# UTILIZATION OF ARECANUT (Areca catechu) HUSK FOR GASIFICATION

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#### ABSTRACT

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### UTILIZATION OF ARECANUT (Areca catechu) HUSK FOR GASIFICATION

Gasification of areca husk was studied in this research. The husk is an agricultural by-product of Arecanut (*Areca catechu*) that could be a potential energy source for the processing of the nut. The problem of slagging during arecanut gasification was investigated using a throat-less, lab-scale downdraft gasifier. The effect of air flow rates from 0.001 to 0.006 m<sup>3</sup>/s on slag formation was studied. With increase of air flow rate, the clinker formation was found to increase ( $r^2 = 0.7191$ ). Subsequent studies consisted of washing the husk to remove external contaminants picked up during sun drying of the husk on ground. Husk samples were washed using water and were gasified to study the slag formation. Statistical analysis of clinker formation between washed and unwashed samples showed that the variation was significant. Ash and clinkers constituents were analyzed and their composition showed typical elements and oxides enhancing deposition problems. The alkali index calculated from ash composition indicates that slagging is practically certain to occur during thermochemical conversions of areca husk.

# RÉSUMÉ

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# LA GAZÉIFICATION DE L'ENVELOPPE FIBREUSE DU FRUIT Areca catechu.

La gazéification de l'enveloppe fibreuse du fruit Areca catechu est étudiée dans cette recherche. Cette enveloppe fibreuse est un sous-produit agricole qui pourrait potentiellement être utilisé comme source d'énergie pour la transformation même du fruit areca. Le problème de formation de scories lors de la gazéification fut étudié à l'aide d'un gazogène à échelle laboratoire sans rétrécissement au niveau de la zone de combustion. L'effet de la variation du débit d'air de l'ordre de 0.001 à 0.006 m<sup>3</sup>/s sur la formation de scories fut étudié. La formation de scories augmenta au fur et à mesure que le débit d'air fut augmenté ( $r^2 = 0.7191$ ). Des études subséquentes consistèrent à laver l'enveloppe du fruit pour en retirer les contaminants minéraux obtenus lors du séchage au soleil par étalement sur le sol. Les échantillons d'enveloppes fibreuses furent lavés à l'eau et gazéifiés afin d'en étudier la formation de scories. Une analyse statistique de la formation de scories entre les échantillons lavés et non-lavés démontra une variation significative. La composition des cendres et scories fut analysée et les résultats montrèrent des éléments et composés typiques favorisant les problèmes de déposition. L'indice d'alcalinité fut évalué à partir de la composition des cendres et le résultat confirme la prédisposition des cendres à occasionner la scorification et autres dépositions lors de conversions thermochimiques de l'enveloppe fibreuse de l'Areca catechu.

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ABSTRACT	ii
RÉSUMÉ	iii
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
1. INTRODUCTION	1
1.1. Gasification	2
1.2. Arecanut Husk	2
2. HYPOTHESES AND OBJECTIVES	
2.1. Hypotheses	4
2.2. Objectives	4
3. LITERATURE REVIEW	5
3.1. Gasification	5
3.1.1. Process Reactions	5
3.1.2. Type of Gasification	
3.1.3. Categories of Gasifiers	9
3.1.4. Factors affecting Gasification	
3.1.5. Gasifier Thermodynamics	
3.2. Ash	14
3.2.1. Ash in Feedstock and its Implications	14
3.2.2. Ash Analysis	
3.2.3. Ash in Biomass	
3.2.4. Ash Melting	16
3.2.5. Methods to Reduce Ash Melting Problems	
3.2.6. Prediction of Ash Melting Behaviour	
3.3. Arecanut Production	
4. MATERIAL AND METHODS	
4.1. Experimental Setup	
4.2. Instrumentation and Control	32

# **TABLE OF CONTENTS**

4.	3. Fee	dstock Material	32
4.	4. Ope	erating the Gasifier	33
	4.4.1.	Reactor Design	33
	4.4.2.	Operational Procedure	35
4.	5. Gas	ification Experiments	36
	4.5.1.	Feedstock Trials	36
	4.5.2.	Gasification at Various Air Flow Rates	36
4.	6. Wa	shing of Areca Husk for Reduction of Ash Content	37
	4.6.1.	Washing Treatment Setup	37
	4.6.2.	Washing Treatment Methodology	37
	4.6.3.	Gasification Test Setup of Washed and Unwashed Feedstock	38
4.	7. Ash	and Clinker Analyses	38
4.	8. Stat	istical Methodology	39
5.	RESUL	IS AND DISCUSSION	40
5.	1. Gas	ification of Areca Husk	40
	5.1.1.	Gasification Experiments	40
5.	2. Effe	ect of Air Flow Rate on Gasification of Arecanut husk	43
	5.2.1.	Clinker Formation	43
	5.2.2.	Equivalence Ratio	53
	5.2.3.	Gasifier Verification	61
5.	3. Wa	shing Treatment	62
	5.3.1.	Clinker Reduction	62
	5.3.2.	Ash Melting Behaviour	63
	5.3.3.	Effect of Washing on Ash Melting Behaviour	66
	5.3.4.	Alkali Index (AI)	66
	5.3.5.	Ash Melting Test	67
	5.3.6.	Ash Preparation	73
5	4. Sur	nmary	74
6.	CONCL	USION	76
REF	ERENCE	ES	78
APP	ENDIX.		82

# LIST OF TABLES

Table 3.1:	Energy content of the producer gases obtained from different types of gasification (Reed, 1981)9
Table 3.2:	Melting temperatures of compounds potentially responsible for low- temperature melting behaviour in biomass feeds
Table 3.3:	Maximum air velocity operation conditions within the inverted downdraft gasifier before occurrence of slag formation (Dasappa <i>et al.</i> , 2003)
Table 3.4:	Properties of common biomass utilized for gasification
Table 5.1:	Results for areca husk gasification at different air flow rate input41
Table 5.2:	Results for wood ( <i>Casuarina equisetifolia</i> ) gasification at different air flow rate input
Table 5.3:	Total amount of residues obtained during gasification of areca husk at various air flow rates
Table 5.4:	Gasification parameters obtained for areca husk and wood during tests at various air flow rates. (E.R.: equivalence ratio)
Table 5.5:	Producer gas ignition at varying air flow rates
Table 5.6:	Air speed in the reactor created by gasifier configuration
Table 5.7:	Residues obtained from gasification of washed and unwashed areca husk
Table 5.8:	Chemical composition of ash and clinker from areca husk
Table 5.9:	SO <sub>x</sub> content in producer gases obtained during gasification of washed and unwashed areca husk 66

# LIST OF FIGURES

Figure 3.1:	Updraft and downdraft gasifiers – Air flow paths and reaction zones (Goswami, 1986)
Figure 3.2:	Main types of gasifier reactors11
Figure 3.3:	Example of K <sub>2</sub> O-CaO-SiO <sub>2</sub> phase diagram used for ash melting prediction of reed-canary-grass (Paulrud <i>et al.</i> , 2001)
Figure 4.1:	Schematic diagram of the lab-scale downdraft gasifier and its dimensions
Figure 4.2:	Schematic representation of experimental setup for gasification experiments
Figure 4.3:	Photograph of the assembled experimental setup for gasification experiments
Figure 4.4:	Gas analyzers, temperature indicator and air flow meter used in the studies
Figure 4.5:	(a) Areca and (b) wood samples used as feedstock for gasification experiments
Figure 4.6:	Dismantled gasifier
Figure 4.7:	Schematic representation of lab-scale gasifier functioning during the gasification experiments
Figure 4.8:	Setup utilized to wash arecanut husk
Figure 5.1:	Slag created during areca husk gasification using lab-scale gasifier.42
Figure 5.2:	Clinker formation and rock residues during gasification of areca husk at different air flow rates
Figure 5.3:	Maximum and average temperatures observed in the gasifier zones during gasification of areca husk
Figure 5.4:	Residues obtained from gasification of areca husk at various input air flow rates
Figure 5.5:	Temperatures observed in oxidation zone of downdraft gasifier during tests with areca husk47

Figure 5.6:	Temperatures in reduction zone of downdraft gasifier during tests with areca husk
Figure 5.7:	Temperatures at the burner zone of downdraft gasifier during tests with areca husk
Figure 5.8:	Percent CO composition in producer gases obtained by gasification of areca husk
Figure 5.9:	Percent CO <sub>2</sub> composition in producer gases obtained by gasification of areca husk
Figure 5.10:	Percent O <sub>2</sub> composition in producer gases obtained by gasification of areca husk
Figure 5.11:	Biomass consumption rate of areca husk and wood ( <i>Casuarina equisetifolia</i> ) during gasification at varying air flow rates
Figure 5.12:	Maximum and average temperatures in the gasifier during tests with wood ( <i>Casuarina equisetifolia</i> ) feedstock
Figure 5.13:	Temperatures in oxidation zone of gasifier during tests with wood ( <i>Casuarina equisetifolia</i> ) feedstock
Figure 5.14:	Temperatures in the reduction zone of gasifier during tests with wood ( <i>Casuarina equisetifolia</i> ) feedstock
Figure 5.15:	Temperatures in the burner zone of gasifier during tests with wood ( <i>Casuarina equisetifolia</i> ) feedstock
Figure 5.16:	Average producer gas composition during gasification of wood ( <i>Casuarina equisetifolia</i> )
Figure 5.17:	<ul><li>(a) Water used for washing treatment for areca husk.</li><li>(b) Mineral material that remained after washing husk</li></ul>
Figure 5.18:	Comparison of average temperature during gasification of washed and unwashed areca husk
Figure 5.19:	Comparison of average temperature during gasification of washed and unwashed areca husk
Figure 5.20:	Schematic representation of ash cone and stainless steel tray utilized for ash fusion test

Figure 5.21:	(a-b) Washed areca husk ash cones exposed to increasing temperatures in laboratory muffle furnace; Progression 525 – 1170 °C
Figure 5.22:	(a-b) Unwashed areca husk ash cones exposed to increasing temperatures in laboratory muffle furnace; Progression 525 – 1170 °C
Figure 5.23:	<ul><li>(a) Manually operated blower utilized for areca husk ash preparation (b) Open perforated cylinder used for ash preparation by natural draft</li></ul>
Figure 5.24:	Ash obtained from the two techniques of ash preparation

### 1. INTRODUCTION

Climate change (commonly referred to as global warming) is now considered as unequivocal and "very likely" caused by human activities, as declared at the Conference on Climate Change in Paris (February 3, 2007). The petroleum resources, despite plenty in few parts of the world, will sooner or later become depleted. Our increasing population and energy driven societies will necessarily have to adopt sustainable solutions to meet these challenges. In an attempt to supply part of our energy needs, the use of biomass (agricultural and forestry residues, dedicated crops and municipal solid wastes) appears as a possible solution. Plant biomass utilized as fuel has the advantage of being neutral in terms of carbon emission. During their growth, plants sequester as much  $CO_2$  that they produce during their transformation for energy production. Some studies estimate that world biomass potential could contribute from 100 EJ to more than 400 EJ of annual energy production by the year 2050 representing a minimum of 20% of the actual world energy consumption (Berndes *et al.*, 2003). In Canada, 6% of energy is currently produced from wood biomass and plant residues (NRCan, 2002; Islam *et al.*, 2004).

Energy scarcity is a major problem in developing countries. In India, a survey (The Hindu, 2005) showed that in 2001, 56% of households did not have access to electricity. Most of these regions are rural based and the agricultural activity generates large amounts of residue biomass and by-products. Agri-processing, representing a means for development, also requires energy; therefore, an efficient use of these residues might contribute significantly in such ventures.

Traditionally, many agricultural residues and by-products are used in processing operations by combustion, which is the simplest and direct form of converting the chemical energy in biomass to usable energy. Wood saw dust in wood processing or bagasse in sugarcane processing are classical examples. However, the efficiency of conversion and the convenience of energy utilization limit the system. Thermochemical conversion comprises combustion process, however other routes for biomass to energy are also available. Gasification is a potential route that may offer better efficiency and flexibility.

1

## 1.1. Gasification

Gasification is the thermochemical breakdown of carbon-containing constituents of biomass to yield a gaseous fuel (termed producer gas or syngas). The technology was developed during early 1800s, but energy crisis (such as the world wars) enhanced the development and refining in this field. During such times, coal and wood were the commonly used fuels in these efforts.

Compared to combustion which requires minimal stoichiometric oxygen input, gasification occurs at partial oxidation conditions (Bridgwater, 1995). Gasification is considered as a clean burning process with homogeneous heating, easy to control and allowing good recovery of heat (Sampathrajan, 2002). The resulting producer gases have the advantage of being easy to handle (Venkatachalam, 2002). The entire gasification process is made up of various chemical and physical processes such as drying, pyrolysis and partial oxidation, reduction and condensation (Bridgwater, 1995; Cetin *et al.*, 2005; Souza-Santos, 2004; Klass, 1998). Some of the processes have been described and modelled. However, gasification still requires significant research and refinement to suit higher energy demands and utilize available biomass.

# 1.2. Arecanut Husk

In India, areca (betel nut, *Areca catechu*) husk is a biomass widely available, especially in the southern part of the country. Arecanut is the kernel obtained from the fruit of the *areca* palm tree and over 0.38 million tonnes of the fruit is harvested annually in India. The nut is of commercial importance and is processed by boiling. The husk of the fruit is removed and it has no other traditional use. Left in piles to dry, it is often a nuisance to the producer/processor. The husk is fibrous (hard and soft fibres) and is predominantly composed of cellulose with varying proportions of hemicellulose, lignin, pectin and protopectin.

The arecanut industry provides a good opportunity for utilization of biomassbased gasifiers. The husk could be potentially utilized as a fuel in gasification and the resulting gases could be used for processing of the nut. Only one such known attempt was made (Angeeswaran, 2002) and the results showed that the initiative was feasible. The study used natural draft and the design of the equipment was not easily adaptable for field operations. For commercial adoption and heating applications, forced, down-draft gasifiers are commonly used. In this research work, tests were done to advance the understanding of arecanut husk gasification and trials were conducted using a fixed bed, lab-scale down-draft gasifier reactor.

# 2. HYPOTHESES AND OBJECTIVES

# 2.1. Hypotheses

The overall theory relies on gasifying arecanut (*Areca catechu*) husk using downdraft gasifier. The only known attempt of arecanut gasification was made by (Angeeswaran, 2002) using a natural-updraft gasifier. Based on advantages of downdraft gasifier over natural-updraft gasifier the first hypothesis was developed:

• It is be possible to gasify arecanut husk using downdraft gasifier.

The results of arecanut husk conversion using downdraft gasifier showed that the husk produced a gas that burned continuously with a stable flame; however its transformation resulted in substantial clinker (slag) formation at the grate. Based on this observation the second hypothesis was developed:

• The airflow rate has an effect on the extent slagging.

The observation that arecanut contained high amounts of sand and contaminants due to sun drying husk on the ground lead to the third hypothesis:

• Washing the husk with water would result in reduction of clinker formation.

# 2.2. Objectives

The following objectives were set to validate the hypotheses in the study:

- 1) To gasify arecanut husk.
- 2) To study the effect of airflow rate.
- 3) To study the effect of a washing pre-treatment for husk.
- 4) To study the composition and fate of mineral constituents during gasification.

#### **3. LITERATURE REVIEW**

#### 3.1. Gasification

Gasification is a thermochemical process in which partial oxidation of organic matter at high temperatures results in a mixture of products, mainly consisting of a gaseous fuel that can be utilized for energy-dependant applications. The gas generated is more usable than the organic feedstock material (used for the gasification process) for generation of heat and power (Priyadarsan *et al.*, 2004). Various oxidizing agents can be utilized for gasification; air, oxygen, steam or a mixture of these gases. For economical reasons, air remains the most commonly utilized oxidizing agent.

The producer gases released from gasification generally contain CO (18-20%), H<sub>2</sub> (18-20%), CH<sub>4</sub> (1-2%), H<sub>2</sub>O (11-12%) and N<sub>2</sub>. With excess air, combustion produces CO<sub>2</sub> and H<sub>2</sub>O, but in sub-stoichiometric conditions, products such as CO and H<sub>2</sub> can be enhanced (Quaak *et al.*, 1998). Gasification of biomass can generate gases with calorific value in the order of 3.9 to 11.8 MJ/m<sup>3</sup> using air, and from 11.8 to 27.5 MJ/m<sup>3</sup> with the use of oxygen. With a greater degree of control leading to higher production of methane and other light hydrocarbons, the value can reach 27.5 to 39.3 MJ/m<sup>3</sup>. The values mentioned for air and oxygen-induced gasification correspond to approximately 20-50% the energy content of natural gases and biogas on volume basis (Reed and Das, 1988).

#### 3.1.1. Process Reactions

In conventional gasifier types such as downdraft, updraft and cross draft, gasification processes occur over four main zones. The chemical reactions happening in these zones must be controlled in order to obtain maximum efficiency of producer gases (Goswami, 1986). These zones are the drying, pyrolysis, oxidation (combustion) and reduction zones (Figure 3.1).

# 3.1.1.1. Drying Zone

Water is removed from the feedstock in the drying zone. During the drying process, the mass transfer from the feedstock to the surrounding depends on: the feedstock temperature, the rate of heat transfer from the surrounding to the biomass and

the relative humidity of the surrounding gas layer. It was observed that the ions present in the surrounding gas layer will affect the partial pressure and water concentrations around the feedstock (Souza-Santos, 2004). At atmospheric pressure, drying is considered to occur at a wide range of temperatures - from ambient (Souza-Santos, 2004) up to 200 °C (Goswami, 1986).

# 3.1.1.2. Pyrolysis Zone

Also known as devolatilization or carbonaceous solid-utilization, pyrolysis is the process by which a mixture of organic and inorganic gases and vapours are released to the surrounding. These products are hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and tars. Tars are composed of heavy organic and inorganic molecules in the form of gases and liquids such as benzene, toluene, phenol and naphthalene. The remaining solid products from pyrolysis are chars made of carbon (Souza-Santos, 2004).

Pyrolysis products are affected by the initial carbon structure and composition, pyrolysis temperature, pressure, residence time in the reactor, heat losses, feedstock consumption and heating rate. Generally, the following transformations are found to occur during these temperatures:

- 1. Moisture evaporation 100 °C and higher
- 2. Decomposition of extractives 100-250 °C
- 3. Decomposition of hemicellulose 250-350 °C
- 4. Decomposition of lignin 500 °C

In addition, from 200 to 280 °C, carbon dioxide, acetic acid and water are released, while between 280 and 500 °C, tars, methyl alcohol, and other gases are produced. From 500 to 700 °C, the gas production is low, but may contain H<sub>2</sub> (Goswami, 1986). The devolatilization process as a function of temperature is fairly similar between coal and biomass (Souza-Santos, 2004). Pyrolysis occurs at different heating rates; categorized as slow, moderate, and fast. Ten degrees Kelvin per second refers to the heating rate of slow pyrolysis, while fast pyrolysis occurs generally at rates above  $10^3$  K/s. The type of reactor influences heating rate, as a result pyrolysis is dependent on the design of the reactor. In moving and fixed bed combustion or gasification, moderate and slow pyrolysis may happen. In fluidized beds, heating rates of  $10^2 - 10^4$  K/s are obtained (Souza-Santos, 2004). An increase in pyrolysis pressure results in a reduction of the yield of volatiles, an increase of H/C ratio in volatiles and a decrease of char gasification reactivity (Souza-Santos, 2004; Cetin *et al.*, 2005). Methane is desired for its high calorific value. Methane formation can be enhanced by increasing operating pressure. The atmosphere surrounding the process also affects the volatiles. Pyrolysis is an anaerobic process; however, the enhancement of hydrogen atmosphere increases the volatile yield. The lack of hydrogen leads to pyrolysis products with longer chains with lower mobility (Souza-Santos, 2004).

## 3.1.1.3. Combustion (Oxidation) Zone

If complete combustion takes place, all carbon in fuel is transformed into carbon dioxide and all hydrogen is transformed into water; the theoretical temperature obtained is 1450 °C.

C + 
$$O_2$$
 =  $CO_2$  ( $\Delta H$  = - 393 MJ/kg mole) (3.1)  
2H<sub>2</sub> +  $O_2$  = 2H<sub>2</sub>O ( $\Delta H$  = + 242 MJ/kg mole) (3.2)

#### 3.1.1.4. Reduction Zone

The amount of fuel which has not been combusted passes into the charcoal bed. The processes in the reduction zone are mainly endothermic reactions and hence there is a drop in temperature. The temperature of the reduction zone varies between 600 and 700 °C. The common reactions are (Goswami, 1986; Sampathrajan, 2002):

C+
$$CO_2$$
= $2CO$  $(\Delta H = + 164.9 \text{ MJ/kg mole})$  $(3.3)$ C+ $H_2O$ = $CO + H_2$  $(\Delta H = + 122.6 \text{ MJ/kg mole})$  $(3.4)$ CO+ $H_2O$ = $CO_2 + H_2$  $(\Delta H = -42 \text{ MJ/kg mole})$  $(3.5)$ C+ $2H_2$ = $CH_4$  $(\Delta H = -75 \text{ MJ/kg mole})$  $(3.6)$  $CO_2$ + $H_2$ = $CO + H_2O$  $(\Delta H = +42.3 \text{ MJ/kg mole})$  $(3.7)$ 



Figure 3.1: Updraft and downdraft gasifiers – Air flow paths and reaction zones (Goswami 1986).

# 3.1.2. Type of Gasification

Conversion of biomass into gases containing the highest energy content possible is the major challenge with gasification. The thermochemical conversion from biomass to gases can be realized in few ways: air gasification, oxygen gasification, hydrogasification, pyrolytic gasification, and by the new prospect of biomass gasification in near and super-critical water (Matsumura *et al.*, 2005). Air and oxygen gasification are the more common and studied methods.

Air gasification is a simple type often used with updraft, downdraft and fluidized bed gasification systems. Air gasifiers, in addition to having a simple configuration are affordable and reliable. The process is most efficient at an equivalence ratio (described in a later section) of about 0.25, representing 1.6 g of air flow per gram of biomass. However, the gas generated with air gasification has low energy content (Table 3.1) which makes it uneconomical for some applications such as pipeline transportation. In addition gases must have proper composition to be used in power engines (Reed, 1981).

gasification (Recu, 1981)			
	Gas	s Ene	ergy
Gasification Type	Content		
	Ν	/JJ/m	3
Air Gasification	5.6	-	7.5
Oxygen Gasification	11.2	-	18.6

Table 3.1: Energy content of the producer gases obtained from different types of gasification (Reed, 1981)

Oxygen gasification can be used with same systems that are designed for air gasification; however, the gases obtained during oxygen gasification have calorific value 2 to 3 times higher. The higher calorific value makes it economical to carry the gases in pipelines unlike the gases obtained from air gasification. In addition, the gases can be used to synthesize methanol, ammonia, gasoline, or methane. The reactions occurring with oxygen gasification have the advantage of occurring faster and requiring lower gas flow. The limitation of oxygen gasification resides in the cost of oxygen compared to air which is free (Reed, 1981).

#### 3.1.3. Categories of Gasifiers

Fixed and moving beds are two different types of gasifier that are sometimes misunderstood. In both cases, air and producer gases pass through the bed upward or downward. Both systems are suitable for small scale applications and have the simplest configuration. Their major difference is with the combustion bed that has a tendency to migrate inside the reactor or not; as a result, the name fixed or moving bed is given. It is important to specify that the moving bed does not refer to fluidized bed; in both cases fixed and moving bed operate at a superficial velocity varying from 0 to the minimum fluidization velocity (in case of upward gas inlet). Fixed and moving bed gasifiers are often utilized for drying, extraction, boiling and calcinations (Reed, 1981). Among the fixed and moving bed gasifiers, the three most popular and studied types are the updraft, downdraft and cross-draft designs (Figure 3.2). Fluidized bed gasifiers are quite commonly used for larger power applications (Quaak *et al.*, 1998).

# 3.1.3.1. Updraft Gasifier

Upward gasifier refers to a counter flow gasifier where biomass fuel moves downward while the producer gas moves upward. Gases follow a natural upward movement as the increasing temperature reduces their density. Updraft gasifier can be designed to work under a natural or forced draft. With this configuration, the air or oxidizing agent entering gets in contact with the chars creating the combustion zone. The gases coming out of the combustion zone have to pass through the layer of chars above them created by the heat of the combustion zone. Here CO<sub>2</sub> and H<sub>2</sub>O are reduced into CO and H<sub>2</sub> (Equations 3.3, 3.4). The reduced gases still contain enough energy to pyrolyse the descending biomass along a range 200 to 500 °C, thus creating the chars that feed the combustion zone. In a reaction chain, pyrolysis gases also have sufficient temperature to dry the wet biomass entering above them. However, during pyrolysis, chemicals, tars, and oils are released and become part of the producer gases. This drawback restrains the application of the updraft gasifier, because these products released from pyrolysis would be detrimental in a heat engine; however, it could be used for heating applications. Another major drawback in updraft gasifier is due to high temperature at the grate melting ashes and leading to slagging (Reed, 1981).

# 3.1.3.2. Downdraft Gasifier

The downdraft is a co-current flow, thus the biomass and air flow both follow a downward movement. In this system air first enters the combustion zone and then passes downwards through the reduction zone made of the charcoal bed. Above the combustion zone, despite the fact air or gases are going down, heat from the combustion zone enhances pyrolysis of biomass feed. The oils and vapours formed due to pyrolysis have to pass through the charcoal bed below and this leads to "flame stabilization". This phenomenon occurs due to the cracking of the oil vapour, maintaining temperature around 800 - 1000 °C. Therefore as temperature rises, the endothermic reactions are favoured from the cracking of oil vapors; and as temperature decreases, release of vapour decreases, enhancing the exothermic reactions. Due to this combination of reactions, the temperature is maintained constant. When the gases are cracked, they become simpler gases leading to reduction in oils and tars; as much as 90% reduction in the value

obtained in updraft gasifier is observed. Some designs add a paddle to mix material in the combustion zone, avoiding preferential flow where tar could pass without getting cracked (Souza-Santos, 2004). Implemented with filters, these gases can be used in fuel spark and diesel engines (Reed, 1981).

# 3.1.3.3. Cross-draft gasifier

Cross-draft is designed similar to downdraft; instead of air or oxygen entering parallel to the fuel movement, the entry is by the side, usually at the same height of the outlet. Outlet is situated on the side of the gasifier (Goswami, 1986).

# 3.1.3.4. Fluidized bed

Fluidized bed gasifiers have been a later development. This design provides a uniform contact temperature between gases and solids (Reed, 1981). Fluidized bed gasifier uses a bed of heating media such as sand for thermal process to occur. The bed is heated at desired temperature and feedstock is inserted to it. The heating media bed and biomass are maintained in a suspended stage as the name indicates.



Figure 3.2: Main types of gasifier reactors.

# 3.1.4. Factors affecting Gasification

Factors affecting gasification can be broadly classified as operating conditions, oxidizing agents and fuel characteristics (Souza-Santos, 2004).

To attain equilibrium conditions, residence times, rate of fuel delivery, temperature and gas-solid contact are major factors of operating conditions (Reed, 1981; Souza-Santos, 2004). Pressure within the reactor also has an effect. Increase in pressure results in a decrease in the equilibrium concentration of carbon dioxide and hydrogen and increase in the carbon monoxide and methane concentrations. Low temperature normally enhances methane, hydrogen and carbon dioxide production.

The oxidizing agent, which is generally air, influences gasification. The main factors are the moisture content, temperature, flow rate, injection position and air-to-fuel ratio (Klass, 1998).

The feedstock parameters affecting gasification process are: calorific value, chemical composition, ash characteristics, ash content, tar formation tendency, size homogeneity, density, flow tendency, and moisture content (Ryu et al., 2006). The chemical composition also affects heating value as it is based on the content of carbon, hydrogen, and oxygen. Volatile content is another important parameter. Compared to coal, biomass is much more reactive due to the higher content of volatiles (70 to 90%). Char reactivity is directly related to gasification efficiency. A fuel which has less volatiles will tend to react longer with the fixed carbon (char), igniting the volatiles instead of enhancing the release of the producer gases. The shape and porosity of particles may also affect process within the reactor. Shape of particle should be as much spherical or cubical as possible. In addition particles should have uniform size and a low tendency for bridging. The gasifiers and combustors are generally designed for particles sized in the range of  $10^{-6}$  to  $10^{-2}$  m (Rvu *et al.*, 2006). Other fuel criteria required for producer gas production in downdraft gasifiers are high inter particle porosity, moisture content less than 20% (wet basis), a low ash content (5-6% maximum), the absence of contaminants (metals, glass or soil), bulk density greater than 160 kg m<sup>-3</sup>, good mechanical strength and resistance to break down during handling (Angeeswaran, 2002). The process of feedstock gasification occurs at lower temperature levels compared to coal due to the high content of cellulose and hemicellulose that react with oxygen (Klass, 1998).

### 3.1.5. Gasifier Thermodynamics

#### 3.1.5.1. Air requirements

A first step in analyzing gasifier performance is determination of stoichiometric oxygen requirements of the fuel. Stoichiometric oxygen requirements can be determined from the ultimate analysis (C, H, O, N content) of the fuel and the completion of the combustion reactions (Equations 3.1 and 3.2). Based on this information, the mass of oxygen required for complete combustion can be determined (Equation 3.8). The oxygen requirements are expressed for a unit mass of fuel.

$$m_{O2 needed} = \frac{m_{C present}}{M_{C}} M_{O2} + \frac{m_{H2 present}}{M_{H2}} \frac{M_{O2}}{2}$$
(3.8)

Where:

- m <sub>O2 needed</sub>: mass of oxygen (kg) required for the completion of reactions 3.1 and 3.2 (based on m<sub>C present</sub> & m<sub>H2 present</sub>).
- m<sub>C present</sub> and m<sub>H2 present</sub>: amount of carbon and hydrogen (kg) present in the fuel.
- M<sub>C</sub>, M<sub>O2</sub> and M<sub>H2</sub>: molecular mass of carbon, oxygen and hydrogen; 12 kg/mol, 32 kg/mol and 2 kg/mol respectively.

Considering the amount of oxygen already in the fuel (m  $_{O2 \text{ present}}$ ), the mass of oxygen to be added (m  $_{O2 \text{ add}}$ ) is calculated (Equation 3.9).

$$m_{O2 add} = m_{O2 needed} - m_{O2 present}$$
(3.9)

The amount of air for combustion (m <sub>air needed</sub>) can then be determined from the oxygen content in air (0.23 kg  $O_2$  per kg of air).

$$m_{air needed} = \frac{m_{O2 add}}{0.23} \tag{3.10}$$

Because the amount of air is expressed per kg of fuel, this value corresponds to the air to fuel ratio (A / F) at stoichiometric requirements. Based on the density of air at room temperature (1.126 kg/m<sup>3</sup>), the volume of air required for complete combustion of fuel (Stoichiometric  $Q_{air}$ ) can be computed.

For gasifier performance analysis, biomass consumption rate and air flow rate can be related to overall performance of the gasifier. Biomass consumption rate can be calculated by monitoring the mass of biomass consumed during a unit time of the gasification process.

Equivalence ratio is a concept used to describe thermochemical conversions such as pyrolysis, gasification and combustion. This parameter is evaluated for a particular fuel as the ratio of the oxidant flow rate to the stoichiometric oxidant flow rate requirements (Equation 3.11). For complete combustion, this ratio must be greater or equal to 1. Pyrolysis occurs at ratios closer to 0, but in the case of gasification, the ratio ranges between 0.19 and 0.43 (Reed, 1981). From the information obtained in previous formulas and monitoring the gasifier air flow rate (Actual  $Q_{air}$ ), equivalence ratio (*E.R.*) can be determined as follows:

$$E.R. = \frac{Actual \ Q_{air}}{Stoichiometric \ Q_{air}}$$
(3.11)

#### 3.2. Ash

#### 3.2.1. Ash in Feedstock and its Implications

One particular problem that is encountered during thermal processes of biomass is the deposition and agglomeration caused from minerals in ash melts. Baxter (1993) stated: "Ash behaviour of agro-residues during thermochemical conversion is one of the most important matters to be studied." The minerals present with the feedstock, when subjected to high temperature and certain conditions, can agglomerate and deposit inside the thermal device leading to slag formation, fouling and bed agglomeration. The principle behind these phenomena has begun to be understood, transformation steps are being explored, and techniques have been defined to anticipate their formation.

# 3.2.2. Ash Analysis

The determination of ash biomass composition assists the prediction and/or prevention of ash deposition by selecting an appropriate technique for mineral reduction; in addition, it allows performing a mass balance of fuel elements, which constitutes a key system analysis (Obernberger *et al.*, 1997). In order to determine ash composition, various methods have been described to first prepare the ash samples. The common method is to maintain the temperature at a maximum between 525-575 °C. At higher temperatures certain elements present in biomass, especially potassium and chlorine are volatilized. In general, ash is prepared within a muffle furnace and samples are placed in crucibles open or closed in order to avoid fuel ignition. In case where large volume of biomass needs to be ashed, bigger containers are used. Thy *et al.* (2005) ashed their wood sample in a semi-closed steel container allowing production in large volume.

#### 3.2.3. Ash in Biomass

Inorganic constituents, such as organically bound cations, inorganic salts and minerals make up the ash present in or on the surface of biomass (Arvelakis and Koukios, 2002). Ashes are usually formed of CaO, K<sub>2</sub>O, Na<sub>2</sub>O, MgO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub> and Cl (Reed, 1981). The type of agricultural residue has a direct effect on ash melting behaviour. Annual crop biomass and annual growth, such as tree trimmings, cannot be utilized as a single fuel in conventional thermal units, especially in boilers. Miles et al. (1996a) observed that most of the deposits occurring in boilers originate from phosphorus, sulphur and chlorine compounds present in the annual growth material of agricultural feedstock. In boilers, these types of biomass must be burned in combination with wood, because the annual growth material composition in volatile alkali (0.34 kg/GJ) reduces the fusion ash temperature enough to vaporize the elements, which then accumulate inside the apparatus (Miles et al., 1996a). Potassium and chlorine are the main ash constituents of straw and rapid-growth plants. This is in contrast to wood biomass where ash and specifically, these two constituents are found in low contents (Dayton et al., 1999; Miles et al., 1996a). Straw has high ash content with a low melting point (1000 °C or less). As was reported by Miles et al. (1996b) and Sander (1997), agro residues and

wood have generally similar C, H, and O content; however, their content varies significantly in terms of nitrogen, ash constituents (Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, Mn), and heavy metals (Cu, Zn, Co, Mo, As, Ni, Cr, Pb, Cd, V, Hg). Compared with coal, agricultural feedstock have higher percentage of K, Cl, Si, but less Ca, Mg, Fe, Al, Na, S (Wei *et al.*, 2005; Baxter, 1993; Miles *et al.*, 1996b; Tran *et al.*, 2004).

# 3.2.4. Ash Melting

Ash can cause problems when it fuses to form slag, which can block the biomass from flowing freely. Slagging can be avoided by managing the temperature – either by reduction where ashes are present or by keeping the ashes at very high temperatures. When ash is not properly removed; its accumulation reduces the range of chemical reactions. Miles *et al.* (1996b) and Wornat *et al.* (1995) describe the process for deposit formation as particle impaction, condensation, thermophoresis and chemical reactions. Deposition can occur in various forms, such as fouling, slagging, bed agglomeration, and sintering. The most important reactions occurring during mineral melting that create slagging and fouling involve alkali metals (K, Na), alkaline earth metals (Ca, Mg), silicon, chlorine, and sulphur (Dayton *et al.*, 1999; Obernberger *et al.*, 1997).

Each mineral has its own behaviour relative to a thermal treatment; nonetheless, the specific behaviour of each individual gets modified when several elements are treated in a group (Table 3.2). In general, ashes in agricultural residues soften between 1240-1310 °C and become fluid at 1330-1410 °C (Vamvuka and Zografos, 2004; Skrifvars, *et al.* 2005). Other parameters influencing the phenomenon are the physical and chemical characteristics of fuel, reactor chamber design and operation, fuel properties and thermochemical reaction conditions. According to Tran *et al.* (2004), vapour pressure of species would affect the arrangement of inorganic ash-forming compounds of alkali and heavy metals. Ash component species having high vapour pressure have more chances to bind with the fine ash fraction or to be expelled from the process in the form of inorganic vapour. It has also been observed that the vaporization of divalent and trivalent metals would have the effect of lowering the loss in inorganic materials by devolatilization (Miles *et al.*, 1996a; Wornat *et al.* 1995).

Group	Mineral	Melting Temperature, °C
Chlorides	NaCl	801
	CaCl <sub>2</sub>	782
	KCI	770
	MgCl <sub>2</sub>	714
	FeCI <sub>3</sub>	306
Carbonates	Na <sub>2</sub> CO <sub>3</sub>	851
	CaCO3	1339
	K <sub>2</sub> CO <sub>3</sub>	891
	MgCO <sub>3</sub>	Decomp. 350
	FeCO3	Decomp. 350
Chlorates	NaClO <sub>3</sub>	248-261
	Ca(CIO <sub>3</sub> ) <sub>2</sub>	340
	KCIO3	356, decomp. 400
	MgClO <sub>3</sub> ,6H <sub>2</sub> O	35
	Iron Fe(CIO <sub>4</sub> ) <sub>2</sub>	Decomp. >400
Sulfates	Na₂SO₄	
	CaSO₄	750-950 (pres. of silicates)
	K₂SO₄	1069 Tr. 558
	MgSO₄	1124 Decomp.
	Fe(SO <sub>4</sub> ) <sub>2</sub>	480 Decomp.
Hydroxides	Na(OH)	318
	Ca(OH) <sub>2</sub>	580-H <sub>2</sub> O
	кон	360
	Mg(OH)	350-Н <sub>2</sub> О
	Fe(OH) <sub>2</sub>	
Sulfides	Na₂S	1180
	K₂S	470
	MgS	
	FeS <sub>2</sub>	1171
Phosphates	Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	1230
	K₃PO₄	1340
	Mg <sub>3</sub> (PH <sub>4</sub> ) <sub>2</sub>	1184

Table 3.2: Melting temperatures of compounds potentially responsible for low-temperature melting behaviour in biomass feeds (Miles *et al.* 1996b).

# 3.2.4.1. Alkali Metals

At conventional boiler temperature (greater than 850 to 950 °C in bed and exit gases), alkalis can volatilize and form compounds such as chlorides, hydroxides and sulphates. These compounds create a salt mixture that easily softens and accumulates on surrounding surfaces. From 900 °C, alkalis have the tendency to react with silica to form silicates that lower melting temperature depending on the composition. In addition, alkalis can react with sulphur to form alkali sulphates with a low melting point and having the tendency to cause fouling on heat transfer surfaces (Arvelakis and Koukios,

2002; Miles *et al.*, 1996a; Baxter *et al.*, 1998; Obernberger, 1998, Ryu, *et al.* 2006; Dayton *et al.*, 1999). Alkali metals have also been shown to reduce char production (Dayton *et al.*, 1999).

Potassium, an essential nutrient for plants, boils at 773.85 °C. It is the alkali metal naturally present at the highest concentration in biomass and is a major element responsible for slag accumulation problems. Potassium is mainly present bound to Cl. and is commonly known as sylvite. At flame temperature, it can accumulate in the form of KCl and KOH (Baxter, 1993; Arvelakis and Koukios, 2002; Miles et al., 1996a; Thy et al., 2006; Jenkins et al., 1998). The gas forms in which potassium tends to be released are mainly KCl, (KCl)<sub>2</sub>, K<sub>2</sub>SO<sub>4</sub>, KOH and K. It can also stay in ash in the form of potassium silicate. Gaseous potassium, when submitted to a cooling process condenses on coarser fly ash and forms solid KCl or K<sub>2</sub>SO<sub>4</sub>. In addition, aerosols can appear and merge with fly ashes during condensation, sulphation and carbonization. Potassium represents a harmful element that causes deposits and corrosion within thermochemical units; the potassium found with deposits can react with sulphur, creating sulphate (Wei *et al.*, 2005; Baxter, 1993). Laboratory experiments have shown that fuel composition affects potassium volatilization; at the same slag melting temperature it remained molten for rice straw ash, but evaporated from wood ash (Thy et al., 2006). Oxygen fugacity is another factor known to affect potassium release (Thy et al., 2006). Despite the negative effect of potassium representing a problem in direct combustion (Fung and Graham, 1980), in gasification reducing atmosphere, it would act as a reaction catalyst and would increase gas production; potassium carbonate and calcium oxide enhance the conversion of char to combustible gases.

Sodium has a boiling point of 882 °C. It can volatilize and form compounds such as Na<sub>2</sub>O and NaCl. However, in the form of silicates, sodium does not tend to form sodium silicates (Wornat *et al.*, 1995). Sodium and potassium carbonate are reported to be stable up to 800 °C (Thy *et al.*, 2006).

# 3.2.4.2. Alkaline Earth Metals

At operating conditions, alkaline earth metals tend to form compounds as sulphates, silicates, chlorides and hydroxides and to create slagging, fouling and bed sintering in a fluidized bed reactor (Dayton *et al.*, 1999; Arvelakis and Koukios, 2002). Calcium has been reported to react with sulphur to form sulphate, which could lower the melting temperature; however, due to its low mobility and its limited quantity in general feedstock, it is not a major problem (Arvelakis and Koukios, 2002). Calcium is often present in the form of calcium carbonate and does not oxidize when ashes are made at low range of temperatures (Skrifvars *et al.*, 2005). In other tests, limestone was used in order to improve bed fluidization, with a positive result; however, the calcium was shown to accumulate on the convection surface of the boiler as CaCO<sub>3</sub> or CaSO<sub>4</sub> (Miles *et al.*, 1996b). Calcium has also been shown to form silicates in the presence of silicon during the end process of char conversion (Wornat *et al.*, 1995). The detection of calcium in the form of calcium carbonate is possible up to about 700-800 °C, when calcite starts decomposing (Thy *et al.*, 2006). Calcium silicates have been reported to form at temperatures between 1100 and 1700 °C (Wornat *et al.*, 1995).

#### 3.2.4.3. Non-metallic elements

Thy et al. (2006) and Thy et al. (2000) reported that halogens are alleged to be a major factor in the behaviour of metallic elements in combustion systems; however, these effects were not studied by means of laboratory experiments. Chlorine facilitates the vaporization and deposition of alkali metals and creates corrosion through development In addition, it inhibits flame development during of corrosive alkali sulphates. combustion. Chlorine evaporates easily, therefore it cannot be evaluated from ash that requires a heating temperature of 575 °C. In case of rice straw, chlorine was observed to decrease the ash melting temperature significantly at levels below 770 °C. It also works as a transport medium for potassium at high temperatures where most K is present in the form of KCl (Baxter et al., 1998; Dayton et al., 1999; Thy et al., 2006). Chlorine can also generate pollution by forming toxic compounds. In the cases of wood and straw, gaseous HCl, an important air pollutant, gets released at temperatures 525 to 825 °C. With straw, at temperatures above 825 °C, gaseous HCl tends to decline, while gaseous KCl formation increases (Wei et al., 2005). Woody biomass usually does not contain chlorine (Dayton et al., 1999).

Pronobis (2005) reported that P<sub>2</sub>O<sub>5</sub>, with a hemispherical temperature of 569 °C,

lowers the melting point temperature for fly ashes. Sulphur present in ash represents a source of fouling, slagging and corrosion in the furnace at high temperatures (Wei *et al.*, 2005).

# 3.2.4.4. Refractory Material

Mineral materials such as silica, alumina and titanium are said to be refractory as they do not vaporize during combustion temperature. Silicon is an element present in plants in the form of hydrated silica or as a cell wall constituent; its content varies with soil conditions (Arvelakis and Koukios, 2002; Miles *et al.*, 1996a). Silica can be present on the surface of biomass as a contaminant due to soil contact. Sand is usually found in the form of quartz (SiO<sub>2</sub>). Some sands, such as alumina sand, have been shown to reduce the agglomeration tendency in circulating fluidized beds; but the pre-existent accumulations before their use did not show any change in composition, especially on the superheated tubes (Miles *et al.*, 1996b).

### 3.2.5. Methods to Reduce Ash Melting Problems

In efforts to reduce deposit problems, leaching tests, fractionation tests and design parameters within a thermal apparatus have been investigated. Some of the works conducted by these methods are presented in this section.

# 3.2.5.1. Leaching Test

Also known as chemical fractionation, the leaching test is utilized to verify the tendency of minerals present at the surface of biomass to be removed using different solvents. In addition leaching is a technique to remove some minerals to reduce combustion-related ash deposition problems. Originally designed for coal, this test can also be utilized for biomass. Standard leaching tests are described in *Alkali Deposits, Summary Report* of (Miles *et al.*, 1996b). Solvents that have been noted in literature are: tap water, distilled water ammonium acetate and hydrochloric acid (Vamvuka and Zografos, 2004; Arvelakis and Koukios, 2002; Dayton *et al.*, 1999; Miles *et al.* 1996b; Skrifvars *et al.* 2005). The minerals that are water soluble or ions exchangeable by ammonium acetate are the portion of minerals that would have vaporized (Miles *et al.*, 1996).

1996b). Those elements leached by water are presumably soluble salts such as alkali sulphates, carbonates and chlorides (Zevenhoven-Onderwater *et al.*, 2000). Many troublesome elements such as chlorine and potassium are water soluble; therefore water leaching can reduce significantly the content of these elements present on the surface of biomass (Miles *et al.*, 1996b) and (Skrifvars *et al.*, 2005). Leaching of most biomass can reduce potassium and sodium by more than 80%, chlorine by more than 90% and in addition, sulphur and phosphorus can also be reduced slightly (Dayton *et al.*, 1999). The ammonium acetate can act as an ion exchanger; therefore, the fraction it can remove can be bound to any organic group within the fuel. Calcium, sulphur, sodium and potassium present in partial and organically bound form can also be removed (Zevenhoven-Onderwater *et al.*, 2000). On the other hand those that are not soluble are present in the form of oxides, silicates or sulphides. Hydrochloric acid affects the carbonates, sulphates and some specific compounds such as crystalline calcium oxalate present in some wood bark (Miles *et al.*, 1996b) and (Skrifvars *et al.*, 2005).

Vamvuka and Zografos (2004) conducted leaching tests with common agroresidues such as olive kernel, olive wood, citrus wood and vine shoots. The leaching treatment was done in pure double distilled water by soaking the feedstock for 2 hourperiods at a temperature of 80 °C. Water leaching reduced the ash content by about 40% and the problematic elemental content of K and Na by 93%, P by 85% and Cl by 97%. Some heavy metals such as V, Co and Pb, the soluble form of minerals such as lime and sylvite were also removed. For olive kernels, chlorine was observed to be more easily extracted than alkali metals; chorine is assumed to be present on the surface area of biomass. This whole change resulted in increasing the ash fusion temperature; on the other hand, it did not have any effect on the sulphur content. Water leaching resulted in a reduction in fouling potential based on the alkali index examined.

Arvelakis and Koukios (2002) conducted leaching tests with wheat straw, olive residues and corn cobs by tying the material into a mesh and soaking it in a barrel filled with tap water. Water pH, electrical conductivity, colour and smell of the leachate were observed at the end of the process. They observed a diminution in problematic elements depending upon the retention time and the mass-to-water ratio. In the case of olive residues, almost all the alkali metals, chlorine, and sulphur were removed, improving the

thermal behaviour. However, in the case of corn and straw, the treatment was not satisfactory. Leaching was shown to have a neutral or positive effect on the calorific value of most of the studied fuels and, similarly, to have a slight positive effect on volatile content.

Dayton *et al.* (1999) conducted similar experiments with tap, deonized and distilled water on wheat straw, rice straw, banagrass (*Pennisetum purpureum*), switchgrass and wood. Leached samples were tested for combustion behaviour within a bench-scale alumina–tube flow; and alkali metal volatile species associated with fouling and slagging were examined. The elements change from the leaching treatments for all the feedstocks resulting in an average depletion of 82% for potassium, 91% for chlorine, sulphur and sodium reduced by 41 and 50% respectively. Phosphorus, magnesium and nitrogen reduced respectively by 43%, 51% and 37%. The observation of alumina, titanium and iron in the samples was explained to be by soil contamination of biomass surface. In case of chlorine the leaching represents a direct reduction in HCl pollution emissions. On the other hand, the reduction in nitrogen from leaching did not reduce the NO<sub>x</sub> gas emissions. Rice straw, switchgrass and wheat straw all presented a beneficial increase in fusion temperature, from 300 °C to 500 °C.

Jenkins *et al.* (1996) tested the effect of washing rice and wheat straw on removal of troublesome elements creating slagging and fouling in thermal conversion systems. Various leaching techniques with the two straw fuels were tried: first by spreading the straw over a wire mesh and spraying water for 1 minute, second technique consists of pouring tap or distilled water over a wire mesh on which straw is spread and the third technique consisted of soaking of straw with distilled water. Tests were also performed with samples in field soaked by natural precipitation. The samples were then analyzed for ash composition and ash fusibility. The treatments resulted in a reduction of about 10% ash for rice straw and up to 68% for wheat straw. For both straws, water treatment resulted in the increase of ash fusion temperature. Significant amount of alkali metals, chlorine and sulphur were released. In addition, observations by scanning electron microscopy showed that washed straw was reduced in most elements other than silica; present in the form of amorphous silica. Tests done in laboratory furnace showed a significant increase in fusion temperature for most treated samples; for ashes like rice

straw that normally fused at 900-1000 °C, the fusion temperature increased as high as 1600 °C. In case of wheat straw the temperature also increased significantly; from 800 to about 1100 °C for one sample and up to 1600 °C for another. Natural rain, in case where straw was not in contact with field soils, presented results as efficient in removing alkali and chlorine as laboratory washing. The observation of ash fusibility seemed to be consistent with the phase relationship for alkali-silica systems diagram of respective fuels.

Leaching is thus considered as a solution in partially removing troublesome elements for deposit formation. The feasibility would depend upon the type of fuel and thermal application (Dayton *et al.*, 1999; Vamvuka and Zografos, 2004). However, based on some ratio tests used for predicting slagging and fouling behavior, Vamvuka and Zografos (2004) observed that in some cases it was not useful. A natural way to use the leaching effect would be to take the advantage of the rain by leaving material in fields.

# 3.2.5.2. Fractionation

Fractionation consists of removing minerals present at the surface of a fuel by a simple sieving and shaking method. Arvelakis and Koukios (2002) did an experiment with a mechanical shaker and a 1mm screen opening in order to verify which element could be eliminated from the biomass. In their experiment, the authors studied wheat straw, olive residue, and corn cobs by separating the material fractionated into two groups, L>1 mm and L<1 mm. All agroresidue ashes were analyzed and characterized for thermal behaviour and elemental analysis after fractionation treatment. The coarse fraction greater than 1 mm demonstrated a reduction in ash content down to 35%, while the L>1 mm significantly increased and showed the presence of extremely troublesome elements in the form of organometalics and chloride salts. Nonetheless, the results obtained during thermal experiments showed an undesirable ash melting behaviour, despite the fact that the ash content had been reduced as much as 50% for certain biomass materials studied.

# 3.2.5.3. Design Parameters affecting Slagging

## a. Additives

Substances can be added in reactors to capture or avoid deposition problems. For heavy metal capture at high temperature, kaolin has been identified as one of most efficient aluminosilicate sorbents. Kaolin was also used in fluidized bed gasifier to avoid problem of slagging, bed agglomeration and fouling caused by alkali metals (Ohman *et al.*, 2000; Steenari and Lindqvist, 1998; Tran *et al.*, 2004). Limestone and alumina sand were two additives used to reduce bed agglomeration, which helped but did not avoid deposition completely (Miles *et al.* 1996b). Straw was shown to limit fouling when mixed with the utilized fuel (Thy *et al.*, 2006).

# b. Construction aspects

Richey *et al.* (1983) developed the channel-flow gasifier which would provide a better control in the high temperature zones allowing the use of some fuels more prone to slagging. The grate can also be maintained at ash melting temperature, which is the case in the slagging gasifier that heats the grate at a temperature of 1300 °C (Reed, 1981). In accordance to (Miles *et al.*, 1996a), alkali volatilization could be avoided operating at gasification temperature conditions less than 760 °C using some additives.

# c. Effect of air flow rate and equivalence ratio on ash melting

During gasification of straw, Wei *et al.* (2005) observed an increase in gaseous HCl released and a reduction in gaseous KCl formation for equivalence ratio between 0.2 and 0.8.

Dasappa *et al.* (2003) studied ash fusion of briquettes made out of biomass. Using an inverted downdraft gasifier they observed the maximum air velocity before occurrence of slag formation. The critical air velocity was found to be around 0.1 m/s. The air velocity was determined using the air flow rate divided by the cross-section of the inverted downdraft gasifier without considering the area occupied by the feedstock (Table 3.3).

Briquettes Type	Air velocity		
Diquettes Type	m/s		
Marigold	0.16		
Ground nut shells	0.26		
Chilly waste	0.17		
Rice husk	0.21		
Rice bran	0.30		
Coirpith	0.10		
Coffee waste	0.17		

Table 3.3: Maximum air velocity operation conditions within the inverted downdraft gasifier before occurrence of slag formation (Dasappa *et al.*, 2003)

# d. Low-High-Low Temperature Reactor (LHL)

Variation of temperature zones along reactor was shown to vary the behaviour of some elements. Eldabbagh *et al.* (2005) observed that low-high-low (LHL) temperature reactor was leading to generation of particles having heavy metals immobilized inside the aluminosilicate matrix. Particles obtained from these tests could be classified as non-hazardous and be reused along nutrients cycling. LHL contributes to the formation of metal-aluminosilicate complexes instead of alkalis. Their formation lowers the fouling and slagging effect compared to standard fluidized bed combustion (FBC). In general it was shown that LHL offered better ash management than classic FBC.

# 3.2.6. Prediction of Ash Melting Behaviour

# 3.2.6.1. Ratio and Indices

a. Alkali Index (AI)

Alkali index was developed for boilers and other similar thermal equipment to express the quantity of alkali oxides (in kg) per unit of fuel calorific value (CV in GJ). The ratio indicates the probability of slagging/fouling for values from 0.17–0.34 kg/GJ (Vamvuka and Zografos, 2004; Miles *et al.*, 1996b). Beyond a value of 0.34, slagging/fouling is guaranteed to happen.

$$AI = \frac{K_2 O + Na_2 O}{CV} \tag{3.12}$$

### b. Base-to-Acid Ratio (B/A)

Based on the knowledge that compounds with alkaline pH lower the risk of fouling, while the acidic ones increase it, an indicative ratio of basic oxides over acidic oxides can be calculated using the following equation (Pronobis, 2005; Vamvuka and Zografos, 2004). Each term in the equation corresponds to the percentage present in fuel. Despite its low content in biomass,  $P_2O_5$  is characterized by a hemispherical temperature of 569°C, which can lower the melting temperature significantly.

$$\frac{B}{A} = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2}$$
(3.13)

# c. Multi Fuel Fouling Index (MFF)

The MFF is another index that was developed during the 1980s. In addition to considering alkali metal content, it takes into account the alkaline-earth metal content and total ash content. The index is elaborated for sulphate deposit and the total ash content; for values of 15-40% the fouling tendency would be medium, low at less than 15% and high for greater than 40% MFF (Skrifvars *et al.*, 2005).

#### d. Bed agglomeration Index (BAI)

This bed agglomeration index has been developed for fluidized-bed reactors, with bed agglomeration occurring for values less than 0.15 (Vamvuka and Zografos, 2004).

$$BAI = \frac{\%(Fe_2O_3)}{\%(K_2O + Na_2O)}$$
(3.14)

#### 3.2.6.2. Ash Melting Test

Analysis of ash melting behaviour is the standard test for ash fusibility. A cone made of the ash sample is subjected to gradually increasing temperature. Stages of deformation are based on visual observations (Jenkins *et al.*, 1998; Skrifvars *et al.*, 1999). Deformation stages occurring along this test are known as initial deformation temperature, softening temperature, hemispherical temperature and fluid temperature. The test was
conducted by Skrifvars *et al.* (2005) and they noted that results did not correlate with the full scale combustor. This situation was explained by the fact that a mixture of several ashes do not melt at a single temperature; consequently it can vary over a range of several hundreds of degrees Celsius. Stallmann and Neavel (1980) similarly observed with coal where the agglomeration temperature did not correlate with the melting temperature obtained during ASTM ash fusion tests. The temperatures were hundred degrees lower than the ASTM test. During the test conducted by Paulrud *et al.* (2001), it was observed that the initial melting during full-scale test started at a lower temperature than the ASTM ash fusion temperature prediction. Although presenting clearly the ash behaviour, Miles *et al.* (1996b) concluded that the method was meaningless to predict full-scale operation deposition. Vamvuka and Zografos (2004) observed that their results for ash melting temperature were consistent with the elemental analysis of ashes, but not within the boiler or other equipment where design and operating conditions differed greatly from the laboratory conditions.

Different equipment for estimation is also available for ash fusibility analysis. Vamvuka and Zografos (2004) used the Ash Fusion Determinator type 789-900, AF-600 (Leco). Thermogravimetric analysis is another technique which can be used to examine the ash fusion constituents (Miles *et al.*, 1996a).



Figure 3.3: Example of K<sub>2</sub>O-CaO-SiO<sub>2</sub> phase diagram used for ash melting prediction of reed-canary-grass (Paulrud *et al.*, 2001).

Jenkins *et al.* (1996) observed that the fusion temperature of their samples corresponded to the expected fusion temperature obtained from the alkali oxide-silica phase systems based on the elemental ash compositions. The phase diagram method (Figure 3.3) can also be utilized for estimating bed agglomeration in fluidized beds (Paulrud *et al.*, 2001).

Ohman and Nordin (1998) mention tests conducted by other authors: the shrinkage test, based on dilatometric measures; the conductance test using the ionic mobility properties of ash constituents; the compression strength test on the ash pellets; and finally the sieving tests. Despite the variety of tests, none was adapted to predict ash agglomeration in fluidized beds. For the special case of fluidized bed agglomeration, Skrifvars *et al.* (1999) and Paulrud *et al.* (2001) used a bench scale fluidized bed and concluded that it was the most reliable technique.

Miles *et al.* (1996b) compared tests such as: the alkali concentration, the water soluble alkali, the tendency to form sulphate or chlorides, and the visual deformation during heating. The best slagging indicators obtained by them is by combining the fuel elemental analysis with the concentration in alkali, sulphur, chlorine and silica.

Sintering test is another test used for verifying ash agglomeration strength, which is standardized by ASTM. Cylindrical ash pellets are formed, cooled and submitted to compression tests (Skrifvars *et al.*, 1999).

In their experiment, Zevenhoven-Onderwater *et al.* (2000) combined the fuel characterization method with a global equilibrium analysis and showed that it was more conclusive than the usual method using fuel ash analysis in the laboratory. They also observed that the composition was not the main aspect, but the fraction of melt in the condensed phases would be of concern.

#### **3.3.** Arecanut Production

Arecanut or areca (*Areca catechu*) is an important cash crop in India. It is estimated that nearly ten million people depend on arecanut industry for their livelihood in India (Padmavathamma, 2004). Annually, over 100 000 tons of dry husk is produced in India. The only use for the husk has been as a fuel in inefficient combustion or as mulch. Different uses have been attempted for this plentiful by-product such as the

manufacturing of thick boards, fluffy cushions, non-woven fabrics, thermal insulation and wrapping paper (Kennedy *et al.*, 2001). Although value added products can be created with the areca husk, these practices have not been adopted due to various difficulties. Boiling is an important step in arecanut processing requiring additional source of energy which is usually supplied in stoves using coconut rachis as fuel.

On wet weight basis, the husk is 60 to 80% of the whole fruit. The major constituents of arecanut fruit are pectin (1.5-3.6%), protopectin (1.5-2.1%), hemi cellulose (35-65.8%), lignin (13-26%), furfuraldehyde (18.8%) and ash (4.4%). The husk fibre itself mainly consists of cellulose (Kennedy *et al.*, 2001). Sun-dried arecanut husk has a mass loss of 28-33% when compared to green husk (Angeeswaran, 2002). The moisture content of the husk at the time of processing is about 74.70% (Kennedy *et al.*, 2000).

A natural updraft gasifier of 60kW with fuel consumption of 20 kg areca husk/hr was designed and studied by Angeeswaran (2002). This gasifier was meant to boil water for arecanut processing. The maximum operating temperature occurred at the grate reaching 900 °C for arecanut husk and 920 °C during trials with wood (*Casuarina* species). An economic analysis of this design in terms of boiling energy costs showed a reduction of 33% compared to conventional methods. In addition, the rate of heating increased by 44%, thereby reducing the process time. Angeeswaran (2002) performed tests for ultimate analysis of arecanut husk (Table 3.4). The ash content of arecanut husk was determined to be 4.0%.

Table 3.4: Properties of common biomass utilized for gasification (percentage of ultimate and ash analysis is expressed on a weight basis).

Feedstock	C	Н	0	N	Ásh Content	Calorific Value
	%	%	%	%	%	MJ/kg
Arecanut husk*	44.7	3.8	51.2	0.4	4.0	17.9
Rice Husk**	38.5	5.7	39.8	0.5	15.5	15.4
Casuarina equisetifolia*	51.0	5.0	43.6	0.17***	1.3***	19.8

\*Angeswaran (2002), \*\*Reed (1981), \*\*\*Puri et al. (1994).

## 4. MATERIAL AND METHODS

#### 4.1. Experimental Setup

A schematic diagram of the experimental lab-scale gasifier used in the studies is presented in Figure 4.1. The unit was developed at the Bioenergy Department of Tamil Nadu Agricultural University, Coimbatore, India. The gasifier is made of plain carbon steel; the dimensions of the unit are also shown in the Figure 4.1.



Figure 4.1: Schematic diagram of the lab-scale downdraft gasifier and its dimensions.

An air blower was utilized for providing the forced draft. The blower had the capacity to provide air flows in the range of  $0.001-0.006 \text{ m}^3/\text{s}$ . Air flow rate was controlled with a manually operated gate valve installed on the flexible pipe system before gasifier air inlet. The complete assembled setup is shown schematically in Figures 4.2 and 4.3. Since part of the experiments was conducted indoors, a fume hood was used to safely remove the unburnt producer gases and the exhaust from the burnt gases.



Figure 4.2: Schematic representation of experimental setup for gasification experiments.
(1 - Air blower, 2 - Air flow meter, 3 - Gate valve, 4 – Gasifier reactor, 5 - Thermocouple for oxidation zone, 6 - Thermocouple for reduction zone, 7 – Thermocouple for burner, 8
Gas sampling ports on each side of the exit pipe, 9 – Support stand, 10 – Burner, 11-Exhaust fume hood, 12 - Unburned gas exhaust blower (negative pressure), 13 - Unburned gas exhausted outdoor)



Figure 4.3: Photograph of the assembled experimental setup for gasification experiments.

#### 4.2. Instrumentation and Control

Producer gas released from the gasifier was analyzed using two gas analyzers (KM 900 Kane-May, Kane International Ltd.), designed for flue gas analysis. O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>x</sub> and SO were the gases monitored. Temperature was monitored in the oxidation, reduction and burner zones using K-type thermocouples. Two Tempstar single-channel and a Mars single-channel temperature indicators were used to read the temperature (Figure 4.4). Air flow rate was monitored using a vertical taper cylinder air flow meter installed in the line before the gasifier air inlet. Two balances, of 1 kg ( $\pm$  2.5 g) and 20 kg ( $\pm$  50g) capacities were utilized to weigh wood char and biomass feedstocks. An electronic balance of 400 g ( $\pm$  0.01 g) capacity was utilized for weighing ash and clinkers.



Figure 4.4: Gas analyzers, temperature indicator and air flow meter used in the studies.

# 4.3. Feedstock Material

The areca husk (Figure 4.5a) used for the tests was obtained from Thondamuthur village near Coimbatore, where arecanut is processed in several local centers. Wood (*Casuarina equisetifolia*) utilized for tests (Figure 4.5b) was obtained from Podur village, located close to Coimbatore.



Figure 4.5: (a) Areca and (b) wood samples used as feedstock for gasification experiments. Rocks were commonly found within arecanut husk samples. Wood was cut into uniform sized and shaped pieces for use in the gasifier.

# 4.4. Operating the Gasifier

# 4.4.1. Reactor Design

The first step before starting gasification was to dismantle the lab-scale downdraft gasifier in order to clean the unit and check the seals (Figure 4.6).



Figure 4.6: Dismantled gasifier. (a) shows the main body of the reactor and (b) the cover with the air inlet and the thermocouple well



Figure 4.7: Schematic representation of lab-scale gasifier functioning during the gasification experiments.

Gasifier functioning is presented schematically in Figure 4.7. Before starting tests, lid (2) is opened and a bed of wood char is inserted in the reactor (1b). The rest of the reactor (1a) is filled with the feedstock. With the top lid closed (2), air is drawn into the gasifier by the blower attached to the inlet (3), swirls around the central reactor (1a-1b) and enters the reactor through a single hole (4). Near this hole, the oxidation of biomass occurs. The gas formed from the oxidation has to pass through a 8-10 cm deep glowing bed of wood char (1b) where reduction occurs. Producer gases created have to escape the reactor by passing through the ash grate (5a) and exit by the burner (6) where they can be ignited (7). Gas samples were taken along this lateral exit pipe (9). Cotton pieces soaked in kerosene and attached to a metal rod with metal wire was pre-ignited and used to ignite producer gases. After the tests, ash was collected by opening the bottom lid (8) and removing the ash grate (5b).

# 4.4.2. Operational Procedure

The procedure followed for each gasification test was as follows:

- 1. Cleaning of gasifier (to remove accumulated ash) by opening the base.
- 2. The gas analyzer was turned on with the sampling pipe not connected in order to calibrate the oxygen percentage.
- 3. The gasifier top lid was opened and wood char (small pieces ~ 5cm long) was added in the reactor cylinder. To facilitate easy flammability some of it soaked in kerosene and thin pieces of cotton cloth residues pre-soaked in kerosene were also thrown in.
- 4. The bed was fired up by dropping a small piece of ignited cotton cloth inside reactor tube.
- 5. The blower was turned on after two minutes at 0.001 m<sup>3</sup>/s air flow rate, with the gasifier top lid open.
- 6. The blower was shut off after three minutes when almost all the wood char in the bed was red hot.
- The biomass feedstock was added to the reactor on the top. The sides of the reactor were knocked using a mallet to ensure adequate and proper biomass flow inside the reactor.
- 8. The top lid of the reactor was closed shut.
- 9. The pump of the gas analyzer was turned on.
- 10. The air blower was turned on and the air flow was adjusted to the desired rate by manipulating the gate valve.
- 11. The producer gas was ignited upon its release. The flame quality was monitored.
- 12. The experimental data displayed on the measuring instruments were recorded periodically. The sides of the reactor were frequently tapped using a mallet to ensure regular flow of the biomass down to the bed.
- 13. When a major and sustained change in appearance of the smoke or when the flame from producer gases was extinguished, the data collection was terminated.
- 14. The blower was shut off and the top lid of the gasifer was opened to verify complete utilization of the biomass feedstock.
- 15. After ensuring that the reactor had cooled down, the bottom grate was opened and the residue was removed.

16. The residue was separated into different constituent materials such as ashes, rocks, clinker, and chars, and weighed to record their respective contents.

#### 4.5. Gasification Experiments

#### 4.5.1. Feedstock Trials

A few preliminary tests were conducted with various feedstocks to set up and test the lab-scale gasifier at the labs of Bioenergy department, Tamil Nadu Agricultural University, Coimbatore, India. Initial testing was done using Jatropha (*Jatropha curcas*) husk and rice (*Oryza sativa*) husk in the unit. Three tests were done using wood (*Casuarina equisetifolia*) pieces and seven trials using areca (*Areca catechu*) husk. Tests with wood and areca husk were done to identify the air flow rate at which maximum gasification was achieved.

During these tests, only the maximum temperature in oxidation zone was monitored and the producer gases were not analyzed. The air flow rate was varied during the test in order to obtain stable gas and flame. Three replicates were initially planned for arecanut husk gasification; however noticing the problem of clinker formation, trials were extended in order to observe clinker mass accumulation.

#### 4.5.2. Gasification at Various Air Flow Rates

Experiments to study the effect of air flow rate on clinker formation were done with areca husk and *Casuarina* wood pieces. Prior to tests, wood was cut into uniform pieces 3 to 4 cm in length (Figure 4.5b). Tests were performed at six air flow rates, three replicates per air flow rate were done for arecanut husk and 1 test per air flow rate for *Casuarina equisetifolia*. Cleaning of the gasifier, opening of grate, removal of residues and wood char ignition was carried out only before the first replicate of each air flow rate test. For the subsequent replicates of the same treatment, fresh feedstock was introduced quickly and the process was continued. Four hundred grams of wood char was placed in the cylinder and an additional 100g of char was added after soaking in kerosene. For each replicate, 1kg of biomass feedstock was introduced into the reactor. The temperature of oxidation, reduction and flame zones were recorded along with the

composition of the gas for CO, CO<sub>2</sub>, O<sub>2</sub>, NO, NO<sub>x</sub> and SO<sub>x</sub>. During the final analysis, all three replicates were merged together to create continuous curves in order to observe gas composition and temperature variation over a longer period. These gas and temperature variations were related to total residues obtained at the end of the three sample runs.

## 4.6. Washing of Areca Husk for Reduction of Ash Content

#### 4.6.1. Washing Treatment Setup

Washing the husk was performed in a rotating cylindrical drum made of iron mesh. The cleaning action occurs by rotating the drum in water and the material inside gets washed by water. The drum cylinder was 71cm long and had a diameter of 51cm. The water container was 75cm wide, 80cm long and 45cm in height. The bottom portion of the drum was immersed in water 10cm deep (Figure 4.8). The drum was rotated manually and the speed of rotation was counted using a stop watch.

## 4.6.2. Washing Treatment Methodology

Drum rotation speed was about 54 rotations per minute. Arecanut husk was washed in batches of 4kg and a total of 32 kg was cleaned. The entire quantity of husk was washed within the same water. After washing was completed, the water was allowed to stagnate for about one hour to allow mineral sedimentation in the container. Water from the container was carefully emptied with a pail and the sediment at the bottom of the container was collected. After cleaning, washed husk and the collected sediment were sun dried on a plastic tarp for over 14 hours and were weighted after drying. The moisture content of arecanut husk was determined following the ASTM method for biomass moisture determination E871-882. There was no significant difference in the final moisture contents of the washed and unwashed husks subjected to gasification.



Figure 4.8: Setup utilized to wash arecanut husk.

## 4.6.3. Gasification Test Setup of Washed and Unwashed Feedstock

The washed and unwashed (control) areca husk samples, both dried to the same moisture content, were subjected to gasification trials in the setup described earlier. Some slight modifications were made for these tests. The experiments were performed outdoors; therefore no fume hood was used. In addition gas analysis was limited to  $SO_x$ . Another modification was the adjustment of the ash grate, placed at a higher level. This modification was tried in order to use less wood char (100g) for the tests that were performed one by one instead of three in a row using the same bed of char. One thermocouple was also added along the lateral pipe going to burner in order to measure producer gas temperature. The tests were performed at a fixed air flow rate of 0.005 m<sup>3</sup>/s, as it was found to provide producer gases easily flammable with stable conditions during previous tests.

## 4.7. Ash and Clinker Analyses

Areca husk ash and clinkers obtained in the residue after gasification were analyzed for their oxides and trace element content. Analyses were done at Earth and Planetary Sciences laboratories of McGill University. Oxides were all determined using an X-Ray Fluorescence spectrometer of model (Philips PW2440 4kW). Clinkers analyzed were a mix of all clinkers obtained at various air flow rates. They were first powdered using ceramic mortar and pestle and were sieved using sieve #60, metric 250 um ASTM E-11. For analysis, clinker powder was melted into pallets that were prepared using AFT 6000/C system and an HERZOG HTP 40 pallet press. Ashes were also analyzed following the same procedure.

# 4.8. Statistical Methodology

Linear regression analysis and testing for significant difference between sample means were done using SAS (SAS Institute Inc., Cary, NC USA). Results of statistical analysis are presented in Appendix.

# 5. RESULTS AND DISCUSSION

#### 5.1. Gasification of Areca Husk

### 5.1.1. Gasification Experiments

Jatropha husk (1.23 kg) was the first feedstock tried in the unit. It produced a gas that burnt with a stable flame at air flow rate of 0.0045  $\text{m}^3/\text{s}$ . The temperature was not monitored during this trial. No clinker formation was observed.

Rice husk was tested in the next trial. It created a fused mass of husk within the reactor above the grate and below the oxidation zone that stopped the process completely without allowing any reaction of the biomass. As shown in Table 3.4, rice husk has an ash content of about 15%. In addition, it is rich in silica, which is known to melt at temperatures as low as 700°C in the presence of alkali (Baxter *et al.*, 1998).

The tests with *Casuarina equisetifolia* showed that the air flow rate maximizing gasification in the lab-scale unit was 0.004 m<sup>3</sup>/s. Temperature in the combustion zone was close to 900°C at this setting. The gasification process proceeded predictably well resulting in stable producer gas easily flammable with no clinker formation. The ash content of wood stem is generally around 1%. Despite the fact that its sap is high in alkali, wood stem is usually low in potassium as it does not accumulate inside the stem. Potassium content is 0.1% compared to straws and grasses that have levels of about 1%. Potassium is an element that melts and vaporizes during combustion process reacting with other elements and lowering their melting temperature. For wood containing alkali and potassium, the deposition tendency is very low. This may be due to the silica content being very low; the quantity of slag that may be created from contact with alkali would be less.

Areca husk gasified satisfactorily producing a stable flame. However it formed clinkers rapidly and the deposition would probably have stopped gasification eventually due to accumulation at the ash grate. The colour of the clinker was a mixture of grey, green and black, and it had a glassy appearance (Figure 5.1 a and b). The tests with areca husk showed that the air flow rate maximizing gasification with the experimental unit was  $0.005 \text{ m}^3/\text{s}$  of air with an average biomass consumption rate of 9.3 kg/h (Table 5.1).

Compared to the consistent performance of the wood feedstock (Table 5.2), the biomass consumption rate of areca husk had more variation.

Table 5.1: Results for areca husk gasification at different air flow rate input					
Trial m	m <sub>Areca</sub>	Gasification Time	Q Air Actual	Biomass Consumption Rate	Air / Fuel
	kg	Min	m³/s	kg/h	kg/kg
1	0.8	7.5	0.0050	6.4	2.74
2	0.9	5.5	0.0045	9.8	1.86
3	1.1	7.0	0.0048	9.4	2.08
4	0.8	6.0	0.0050	8.0	2.74
5	0.8	6.0	0.0054	8.0	2.74
6	0.9	5.5	0.0050	9.8	2.44
7	1	4.5	0.0054	13.3	2.01
			Average:	9.3	2.33
			Standard Deviation:	2.2	0.39

Table 5.2: Results for wood (Casuarina equisetifolia) gasification at different air flow

rate input.					
Trial	m <sub>Wood</sub>	Gasification Time	Q Air Actual	Biomass Consumption Rate	Air / Fuel
	kg	min	m³/s	kg/h	kg/kg
1	2.72	27.0	0.0042	6.0	2.57
2	2.16	21.0	0.0038	6.2	2.74
3	2.00	17.0	0.0039	7.1	2.24
			Average:	6.4	2.52
			Standard Deviation:	0.6	0.25

Ash melting behaviour of areca husk is discussed in detail in a later section. Based on the ash analysis (Table 5.8), areca husk is expected to form clinkers as it contains high levels of all major troublesome elements such as potassium, phosphorus, calcium and silica.



Figure 5.1: Slag created during areca husk gasification using lab-scale gasifier. (a) shows a complete mass of slag agglomerated into charcoal bed. (b) shows a closer look at the slag formation similar to a glass surface.

# 5.2. Effect of Air Flow Rate on Gasification of Arecanut husk

# 5.2.1. Clinker Formation

#### 5.2.1.1. Melting Process

The amount of residues obtained with different flow rates are shown in Table 5.3. A tendency towards increased clinker formation was observed with increasing air flow rate (Figure 5.2). The behaviour was weakly linear ( $r^2 = 0.72$ ); but the linear model was significant at 5% level. Generally, increase in clinker formation could be due to a temperature increase that would melt minerals reaching their fusion temperature. As oxygen is added into combustion bed, it enhances the reactions of combustion which are exothermic, thus increasing the temperature. However, the maximum temperature observed in the combustion (oxidation) zone, did not increase proportionally with the air flow (Figure 5.3). On the other hand, the average and maximum temperature obtained within the reduction zone did show a tendency of increase with the air flow rate. Baxter et al. (1998) mentioned that alkali metals, especially potassium, tend to react with silica to form alkali silicates melting at temperatures above 700 °C. The cohesion of these two elements into alkali silicates may have occurred within the oxidation zone and migrated downwards; reaching the reduction zone where the maximum value was 737 °C. The slight increase in temperature within the reduction zone may have been enough to cause increased clinker formation. A second explanation for the increase in clinker formation could be that a part of the oxygen that was not able to react in combustion zone, enhanced the charcoal combustion in the reduction zone. On the other hand, looking at the fairly unchanged gas composition as the temperature increased within the reduction zone, it seems improbable and the former assumption seems more appropriate.

Another reason why clinker increased and the maximum and average temperature in the oxidation zone did not increase may be because of the increase in temperature happened below the zone monitored by thermocouples. Referring to Figure 4.1, there is a distance of about 15-16 cm between the tip of the thermocouple monitoring oxidation zone (at the air entrance) and the thermocouple below in the reduction zone. A temperature increase may have occurred in that zone as the air flow increased, with no means of monitoring it.

Air Flow Rate	Residue	
(m³/s)	(g/kg Husk)	
0.001	129.97	
0.002	105.95	
0.003	153.97	
0.004	130.18	
0.005	105.70	
0.006	131.63	
Average:	126.23	
Standard Deviation:	18.22	

Table 5.3: Total amount of residues obtained during gasification of areca husk at various air flow rates.



Figure 5.2: Clinker formation and rock residues during gasification of areca husk at different air flow rates.



Figure 5.3: Maximum and average temperatures observed in the gasifier zones during gasification of areca husk.



Figure 5.4: Residues obtained from gasification of areca husk at various input air flow rates.

## 5.2.1.2. Reasons for Reduction Zone Temperature Increase

Temperature within the reduction zone increased with increase in air flow rate while the same was not observed within the oxidation zone (Figure 5.3). Firstly, the higher air flow may have transported the excess exothermic energy created in the combustion zone to the reduction zone by transporting the sensible heat. The reaction rates within the reduction zone vary with temperature, following an Arrhenius relationship (Babu and Sheth, 2006). As a result, reaction rate should have slightly increased, resulting in higher amount of products from the reduction zone, such as CO. By observing Figures 5.8 to 5.10, changes in gas composition with varying air flow rate do not seem significant; for air flow from 0.002 to 0.006 m<sup>3</sup>/s, the CO content varied between 20-25%. Only at 0.001m<sup>3</sup>/s air flow, CO content was slightly lower and this may be due to poor reduction zone stimulation from heat produced within the combustion zone.

## 5.2.1.3. Effect of Rocks

During experiments, the presence of rocks was observed in the feedstock (Figure 4.5 a). These rocks were probably contaminations incorporated with the feedstock during sun drying on the ground. From Figure 5.2, a tendency for the rock content to decrease as the clinker formation increased with the increasing air flow rate was observed ( $r^2 = 0.71$ ). This  $r^2$  value was significant at 5% level. Despite the fact more replicates should be performed prior to further conclusion, it seems that the minerals responsible for clinker formation could simply come from these rocks vulnerable to the melting conditions. The composition of the rocks was not determined; however they are expected to be an important source of silica. Silica would simply react with alkali metals as mentioned earlier.























# 5.2.2. Equivalence Ratio

#### 5.2.2.1. Air Flow and Biomass Consumption

The primary objective of varying the air flow rate was to try relating clinker formation with an increasing equivalence ratio (Equation 3.11). It was expected that as the air flow rate increases, the equivalence ratio would also increase. However, the experimental results presented a different trend - as air flow rate increased, biomass consumption rate also increased linearly (Figure 5.11). The relationship was quite strong, with  $r^2 = 0.99$  (p<0.0001) in the case of areca husk and  $r^2 = 0.99$  (p<0.0001) in the case of *Casuarina equisetifolia* wood feedstock. As a result, the equivalence ratio remained the same for the six different air flow rates (Table 5.4). This result is consistent with the temperature and gas compositions, which did not change considerably as air flow rates were changed (Figures 5.5 to 5.10).



Figure 5.11: Biomass consumption rate of areca husk and wood (*Casuarina equisetifolia*) during gasification at varying air flow rates.

۸ir	Areca Hus	k	Casuarina equisetifolia
Flow Rate	Average Biomass Consumption	E.R.	Biomass E.R. Consumption
m <sup>3</sup> /s	kg/h		kg/h
0.001	2.0	0.47	2.6 0.26
0.002	4.2	0.45	4.0 0.34
0.003	6.0	0.47	7.5 0.27
0.004	8.2	0.46	9.2 0.30
0.005	10.7	0.44	12.3 0.28
0.006	11.3	0.50	13.7 0.30
	Average:	0.47	Average: 0.29
	Standard Deviation:	0.02	Standard 0.03 Deviation:

Table 5.4: Gasification parameters obtained for areca husk and wood during tests at various air flow rates. (E.R.: equivalence ratio)

It should be noted that the biomass feeding rate was self-controlled. The throat-less gasifier simply compensates the biomass depletion by dropping more fuel to the oxidation zone by gravity. Ryu *et al.* (2006) examined the factors affecting burning rate and the ignition front. They mentioned that the rate of reaction can be classified into three regimes varying as a function of the airflow rate: oxygen limitation, reaction limitation and extinguishment from excess air (which is not applicable to gasification). In limited oxygen conditions, the amount of oxygen restricts the propagation of the ignition front and the process rate varies proportionally to the air flow rate. In limited regimes, the reaction rate is a function of the fuel reaction itself. It appears that the first case (limited oxygen conditions) describes the observed phenomenon.



















Figure 5.16: Average producer gas composition during gasification of wood (*Casuarina equisetifolia*).

## 5.2.2.2. Flame Ignition

The capacity of producer gases to be ignited was observed as an indication of the extent of gasification and the performance of areca husk is compared with wood (Table 5.5). At lower air flow rates with areca husk, the gases were harder to ignite. It can be observed in case of areca husk that the temperature of reduction zone did not reach 500°C at the lowest air flow rate (Figure 5.6). Though the gas composition does not provide much insight into the possibilities, it could be assumed that the temperature developed at the reduction zone could not initiate or sustain the reactions leading to formation of flammable producer gases.

Table 5.5: Producer gas ignition at varying air flow rates.

Air Flow Rate	Flame Characteristic		
m³/s	Areca Husk	Wood	
0.001	No Flame	Sustainable flame	
0.002	Partially sustainable	Sustainable flame	
0.003	Sustainable flame	Sustainable flame	
0.004	Sustainable flame	Sustainable flame	
0.005	Sustainable flame	Sustainable flame	
0.006	Sustainable flame	Sustainable flame	

#### 5.2.2.3. Fuel Characteristics

It is clear from Table 5.4 that the consumption of wood was faster than the husk. As mentioned in literature review, the bulk density and porosity of biomass are two factors affecting gasification. According to Ryu *et al.* (2006), the burning rate decreases as bulk density increases. Bulk density of areca was determined experimentally to be about 250 kg/m<sup>3</sup>. Bulk density for *Casuarina* is estimated to be 870 kg/m<sup>3</sup> (Puri *et al.*, 1994). The physical structure of areca appears to be favourable for easy combustion - the surface area created by the porosity, the fibrous characteristic, and the outer and inner shell available would be expected to stimulate the burning reaction. Wood pieces have only the outer surface area exposed to burning. However, the denser wood probably moves better in the reactor compared to the lighter husk, which is prone to bridging within the reactor.

In order to control the biomass feeding rate two methods could be utilized - creating a throat at the bed which would control the flow of fuel due to its flow properties. According to Giltrap *et al.* (2003), the flow properties of biomass and the air flow rate requirements for gasification determine the cross-sectional area of a gasifier. Feeding the biomass with a metering device such as a screw auger or a star valve with variable flow rate could also control fuel feeding rate with desirable results.

#### 5.2.2.4. Air Velocity Effect

The velocity of air within the reactor is also important for formation of slag (Dasappa *et al.*, 2003). Studying the effect of air velocity on slag formation in briquettes biomass, it was observed that critical air speed for most of the briquettes tested was about 0.1 m/s. Above that value, slag agglomeration was initiated. In this study, the velocity of air based on the air flow rates and the cross sectional area of the openings was calculated (Table 5.6). It is interesting to ponder on the importance of air velocity on clinker formation. Higher air flow rates in reactors with narrow openings lead to high air velocities. It could be assumed that the higher velocity of the air leads to increased mobility of molecules in the reactor, with various implications, including development of clinkers. If this assumption is proven correct, it has a major impact on the design of reactors with respect to the delivery of air and its movement through the reactor. This

feature would be very important for feedstock such as areca husk. The irregular, fibrous surface of the husk can be expected to result in velocity profiles quite different from the more regular shape of wood feedstocks.

Air Flow Rate	Air speed at nozzle entrance	Air speed within reactor
m³/s	m/s	m/s
0.001	1.41	0.06
0.002	2.83	0.13
0.003	4.24	0.19
0.004	5.66	0.26
0.005	7.07	0.32
0.006	8.49	0.39

Table 5.6: Air speed in the reactor created by gasifier configuration.

\* Nozzle entrance corresponds to the opening where air enters the reactor (Figure 4.7).

## 5.2.3. Gasifier Verification

Wood tests using *Casuarina equisetifolia* were done in order to substantiate the studies with areca husk and compare its performance. The results are shown in Figures 5.12 to 5.16. *Casuarina equisetifolia* wood was tested for gasification by Weber (1985) and the gas composition obtained was 19% CO, 19.6% H<sub>2</sub>, 10.4% CO<sub>2</sub>, 49.8% N<sub>2</sub>, 0.4% O<sub>2</sub> and 0.8% CH<sub>4</sub>. Results for the same wood used in this study are 25% CO, 13% CO<sub>2</sub> and 3% O<sub>2</sub>. Assuming N<sub>2</sub> was at the same level, H<sub>2</sub> for test with lab-scale gasifier is estimated at a maximum of 10%.

# 5.3. Washing Treatment

# 5.3.1. Clinker Reduction

Results for clinker formation during gasification of washed husk and unwashed husk showed that there is a significant reduction in clinker formation by washing the husk (Table 5.7). There was a reduction of 8.6 g of clinker per kg of unwashed husk, corresponding to an average 36% reduction in clinker formation. Ash content, wood char and rock residues were statistically analyzed for the same treatment; however the results did not show significant difference between the other parameters for washed and unwashed husk (Table 5.7). The material removed from washing was not analyzed; however its physical appearance strongly resembled sand and small stones (Figure 5.17 b).

The washing treatment did not seem to affect the gasification process as indicated by the observation of temperatures in the reactor (Figures 5.18 and 5.19). However, the formation and accumulation of clinkers are important in the long run. Build up of slag and agglomeration leads to variations in the operating characteristics of the gasifier and even shuts down the process entirely. Hence, the washing treatment needs to be tested in a larger reactor for longer periods to evaluate the benefits.



Figure 5.17: (a) Water used for washing treatment for areca husk. (b) Mineral material that remained after washing husk.
	Poplicato -	Residues						
Treatment	Replicate	m <sub>total</sub>	m <sub>clinker</sub>	m <sub>charcoal</sub>	m <sub>rocks</sub>	m <sub>ash</sub>		
	#	g	g	g	g	g		
	1	103.5	18.0	64.9	0.0	20.65		
Washed	2	138.8	11.6	52.7	49.1	25.39		
	3	110.6	16.0	65.9	0.0	28.62		
	Average:	117.6	15.2	61.2	16.4	24.9		
	1	121.4	22.8	70.5	0.0	28.07		
Unwashed	2	104.5	24.6	46.3	3.8	29.78		
	3	127.8	24.0	47.3	28.7	27.72		
	Average:	117.9	23.8	54.7	10.8	28.5		

Table 5.7: Residues obtained from gasification of washed and unwashed areca husk.

Table 5.8: Chemical composition of ash and clinker from areca husk.

		1	2	3	4	5
Maria		Ash	Ash	Ash	Ash	Clinker
Main Constituents	Unit	Muffle	Muffle	Simple	Simple	Gasification
Constituents		Furnace	Furnace	Combustion	Combustion	test
		Unwashed	Washed	Unwashed	Washed	Unwashed
SiO <sub>2</sub>	%	12.21	9.46	30.18	28.49	43.76
TiO <sub>2</sub>	%	0.06	0.00	0.11	0.05	0.36
Al <sub>2</sub> O <sub>3</sub>	%	0.25	0.15	0.92	0.60	4.76
$Fe_2O_3$	%	0.76	0.51	0.85	0.62	3.64
MnO	%	0.03	0.03	0.05	0.02	0.13
MgO	%	1.98	1.63	6.29	6.06	4.14
CaO	%	6.06	5.23	7.78	7.01	14.41
Na <sub>2</sub> O	%	0.24	0.23	0.57	1.36	1.55
K <sub>2</sub> O	%	21.00	16.11	25.28	22.64	19.72
$P_2O_5$	%	3.17	2.49	6.88	6.51	4.72
BaO	ppm	1045	700	1260	800	2820
Cu	ppm	370	350	165	145	250
Ni	ppm	275	155	75	<d l<="" td=""><td>150</td></d>	150
Rb	ppm	590	410	380	380	242
Sr	ppm	715	695	645	630	1130
Zn	ppm	330	210	225	280	175
Zr	ppm	n.d.	n.d.	n.d.	n.d.	110
LOI	%	68.69	75.54	20.77	26.43	2.26
Total	%	114.78	111.63	99.96	100.01	99.93
CI	%	n.d.	n.d.	n.d.	n.d.	0.17
SO <sub>3</sub>	%	1.88	1.78	3.70	4.49	0.70

n.d.: non detectable.

# 5.3.2. Ash Melting Behaviour

Information about ash composition is considered essential to explain ash melting behaviour (Miles *et al.*, 1996b). The analysis of washed and unwashed ashes as well as clinker is presented in Table 5.8. The results present ash constituents for ash samples

prepared in muffle furnace and by open air combustion. It has to be noted that results from muffle furnace provide a total of 114.78 and 111.63% which was explained to be from the samples expressed as oxides, while some constituents could be present in their elemental form, thus affecting the total mass. Despite these unknown possibilities, the results confirm that the most troublesome elements such as K, Ca, P, and silica are present at high levels in areca husk biomass. In addition Al, Ti, Fe, Mg, and S that also enhance ash melting, are found in the ashes of areca husk. K, S, Cl, alkali sulphates, carbonates and chlorides are the most common elements participating in slagging formation. These constituents react with silica creating compositions prone to ash melting.

Water leaching removed significant amount of residues, however referring to Table 5.7, it can be noted that rocks still remained after washing. Some amount of sand could be retained in the biomass. The fibrous and shelled nature of the husk results in a tendency for minerals to get trapped intricately. Thus preventing from removal by leaching. Washing duration might then have an impact or a system of using water in circulation to remove the suspended particles might be favourable. However, these add to the cost and drudgery of utilizing a by-product efficiently. On the other hand a solution to avoid the sand particles would be to dry the husk on the surface free of such contamination. Based on the value of the husk, a cheaper solution should be found, such as drying the material on large tarps or a ground free of sand and rocks.

It can be noted from Table 5.7 that the residual content from gasification of washed and unwashed arecanut husk had varying contents of rocks, with higher content in the former. This could be an anomaly. It could also be due to the removal of other ash components from the husk which reduces the participation of such silica contaminants in reactions leading to formation of clinkers at lower temperatures.



Figure 5.18: Comparison of average temperature during gasification of washed and unwashed areca husk.



Figure 5.19: Comparison of maximum temperature during gasification of washed and unwashed areca husk.

### 5.3.3. Effect of Washing on Ash Melting Behaviour.

Observing the ash composition in Table 5.8, it is clear that there was a reduction in the ash percentage by washing. As mentioned earlier, washing treatment can remove a portion of soluble elements as well as elements present as surface contaminants. Silica falls into the last category where, the fraction of silica biologically incorporated to biomass is considered refractory to water leaching treatments (Miles *et al.*, 1996b). Silicon in the form of quartz sand (SiO<sub>2</sub>) is known to melt at high temperatures; however the melting temperature decreases in contact with elements such as K, Na, and Ca. Other elements analyzed in the form of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> are also considered refractory material (Miles *et al.*, 1996b) and they showed a tendency to reduce from water leaching. Therefore, it suggests that a portion of these elements were present in contaminants. The absence of SO<sub>x</sub> in gases from washed sample (Table 5.9) may suggest that some element affects vaporization of SO<sub>x</sub> and that it was affected by washing.

unwasheu areca nusk.					
Treatment	Renlicate	SO <sub>x</sub> Content			
	Replicate	Reading 1	Reading 2		
	#	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	ppm		
	1	0	0		
Washod	2	0	0		
Washeu	3	0	0		
	SOx Content           Replicate         SOx Content           Reading 1 Reading         Reading 1 Reading           #         ppm         ppm           1         0         0           2         0         0           3         0         0           Average:         0         11           2         19         20           3         10         0           Average:         14         14	0			
	1	23	11		
Linwachod	2	19	20		
Uliwasheu	3	10	0		
	Average:	1	4		

Table 5.9:  $SO_x$  content in producer gases obtained during gasification of washed and

## 5.3.4. Alkali Index (AI)

The alkali index (Equation 3.12) was determined using the ash composition in  $K_2O$  and  $Na_2O$  (Table 5.8; Samples 1 and 2), the ash content of areca (4.0%) and its calorific value (17.9 MJ/kg) (Table 3.8).  $K_2O$  and  $Na_2O$  are the values of unwashed ashes prepared with muffle furnace. These values were chosen, because of the standard preparation method using muffle furnace, which limits loss on ignition (LOI). The value for alkali index obtained is 0.48. In accordance to Vamvuka and Zografos (2004) and

Miles *et al.* (1996b), beyond a value of 0.34, slagging and other deposition problems are guaranteed to happen during thermochemical reactions. Therefore in the case of areca husk, the alkali index corroborates with the results of the current study concerning the tendency of arecanut husk in creating slag formation. It suggests that the thermochemical conversions using arecanut husk as fuel may require the use of adapted equipment or a pre-treatment for the feedstock.

### 5.3.5. Ash Melting Test

Ash melting test was performed in order to verify the temperature at which ashes would become fluid. Ash cones (Figure 5.20) were prepared and the tests were carried out in a muffle furnace with no gas control. The ash melting behaviour of both washed and untreated husk was similar. In both cases the liquid temperature appeared to be about 1150 °C (Figure 5.21b and 5.22b). However, this temperature was not attained in any section of the gasifier.



Figure 5.20: Schematic representation of ash cone and stainless steel tray utilized for ash fusion test.

The melting test was done in order to determine if the reactor could be maintained at a certain temperature in order to remove the ashes in a liquid form. In a downdraft gasifier with the reduction zone at the bottom this approach is not useful. However, the updraft gasifier which has its oxidation zone with higher temperature at the bottom may reserve a potential for that application. The temperature at which ashes become liquid in a particular gasifier must be determined under those specific conditions, as laboratory tests are known to fail in representing the melting temperatures obtained under operating conditions (Vamvuka and Zografos, 2004; Skrifvars *et al.* 2005).



n.a.



Figure 5.21 a: Washed areca husk ash cones exposed to increasing temperatures in laboratory muffle furnace; Progression 525 – 1000 °C.









Figure 5.21 b: Washed areca husk ash cones exposed to increasing temperatures in laboratory muffle furnace; Progression 1015 – 1170 °C.









Figure 5.22 a: Unwashed areca husk ash cones exposed to increasing temperatures in laboratory muffle furnace; Progression 525 – 1000 °C.



T: 1015 °C T: 1020 °C T: 1030 °C T: 1040 °C T: 1050 °C



 T: 1060 °C
 T: 1070 °C
 T: 1080 °C
 T: 1090 °C
 T: 1100 °C

 Image: Strain Stra



T: 1160 °C T: 1170 °C

Figure 5.22 b: Unwashed areca husk ash cones exposed to increasing temperatures in laboratory muffle furnace; Progression 1015 – 1170 °C.

## 5.3.6. Ash Preparation

Prior to the ash fusion test, ashes had to be prepared. Despite the fact that the ash fusion test experiment was not reliable, the preparation of ash samples provided some interesting observations.

To obtain larger volumes of ash (as using the muffle furnace method yielded only small batches) two techniques were tried for the sake of convenience. The first consisted of simply blowing air on burning biomass (Figure 5.23 a) and a second method was by igniting the biomass in a perforated cylinder and allowing it to burn by itself (Figure 5.23 b). The ashes produced using the cylinder was used for ash melting test.

It was observed during this ash preparation that biomass that burnt naturally produced a grey ash and the sample prepared with forced air resulted in black ash (indicating higher carbon content), mixed with clinkers (Figure 5.24).



Figure 5.23: (a) Manually operated blower utilized for areca husk ash preparation (b) Open perforated cylinder used for ash preparation by natural draft.



Figure 5.24: Ash obtained from the two techniques of ash preparation. Darker ash was prepared using manual blower and grey ash was obtained using open cylinder.

This simple observation may not be conclusive; however, it may be linked to observation made earlier regarding the reactivity of biomass fuel based on it shape, porosity and bulk density. It is also interesting to note that in the studies of Angeeswaran (2002) on use of areca husk for gasification in a natural, updraft gasifier, clinker formation is not mentioned. This unit seemed to function adequately during the experiments, producing a gas that burned well with no apparent sign of clinker formation even though the temperatures reached 900 °C in the reactor. Perhaps there is a relationship between the biomass characteristics and the rate of combustion that needs to be investigated and understood for better utilization of their potential in energy applications.

## 5.4. Summary

Arecanut husk was successfully gasified in a forced, downdraft lab-scale gasifier. The clinker formation was found to be high compared to wood biomass feedstock which did not form accumulation. The clinker formation was found to increase almost linearly with the air flow rate. However, only minor changes were observed in the development of temperatures in the different zones of the reactor. Hence, no significant changes were observed in the composition of the producer gases resulting from different air flow rates. A simple washing pre-treatment was applied to the areca husk feedstock to remove external contaminants that were probably picked up during the drying of husk on ground. Washing not only reduced the ash content of the feedstock, but also significantly decreased the incidence of clinkers during gasification of the treated husk. Ash analysis of areca husk indicates presence of problematic elements in levels high enough to guarantee slagging during gasification.

## 6. CONCLUSION

The research investigated the potential of utilizing an agricultural by-product for biomass energy. Arecanut processing in India involves consumption of large amounts of heat and rejection of a significant amount of biomass as by-products. Redirecting the energy from the solid waste to the processing inputs would not only enhance the efficiency of the industry, but also contribute in solving the problem of managing the nuisance created by the rejected husk. With this focus, the feasibility of gasifying areca husk in a downdraft reactor was studied.

Determining the limitation of a technology helps to identify its range of applications. Downdraft gasifiers are preferred for production of cleaner producer gases that can be used in heat engines. However, it was realized during this investigation that downdraft gasifiers are probably not suitable for economic utilization of agricultural residues as biomass feedstock.

Based on information available on updraft gasification for areca husk and current experiments done on downdraft gasifier, updraft gasifier may have an advantage concerning ash deposition. Despite the fact it should be investigated more thoroughly, a natural updraft design may lead to lower formation of slag compared to downdraft systems that are predisposed to accumulation of slag when dealing with high mineral containing feedstock. The natural draft design could also be used to maintain a high temperature in the oxidation zone situated above the grate. This could allow removal of ash in liquid form. The downdraft gasifier does not allow this operating condition because of the reduction zone being at the lower level of the gasifier and creating a cooler zone. This cooler zone would be expected to solidify liquid ashes that are believed to be created within the oxidation zone where temperature reaches the highest level within the reactor.

On the other hand, this study allowed the investigation of the pre-treatment of biomass contaminated by soil particles. Washing was found to reduce the predisposition of the feed towards slagging. However the use of large quantities of water and its associated problems, as well as the additional energy required for the process disqualify the treatment as an effective recommendation in this context. Implementing good

management practices such as drying on soil or dirt free surfaces could be a better suggestion.

Further work could be done on palletizing or cutting arecanut husk into smaller, uniform pieces. The actual shape of the husk results in a tendency for the feedstock to clog in the reactor, causing an uneven flow within. It might be interesting to investigate the benefits of mixing the husk with a denser, cheap feedstock in the gasifier feed. A feedstock with small particle size and easy flow property could be used to stabilize the gasifying conditions.

Gasification of areca husk is a desirable technology that has potential applications in the third world. However, further studies are suggested in designing continuous, updraft, natural draft systems that could be easily constructed, installed and operated by the processing industry.

## REFERENCES

- Angeeswaran, R. 2002. *Energy Recovery from Agricultural Byproduct*. M Sc. Thesis, Department of Bio Energy, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India.
- Arvelakis, S. and Koukios, E. G. 2002. Physicochemical upgrading of agroresidues as feedstocks for energy production via thermochemical conversion methods. *Biomass and Bioenergy*, 22(5): 331-348.
- Babu, B. V. and Sheth, P. N. 2006. Modeling and simulation of reduction zone of downdraft biomass gasifier: Effect of char reactivity factor, *Energy Conversion* and Management, 47(15-16): 2602-2611.
- Baxter, L. L. 1993. Ash deposition during biomass and coal combustion: A mechanistic approach. *Biomass and Bioenergy*, 4(2): 85-102.
- Baxter, L. L., Miles, T. R., Miles Jr, T. R., Jenkins, B. M., Milne, T., Dayton, D., Bryers, R. W. and Oden, L. L. 1998. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Processing Technology*, 54(1-3): 47-78.
- Berndes, G., Hoogwijk, M., and Broek, R. 2003. The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass and Bioenergy*, 25(1): 1-28.
- Bridgwater, A. V. 1995. Technical and economic feasibility of biomass gasification for power generation. *Fuel*, 74(5): 631-653.
- Cetin, E., Moghtaderi, B., Gupta, R. and Wall, T. F. 2005. Biomass gasification kinetics: Influences of pressure and char structure. *Combustion Science and Technology*, 177(4): 765-791.
- Dasappa, S., Mukunda, H. S., Paul, P. J. and Rajan, N. K. S. 2003. Biomass to Energy, The Science and Technology of the IISc Bio-energy Systems. Advanced Bioresidue Energy Technologies Society, Combustion Gasification and Propulsion Laboratory, Indian Institute of Science, Bangalore, India.
- Dayton, D. C., Jenkins, B. M., Turn, S. Q., Bakker, R. R., Williams, R. B., Belle-Oudry, D. and Hill, L. M. 1999. Release of Inorganic Constituents from Leached Biomass during Thermal Conversion. *Energy Fuels*, 13(4): 860-870.
- Eldabbagh, F., Ramesh, A., Hawari, J., Hutny, W. and Kozinski, J. A. 2005. Particlemetal interactions during combustion of pulp and paper biomass in a fluidized bed combustor. *Combustion and Flame*, 142(3): 249-257.
- Fung, D. P. C. and Graham, R. 1980. The Role of Catalysis in Wood Gasification. Thermal conversion of solids wastes and biomass. ACS Symposium Series 130. American Chemical Society. Washington, D.C., USA.
- Giltrap, D. L., McKibbin, R. and Barnes, G.R.G. 2003. A steady state model of gas-char reactions in a downdraft biomass gasifier. *Solar Energ*, 74(1): 85-91.
- Goswami, D. Y. 1986. *Alternative Energy in Agriculture*..Boca Raton, CRC Press, FL, USA.
- Islam, M., Fartaj, A. and Ting, D. S. K. 2004. Current utilization and future prospects of emerging renewable energy applications in Canada. *Renewable and Sustainable Energy Reviews*, 8(6): 493-519.

- Jenkins, B. M., Bakker, R. R. and Wei, J. B. 1996. On the properties of washed straw. *Biomass and Bioenergy*, 10(4): 177-200.
- Jenkins, B. M., Baxter, L. L., Miles Jr, T. R. and Miles, T. R. 1998. Combustion properties of biomass. *Fuel Processing Technology*, 54(1-3): 17-46.
- Kennedy, J. Z., Viswanathan, R. and Devadas, C.T. 2001. *Status Report of Arecanut in India*. Department of Agricultural Processing, Agricultural Engineering College and Research Institute, Tamil Nadu Agricultural University, Coimbatore, India.
- Klass, D. L. 1998. *Biomass for Renewable Energy, Fuels, and Chemicals*. Academic Press. San Diego. USA.
- Matsumura, Y., Minowa, T., Potic, B., Kersten, S. R. A., Prins, W. and van Swaaij, W. P. M., Willibrordus, P.M., Van De Beld, B., Elliot, D. C., Neunenschwander, G. G., Kruse, A. and Antal Jr., M. J. 2005. Biomass gasification in near- and supercritical water: Status and prospects. *Biomass and Bioenergy*, 29(4): 269-292.
- Miles, T. R., Miles, J. T. R., Baxter, L. L., Bryers, R. W., Jenkins, B. M. and Oden, L. L. 1996a. Boiler deposits from firing biomass fuels. *Biomass and Bioenergy*, 10(2-3): 125-138.
- Miles, T. R., Miles, T. R., Baxter, L. L., Bryers, I. W., Jenkins, B. M. and Ode, L. L. 1996b. Alkali deposits found in biomass power plants a preliminary investigation of their extent and nature. *Summary Report for National Renewable Energy Laboratory*.
- Natural Resources Canada. 2002. *Renewable energy in Canada: status report 2002.* Natural Resources Canada, Ontario, Canada.
- Obernberger, I. 1998. Decentralized biomass combustion: State of the art and future development. *Biomass and Bioenergy*, 14(1): 33-56.
- Obernberger, I., Biedermann, F., Widmann, W. and Riedl, R. 1997. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass and Bioenergy*, 12(3): 211-224.
- Ohman, M. and Nordin, A. 1998. A new method for quantification of fluidized bed agglomeration tendencies: a sensitivity analysis. *Energy Fuels*, 12(1): 90-94.
- Ohman, M., Nordin, A., Skrifvars, B. J., Backman, R., and Hupa, M. 2000. Bed agglomeration characteristics during fluidized bed combustion of biomass fuels. *Energy Fuels*, 14(1): 169-178.
- Padmavathamma, V. 2004. Arecanut in Indian economy; present status and future strategies. Seminar University Agricultural Sciences Bangalore 2004, University of Agricultural Sciences, Bangalore, India.
- Paulrud, S., Nilsson, C. and Ohman, M. 2001. Reed canary-grass ash composition and its melting behaviour during combustion. *Fuel*, 80(10): 1391-1398.
- Pronobis, M. 2005. Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. *Biomass and Bioenergy*, 28(4), 375-383.
- Priyadarsan, S., Annamalai, K., Sweeten, J. M., Mukhtar, S. and Holtzapple, M. T. 2004. Fixed-bed gasification of feedlot manure and poultry litter biomass. *Transactions of the ASAE*, 47(5): 1689-1696.
- Puri, S., Singh, S. and Bhushan, B. 1994. Evaluation of fuel wood quality of indigenous and exotic tree species of india's semiarid region. *Agroforestry Systems*, 26, 123-130.
- Quaak, P., Knoef, H. and Stassen, H. 1999. Energy from biomass; a review of combustion

and gasification technologies. *World Bank Technical Paper no. 422. Energy Series.* World Bank, Washington, D.C., USA.

- Reed, T. B. 1981. *Biomass Gasification; Principles and Technology*. Solar Energy Research Institute (Noyes Data Corporation), Park Ridge, New Jersey, USA.
- Reed, T. B. and Das, A. 1988. *Handbook of Biomass Downdraft Gasifier Engine Systems*, Solar Energy Research Institute (U.S. Department of Energy), Colorado, USA.
- Richley, C. B., Barrett, J. R. and Klutz, L. J. 1983. *Development of a downdraft-channel gasifier furnace with mechanical fueling for crop drying*. Third Annual Solar and Biomass Workshop, Atlanta, Ga., USA.
- Ryu, C., Yang, Y. B., Khor, A., Yates, E. N., Sharifi, V. N. and Swithenbank, J. 2006. Effect of fuel properties on biomass combustion: Part I. Experiments - Fuel type, equivalence ratio and particle size. *Fuel*, 85(7-8): 1039-1046.
- Sampathrajan, A. 2002. Gasification of biomass. *Biomass Handling, Conversion and Management*. Tamil Nadu Agricultural University, Coimbatore, India.
- Sander, B. 1997. Properties of Danish biofuels and the requirements for power production. *Biomass and Bioenergy*, 12(3): 177-183.
- Souza-Santos, M. L. D. 2004. Solid Fuels Combustion and Gasification : Modeling, Simulation, and Equipment Operation. Marcel Dekker, New York, USA.
- Skrifvars, B. J., Ohman, M., Nordin, A. and Hupa, M. 1999. Predicting bed agglomeration tendencies for biomass fuels fired in fbc boilers: a comparison of three different prediction methods. *Energy Fuels*, 13(2): 359-363.
- Skrifvars, B. J., Yrjas, P., Kinni, J., Siefen, P. and Hupa, M. 2005. The fouling behavior of rice husk ash in fluidized-bed combustion. 1. Fuel characteristics. *Energy and Fuels*, 19(4): 1503-1511.
- Stallmann, J. J. and Neavel, R. C. 1980. Technique to measure the temperature of agglomeration of coal ash. *Fuel*, 59(8): 584-586.
- Steenari, B. M. and Lindqvist, O. 1998. High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite. *Biomass and Bioenergy*, 14(1): 67-76.
- Tijmensen, M. J. A., Faaij, A. P. C., Hamelinck, C. N. and van Hardeveld, M. R. M. 2002. Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. *Biomass and Bioenergy*, 23(2): 129-152.
- The Hindu, 2005. Survey of the Environment, The Hindu, Special Edition 2005, India.
- Thy, P., Grundvig, S., Jenkins, B. M., Shiraki, R. and Lesher, C. E. 2005. Analytical controlled losses of potassium from straw ashes. *Energy and Fuels*, 19(6): 2571-2575.
- Thy, P., Jenkins, B. M., Grundvig, S., Shiraki, R. and Lesher, C. E. 2006. High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel*, 85(5-6): 783-795.
- Thy, P., Lesher, C. E. and Jenkins, B. M. 2000. Experimental determination of high-temperature elemental losses from biomass slag. *Fuel*, 79(6): 693-700.
- Tran, Q. K., Steenari, B.-M., Iisa, K. and Lindqvist, O. 2004. Capture of potassium and cadmium by kaolin in oxidizing and reducing atmospheres. *Energy and Fuels*, 18(6): 1870-1876.
- Vamvuka, D. and Zografos, D. 2004. Predicting the behaviour of ash from agricultural wastes during combustion. *Fuel*, 83(14-15 SPEC ISS): 2051-2057.
- Venkatachalam, P. 2002. Biomass gasification systems. *Biomass Handling, Conversion and Management*. Tamil Nadu Agricultural University, Coimbatore, India.

- Weber, R. G. 1985. Performance of modified Inbert, downdraft gasifier dual fuelled and all gas using coconut husk and wood as the biomass fuel, *Republic of syeychelles* second International Producer Gas Conference, Bandung, Indonesia.
- Wei, X., Schnell, U. and Hein, K. R. G. 2005. Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation. *Fuel*, 84(7-8): 841-848.
- Wornat, M. J., Hurt, R. H., Yang, N. Y. C. and Headley, T. J. 1995. Structural and compositional transformations of biomass chars during combustion. *Combustion* and Flame, 100(1-2): 131-143.
- Zevenhoven-Onderwater, M., Blomquist, J. P., Skrifvars, B. J., Backman, R. and Hupa, M. 2000. The prediction of behaviour of ashes from five different solid fuels in fluidised bed combustion. *Fuel*, 79(11): 1353-1361.

# APPENDIX

Statistical Analyses

Hypothesis 2.1: Clinker Formation Increase in Function of Air Flow Rates; Linear Regression Analysis.

```
DATA Clinker_airflow_regr;
INPUT ind airflow clinker;
CARDS;
1 0.001 41.96
2 0.002 49.80
3 0.003 50.96
4 0.004 47.82
5 0.005 52.54
6 0.006 63.82
;
PROC REG data=Clinker_airflow_regr;
MODEL clinker=airflow;
RUN;
```

The SAS System 20:39 Wednesday, January 24, 2007 1 The REG Procedure Model: MODEL1 Dependent Variable: clinker Number of Observations Read 6 Number of Observations Used 6

### Analysis of Variance

		Sum of	Mean		
Source	DF	Squares	Square	F Value	Pr > F
Model	1	186.89692	186.89692	10.25	0.0329
Error	4	72.96768	18.24192		
Corrected Total	5	259.86460			

Root MSE	4.27106	R-Square	0.7192
Dependent Mean	51.15000	Adj R-Sq	0.6490
Coeff Var	8.35006		

### Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	39.71200	3.97614	9.99	0.0006
airflow	1	3268.00000	1020.97768	3.20	0.0329

Hypothesis 2.2: Rock Diminution in Function of Air Flow Rates; Linear Regression Analysis.

;

```
DATA Rocks airflow regr;
INPUT ind airflow rocks;
CARDS;
1 0.001 38.63
2 0.002 21.43
3 0.003 34.45
4 0.004 20.19
5 0.005 16.32
6 0.006 10.51
PROC REG data=Rocks_airflow_regr;
MODEL rocks=airflow;
RUN;
                   The SAS System
                                     20:52 Wednesday, January 24, 2007
                                                                        1
                                      The REG Procedure
                                        Model: MODEL1
                                  Dependent Variable: rocks
                           Number of Observations Read
                                                                6
                           Number of Observations Used
                                                                6
                                     Analysis of Variance
                                            Sum of
                                                            Mean
        Source
                                 DF
                                           Squares
                                                          Square
                                                                    F Value
                                                                               Pr > F
        Model
                                  1
                                         413.78052
                                                       413.78052
                                                                       9.71
                                                                               0.0357
        Error
                                         170.52557
                                                        42.63139
                                  4
                                         584.30608
        Corrected Total
                                  5
                     Root MSE
                                                     R-Square
                                                                  0.7082
                                           6.52927
                     Dependent Mean
                                          23.58833
                                                     Adj R-Sq
                                                                  0.6352
                     Coeff Var
                                          27.68009
                                     Parameter Estimates
                                  Parameter
                                                 Standard
             Variable
                          DF
                                   Estimate
                                                    Error
                                                             t Value
                                                                        Pr > |t|
              Intercept
                           1
                                   40.60733
                                                  6.07842
                                                                6.68
                                                                          0.0026
```

1560.79452

-3.12

0.0357

airflow

1

-4862.57143

Hypothesis 2.3: Biomass Consumption Rate in Function of Air Flow Rates; Linear Regression Analysis.

```
DATA BiomConsump_airflow_regr;
INPUT ind airflow BCRA BCRW;
CARDS;
1 0.001 2.0 2.6
2 0.002 4.2 4.0
3 0.003 6.0 7.5
4 0.004 8.2 9.2
5 0.005 10.7 12.3
6 0.006 11.3 13.7
;
PROC REG data=BiomConsump_airflow_regr;
MODEL BCRA=airflow;
MODEL BCRW=airflow;
RUN;
```

Coeff Var

1) Arecanut Husk Consumption Rate:

The SAS System 20:04 Sunday, February 18, 2007 16 The REG Procedure Model: MODEL1 Dependent Variable: BCRA Number of Observations Read 6 Number of Observations Used 6 Analysis of Variance Sum of Mean Source DF Squares Square F Value Pr > FModel 1 66.44629 66.44629 269.27 <.0001 Error 4 0.98705 0.24676 Corrected Total 5 67.43333 Root MSE 0.49675 R-Square 0.9854 Dependent Mean 7.06667 Adj R-Sq 0.9817

#### Parameter Estimates

7.02950

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	0.24667	0.46245	0.53	0.6220
airflow	1	1948.57143	118.74629	16.41	<.0001

# 2) Casuarina Equisetifolia Consumption Rate:

The SAS System 20:04 Sunday, February 18, 2007 17

### The REG Procedure Model: MODEL2 Dependent Variable: BCRW

Number	of	Observations	Read	6
Number	of	Observations	Used	6

## Analysis of Variance

		Sum of	Mean		
Source	DF	Squares	Square	F Value	Pr > F
Model	1	96.29157	96.29157	306.48	<.0001
Error	4	1.25676	0.31419		
Corrected Total	5	97.54833			

Root MSE	0.56053	R-Square	0.9871
Dependent Mean	8.21667	Adj R-Sq	0.9839
Coeff Var	6.82183		

### Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t
Intercept	1	0.00667	0.52182	0.01	0.9904
airflow	1	2345.71429	133.99157	17.51	<.0001

Hypothesis 3.1: Washing Treatment, Clinker Formation, Significant Difference between Sample Means; Washed vs. Unwashed.

```
Data Clinker_Formation;
Input quadrat treatment$ clinker;
cards;
1 UW 22.8
2 UW 24.6
3 UW 24.0
4 W 18.0
5 W 11.6
6 W 16.0
;
proc GLM data=Clinker Formation;
class treatment;
model clinker = treatment;
means treatment/LSD SNK;
run;
                                20:49 Wednesday, January 24, 2007 1
                 The SAS System
                                   The GLM Procedure
                                Class Level Information
                            Class
                                         Levels
                                                   Values
                                                   UW W
                            treatment
                                              2
                         Number of Observations Read
                                                           6
                         Number of Observations Used
                                                           6
                               The GLM Procedure
Dependent Variable: clinker
```

			Sum	of				
Source		DF	Squai	res	Mean	Square	F Value	Pr > F
Model		1	110.94000	000	110.9	400000	19.19	0.0119
Error		4	23.12000	000	5.7	800000		
Corrected Total		5	134.06000	000				
	R-Square	Coeff	Var	Root M	SE	clinker Me	an	
	0.827540	12.32	2904	2.40416	63	19.500	00	
Source		DF	Type I	SS	Mean	Square	F Value	Pr > F
treatment		1	110.94000	000	110.9	400000	19.19	0.0119

Source	DF	Type III SS	Mean Square	F Value	Pr > F
treatment	1	110.9400000	110.9400000	19.19	0.0119
	Ţ	The GLM Procedure	e		

## t Tests (LSD) for clinker

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error  $% \left[ {\left[ {{{\rm{T}}_{\rm{T}}} \right]_{\rm{T}}} \right]$ 

rate.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	5.78
Critical Value of t	2.77645
Least Significant Difference	5.4501

Means with the same letter are not significantly different.

t Grouping	Mean	Ν	treatment
А	23.800	3	UW
В	15.200	3	W

The SAS System 20:49 Wednesday, January 24, 2007 4

The GLM Procedure

Student-Newman-Keuls Test for clinker

NOTE: This test controls the Type I experiment wise error rate under the complete null hypothesis but not under partial null hypotheses.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	5.78

Number of Means2Critical Range5.4501394

Means with the same letter are not significantly different.

SNK Grouping	Mean	Ν	treatment
А	23.800	3	UW
В	15,200	3	W

Hypothesis 3.2: Washing Treatment, Moisture Content Variation in Husk, Significant Difference between Sample Means; Washed vs. Unwashed.

```
Data Moisture Content;
Input quadrat husk treatment$ moisture;
cards;
1 UW 11.88
2 UW 14.00
3 UW 11.88
4 UW 10.89
5 W 12.87
6 W 9.90
7 W 10.00
8 W 10.00
;
proc GLM data=Moisture Content;
class husk treatment;
model moisture = husk treatment;
means husk treatment/LSD;
run;
```

The SAS System

	The GLM P	rocedure		
	Class Level	Informatio	ı	
	Class	Levels	Values	
	husk_treatment	2	UW W	
	Number of Observatio Number of Observatio	ns Read ns Used	8 8	
	The GLM P	rocedure		
Dependent Variable: mois	sture			
	Su	m of		
0	55 0		•	

20:41 Wednesday, January 24, 2007 1

Source		DF	Squ	ares	Mean Square	F Va	lue	Pr > F
Model		1	4.3218	0000	4.32180000	2	.26	0.1836
Error		6	11.4839	5000	1.91399167			
Corrected Tota	1	7	15.8057	5000				
	R-Square	Coeff	Var	Root MS	E moisture	e Mean		
	0.273432	12.10	0651	1.38347	'1 11	.42750		

Source	DF	Type I SS	Mean Square	F Value	Pr > F
husk_treatment	1	4.32180000	4.32180000	2.26	0.1836
Source	DF	Type III SS	Mean Square	F Value	Pr > F
husk_treatment	1	4.32180000	4.32180000	2.26	0.1836

### The GLM Procedure

t Tests (LSD) for moisture

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error

rate.

Alpha	0.05
Error Degrees of Freedom	6
Error Mean Square	1.913992
Critical Value of t	2.44691
Least Significant Difference	2.3937

Means with the same letter are not significantly different.

t Grouping	Mean	Ν	husk_ treatment
A	12.1625	4	UW
A	10.6925	4	W

Hypothesis 3.3: Washing Treatment, Ash Formation, Significant Difference between Sample Means; Washed vs. Unwashed.

```
Data Ash_Formation;
Input quadrat treatment$ ash;
cards;
1 UW 28.07
2 UW 29.78
3 UW 27.72
4 W 20.65
5 W 25.39
6 W 28.62
;
proc GLM data=Ash_Formation;
class treatment;
model ash = treatment;
means treatment/LSD SNK;
run;
```

The	SAS	System	20:45	Wednesday,	January	24,	2007	1

The GLM Procedure

Class Level Information

Class	Levels	Values
treatment	2	UW W

Number	of	Observations	Read	6
Number	of	<b>Observations</b>	Used	6

The GLM Procedure

Dependent Variable: ash

		Sum of			
Source	DF	Squares	Mean Square	F Value	Pr > F
Model	1	19.83801667	19.83801667	2.30	0.2043
Error	4	34.57053333	8.64263333		
Corrected Total	5	54.40855000			

	R-Square 0.364612	Coe 1	eff Var 1.00856	Root 2.93	MSE 9836	ash M 26.70	ean 500	
Source treatment		DF 1	Type 19.8380	I SS 1667	Mean \$ 19.838	Square 301667	F Value 2.30	Pr > F 0.2043
Source		DF	Type II	I SS	Mean S	Square	F Value	Pr > F
treatment		1	19.8380	1667	19.83	801667	2.30	0.2043

#### The GLM Procedure

## t Tests (LSD) for ash

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error  $% \left[ {\left[ {{{\rm{T}}_{\rm{T}}} \right]_{\rm{T}}} \right]$ 

rate.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	8.642633
Critical Value of t	2.77645
Least Significant Difference	6.6645

Means with the same letter are not significantly different.

t Grouping	Mean	Ν	treatment
А	28.523	3	UW
A	24,887	3	W

Hypothesis 3.4: Washing Treatment, Wood char formation, Significant Difference between Sample Means; Washed vs. Unwashed.

```
Data WoodChar_residues;
Input quadrat treatment$ woodchar;
cards;
1 UW 70.5
2 UW 46.3
3 UW 47.3
4 W 64.9
5 W 52.7
6 W 65.9
;
proc GLM data=WoodChar_residues;
class treatment;
model woodchar = treatment;
means treatment/LSD SNK;
run;
```

The GLM Procedure

Dependent Variable: woodchar

			Su	m of			
Source		DF	Squ	ares	Mean Square	F Value	Pr > F
Model		1	62.726	6667	62.7266667	0.52	0.5109
Error		4	482.986	6667	120.7466667		
Corrected Tota	1	5	545.713	3333			
	R-Square 0.114944	Coeff 18.90	Var 6745	Root MS 10.9884	E woodcha 8 57	r Mean .93333	

The GLM Procedure

t Tests (LSD) for woodchar

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error

rate.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	120.7467
Critical Value of t	2.77645
Least Significant Difference	24.91

Means with the same letter are not significantly different.

t	Grouping	Mean	Ν	treatment
	А	61.167	3	W
	А			
	А	54.700	3	UW

Hypothesis 3.5: Washing Treatment, Rock Residues, Significant Difference between Sample Means; Washed vs. Unwashed.

```
Data Rocks residues;
Input quadrat treatment$ rocks;
cards;
1 UW 0.0
2 UW 3.8
3 UW 28.7
4 W 0.0
5 W 49.1
6 W 0.0
;
proc GLM data=Rocks_residues;
class treatment;
model rocks = treatment;
means treatment/LSD SNK;
run;
                                     20:57 Wednesday, January 24, 2007
                    The SAS System
                                                                      1
                                     The GLM Procedure
                                  Class Level Information
                              Class
                                             Levels
                                                      Values
                               treatment
                                                  2
                                                      UW W
                           Number of Observations Read
                                                               6
                           Number of Observations Used
                                                               6
                   The GLM Procedure
Dependent Variable: rocks
                                            Sum of
      Source
                         DF
                                               Mean Square
                                                                        Pr > F
                                   Squares
                                                             F Value
     Model
                         1
                                45.926667
                                                45.926667
                                                               0.09
                                                                       0.7818
                                                       523.313333
     Error
                                 4
                                       2093.253333
      Corrected Total
                                 5
                                       2139.180000
                      R-Square
                                  Coeff Var
                                                 Root MSE
                                                            rocks Mean
                      0.021469
                                   168.2062
                                                 22.87604
                                                              13.60000
      Source
                      DF
                              Type I SS
                                            Mean Square
                                                          F Value
                                                                     Pr > F
```

45.92666667

0.09

0.7818

45.92666667

1

treatment

Source	DF	Type III SS	Mean Square	F Value	Pr > F
treatment	1	45.92666667	45,92666667	0.09	0.7818

The GLM Procedure

### t Tests (LSD) for rocks

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error  $% \left[ {\left[ {{{\rm{T}}_{\rm{T}}} \right]_{\rm{T}}} \right]$ 

rate.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	523.3133
Critical Value of t	2.77645
Least Significant Difference	51.859

Means with the same letter are not significantly different.

t Grouping	Mean	Ν	treatment
А	16.37	3	W
A A	10.83	3	UW

The SAS System 20:57 Wednesday, January 24, 2007 4

The GLM Procedure

#### Student-Newman-Keuls Test for rocks

NOTE: This test controls the Type I experimentwise error rate under the complete null

hypothesis but not under partial null hypotheses.

Alpha	0.05
Error Degrees of Freedom	4
Error Mean Square	523.3133
Number of Means	2
Critical Range 5	1.859054

Means with the same letter are not significantly different.

SNK Grouping	Mean	Ν	treat	ment
A	16.37	3	W	
A	10.83	3	UW	