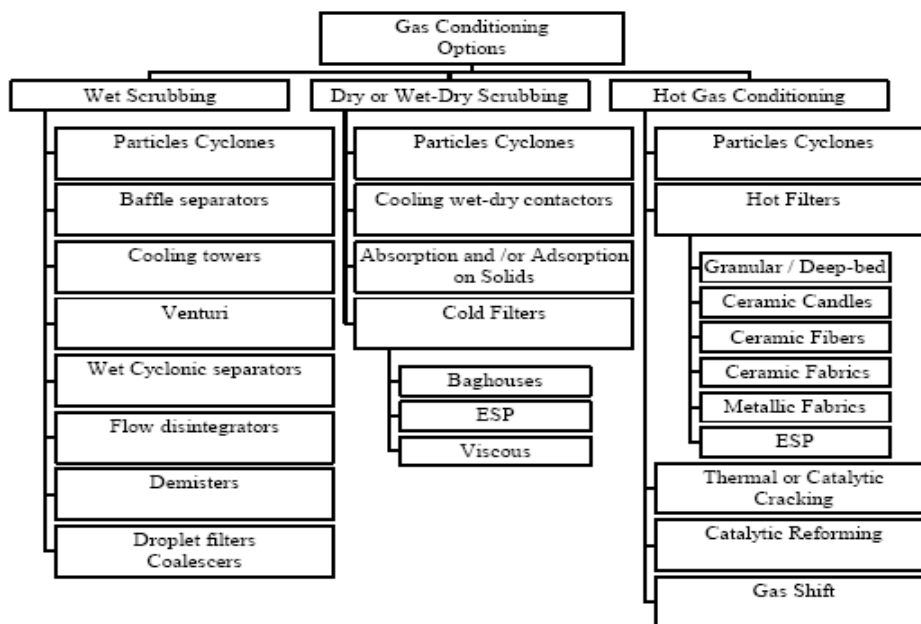


Figure 2.6: Various Options of Gas Cleaning Technologies (Milne *et al.*, 1998)

Table 2.5: Reduction of Tars and Particulates in Various Producer Gas Cleaning Systems

Techniques	Temperature (°C)	Particles Reduction (%)	Tars Reduction (%)
Sand bed filter	10-20	70-99	50-97
Wash tower	50-60	0-98	10-25
Venturi scrubber	n/a	n/a	50-90
Rotational atomizer	<100	95-99	n/a
Wet electrostatic Precipitator	40-50	>99	0-60
Fabric filter	130	70-95	0-50
Rotational particle separator	130	85-90	30-70
Fixed bed tar adsorber	80	n/a	50
Catalytic tar cracker	900	n/a	>95

Source: Hasler *et al.*, (1999)

## **CHAPTER 3: A NEW PROTOCOL FOR TARS AND PARTICULATES CHARACTERIZATION**

### **3.1 Introduction**

One of the most challenging issues concerning biomass gasification is the tar and particulates formed during the process. Tars are considered to be a complex mixture of the condensable fraction of the organic gasification products and are largely aromatic hydrocarbons (Milne *et al.*, 1998). Tars and particulates are problematic in integrated biomass gasification systems as they may condense on valves and fittings, hampering the ability of valves to function properly. They also clog fuel lines and injectors in internal combustion engines (Devi *et al.*, 2005). Currently, there is no specific method for determining the concentration of tars and particulates from biomass gasification. Reliable sampling and analysis of these impurities from biomass gasification is needed for an efficient process development and economical operation of gasifiers. In this study, a pilot scale downdraft gasifier with an average throughput of 6.6 kg/h was used to establish the characterization of tar and particulates from gasification of woodchips.

This chapter presents a simple and effective procedure for measuring the tar and particulates produced from biomass gasification operated at atmospheric pressure using EPA standard.

### **3.2 Material Description and Preparation**

A pilot scale downdraft gasifier was designed and constructed in the Biological and Agricultural Department of the Louisiana State University AgCenter. The gasifier was constructed using a cylindrical vessel with 85 cm in height and 60 cm in diameter. Cypress mulch woodchips obtained from hardware stores in Baton Rouge, Louisiana dried to between 11 and 17% moisture content were used for this study. The woodchips were chipped to sizes less than 5 cm with a 2.5 Horsepower rotary tree limb chipper/shredder from Chicago Electric Power Tools (Model No. 92281). In addition, pine pellets obtained from a hardware store in Baton Rouge, Louisiana, were

also used for experimentation. The pellets were about 1.27 cm long, 0.635 cm in diameter, and dried to 3.2% moisture content. The gasification process was carried out at atmospheric pressure and air was used as the gasification agent. The determination of tars and particulates in the syngas produced was carried out in two steps: sampling and analysis.

### **3.3 Gasifier System Operation**

The fixed bed gasifier system used in this project was designed and constructed in the Biological and Agricultural Department of the Louisiana State University AgCenter. After a series of initial tests, the system was modified for this study. The gasifier consists of a feeder unit, gasification furnace, a gas flare, and a temperature monitoring system.

#### **3.3.1 Feeder Unit**

The gasifier feeder unit was designed to allow for batch process gasification. It consists of two 7.62 cm pipes with knife gate valves between and at the top of the pipes. Feed level detectors were incorporated into the feed system. The detectors were made from metal rods inserted through the feeder pipes and the depth of the feed in the unit was gauged by the movement of the rod. After the feed was weighed, it was manually loaded into the system. Using the gate valves and feed level detector, materials were reloaded during gasification.

#### **3.3.2 Gasifier Furnace**

The gasification system was a fixed bed downdraft gasifier with air as the oxidant. A cylindrical furnace height was 72.5 cm and 10 cm in diameter. The gasification chamber was open to atmospheric conditions from the air blower. A grate at the bottom of the chamber provided support for the bio-fuel and maintained a stationary reaction bed. Six K-type thermocouples were connected to the wall of the furnace from top to bottom with approximately 7cm distance between adjacent thermocouples.

At the beginning of an experiment, the temperature monitoring system was initialized and the gasifier was started. During the course of the project, two temperature monitoring systems were used. Initially a Campbell Scientific Micrologger (21X) was used and was later replaced with a USB-based data acquisition hardware (Model: USB-TC, Measurement Computing Corporation). During start up, the air blower was first turned on, drawing atmospheric air into the gasifier at approximately 5 m<sup>3</sup>/h to 8.5 m<sup>3</sup>/h. Generally a high air flow was favored during start up to generate a faster warm up and ignition of the system. The grate vibrator cycled on and off at a pre-determined frequency to move the biomass feed through the gasifier. As the biomass was combusted, more material was fed into the gasifier through the feeder system. The gasification process followed that described for downdraft gasifiers. Generally, biomass undergoes four steps during gasification: drying, pyrolysis, oxidation, and reduction. The syngas, including impurities, was designed to flow through a pipe connected to the furnace.

### **3.3.3 Gas Flare**

The syngas exiting the gasifier was channeled to a gas flare chamber for combustion. This was necessary to minimize air pollution during the process of experimentation and to confirm the presence of combustible gases.

### **3.4 Syngas Sampling**

The syngas sampling was performed during stable operating conditions of the gasification process. This is indicated by the generation of a steady self sustainable flame from the burning of the gas being produced. To get reliable data, it was important that the sampling conditions are maintained at defined values during the experiment. The sample gas flow rate decreased from approximately 94.4 cm<sup>3</sup>/s to 78.7 cm<sup>3</sup>/s after 30 minutes of sampling because of plugging in the connection lines and in the filter assembly. This factor was considered when planning the setup for

sampling line. One measurement point from the gasifier was sufficient to produce a representative data on the level of impurities.

### 3.4.1 Preparation of Sampling Equipment

It was important to ensure that all sampling equipment was in good operational condition before startup. The sampling line was kept as short as possible and a leak test was performed on the sampling train to ensure gas tight connection. Prior to using the equipment in connection with a site measurement, all glass equipment was cleaned according to an internal laboratory instruction.

### 3.4.2 Outline and Principle of Syngas Sampling

The structure of the gas sampling process is shown in Figure 3.1 below. It was based on EPA Method 5 for measuring particulate matter emissions from stationary sources but was adapted to measure gravimetric tar and particulate matter generated during biomass gasification. Unlike the EPA standard, it does not include determination of moisture content in the gas. The probe and pitot tube assembly was not used in this protocol to measure the gas velocity; however, the gas flow analysis was done using the flow regulator and flow meter.

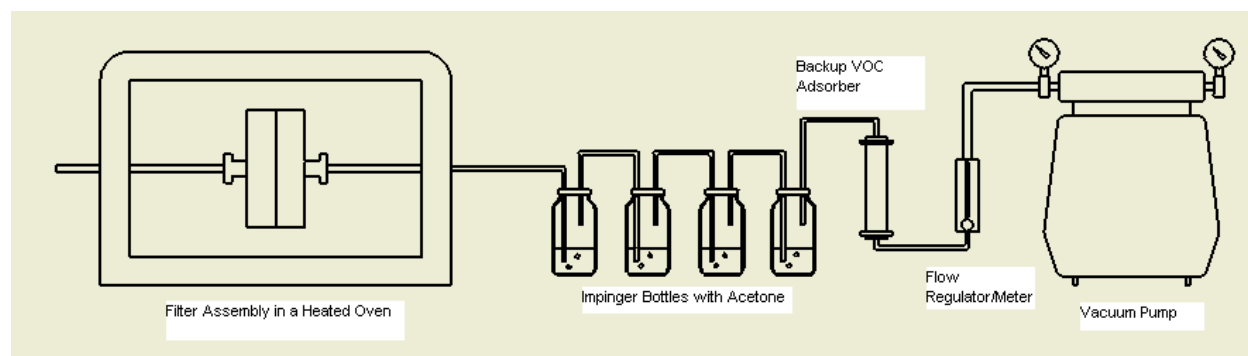


Figure 3.1: Tars and Particulates Sampling Train

Gas produced from the gasifier traveled through copper connection tubing to the filter assembly where the particulates are collected. At temperatures around 250°C, most of the tar contained in the gas passed through the connection tubing to a series of impinger bottles containing

acetone in which it was dissolved. A backup tar adsorber is optional and may not be needed. The vacuum pump generated suction for the process and the flow regulator controlled and measured the volume of gas sampled.

The measurement principle of this procedure was based on the discontinuous sampling of a gas stream containing tar and particulates under iso-kinetic conditions. The sampling of tar and particulates was performed simultaneously, and the system was set up to measure the impurities quantitatively. The procedure is described in the following sections.

#### **3.4.2.1 Particulate Collection**

The particles were collected in an external filter assembly placed in an oven and heated to 250°C to prevent the condensation of tars in the filter and in the copper tubing. Glass microfiber filter with particle retention size 0.7 µm and 90 mm diameter (Whatman: GF/F Cat No 1825 090) was used. The filter paper was preheated to more than 250°C for about 15 minutes before being used to obtain the tare weight. Millipore stainless steel pressure filter holder was used to ensure a gas tight filter system.

#### **3.4.2.2 Tar Collection**

A sampling train comprising four (4) impinger bottles connected in series was used for collecting the tars in the sampled gas stream. The tars were dissolved in approximately 50 ml of solvent in each bottle. Acetone was found to be an appropriate solvent because of its high solubility (EPA Method 5).

#### **3.4.2.3 Volume Measurement**

The sampling train was connected to a vacuum pump and gas flow meter. The pump generated the needed suction for the syngas sampling. The gas flow rate was 94.4 cm<sup>3</sup>/s. The gas meter readings and start times were noted and recorded. The volume of gas sampled was determined from the flow meter/regulator.

### 3.4.3 Duration of Sampling

The amount of time needed to collect a representative quantity of tars and particulates depended on the concentration observed which has the effect of clogging the filter paper. It also depended on the size of the connection tubing. This protocol was prepared using one-quarter inch diameter copper tubing in the sampling process, and sampling lasted for approximately 30 minutes.

### 3.4.4 Sample Analysis

Analysis was done within 24 hours after sampling to avoid contamination of the collected syngas and impurities. The techniques used in determining the tar composition could be GC-MS in which positive identification of individual tar compounds is performed or by gravimetric method, or a combination of both depending on the end use of the of the gasification products. This procedure describes the gravimetric method of analyzing both the tars and particulates.

### 3.4.5 Determination of Gravimetric Tar

All condensed tar particles were washed from the transfer lines (e.g. copper tubing) using the high purity acetone and combined with the tar collected in the impinger bottles. The mass of gravimetric tar was determined through solvent evaporation. The results were calculated using the following equation:

$$C_t = \frac{W_t}{V_g} \quad (3.1)$$

Where:  $C_t$  = Concentration of tar in syngas ( $\text{g}/\text{m}^3$ )

$W_t$  = Weight of tar (g)

$V_g$  = Volume of sampled gas ( $\text{m}^3$ )

### 3.4.6 Determination of Particulates

The particulate concentration was calculated from the difference in weight between the tare weight of the filter and the dry particulate containing filter obtained after drying in oven set at 60°C for approximately 30 mins and allowed to acclimatize in a desiccator. The following equation was used to quantify the particulates in the gas stream:

$$C_p = \frac{W_p}{V_g} \quad (3.2)$$

Where:  $C_p$  = Concentration of particulates in syngas ( $\text{g/m}^3$ )

$W_p$  = Weight of particulates (g)

$V_g$  = Volume of sampled gas ( $\text{m}^3$ )

### 3.4.7 Estimation of Syngas Flow Rate and Yield

The following procedure describes the determination of the syngas flow rate from the gas yield and the gasifier load. It is based on a total carbon balance and can be applied when the following are established:

- Stable gasifier operation
- Syngas composition is known
- Fuel feeding rate (kg/h), fuel moisture and carbon content are known
- Solid or liquid carbonaceous effluent streams (bottom ashes, particles, tar) and their carbon content are known.

The calculation of the syngas flow rate based on an elemental carbon balance can be written as:

$$q_{m,\text{fuel}} cc_{\text{fuel}} + \sum q_{v,\text{agent}} cc_{\text{agent}} = q_{v,\text{gas}} \cdot (c_{\text{gas}} + c_{\text{tar}} cc_{\text{tar}} + c_{\text{particles}} cc_{\text{particles}}) + q_{m,\text{ash}} cc_{\text{ash}} \quad (3.3)$$

Where:  $q_{m,\text{fuel}}$  = Fuel feeding rate (kg dry biomass/h)

$cc_{\text{fuel}}$  = Carbon content of fuel (kg C/kg dry biomass = 0.47 for woody biomass)

$q_{v,agent}$  = Gasification agent feeding rate (m<sup>3</sup>/h)

$cc_{agent}$  = Carbon content of gasification agent (kg C/m<sup>3</sup>)

$q_{v,gas}$  = Syngas generation rate (m<sup>3</sup>/h)

$cc_{gas}$  = Carbon content of non-condensable gases (CO, CO<sub>2</sub>, CH<sub>4</sub>) in the syngas (kg C/m<sup>3</sup>)

$c_{tar}$  = Tar concentration in the syngas (kg/m<sup>3</sup>)

$cc_{tar}$  = Carbon content of tar (kg C/kg tar)

$C_{particles}$  = Particulate concentration in syngas (kg/m<sup>3</sup>)

$cc_{particles}$  = Carbon content of particulates (kg C/kg dry biomass)

$q_{m,ash}$  = Bottom ash rate (kg dry ash/h)

$cc_{ash}$  = Carbon content of bottom ash (kg C/kg dry ash)

Generally, the gasification agent does not contain carbonaceous gas components, thus  $cc_{agent} = 0$ .

Rearranging the equation gives:

$$Y_{gas} = \frac{q_{v,gas}}{q_{m,fuel}} = \frac{cc_{fuel} - c_{ash,fuel}cc_{ash}}{cc_{gas} + c_{tar}cc_{tar} + c_{particles}cc_{particles}} \quad (3.4)$$

Where  $Y_{gas}$  = producer gas yield (m<sup>3</sup>/kg dry biomass)

$C_{ash,fuel}$  = Ash content of fuel (kg/kg dry biomass)

However, a simple and direct analysis of the volume of gas produced can be determined from the biomass conversion rate using the following equation:

$$CR = \frac{V_{tg}}{W_f} \quad (3.5)$$

Where:  $CR$  = Conversion rate of biomass

$V_{tg}$  = Total volume of syngas produced

$W_f$  = Weight of biomass consumed

### 3.5 Syngas Composition Measurement and Heating Value

The syngas produced from the woodchip gasification contains many components, but only CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub> were considered in this project. The gas mixture was measured with a TCD gas chromatograph (SRI MG #1). The gas was collected over a 0.3 μm filter using a syringe and the sample was immediately injected into the already calibrated GC. The calibration of the GC was done with a known mixture of Airgas containing the gases in the syngas to be identified.

The heating value of a gas cannot be measured directly, but only with respect to a reference state. The most widely used is the Lower Heating Value (LHV). This uses water vapor as its reference state. The heating value of the syngas was calculated from the concentration of combustible gases in the mixture.

$$\text{Lower Heating Value (LHV)} = \%H_2 * LHV_{H_2} + \%CH_4 * LHV_{CH_4} + \%CO * LHV_{CO} \quad (3.6)$$

## **CHAPTER 4: RESULTS AND DISCUSSION OF EXPERIMENTAL DATA**

### **4.1 Introduction**

In this section, results of experiments conducted to test the suitability of the sampling protocol developed for tar and particulates from biomass gasification. This Chapter also presents the experimental procedure and results obtained from using calcined dolomite, proprietary catalyst, and bag-filter as tars and particulates removal techniques. Conditions identical to those used in the base study were used in all experiments involving gas cleaning.

### **4.2 Experimental Results Summary**

A total of 9 runs for cypress mulch woodchips and 16 runs for pine pellets were included in this study. Due to the complex nature of the gasification process, some problems were observed during the initial phase of this project. A major problem had to do with the feed unit operation which meant that the biomass feedstock got stuck in the pipe-like hopper and did not flow through to the furnace easily. Even after repeated modifications there were still quite a few problems with the feed mechanism as described above. Another problem was that the temperature monitoring and recording instrument used at the early stage (21X Micrologger) did not give real time temperature data, thereby making it difficult to monitor fluctuations in gasifier temperature. The USB-TC system was installed to solve this problem but there were difficulties in getting it to work properly.

### **4.3 Gasifier Temperature Profile**

The process occurring in the gasification chamber was the most complex development in this study because temperatures varied by location and with time and showed unsteady distribution trends. The temperatures of the gasifier wall (T1, T2, T3, T4, T5, T6), within the furnace, were continuously measured and recorded by the computerized control system. Temperature averages were calculated within a 30 seconds interval, and average temperature profiles were created. Figure 4.1 shows typical gasification temperature profiles during different test runs.

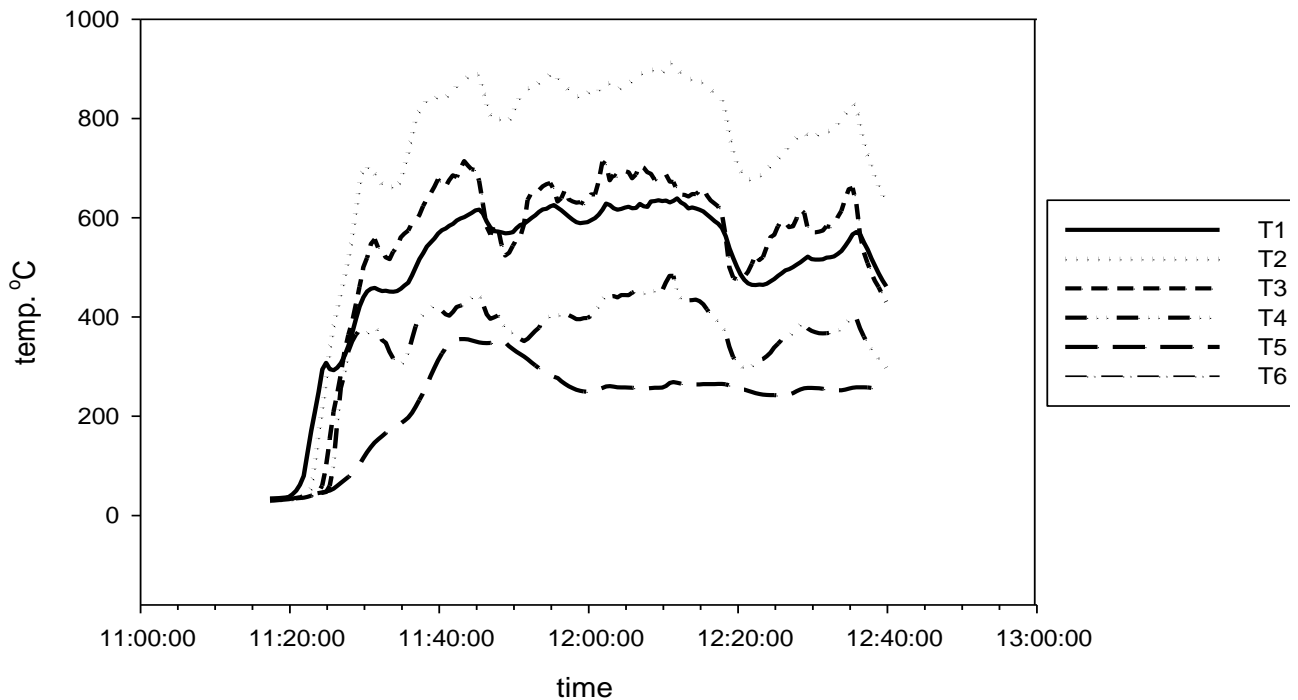


Figure 4.1 Typical Gasifier Wall Temperature Profile from Gasification of Woodchips

In the above temperature profile, T1 represents the thermocouple immediately above the grate, and T2 to T6 represent the thermocouples were placed approximately 7 cm adjacent to one another. The wall temperatures generally increased with increase in air flow from the air blower. The average air flow rates were between 5.0 and 8.5 m<sup>3</sup>/h. The gasifier was designed so that pyrolysis occurred around the zone defined by T2 to T4.

#### 4.4 Gas Composition and Heating Value

The average yields of measured syngas components for woodchips are listed in Table 4.1, and average yields for pine pellets are listed in Table 4.2. The results indicated a more consistent data for pine pellets when compared to woodchips. This due to the variability in the moisture content of the woodchips (11 to 17 %) while the pellets were actually treated and had a consistent moisture content of 3.2%. A comparison with data published on gasification with similar systems is presented in Table 4.3. Due to the difficulty in measuring H<sub>2</sub> with a TCD chromatograph using helium as mobile phase, the data for H<sub>2</sub> may not be as precise as it could have been. The average

concentrations of the combustible gases namely: carbon monoxide (CO), hydrogen (H<sub>2</sub>), and methane (CH<sub>4</sub>) obtained were within the limits reported in previous work (Heesch *et al.*, 1999). However, the rather high percentage of Nitrogen (N) in the gas mixture could be explained by the fact that air was used as the gasification medium. The use of pure oxygen will result in higher percentages of the combustible gases. However, no additional efforts were made to lower the nitrogen content. The attempt to minimize the air flow from the blower did not seem to have any noticeable effect on the gas composition, but rather reduced the velocity of the syngas flowing from the gasification chamber.

Table 4.1: Summary of Syngas Composition and Lower Heating Value for woodchips

Run No.	CH <sub>4</sub> (% Vol.)	CO (% Vol.)	H <sub>2</sub> (% Vol.)	CO <sub>2</sub> (% Vol.)	N <sub>2</sub> (% Vol.)	LHV (MJ/Nm <sup>3</sup> )
1	1.58	10.42	10.62	12.56	64.82	3.03
2	1.45	14.70	13.82	11.22	58.79	3.87
3	1.20	9.05	12.47	13.34	63.93	2.92
4	1.87	10.65	10.82	12.03	64.72	3.18
5	1.95	13.98	10.39	12.75	60.92	3.58
6	2.17	13.75	11.22	13.09	59.77	3.72
Average	1.70	12.09	11.56	12.5	62.16	3.38
STD	0.36	2.33	1.33	0.77	2.66	0.39

Table 4.2: Summary of Syngas Composition and Lower Heating Value for pine pellets

Run No.	CH <sub>4</sub> (% Vol.)	CO (% Vol.)	H <sub>2</sub> (% Vol.)	CO <sub>2</sub> (% Vol.)	N <sub>2</sub> (% Vol.)	LHV (MJ/Nm <sup>3</sup> )
1	2.08	13.55	11.77	13.65	58.30	3.73
2	2.10	14.12	10.95	12.58	60.04	3.72
3	1.96	12.80	11.60	12.72	60.85	3.57
Average	2.05	13.49	11.44	12.98	59.73	3.67
STD	0.08	0.66	0.43	0.58	1.30	0.09

Table 4.3: Comparison of Syngas Composition with Published Data

Parameters	Published Data	Experimental Results	
		Woodchips (Average)	Pine pellets (Average)
H <sub>2</sub> (% Vol.)	15-21	11.56	11.44
CO (% Vol.)	10-22	12.09	13.49
CO <sub>2</sub> (% Vol.)	11-13	12.50	12.98
CH <sub>4</sub> (% Vol.)	1-5	1.70	2.05
N <sub>2</sub> (% Vol.)	39-63	62.16	59.73
LHV (MJ/Nm <sup>3</sup> )	4.0-5.6	3.38	3.67

#### 4.5 Gravimetric Tar and Particulates

The process of tar and particulate sampling was initiated only after the temperatures in the gasifier approached steady state and there was evidence of combustible gases produced, indicated by a self sustaining flame. Tables 4.4 and 4.5 show the results obtained for gravimetric tar and particulates of the pre-filtered syngas for woodchips and pine pellets.

Table 4.4: Summary of Tar and Particulates Concentration before gas cleaning (Woodchips)

Run No.	Tar Concentration (g/Nm <sup>3</sup> )	Particulate Concentration (g/Nm <sup>3</sup> )
1	2.12	4.35
2	1.45	2.51
3	2.23	5.30
4	1.45	4.88
5	1.52	3.25
6	1.02	2.76
Average	1.63	3.84
STD	0.46	1.16

Table 4.5: Summary of Tar and Particulates Concentration before gas cleaning (Pine Pellets)

Run No.	Tar Concentration (g/Nm <sup>3</sup> )	Particulates Concentration (g/Nm <sup>3</sup> )
1	0.97	4.78
2	0.91	4.79
3	0.67	4.67
Average	0.85	4.75
STD	0.16	0.07

#### 4.6 Biomass Conversion Rate

The analysis for biomass conversion rate was determined from the amount of syngas yield per unit weight of biomass. The average yield for woodchips and pine pellets are tabulated below:

Table 4.6: Summary of Weight of Biomass Consumed, Total Volume of Syngas, and Biomass Conversion Rate for Woodchips

Run No.	Weight of Biomass Consumed (kg)	Total Volume of Syngas (Nm <sup>3</sup> )	Biomass Conversion Rate (Nm <sup>3</sup> /kg)
1	6.50	7.65	1.18
2	9.75	10.20	1.05
3	9.75	10.84	1.11
4	9.75	9.56	0.98
5	6.50	7.01	1.08
6	6.50	7.27	1.12
Average	8.12	8.75	1.09
STD	1.78	1.65	0.07

Table 4.7: Summary of Weight of Biomass Consumed, Total Volume of Syngas, and Biomass Conversion Rate for Pine Pellets

Run No.	Weight of Biomass Consumed (kg)	Total Volume of Syngas (Nm <sup>3</sup> )	Biomass Conversion Rate (Nm <sup>3</sup> /kg)
1	12	15.30	1.28
2	12	15.94	1.33
3	12	15.94	1.33
Average	12	15.73	1.31
STD	0	0.37	0.03

#### **4.7 Gas Cleaning and Conditioning**

As mentioned earlier, the successful implementation of biomass gasification for gas engine and turbine based power projects or for fuel cell applications or Fischer-Tropsch depends on the effective and efficient removal of tar from the syngas. Chapter 2 provided an overview of various gas cleaning and conditioning equipment.

#### **4.8 Catalytic Bed Setup and Experimentation.**

The catalytic bed conversion system was arranged to treat a portion of the syngas produced just before the sampling train. The experiments for cracking the tar component were carried out using a fixed-bed reactor packed with granulated dolomite (more than 2.36 mm diameter). The fixed-bed had an internal diameter of 19 mm and length of 152.4 mm made from a steel pipe. This catalyst bed was placed inside a muffle furnace. A schematic diagram of the experimental setup is shown in Figure 4.2. Catalyst depth in the pipe was 101.6 mm and supported by wire mesh at both ends of the pipe. Prior to the experimentation involving dolomite, calcination was done at 850°C in an oven for 2 hours. Albermale proprietary catalyst was also used as tars removal material. Finally, a combination of the proprietary catalyst and bag-filter was used to minimize both tars and particulates to within acceptable limits. During each run, samples of the raw syngas were drawn into the catalytic bed by the vacuum pump before passing through the tar and particulate sampling system. The gas sampling flow rates were equivalent to that used during the initial experimentation process (approximately 94 cm<sup>3</sup>/s).

#### **4.9 Effect of Dolomite Bed on Tars and Particulates Yield**

The dolomite bed was designed to minimize the tars and capture fine particulates generated in the syngas. The amount of these impurities passing through the sampling train after leaving the dolomite bed was considerable less than what was determined before the gas treatment.

Experimental data showed about 90% tar removal and 50% reduction in particulates collected. Tables 4.8 and 4.9 show the experimental results obtained at 850°C operation of the dolomite bed.

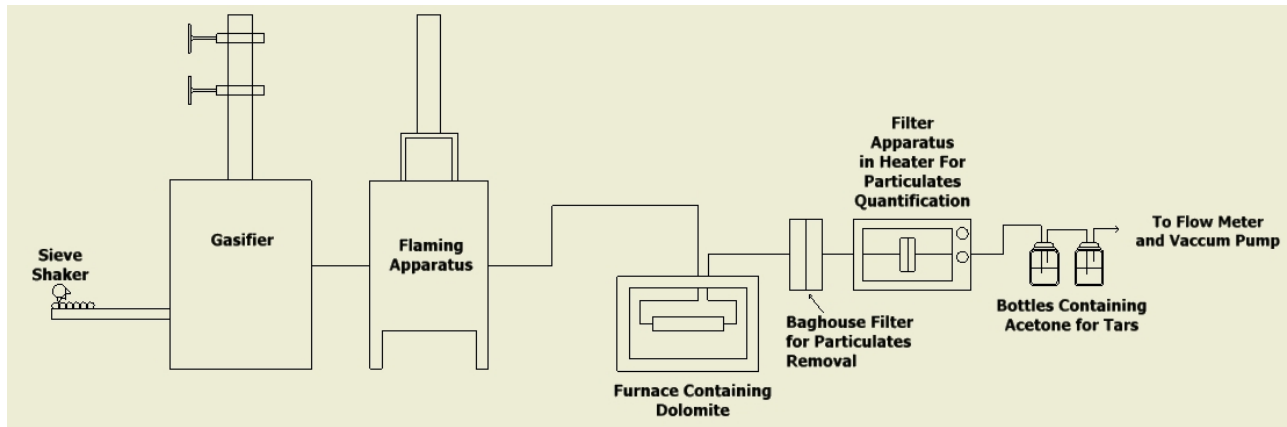


Figure 4.2: Gasification Setup Showing Dolomite Arrangement.

The setup above shows the operational arrangement of biomass gasification with the tars and particulates reduction equipment.

Table 4.8 Summary of Tars and Particulates Concentration after Dolomite Bed (Pine Pellets)

Run No.	Tar Concentration (g/m <sup>3</sup> )	Particulate Concentration (g/m <sup>3</sup> )
1	0.12	2.09
2	0.07	2.08
3	0.09	1.86
Average	0.09	2.01
Standard Deviation	0.02	0.13

Table 4.9 Summary of Tars and Particulates Concentration after Dolomite Bed (Woodchips)

Run No.	Tar Concentration (g/Nm <sup>3</sup> )	Particulate Concentration (g/Nm <sup>3</sup> )
1	0.19	1.97
2	0.17	2.33
3	0.20	2.50
Average	0.19	2.27
Standard Deviation	0.015	0.27

#### 4.9.1 Effect of Temperature on Dolomite Performance

The catalytic bed temperature was varied to analyze its effect on syngas cleaning. Using the same amount of dolomite (8.5g), bed temperatures ranging from 650°C to 950°C were chosen for this study. Experimental data showed a fairly sharp increase in the performance of the dolomite as temperature increased up to 850°C, but at remained quite steady between 850°C and 950°C. The results are tabulated below:

Table 4.10: Effect of the Dolomite Bed Temperature (Pine Pellets)

Temperature (°C)	Tars Concentration (g/Nm <sup>3</sup> )	Particulates Concentration (g/Nm <sup>3</sup> )
650	0.34	3.42
750	0.10	2.85
850	0.09	2.10
950	0.08	2.14

#### 4.10 Effect of Albermale Proprietary Catalyst on Tars and Particulates.

The proprietary catalyst was used at different bed temperatures for the gasification of pine pellets. Tests showed little effects in the operation of the catalyst at the temperatures investigated.

Table 4.11 summarizes the results obtained.

#### 4.11 Tars and Particulates Concentration after Proprietary Catalyst and Bag-Filter.

A final tars and particulates removal experimentation using the proprietary catalyst at 250°C and bag-filter was done using pine pellets. The results showed considerable reduction of tars and particulates impurities to within the limit referenced in the literature as the minimum for operating an IC engine. The results are tabulated in table 4.12.

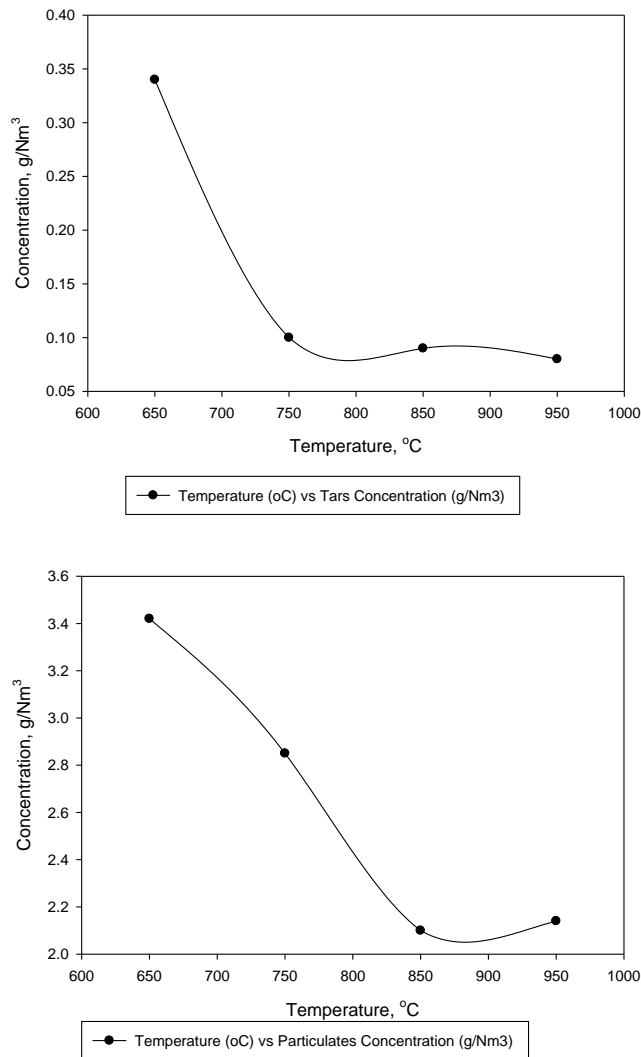


Figure 4.3: Plots Showing the Effect of Temperature on Dolomite Performance

Table 4.11 Summary of Tars and Particulates after Proprietary Catalyst

Temperature, °C	Tars concentration g/m <sup>3</sup>	Particulates concentration, g/m <sup>3</sup>
600	0.08	1.96
500	0.09	2.00
250	0.09	2.07

Table 4.12 Tars and Particulates after Proprietary Catalyst and Bag-Filter

Temperature, °C	Tars concentration, g/m <sup>3</sup>	Particulates concentration, g/m <sup>3</sup>
250	0.08	0.07
250	0.06	0.06
250	0.06	0.07

## **CHAPTER 5: OVERALL CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH**

### **5.1 Overall Conclusions**

Gasification of woodchips and pine pellets at atmospheric pressure showed that it was possible to produce a combustible gas from a downdraft gasifier. The syngas composition and an estimation of the resulting heating value were presented in Chapter 4. Tars and particulates analysis and control were experimentally tested with dolomite, Albermale proprietary catalysts, and bag-filter. The dolomite was treated to varying temperatures of 650°C, 750°C, 850°C, and 950°C. The proprietary catalyst was treated to 600°C, 500°C, and 250°C. The following conclusions can be drawn from this research.

- A protocol for characterizing the tar and particulates generated from a biomass gasification process was designed from existing EPA procedure (EPA Method 5).
- The tars and particulates concentration in the raw gas analysis for woodchips was found to be quite inconsistent and did vary appreciably. A reason for this might be due to different temperature profiles observed during different test runs. However, gasification of pine pellets did produce a more consistent set of data.
- Dolomite and the Albermale proprietary catalysts had significant effect on the presence of tars in the syngas produced from gasification.
- Experimental results showed an even distribution of tars and particulates concentration for the different runs in the post-cleaning analysis of the syngas produced from both woodchips and pine pellets.
- The temperature of the catalyst bed was a factor in the performance of the dolomite. As temperatures increased from 650°C, there was a visible increase in the effectiveness of the catalyst as a tar removal technique.

- The Albermale proprietary catalyst used did not show any difference in its ability to reduce the tars concentration between 600°C and 250°C.
- Gas cleaning and conditioning using a combination of the proprietary catalyst and the bag-filter showed a significant reduction in the level of tars and particulates to within acceptable limits for use in an IC engine.

## **5.2 Suggestions for Future Research**

The experiments conducted in this research were to characterize the tar and particulate using gravimetric analysis. More work needs to be done in understanding the chemistry of the tar generated. It would also be desirable to investigate the particulate size distribution.

The biomass feedstock was manually loaded into the gasifier which made the whole process quite tedious. It is recommended that the feeding system should be automated to ensure easy loading of feedstock during the gasifier operation. The energy conversion efficiency of the gasifier was lower than expected and therefore, performance evaluation and modification of the gasifier need to be carried. Data collection conditions and measurement accuracy should be improved, such as by using a more sensitive gas chromatograph (GC) for analyzing the syngas composition, especially for more accurate hydrogen gas determination. It would also be of interest to determine the water vapor content in the syngas.

In the research described in this thesis, the amounts of dolomite used in all the test runs were kept constant. Further work needs to be done to study the effect of space velocity on the cleaning efficiency of the dolomite and proprietary catalysts. Finally, more species of biomass should be tested to evaluate the performance of the gasifier design and the characterization of tar and particulate impurities.

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## APPENDIX A BIOMASS USED IN GASIFICATION PROJECT



**Photo A1: Cypress Mulch Woodchips**



**Photo A2: Pine Pellets**

## APPENDIX B COLLECTED TAR AND PARTICULATE



**Photo B1: Filter Assembly showing filter paper with collected particulates after syngas sampling**



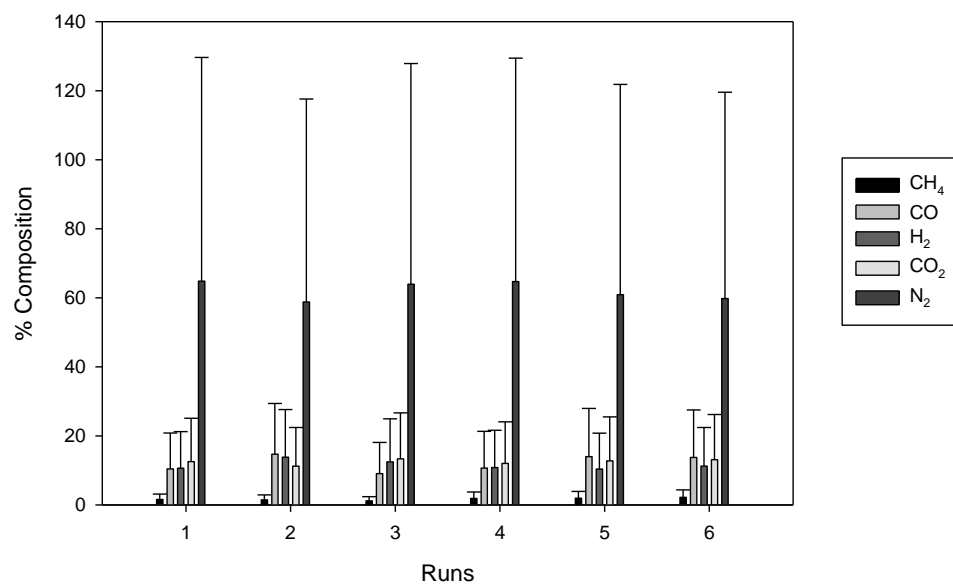
**Photo B2: Aluminum pan with tar collected after evaporation of acetone**

## APPENDIX C GAS FLARE

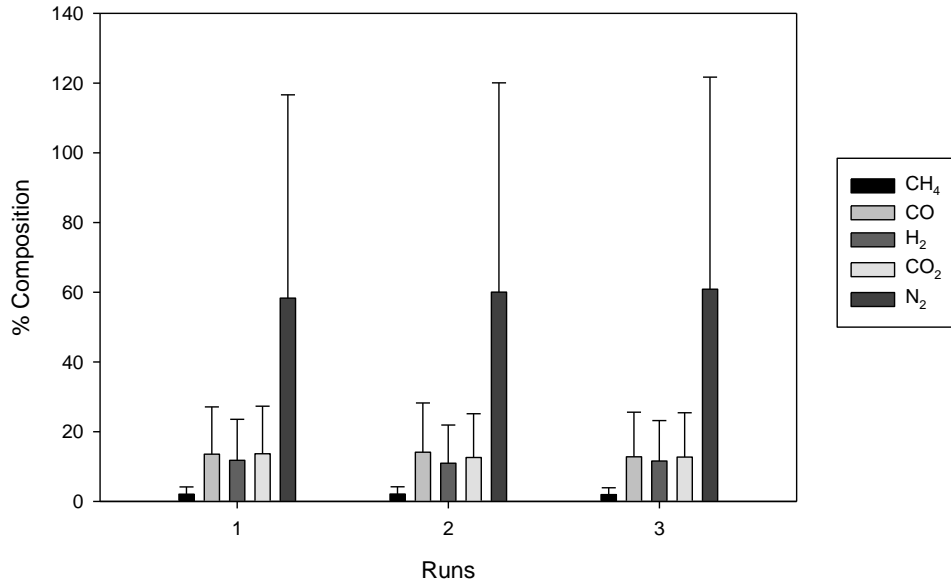


**Photo C: Syngas being flared during gasification.**

## APPENDIX D GAS COMPOSITION FROM WOODCHIPS GASIFICATION



# APPENDIX E GAS COMPOSITION FROM GASIFICATION OF PINE PELLETS



## APPENDIX F STATISTICAL INFORMATION

SAS Output Report

Randomize complete design (one-way anova)

Effect of dolomite on tars and particulates from woodchips

Treatment appears as 0 for “no treatment” and 1 for “treatment” throughout.

List of data

Obs	tars	particulates	trt
1	2.12	4.35	0
2	1.45	2.51	0
3	2.23	5.30	0
4	1.45	4.88	0
5	1.52	3.25	0
6	1.02	2.76	0
7	0.19	1.97	1
8	0.17	2.33	1
9	0.20	2.50	1

The ANOVA Procedure

Class Level Information

Class	Levels	Values
trt	2	0 1

Number of Observations Read 9

Number of Observations Used 9

The ANOVA Procedure

Dependent Variable: tars

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	4.17605000	4.17605000	27.85	0.0012
Error	7	1.04955000	0.14993571		
Corrected Total	8	5.22560000			

R-Square	Coeff Var	Root MSE	tars Mean
0.799152	33.67090	0.387215	1.150000

Source	DF	Anova SS	Mean Square	F Value	Pr > F
trt	1	4.17605000	4.17605000	27.85	0.0012

The ANOVA Procedure

Class Level Information

Class	Levels	Values
trt	2	0 1

Number of Observations Read 9

Number of Observations Used 9

The ANOVA Procedure

Dependent Variable: particulates

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	4.96125000	4.96125000	5.03	0.0598
Error	7	6.90315000	0.98616429		
Corrected Total	8	11.86440000			

R-Square	Coeff Var	Root MSE	particulates Mean
0.418163	29.94145	0.993058	3.316667

Source	DF	Anova SS	Mean Square	F Value	Pr > F
trt	1	4.96125000	4.96125000	5.03	0.0598

The REG Procedure

Model: MODEL1

Dependent Variable: tars

Number of Observations Read 9

Number of Observations Used 9

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	4.17605	4.17605	27.85	0.0012
Error	7	1.04955	0.14994		
Corrected Total	8	5.22560			
Root MSE	0.38722	R-Square	0.7992		
Dependent Mean	1.15000	Adj R-Sq	0.7705		
Coeff Var	33.67090				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	1.63167	0.15808	10.32	<.0001
trt	1	-1.44500	0.27380	-5.28	0.0012

The REG Procedure

Model: MODEL1

Dependent Variable: particulates

Number of Observations Read 9

Number of Observations Used 9

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	4.96125	4.96125	5.03	0.0598
Error	7	6.90315	0.98616		
Corrected Total	8	11.86440			
Root MSE	0.99306	R-Square	0.4182		
Dependent Mean	3.31667	Adj R-Sq	0.3350		
Coeff Var	29.94145				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	3.84167	0.40541	9.48	<.0001
trt	1	-1.57500	0.70220	-2.24	0.0598

## The Mixed Procedure

### Model Information

Data Set WORK.GASIFICATION  
Dependent Variable tars  
Covariance Structure Diagonal  
Estimation Method REML  
Residual Variance Method Profile  
Fixed Effects SE Method Model-Based  
Degrees of Freedom Method Residual

### Class Level Information

Class	Levels	Values
trt	2	0 1

### Dimensions

Covariance Parameters	1
Columns in X	3
Columns in Z	0
Subjects	1
Max Obs Per Subject	9
Number of Observations	
Number of Observations Read	9
Number of Observations Used	9
Number of Observations Not Used	0

### Covariance Parameter

#### Estimates

Cov Parm	Estimate
Residual	0.1499

#### Fit Statistics

-2 Res Log Likelihood	9.5
AIC (smaller is better)	11.5
AICC (smaller is better)	12.3
BIC (smaller is better)	11.4

## The Mixed Procedure

### Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
trt	1	7	27.85	0.0012

## The Mixed Procedure

### Model Information

Data Set WORK.GASIFICATION  
Dependent Variable particulates  
Covariance Structure Diagonal  
Estimation Method REML  
Residual Variance Method Profile

Fixed Effects SE Method    Model-Based  
Degrees of Freedom Method    Residual

#### Class Level Information

Class	Levels	Values
trt	2	0 1

#### Dimensions

Covariance Parameters	1
Columns in X	3
Columns in Z	0
Subjects	1
Max Obs Per Subject	9
Number of Observations	
Number of Observations Read	9
Number of Observations Used	9
Number of Observations Not Used	0

#### Covariance Parameter

#### Estimates

Cov Parm	Estimate
Residual	0.9862

#### Fit Statistics

-2 Res Log Likelihood	22.7
AIC (smaller is better)	24.7
AICC (smaller is better)	25.5
BIC (smaller is better)	24.6

#### The Mixed Procedure

#### Type 3 Tests of Fixed Effects

Effect	Num		Den	
	DF	DF	F Value	Pr > F
trt	1	7	5.03	0.0598

SAS Output Report  
Randomize complete design (one-way anova)  
Effect of dolomite on tars and particulates from pine pellets

List of data

Obs	tars	particulates	trt
1	0.97	4.78	0
2	0.91	4.79	0
3	0.67	4.67	0
4	0.12	2.09	1
5	0.07	2.08	1
6	0.09	1.86	1

The ANOVA Procedure

Class Level Information

Class	Levels	Values
trt	2	0 1

Number of Observations Read 6

Number of Observations Used 6

The ANOVA Procedure

Dependent Variable: tars

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.85881667	0.85881667	66.49	0.0012
Error	4	0.05166667	0.01291667		
Corrected Total	5	0.91048333			
R-Square	Coeff Var	Root MSE	tars Mean		
0.943254	24.09573	0.113652	0.471667		

Source	DF	Anova SS	Mean Square	F Value	Pr > F
trt	1	0.85881667	0.85881667	66.49	0.0012

The ANOVA Procedure

Class Level Information

Class	Levels	Values
trt	2	0 1

Number of Observations Read 6

Number of Observations Used 6

The ANOVA Procedure

Dependent Variable: particulates

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	11.23401667	11.23401667	1053.19	<.0001
Error	4	0.04266667	0.01066667		
Corrected Total	5	11.27668333			
R-Square	Coeff Var	Root MSE	particulates Mean		
0.996216	3.057116	0.103280	3.378333		

Source	DF	Anova SS	Mean Square	F Value	Pr > F
trt	1	11.23401667	11.23401667	1053.19	<.0001

The REG Procedure

Model: MODEL1

Dependent Variable: tars

Number of Observations Read 6

Number of Observations Used 6

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.85882	0.85882	66.49	0.0012
Error	4	0.05167	0.01292		
Corrected Total	5	0.91048			
Root MSE		0.11365	R-Square	0.9433	
Dependent Mean		0.47167	Adj R-Sq	0.9291	
Coeff Var		24.09573			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	0.85000	0.06562	12.95	0.0002
trt	1	-0.75667	0.09280	-8.15	0.0012

The REG Procedure

Model: MODEL1

Dependent Variable: particulates

Number of Observations Read 6

Number of Observations Used 6

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	11.23402	11.23402	1053.19	<.0001
Error	4	0.04267	0.01067		
Corrected Total	5	11.27668			
Root MSE		0.10328	R-Square	0.9962	
Dependent Mean		3.37833	Adj R-Sq	0.9953	
Coeff Var		3.05712			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	4.74667	0.05963	79.60	<.0001
trt	1	-2.73667	0.08433	-32.45	<.0001

The Mixed Procedure

Model Information

Data Set WORK.GASIFICATION  
Dependent Variable tars  
Covariance Structure Diagonal  
Estimation Method REML  
Residual Variance Method Profile  
Fixed Effects SE Method Model-Based  
Degrees of Freedom Method Residual  
Class Level Information  
Class Levels Values  
trt 2 0 1

Dimensions

Covariance Parameters 1  
Columns in X 3  
Columns in Z 0  
Subjects 1  
Max Obs Per Subject 6  
Number of Observations  
Number of Observations Read 6  
Number of Observations Used 6  
Number of Observations Not Used 0

Covariance Parameter

Estimates

Cov Parm Estimate  
Residual 0.01292

Fit Statistics

-2 Res Log Likelihood -3.8  
AIC (smaller is better) -1.8  
AICC (smaller is better) 0.2  
BIC (smaller is better) -2.5

The Mixed Procedure

Type 3 Tests of Fixed Effects

	Num	Den		
Effect	DF	DF	F Value	Pr > F
trt	1	4	66.49	0.0012

The Mixed Procedure

Model Information

Data Set WORK.GASIFICATION  
Dependent Variable particulates  
Covariance Structure Diagonal  
Estimation Method REML

Residual Variance Method Profile  
 Fixed Effects SE Method Model-Based  
 Degrees of Freedom Method Residual  
 Class Level Information  
 Class Levels Values  
 trt 2 0 1

Dimensions  
 Covariance Parameters 1  
 Columns in X 3  
 Columns in Z 0  
 Subjects 1  
 Max Obs Per Subject 6  
 Number of Observations  
 Number of Observations Read 6  
 Number of Observations Used 6  
 Number of Observations Not Used 0

Covariance Parameter

Estimates

Cov Parm Estimate

Residual 0.01067

Fit Statistics

-2 Res Log Likelihood -4.6

AIC (smaller is better) -2.6

AICC (smaller is better) -0.6

BIC (smaller is better) -3.2

The Mixed Procedure

Type 3 Tests of Fixed Effects

Effect	DF	DF	F Value	Pr > F
trt	1	4	1053.19	<.0001

SAS Output Report

Randomize complete design (one-way anova)

Effect of Proprietary catalyst + bagfilter on tars and particulates from pine pellets

List of data

Obs	tars	particulates	trt
1	0.97	4.78	0
2	0.91	4.79	0
3	0.67	4.67	0
4	0.08	0.07	1
5	0.06	0.06	1
6	0.06	0.07	1

The ANOVA Procedure

Class Level Information

Class	Levels	Values	
trt	2	0 1	
Number of Observations Read			6
Number of Observations Used			6

The ANOVA Procedure

Dependent Variable: tars

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.92041667	0.92041667	72.66	0.0010
Error	4	0.05066667	0.01266667		
Corrected Total	5	0.97108333			
R-Square	Coeff Var	Root MSE	tars Mean		
0.947825	24.55555	0.112546	0.458333		
Source	DF	Anova SS	Mean Square	F Value	Pr > F
trt	1	0.92041667	0.92041667	72.66	0.0010

The ANOVA Procedure

Class Level Information

Class	Levels	Values	
trt	2	0 1	
Number of Observations Read			6
Number of Observations Used			6

The ANOVA Procedure

Dependent Variable: particulates

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	32.85360000	32.85360000	14710.6	<.0001
Error	4	0.00893333	0.00223333		
Corrected Total	5	32.86253333			
R-Square	Coeff Var	Root MSE	particulates Mean		
0.999728	1.963635	0.047258	2.406667		
Source	DF	Anova SS	Mean Square	F Value	Pr > F
trt	1	32.85360000	32.85360000	14710.6	<.0001

REG Procedure

Model: MODEL1

Dependent Variable: tars

Number of Observations Read 6

Number of Observations Used 6

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.92042	0.92042	72.66	0.0010
Error	4	0.05067	0.01267		
Corrected Total	5	0.97108			
Root MSE	0.11255	R-Square	0.9478		
Dependent Mean	0.45833	Adj R-Sq	0.9348		
Coeff Var	24.55555				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	0.85000	0.06498	13.08	0.0002
trt	1	-0.78333	0.09189	-8.52	0.0010

The REG Procedure

Model: MODEL1

Dependent Variable: particulates

Number of Observations Read 6

Number of Observations Used 6

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	32.85360	32.85360	14710.6	<.0001
Error	4	0.00893	0.00223		
Corrected Total	5	32.86253			
Root MSE	0.04726	R-Square	0.9997		
Dependent Mean	2.40667	Adj R-Sq	0.9997		
Coeff Var	1.96364				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	4.74667	0.02728	173.97	<.0001
trt	1	-4.68000	0.03859	-121.29	<.0001

## The Mixed Procedure

### Model Information

Data Set WORK.GASIFICATION  
Dependent Variable tars  
Covariance Structure Diagonal  
Estimation Method REML  
Residual Variance Method Profile  
Fixed Effects SE Method Model-Based  
Degrees of Freedom Method Residual  
Class Level Information  
Class Levels Values  
trt 2 0 1

### Dimensions

Covariance Parameters 1  
Columns in X 3  
Columns in Z 0  
Subjects 1  
Max Obs Per Subject 6  
Number of Observations  
Number of Observations Read 6  
Number of Observations Used 6  
Number of Observations Not Used 0

### Covariance Parameter

#### Estimates

Cov Parm Estimate  
Residual 0.01267

#### Fit Statistics

-2 Res Log Likelihood -3.9  
AIC (smaller is better) -1.9  
AICC (smaller is better) 0.1  
BIC (smaller is better) -2.5

### The Mixed Procedure

#### Type 3 Tests of Fixed Effects

	Num	Den		
Effect	DF	DF	F Value	Pr > F
trt	1	4	72.66	0.0010

## The Mixed Procedure

### Model Information

Data Set WORK.GASIFICATION  
Dependent Variable particulates  
Covariance Structure Diagonal  
Estimation Method REML

Residual Variance Method Profile  
Fixed Effects SE Method Model-Based  
Degrees of Freedom Method Residual

Class Level Information

Class	Levels	Values		
trt	2	0 1		

Dimensions

Covariance Parameters	1		
Columns in X	3		
Columns in Z	0		
Subjects	1		
Max Obs Per Subject	6		
Number of Observations			
Number of Observations Read	6		
Number of Observations Used	6		
Number of Observations Not Used	0		

Covariance Parameter

Estimates

Cov Parm	Estimate
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Residual	0.002233
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Fit Statistics

-2 Res Log Likelihood	-10.9
AIC (smaller is better)	-8.9
AICC (smaller is better)	-6.9
BIC (smaller is better)	-9.5

The Mixed Procedure

Type 3 Tests of Fixed Effects

	Num	Den		
Effect	DF	DF	F Value	Pr > F
trt	1	4	14710.6	<.0001

## **VITA**

Christopher Osita Akudo obtained his Bachelor of Science in Agricultural Engineering degree from the Federal University of Technology at Minna, Nigeria, in 2003. He plans to receive his Master of Science in Biological Engineering degree at the spring 2008 commencement while continuing with his doctoral program in civil and environmental engineering.