INVESTIGATION OF BIOMASS BRIQUETTES AS ENERGY SOURCES THROUGH THEIR CALORIFIC VALUES IN RELATION TO THEIR TOTAL CARBON/HYDROGEN CONTENT FOR EFFICIENT BIOFUEL UTILIZATION

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NOVEMBER, 2012

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DECLARATION

I hereby declared that:

(i) The report presented in this thesis is the results of my original research work,

(ii) This thesis has not been submitted to any other institution, for any award other than Ahmadu Bello University, Zaria,

(iii) All inclusions from other research works have been duly referenced and acknowledged.

Ismaila Aminu _____ _____

Signature Date

CERTIFICATION

This thesis entitled Investigation on Biomass Briquettes as Energy Sources through Their Calorific Values in Relation to Their Total Carbon/Hydrogen Content for Efficient Biofuel Utilization by Ismaila Aminu meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

To my family

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ABSTRACT

The relationship between the high heating values (HHVs) and total hydrogen and carbon contents of fourteen (14) selected biomass briquettes in terms of grain size, pressure and binders is studied. Analyses of the experimental results show that the high heating values of the biomass tested are not linearly related to their total hydrogen contents but directly related to their total Carbon contents. Comparison of the measured and calculated HHVs of the biomass samples reveal that the calculated measurement of the HHVs compared well with that of the American Standard of Testing Materials (ASTM) results and also in agreement with the widely reported values in the acceptable range of 17-21MJ/kg. The investigation of the effect of particle size and added binder in the biofuel preparation indicates that finely ground particles (about 125μm) had low calorific values as the grinding resulted in a loss of some heat and made the sample vulnerable to air oxidation while addition of Poly Vinyl Cloride (PVC) dissolved in toluene organic binder tend to decerease the HHVs to about half the original values for the range of biomass tested.

TABLE OF CONTENTS

Title Page……..……i

Declaration……..……iii

Certification…….……iv

Dedication…….……..……..ii

Acknowledgements ……..…….…….……...v

Abstract…….…….……vi

Table of contents ……..…….……vii

List of Tables……..…….…….……...xi

List of Figures……..…….……..….....x

List of Appendices and Plates……...……...…..…xii

Nomenclature ……..……..xiii

CHAPTER ONE

1.0 **GENERAL INTRODUCTION**……...…….....1.0

1.1 Statement of Research Problem ……..…….....4.0

1.2 Aims and Objectives……..…….……5.0

1.3 Justification……...…….…….…….....5.0

1.4 Research Scope…….....6.0

CHAPTER TWO

2.0 **LTERATUTRE REVIEW**……..……...….....7.0

2.1 The Calorific Value or Heating Value…….……..….....12

2.2 Biomass Types…….....14

2.3 Plant Characteistics……...…….....16

2.4 Hydrogen as Fuel/Hydrogen Economy……...…17

2.5 Theoretical Aspects of Neutron Reflection Technique……..……19

2. 5.1 General……..……..……19

2.6 The Neutron…….……..….20

2.6.1 Neutron Energy Classification……..…..……....21

2.7 Neutron Sources……..…….……..22

2.7.1 Isotopic Neutron Sources (ISNS)……..…..…….....22

2.7.1.1 Alpha (α, n)…….…….....22

2.7.1.2 Photo-Neutron (γ, n) Sources (PNS)…….....23

2.7.1.3 Spontaneous Fission Sources (SFS)…….....24

2.7.2 Neutron Generators (NG)…….....24

2.7.3 Nuclear Reactors (NR)……..…..…..25

2.8 Theory of Neutron Thermalization…….…….....26

2.8.1 Interaction of Neutron with Matter…….……...……..27

2.8.2 Neutron Detection…….....30

2.8.3 The Concept of Neutron Reflection…….....31

2.8.4 Neutron Reflection Property (Albed……...…….....33

CHAPTER THREE

3.0 Research Methodology…….……...……..….35

3.1 Sampling of Biomass Materials.....……..35

3.2 Analytical Procedure Using Bomb Calorimeter…….…..……..…35

3.2.1 Sample Preparation……..……..35

3.2.2 Experimental Set-up for the Bomb Measurement……...…….……...36

3.2.3 Analysis Procedures for the Bomb Measurement……..38

3.3: Analytical Procedure Using Neutron Reflection Set up…….……40

3.3.1 Sample Preparation…….……42

3.3.2 Experimental Arrangement for the Determination of H Using n- Reflection Technique……..42

3.3.2.1 The ^{3}He Neutron Probe……...……..43

3.3.2.2 Electronic Counting Set-up…….……..44

3.3.2.3 Analysis Procedure……...45

3.4 Density Measurement ……..……...……47

3.5 Determination of Nitrogen Sulphur and Carbon……...…….…..47

3.5.1 Determination of Nitrogen by Kjeldahl Method……..…48

3.5.2 Determination of Sulphur……...49

3.5.3 Determination of Carbon Content……...….49

3.6 Determination of Ash Content……...50

3.7 The Use of Empirical Equations to Estimates HHVs……..……..…50

CHAPTER FOUR

4.0 **RESULTS AND DISCUSSION**……..…….....51

4.1: Samples' Densities ……...…….....……51

4.1.1 Excess Count Rates for Fourteen biomass Samples…….……..…51

4.1.2 Densisitis and Excess Count Rates for Fourteen biomass Samples……..52

4.2: Relationship Between HHVs (MJ/Kg) and Hydrogen Contents (%wt) of Samples 54

4.3: Ultimate Analysis of the Biomass Samples…….....57

4.4: Effectct of Particle Size on HHVs of the Samples……..…….....60

4.5: Effect of Binder on High Heating Values……..……62

4.6: Comparison Between Direct and Indirect HHVs of the Samples …..……....64

CHAPTER FIVE

5.0 **SUMMARY, CONCLUSION AND RECCOMMENDATION FOR FURTHER WORK**…….……...…....67

5.1 Summary……..…….....67

5.2 Conclusion …….…....68

5.3 Reccommendation for Further work: …..……..….....69

REFERENCES:……..…….…..….71

LIST OF TABLES

Table 2.1: HHV, Ultimate and Proximate Analysis of Some Selected Biofuels.....13

Table 2.2: Cellulose/Lignin Content of Some Selected Biomass (wt%) …….....16

Table 3.1: Reflection Parameter of Compound Used for the determination of Hydrogen..41

Table 4.1: Densities and Excess Count Rates for Fourteen biomass Materials……..53

Table 4.2: Relationship Between HHVs and H-contents (%wt) of the Samples…….55

Table 4.3: Ultimate Analysis (%mass, dry basis) of Plant Bomass Samples…….57

Table 4.4: Ultimate analysis % by wt (dry basis) Compared……..……59

Table 4.5: Effectct of Particle Size on HHVs of the Samples ……..…….61

Table 4.6: Effect of Binders on Gross Calorific Values…. …….…….....64

Table 4.7: Comparison Between Direct and Indirect HHVs of the Biomass Fuels…..…..66

LIST OF FIGURES

Figure 2.0: DSC Curves of Common Milkweed……..…….....….8.0

Figure 2.1: Hydrogen Cycle…….……..……..…19

Figure 3.1: Schematic diagram of the experimental set up ……..…….....37

Figure 3.2: Schematic Diagram of the Bomb Calorimeter……..38

Figure 3.3: Calibration Line for Materials used for the determination of H…….....…..41

Figure 3.4: Arrangement of Neutron reflection Technique……..……...…….43

Figure 3.5: The ^{3}He Detector……...…..…..…44

Figure 4.0: HHVs Against Total Hydrogen Content (%wt)…….……...56

Figure 4.1: HHVs Against Total Carbon Content (%wt)……...56

Figure 4.2: Comparison between ultimate analysis of this work and that of Chaniwala et al.……..59

Figure 4.3: Effect of Particle Size on HHV……..……..…62

Figure 4.4: Measured HHV with and without Binder…….63

Figure 4.5: Comparison between Direct and Indirect HHVs……..65

LIST OF PLATES

Plate I: Source Holder with Sample Holder in Place……..……....42

Plate II: Electronic Counting Set Up……...45

NOMENCLATURE

ASTM-American Standard of Testing Materials

CV-Calorific Value

CO_2-Carbon dioxide

CPS-Count per Second

COSHH-Control of Substances Hazardous to Health

CHNOS-Carbon, Hydrogen, Nitrogen, Oxygen and Sulfur

DSC-Differential Scanning Calorimetry

etc- and so forth

HC-Hydrocarbon

^{3}He- Helium-3

HHV-Higher Heating Value

i.e. - that is

LHV-Lower Heating Value

MJ/Kg-Mega Joule per Kilogram

NCV-Net Calorific Value

PVC-Poly Vinyl Chloride

Vs-Versus

Wt%-Weight Percent

CHAPTER ONE

GENERAL INTRODUCTION

1.0 INTRODUCTION

Since the beginning of the last century fossil fuels had became the major source of global energy. In the last 110 years large quantities of oil, gas and coal were removed from their ground deposits. These fuels are generally used as sources of energy in transport engines, heating applications and electricity, and in some instances as raw-materials for the petrochemical industries. Although, the fossil fuels play a key role in the global economic and political situations, their numerous challenges accounted for a shift to more sustainable energy sources (El Shinnawi *et al.,* 1989; Hodgson, 1999, Fabian, 2003). Environmental and ecological problems are the major issue of concern associated with exploitation of these fuels. There are currently about 750 Giga tones of CO_2 in the atmosphere, a greenhouse gas that was identified as the major contributor to the current global warming problems (Abdullahi *et al,* 2011). Reports by Intergovernmental Panel on Climate Change (IPCC, 2007) revealed that, the world is experiencing severe consequences ranging from drought, melting of sea ice, diminishing of important plant and animal species, acid rain to overspread of diseases especially in the developing countries like Nigeria. Oil spill and gas flaring are another environmental threats associated with exploitation of fossil fuels particularly in a regions that are so close to the fossil fuel source. Burgher (2007) had shown that between 1970 and 2004 more than 700 tons of oil were accidentally spilled from tankers across the globe, the consequences of which include economic loses and destruction of marine plants and animals (Hischberg *et al.,* 2004). Another major challenge with these fuels is their un-sustainability and projected depletion over the years. Campbell

and Laherrere (1998), Shell global and Exxon Mobil (2006) use several technological methods to quantify the current known crude oil reserves and reserves that are yet undiscovered. They predicted that worldwide crude oil production will begin to decline by 2010 and resources will last for the next 40 years at the current rate of consumption and this has been a constant ratio for at least the last 15 years (Andrews, 2010). They also concluded that annual global oil production would decline from current twenty five (25) billion barrels to approximately five (5) billion barrels per day by 2050 (Sun and Cheng, 2002; Nigam and Singh 2010). Similar predictions were made by Hodgson (1999), as he predicted that increased production from large oil fields (e.g. that of Alaska) is declining at the rate of 4 – 5% annually. While the total reserves would only last for the next few decades, the consumption is seriously projected to increase worldwide. For example, analysis by Hodgson (1999) showed that the energy consumption in the decade 1984-94 rose by 1.6% per year worldwide, 1.4% in Western Europe, 2.3% in Africa, 4.3% in China, and 6.1% in India. In 1996 the use of oil increased by 2.3%, natural gas by 4.5%, coal by 2.3% nuclear by 2.3% and hydro by 1%. There is increasing energy demand in many countries around the world.

The use of fuel wood in large scale without replenishing poses serious environmental consequences in many countries, desertification being the most important one. The increase in Nigeria's population places more demands on energy to light and heat homes, to cook food, to drive our transport, and communication devices and provide power for industries. To address the various energy challenges associated with non-renewable fuels, many countries have indicated commitment to biofuels production that are renewable,

sustainable, cheap, efficient, safe and geographically diversified. Solid and liquid biofuels in particular, had become an important source of energy even in the rural communities. Brazilian efforts to reduce fossil fuels consumption by using blends fuels is a good attempt in this direction. Today, majority of transport vehicle in Europe and North America are designed to run on blend of at least 5% biofuels. The main advantage of biofuels are its domestic origin, potential for reducing total dependence on oil and gas economy, it also offers benefits of regional development, and social structure, especially to developing countries like Nigeria. Despite the international commitments to sustainable energy development, the Nigerian government and the local communities have only indicated a partial concern. In fact very few biofuels producing units, operating mainly on a significantly low level of technology are available in Nigeria. The bush biomass, agricultural edible and non-edible oil seeds and grains, other agricultural and industrial wastes that are largely produced daily in the country could be employed as raw-materials for both small and large scale solid and liquid biofuels production. In addition to energy security and waste management, the biofuels production has strong potentials for jobs creation and source of revenues to the government and rural farmers.

In order to provide a means of quantification of energy content of biomass, this work investigated the relationship between gross calorific values (GCV) and total hydrogen and carbon content of fourteen (14) selected plant biomass. The work also determined the key effects of particle size and addition of binder on the calorific values (heat value) for various biofuels samples. It was an experimentally based project and employed the used Oxygen bomb calorimeter (Parr 6100 model) and ultimate analysis in determining the

calorific values of biofuels either directly or indirectly. Total hydrogen contents of various biomass samples were also determined by neutron reflection technique.

1.1 STATEMENT OF RESEARCH PROBLEMS

The key problems of using solid biofuels for heat and electricity applications is that they have

(i) a relatively low energy density compared with conventional fuels

(ii) Can easily absorb moisture on storage which may consequently reduce its energy contents.

(iii) There is also problem of high energy consumption during collection and

(iv) Problem of high energy consumption during transportation of the raw materials.

Since it is very difficult to solve all the problems at the same time, this study focus on the first and fourth problems and attempts to answer the following questions

- Can the abundant solid biomass resources of energy have the potential to substitute or largely supplement the conventional fuel in domestic and industrial heating processes in Nigeria?
- Does the biomass particle size and addition of binders in the biofuel preparation have effects on the calorific value of particular biomass material?
- How does the hydrogen and carbon content relates to the calorific value of biomass?

1.2 AIM AND OBJECTIVES OF THE RESEARCH

The aim of the project is to investigate the relationship between calorific values and the total hydrogen and carbon contents (%wt) of fourteen (14) selected solid biofuels available either as waste or specifically grown for the energy generation.

The objectives include:

- Investigation of the effect of biomass particle size and effect of binder on the thermal (calorific) value of particular biomass specie.
- To compare measured and calculated calorific values and see how well the empirical correlations by Channiwala and Parikh and Boie predict experimental results.
- Analytically measure the total sulphur and nitrogen contents of biomass in order to observe their potential as environmentally safe energy source.

1.3 JUSTIFICATION

Industries worldwide are faced with regulatory and competitive pressures to control emissions and reduce operating costs. Consequently, Biofuel Briquettes for Utilization as Energy Source for domestic and industrial heating processes can significantly reduce emissions of air pollutants and enhance research on the development and application of alternative and cost-effective energy sources which will make a significant contribution to improving national energy efficiency, optimised profit as well as enhance rural development goals and global competitiveness for Nigerian industries. Knowing the energy potentials (thermal values and elemental composition) of some selected plant biomass most of which are currently thrown away or burned in our farmlands, can certainly contribute in prospective and diagnostic studies regarding the use of renewable

energies especially solid bioresources and enhance research for changing waste to wealth in any sector of national economy.

1.4 RESEARCH SCOPE

The research covers determination of the high heating (calorific) values and total hydrogen (H), carbon (C), oxygen (O), nitrogen (N), and sulphur (S) of fourteen (14) selected plant biomass. The work considered combination of solid fuel from energy crops (fast-growing plants, trees and herbaceous biomass) and agricultural residues (rice straw/husk, wheat straw, cotton stalks, sugarcane waste, groundnut shell, saw dust, corn stalks, flamboyant). The relationship between the high heating values (HHV) and total hydrogen and carbon contents of the biomass was investigated. The work also considered the effect of biomass particle size and effect of binder on the calorific value of a particular biomass material. Comparisons between measured and calculated calorific values were made in order to see how well the empirical correlations by Boie and Channiwala and Parikh may predict experimental results.

CHAPTER TWO

LITERATURE REVIEW

2.0 INTRODUCTION

The determination of the calorific values and percentage of C, H, N, S and O of biofuels are important in considering their suitability as environmentally safe energy sources and their potential to produce a particular bio-energy that can be used for industrial and domestic process heat (Kumar and Pratt, 1996). Estimation of high heating value from the elemental composition of fuel is also important in performance modeling calculations on thermal system (Kumar and Pratt, 1996).

"The direct determination of calorific values of fuel materials by differential scanning calorimetry (DSC) was introduced by Fayans in 1977. This technique measures heat flow as a function of temperature with total area under the curve being proportional to the heat of combustion. A typical thermocurve shows two-step decomposition with the first peak relating to the combustion of volatiles and the second to the fixed carbon in the sample" Figure 2.1 (Kumar and Pratt, 1996). Kumar and Pratt (1996) quoted Varhegyi et *al.* (1986) that DSC curves reveal considerably less energy release than the true heat of combustion due to experimental conditions; they proposed the use of metallic catalysts as aids to material combustion so as to correct this shortcoming.

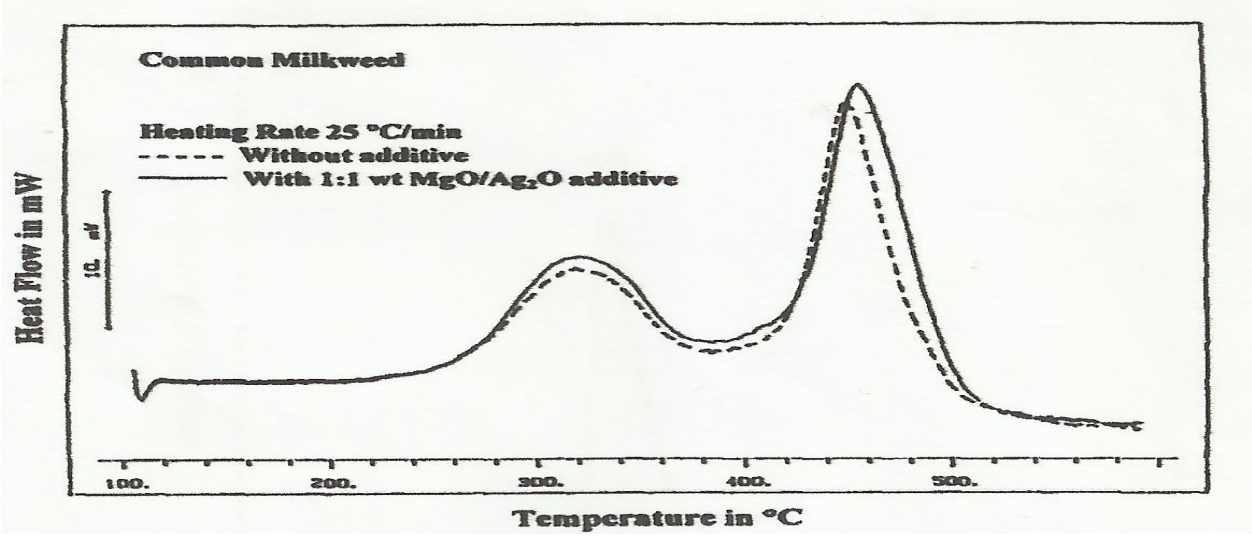


Figure 2.1: DSC Curves of common milkweed (Source: Kumar and Pratt, 1996)

Kumar and Pratt (1996) extend the use of differential scanning calorimetry (DSC) and elemental analysis (EA) to measure calorific values of some biofuels such as common milkweed, dogbane, kudzu, and eucalyptus tree. The biofuels were analyzed under the same conditions as the standard coal samples and the calorific values of direct and indirect determinations were compared. They obtained calorific values that are in quite agreement with that published by American Standard of Testing Materials (ASTM) using Bomb calorimeter.

A method for calculating the calorific values of coal from the elemental composition has been introduced by Culmo in 1977. Percents of carbon, hydrogen, oxygen, sulphur, moisture and ash were used to calculate the calorific values from the Dulong equation as shown in (2.00) (Kumar and Pratt, 1996):

$$CV = 144.4(\%C) + 610.2(\%H) - 65.9(\%O) - 0.39(\%O)^2 \qquad (2.00)$$

%C, %H, %N, %O are the respective C, H, N, O contents of the coal on a dry ash free (daf) basis. Dulong suggests the following formula for gross calorific value (GCV) of fossil fuels when oxygen content is less than 10%

$$GCV = 337\ C + 1442\ (H - O/8) + 93\ S \qquad (2.01)$$

GCV is in (KJ/kg). C, H, O, S is percentages on weight basis for carbon, hydrogen, oxygen and sulphur. The net calorific value for constant pressure combustion is:

$$NCV = GCV - mc * hfg \qquad (2.02)$$

mc is the mass of condensate per unit quantity of fuel and hfg is the latent heat of steam at 25 degree Celsius which is 2442 kJ/kg (www.taftan.com).

There have been many attempts at correlating the heating value with the elemental composition of biomass. The published correlations are divided into two:

(a) The correlations based on the assumption that the combustion reactions of C, H, and S to CO_2, H_2O and SO_2 respectively with different assumptions regarding association of oxygen with hydrogen or carbon

(b) the correlations based on the assumption that the HHV of fuel is proportional to the amount of oxygen/air required for complete combustion, the constant of proportionality being represented either as a function of oxygen or hydrogen content in the fuel (Channiwala and Parikh, 2002). In the earlier work by Channiwala and Parikh (2002), they presented about 22 important empirical correlations with their corresponding basis and assumptions, though many of the relations have been derived for coals. Tillman (1978) observed that the high heating value of biomass materials is a very strong function of its

carbon content and based on this he derived the following correlation for wood and wood barks combustion:

$$HHV = 0.4373C-0.3059 \text{ MJ/Kg} \quad (2.03)$$

The above equation was later modified to equation 2.04 to cover whole range of biomass materials (Channiwala and Parikh, 2002)

$$HHV = 0.4373C-1.6701 \text{ MJ/Kg} \quad (2.04)$$

Yin (2011) developed a new empirical correlation for estimating the HHVs of various lignocellulosic materials, using their ultimate analysis data. The relation between the observed HHV and C, H and O contents of the samples (wt %) was investigated. Thus the HHV (MJ/kg) of lignocellulosic materials including C, H and O can be calculated from equation 2.05.

$$HHV \text{ (MJ/kg)} = 0.335C + 1.423H – 0.154O \quad (2.05)$$

The above equation indicates that hydrogen and carbon atoms are contributing to the heating value positively, and oxygen content is contributing negatively. It is therefore an important step in some biomass conversion routes to de-oxidize the biomass in order to increase the heating value.

Cellulose has a smaller heating value than lignin because of its higher degree of oxidation. Other compounds, such as HC in the fuel with lower degrees of oxidation, tend to raise the heating value of the biomass (Demirbas, 2001). This work will use a unified correlation for estimating HHV of solid, liquid, and gaseous fuels developed by Channiwala and Parikh (2002) and that of Boie's (1953) given by equations 2.06 and 2.07 respectively.

$$HHV= 0.3491C + 1.1783H + 0.1005S – 0.1034O – 0.0151N – 0.0211A \quad (2.06)$$

$$HHV = 0.3517C + 1.1626H + 0.1047S + 0.0628N - 0.111O \text{ MJ/Kg} \quad (2.07)$$

The above correlations make it possible to accurately predict the gross heating values of most biomass fuels of known ultimate composition and ash content (Annamalai and Ramalingam, 1987; Chaniwala and Parikh, (2002). Where C, H, O, N and A in equation 2.06 or 2.07, represents carbon, hydrogen, oxygen, nitrogen, sulfur and ash contents of materials expressed in mass percentage on dry basis.

The simultaneous determination of C, H, N, O and S in organic compounds was done by Pella and Colombo in 1978 using a Carlo Erba Elemental Analyzer, Model 1106. Sadek and deBot (1987) determined C, H, N, and S simultaneously along with oxygen (O) in coal samples using this analyzer. Kumar and Pratt (1996) also used this same analyzer to determine simultaneously C, H, O, and S for biofuels. These determined elements were used to estimate the calorific values of various biomasses. The calorific value of biomass is much lower than coal, hydrocarbon oil and gas because of its high oxygen contents see table 2.1 for comparison.

There are a number of technologies in use and many under development for production of biofuels depending on their states. The well-know technologies for conversion of biomass to liquid biofuels include: fermentation of sugars and starchy substrates to bio-ethanol, hydrolysis of cellulose materials to bio-ethanol, catalytic technology of converting ethanol to mixed hydrocarbon, bio-butanol by fermentation, transesterificaiton of natural oils and fats to biodiesel, hydro cracking of natural oils and fats, pyrolysis and gasification of various organic materials etc (Demirbas, 2005).

Biomass can be transformed to solid biofuels as briquettes, logs, bales, chips, pellets, etc and this is the main concern of this work.

2.1 THE CALORIFIC VALUE OR HEATING VALUE

The calorific value (CV) of a fuel is an expression of the energy content, or heat value, released when a unit value of it is burnt in air (McKendry, 2002; Jones 2009). It is the amount of heat in, or work obtainable from, a unit amount of the energy resource. It is another important parameter, which determines the quality of an energy source. The energy resources being analysed in this work contain C, O and H in major concentrations, while S, N, and a number of other elements in minor or trace concentrations. The calorific value is measured in a standard test in a bomb calorimeter. It can also be estimated from the ultimate analysis usually reported on a "dry" or dry ash free "daf" basis. The CV is usually given in terms of the energy content per unit mass, or volume of substance; hence MJ/kg for solids, MJ/L for liquids, or MJ/Nm^3 for gases. The CV of a fuel can be expressed in two forms, the gross CV (GCV), or higher heating value (HHV) and the net CV (NCV), or lower heating value (LHV). The high heating value (HHV) or gross calorific value (GCV) is the total energy content released when the fuel is burnt in air, including the latent heat contained in the moisture and water from combustion and therefore represents the maximum amount of energy potentially recoverable from a given biomass source (Annamalai *et al.,* 1987; McKendry, 2002).The actual amount of energy recovered will vary with the conversion technology, as will the form of that energy i.e. combustible gas, oil, steam, etc. In practical terms, the latent heat contained in the water vapour cannot be used effectively and therefore, the LHV is the appropriate value to use for the energy available for subsequent use (McKendry, 2002).The lower heating value (LHV) or net

calorific value (NCV) measures the maximum amount of sensible heat which can be extracted from the combustion of fuel if water in the fuel and water generated during combustion exit as steady flow in gaseous state (www.handbook.ifrf.net, Chandra and Payne, (1986) and McKendry, (2002). It is assume that the latent heat of vaporisation of the water cannot be recovered. Table 2.1 (adapted from McKendry, P., (2002); Annamalai *et al, (*1987) with modification) shows the ultimate analysis and calorific values (CV) of some typical biomass materials. It can be seen that the energy content of biomass (on dry ash-free basis) is similar for all plant species, ranging from 17-21 MJ/Kg.

Table 2.1: High heating value, ultimate and proximate analysis of some biofuels (Source: McKendry, P., (2002); Annamalai *et al,* (1987) and Channiwala and Parikh, (2002)

Fuel common name	Moisture (wt%of fuel)	Ash(wt% of dryfuel)	HHV(MJ/kg Daf)	C	H	O	N	S
Almond shells	7.5	2.9	19.8	-	-	-	-	-
Almond hulls	8.0	5.8	20.0	-	-	-	-	-
Beech wood	6.5	0.6	19.6	51.6	6.3	41.4	-	-
Oak wood	`1	1.7	19.8	51.6	6.3	41.5	0	0.1
Olive husk	6.8	2.1	21.8	-	-	-	-	-
Rice straw	11.12	19.2	18.7	41.4	5.0	39.9	0.7	0.1
Rice husk	8.47	21.24	14.693	38.5	5.2	34.6	0.5	-
C/nut shell	8.27	0.71	20.498	50.3	5.7	43.4	0.0	-
Saw dust	-	5.83	19.970	47.2	5.9	40.4	0.7	0.16
Bagasse	-	11.27	17.330	44.8	5.4	39.6	0.4	0.01
Switch grass	13.1-15	4.5-5.9	17.4-19.9	-	-	-	-	-
Wheat straw	6.4-16	8.1	19.3	42.8	5.5	1.0	0.7	0
Berley straw	30	6	16.1	45.7	6.1	38.3	0.4	0.1
Walnut shell	-	2.8	-	53.6	6.0	35.5	1.5	0
Cereal straw	6.0	4.3	17.3	-	-	-	-	-
Miscanthus	11.5	2.8	18.5	48.1	5.4	42.2	0.5	<0.1
Coal (Bituminous)	8-12	8.0	26	81.5	4.0	3.3	1.2	3
Hydrocarbon Oil	-	-	44	-	-	-	-	-
Natural Gas (Methane)	-	-	55	-	-	-	-	-

When quoting a CV, the moisture content needs to be stated, as this reduces the available energy from the biomass. It appears normal practice to quote both the CV and crop yield on the basis of dry matter tonnes (dmt), which assumes zero percent moisture content. If any moisture is present, this reduces the CV proportional to the moisture content (McKendry, 2002). Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is negligible. Moisture content in coals varies in the range 2-30%. However, the bulk density (and hence energy density) of most biomass feedstock is generally low, even after densification – between 10% and 40% of the bulk density of most fossil fuels. Liquid biofuels however have bulk densities comparable to those for fossil fuels.

2.2 BIOMASS TYPES

Biomass is the name given to any natural material considered as a source of energy or chemicals (Jones, 2009). It includes woods, grasses, straws, forestry residues, agricultural wastes etc. All biomass convert CO_2 and sunlight into the organic substances that make up plants (through the process of photosynthesis). Biomass is (in theory) also 'CO_2 neutral'.

Solid fuels are characterised by their ultimate analysis (C, H, N, S, O contents), proximate analysis (moisture, volatiles, fixed carbon and ash) and heating value. This data can be reported on "as received (a.r)", "dry" or "dry ash free (d.a.f.)" and these bases can be readily inter-converted. Compared to coal, biomass, in general, has lower ash, higher moisture, higher O content, lower N & S contents and lower heating value and energy content.

In general, researchers have characterized the various types of biomass in different ways but simply can be classified into four main groups, namely:

•Woody plants (e.g. trees),

• Herbaceous plants/grasses (perennial crops)

• Aquatic plants, and

• Manures.

Within this categorization, herbaceous plants can be further subdivided into those with high- and low-moisture contents. Apart from specific applications or needs, most commercial activity has been directed towards the lower moisture-content types, woody plants and herbaceous species and these are the types of plant biomass that were investigated in this study. Aquatic plants and manures are intrinsically high-moisture materials and as such, are more suited to 'wet' processing techniques (McKendry, 2002). High moisture content biomass, such as the herbaceous plant sugarcane, lends itself to a 'wet/aqueous' conversion process, involving biologically mediated reactions, such as fermentation, while a 'dry' biomass such as wood chips, and plant residues are more economically suited to thermal conversion technologies such as gasification, pyrolysis or combustion. On this basis, woody and low moisture content herbaceous plant species are the most efficient biomass sources for thermal conversion to liquid fuels such as bio-ethanol, biodiesel, and methanol. However, there are other factors which must be taken into consideration in determining the selection of the conversion process, apart from simply moisture content, especially in relation to those forms of biomass which lie midway between the two extremes of 'wet' and 'dry'. Examples of such factors are the ash/residue, alkali and trace component contents, which impact adversely on thermal conversion

processes and the cellulose content, which influences biochemical fermentation processes (McKendry, 2002).

2.3 PLANT CHARACTERISTICS

The main components of all biomass are CELLULOSE (($C_6H_{10}O_5$) n, HEMICELLULOSE (($C_5H_8O_4$) n), LIGNIN (polymer with phenol units or cross linked phenyl propane polymer) and small amount of other extractives. Woody plant species are typically characterised by slow growth and are composed of tightly bound fibres, giving a hard external surface, while herbaceous plants are usually perennial, with more loosely bound fibres, indicating a lower proportion of lignin, which binds together the cellulosic fibres: both materials are examples of polysaccharides; long-chain natural polymers (McKendry, 2002, Jones 2009). Table 2.2 present the proportions of cellulose, hemicelluloses and lignin content of some selected biomass.

Table 2.2: Cellulose/lignin content of some selected biomass (wt %)

Biomass	Lignin (%)	Cellulose (%)	Hemicelluloses (%)
Softwood	27-30	35-40	25-30
Hardwood	20-25	45-50	20-25
Wheat straw	15-20	33-40	20-25
Switch grass	5-20	30-50	10-40

Source: McKendry, 2002

The relative proportions of cellulose and lignin is one of the determining factors in identifying the suitability of plant species for subsequent processing as energy crops. Cellulose is a glucose polymer, consisting of linear chains of (1, 4)-D-glucopyranose units,

in which the units are linked 1–4 in the b-configuration, with an average molecular weight of around 100,000.

“Hemicelluloses is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylems and arabinose and methylglucuronic and galaturonic acids, with an average molecular weight of <30,000. In contrast to cellulose, hemicellulose is a heterogeneous branched polysaccharide that binds tightly, but non-covalently, to the surface of each cellulose micro fibril. Hemicelluloses differs from cellulose, in consisting primarily of xylose and other five-carbon monosaccharide” (McKendry, 2002).

“Lignin can be regarded as a group of amorphous, high molecular-weight and chemically related compounds. “The building blocks of lignin are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propane. These may have zero, one or two methoxyl groups attached to the rings, giving rise to three structures, termed I, II and III, respectively. The proportions of each structure depend on the source of the polymer i.e. structure I is found in plants such as grasses; structure II in the wood of conifers; while structure III is found in deciduous wood. Cellulose is generally the largest fraction, representing about 40–50% of the biomass by weight; the hemicelluloses portion represents 20–40% of the material by weight” (McKendry, 2002).

2.4 HYDROGEN AS FUEL/HYDROGEN ECONOMY

Hydrogen fuel does not occur naturally on earth and thus is not an energy source, but is an energy carrier. Currently it is most frequently made from methane or other fossil fuels. This has problems as energy in the natural gas is greater than the energy content that the hydrogen produces. For every MJ of fossil fuel consumed by the system, 0.66 MJ of

hydrogen are produced (Dupont, 2010). However, it can be produced from a wide range of sources (such as wind, solar, or nuclear) that are intermittent, too diffuse or too cumbersome to directly propel vehicles. Integrated wind-to-hydrogen plants, using electrolysis of water are exploring technologies to deliver costs low enough, and quantities great enough, to compete with traditional energy. Hydrogen is the densest energy carrier in the universe. It is 3 times more energy dense than petrol and its combustion releases 3 times more energy than natural gas (mass basis) and 6 times more than coal (Dupont, 2010). Its combustion emissions are just water and heat (no smoke, no soot, no carbon monoxide, no carbon dioxide, no sulphur oxides, and if oxygen (not air) is used as oxidant, no nitrogen oxides. It has very little thermal radiation because of absence of soot and carbon products: reduced risks of burns. However, H_2 explosion risks arise mainly from significant leakages in non ventilated enclosures. Hydrogen is not found alone in nature, (but makes up for 75% of the matter in the universe) as a result it is termed an 'energy carrier', used in transport, heat, and power generation. It can be stored in large amounts as compressed gas, or better, super cold liquid.

Hydrogen can be produced from renewable sources (plant biomass) by a number of processes. This includes: thermo chemical Production (e.g. gasification and reforming processes of biomass feedstock), Biohydrogen (dark fermentation of carbohydrates and anaerobic digestion), photobiological (H_2 from microalgae) (Dupont, 2010). When generated from renewable sources, hydrogen production and use is part of a clean, cyclic process. The source of Hydrogen can be replenished at the end of the cycle; the net result is

the conversion of an abundant energy source into used energy (heat + mobile/stationary power). The hydrogen cycle is presented in Figure 2.2.

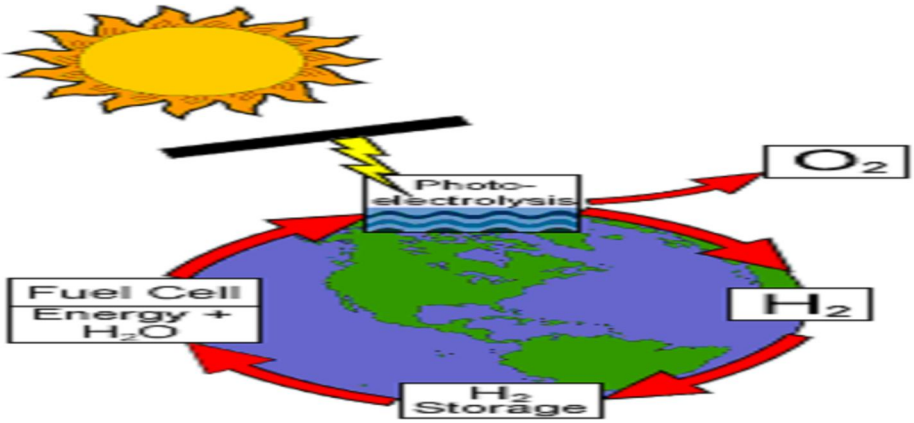


Figure 2.2: The hydrogen cycle Source: Dopont, 2009

2.5 THEORETICAL ASPECTS OF NEUTRON REFLECTION TECHNIQUE

2.5.1 General

Neutron absorption, transmission and reflection methods are widely used, in chemical analysis of bulk samples especially for the determination of hydrogen and moisture contents (Isa, 2002, Zakari, 1997). A fast, non destructive technique used based on thermal neutron reflection was used to determine hydrogen contents in many organic compounds. This technique utilizes the relative thermal intensity of thermal neutrons reflected by a bulk sample to determine its total hydrogen/moisture content of the sample. The reflection property of a sample can be characterized by the albedo of thermal neutrons; a principle introduced by Amaldi and Fermi (1936). This principle of albedo was subsequently generalized for two media of different neutron diffusion properties by Csikai (1987). Buczeko *et al* (1975) used the method to determine content of asphalt concrete. Csikai and Buczko (1999) introduced the reflection cross section of the thermal neutrons as a

microscopic parameter for the characterization of the reflection property of substances. Kirally and Csikai (2000) compared prompt neutron detection and the foil activation methods for the determination of the reflection cross section of thermal neutrons and the hydrogen content of bulk samples. De Hevesy developed neutron activation analysis (NAA) in 1935. These methods and other recommended one such as prompt gamma ray neutron activation analysis (PGNAA), X-ray diffraction (XRD); X-ray fluorescent Spectroscopy (XRFS) etc are widely used in elemental analysis of various mineral samples. Zakari (1997) used neutron transmission and reflection technique in determining the H content $\frac{(O+C)}{H}$ atomic ratio in hydrocarbon and solid mineral samples. Isa (2002) and Akaho *et al* (2001) used the neutron reflection technique to determine the total hydrogen content of some mineral substance and Palm oil respectively. The result obtained by Isa (2002) indicates that the CV and excess count rate, R are proportional to hydrogen content of the three mineral samples. Jonah *et al* (1999) used neutron reflection method in determining the total hydrogen content of oil samples in Nigeria. Zakari *et al* (2009) used the neutron transmission technique to analyze the chemical composition and concentration of three Nigerian mineral rocks.

2.6 THE NEUTRON

Neutron has played significant analytical roles in various fields of knowledge mainly due to its intense penetrating power into the materials (Meyerhof, 1988).

The neutron has only slightly greater mass than that of the proton but has no electrical charge. This neutrality allows it to wonder through matter practically free from electric or

magnetic effects and to reside in the nucleus of an atom without contributing to the internal electrical forces (Murray and Cobb, 1970). Since a neutron has no charge it can easily enter into a nucleus and cause reaction.

The neutron has a rest mass of 935.550± 0.005MeV/C^2, with at least seven excited states below 1500MeV, of spins ½ and 3/2. It has a volume of 10^{-44} cm^3, Spin J = ½, in units of $\hbar$ and isotopic spin, T = ½ and magnetic Moment = -1.91 μN. The projection of isotopic spin is (-1/2, +1/2), its strangeness S =0 and its mean life time is, $\tau = 1.01 \pm 0.03x10^3 s$. The probability that it will decay, thereafter, to a proton, an electron and anti-neutrino via the reaction

$$N \rightarrow p + e^- + \upsilon_e \qquad (Q = +0.78MeV) \qquad (2.08)$$

is 100% (Yavorsky and Detlaf,1980)

It is said to contain three quarks: 2 "down" quarks of spin 1/2., charge –e/3 and 1 "up" quarks of spin1/2, charge +2e/3. Survives for ≈ 1ms in liquid or solids and has penetrating power in lead

$= 2 \times 10^{-3} m^2$

2.6.1 Neutron-Energy Classification

Neutron interaction with matter depends on its energy and it has become necessary to classify neutrons according to their energy E. In general, neutrons are classified into cold or sub thermal neutrons (0 < E < 0.005eV), thermal (0.005 < E <0.5eV), epithermal (0.5eV < E < 1 KeV), intermediate (1 KeV < E < 100 KeV), fast (100 KeV < E < 10 MeV) and high-energy neutrons (E ≈ 100 MeV) (IAEA, 1988). Neutrons of energy E > 100 MeV are called spallation neutrons. These energy ranges are obtainable from different sources of neutrons.

The neutron's energy class of interest in this work is the thermal neutrons where the dominant interaction of neutron is elastic scattering.

2.7 NEUTRON SOURCES

The neutron sources used in radiation laboratories are wide and varied produced in a variety of nuclear reactions. Such nuclear reactions can be induced by alpha and gamma radiation from radioactive nuclides (in isotopic sources), charged particles from accelerating devices (in neutron generators) and or nuclear fission (in nuclear reactors). The neutron flux and energy spectrum -vary with type of source. Further, the sources vary in construction size and cost from the simple, low-cost, low-flux, radioisotope sources to complex expensive high-flux nuclear reactors" (Isa *et al*, 2002). The above neutron sources are described in the next sections.

2.7. 1 Isotopic Neutron Sources (INS)

There are three main types of INS:

a. Alpha-emitters which produce neutrons through an (α, n) reaction

b. Gamma-emitters through (γ, n) reaction and

c. Isotopes of heavy elements, which undergo spontaneous fission

2.7.1.1 Alpha (α, n)

The nuclear reaction mostly used for the (α, n) production of neutrons, is that which led to the discovery of the neutron

$$^{9}Be + {}^{4}He \rightarrow {}^{12}C + n \qquad (Q = 5.70Mev) \qquad (2.09)$$

In this reaction, beryllium was irradiated with α particle from naturally occurring radio nuclides like ^{241}Am, ^{238}Pu. Other light elements like ^{10}B, ^{11}B, ^{11}F, ^{15}C, ^{7}Li can be used as targets, but their neutron yields are small compared to that of $^{9}B_e$ (Garg ,1989).

2.7.1.2 Photo-Neutron (γ, n) Sources (PNS)

Whenever the γ- ray energy exceeds the neutron binding energy in the nucleus, a (γ, n) reaction becomes possible only. Only $^{9}B_e$ (Q = -1.665MeV) and ^{2}H (Q = -2.226MeV) are of practical interest as targets, since most nuclei have a neutron binding energy above 8MeV (Hoste, 1988). Typical reactions are:

$$^{9}B_e + \gamma \rightarrow {}^{8}B_e + {}^{1}n \qquad (Q = -1.665MeV) \qquad (2.10)$$

$$^{2}H + \gamma \rightarrow {}^{1}H + {}^{1}n \qquad (Q = -2.226MeV) \qquad (2.11)$$

A γ- ray, of at least negative Q-value energy is needed to make the reactions energetically possible; as such only γ- rays of relatively high energy can be applied. For γ-energies exceeding this minimum, the corresponding neutron energy can be obtained from

$$E_n(\theta) = \frac{E_{\alpha+Q}}{m+M} \quad \frac{E_r\,[(2mM)(m+M)[E_r+Q]cos\theta}{(m+M)^2} \qquad (2.12)$$

where θ = angle between γ- photon and neutron directions

E_r = γ- ray energy

M = mass of recoil nucleus (x c^2)

m = mass of neutron (x c^2)

c = speed of light

Photo-neutron sources have an advantage that with mono-energetic γ-rays, the neutrons produced are also nearly mono-energetic. Their disadvantages are relatively low neutron yield and large shielding requirements for high activity γ-rays needed to produce the

required neutrons intensities. This large γ-ray background is difficult to filter out and may interfere with many experiments (Hunt, 1987).

2.7.1.3 Spontaneous Fission Sources (SFS)

Spontaneous fission can occur in many trans-uranium elements, with the release of neutrons alongside the fission fragments. The fragments can as well promptly decay, emitting, β and γ radiation. The latter radiation can be absorbed by enveloping the source in sufficiently thick container, thus leaving only the more penetrating neutrons.

The most common SFS is ^{252}Cf with $T_{1/2} = 2.65$ yrs emitting 3.75 neutrons per fission (or $2.34 \times 10^{12} ng^{-1}s^{-1}$) of average energy 2.14 MeV (Hoste, 1988).

2.7.2 Neutron Generators (NG)

A wide variety of (p, n), (d, n) and (α, n) reaction may be produced using energetic particles beams from particle accelerators such as Cockcroft Walton, Van-de Graaf and the electrostatic rotor high voltage (HV) generators. The charged particles originate from ion sources like radio frequency (Rf) and the Duo plasmation types. The interaction of this accelerated ions with target (usually ^{3}H, ^{9}Be, ^{12}C etc) result in production of approximately mono-energetic neutrons. The most commonly used is the D-T reaction of equation (2.13) with a cross section approximately 1 barn.

$$^{2}H + ^{3}H \rightarrow ^{4}He + ^{1}n \qquad (Q = 17.6MeV) \qquad (2.13)$$

The particles produced here are of high intensity and energy than those available from the decay of a limited number of radioisotopes.

2.7.3 Nuclear Reactor (NR)

Nuclear Reactors are of many type and these may be classified by their purpose, their fuel and moderator and the speed of the neutrons when they cause fission. A reactor may be built for experimental (research) purposes, or to produce fissile material or generate useful power. The fuel can be natural uranium, or uranium enriched with high proportion of fissile uranium isotopes, or with plutonium. The moderator can be any materials that slows the neutrons down efficiently without capturing too many of them, and ordinary water, deuterium in the form of heavy water and graphite are often used. Reactors with moderator are called thermal reactors, whereas those without a moderator are called fast reactors.

Research reactors are more commonly used as sources of neutrons for experiments involving irradiation of sample or NAA. They all utilize the fact that a self-sustained fission chain reaction e.g.

$$^{235}U + {}^{1}n \rightarrow {}^{236}U^{*} \rightarrow {}^{144}Ba + {}^{90}Kr + 2n + Q \qquad (2.14)$$

involving repeated fission processes provides the required neutrons. Research reactors provide a useful high neutron flux of the order $10^{12}ncm^{-2}s^{-1}$ and above and the produced neutrons have an energy spectrum extending beyond 6MeV and a mean energy of about 2MeV.

These energies are quite high for most experimental purposes are mostly reduced to energies in the fractional –eV region by elastic collisions with the reactor moderator (Hunt, 1987)

The neutron radiation in the interior of a reactor is characterized by the neutron flux Ø, the number of neutrons passing in all directions through a sphere of cross section $\pi r^2 = 1cm^2s^{-1}$.

A most common research reactor is the Miniature Neutron Source Reactor (MNSR).

Most important is the region of high neutron-flux must be made accessible to the experimenter so that specimens to be irradiated may be inserted without disturbing reactor operation. It is also desirable to have regions of predominantly thermal neutron flux made available as free as possible from high energy neutrons, and with as low a γ-background as possible.

Power reactors are generally used for energy (electricity) generation. The fission products are slowed by the water moderator through friction, and the water is heated to a very high temperature and pressure. This water than enters a heat exchanger, where it heats a secondary water coolant. Because of the high temperature of the primary coolant, the secondary coolant, which is relatively at normal pressure, is immediately converted to steam. This steam is passed to a turbine, which drive an electric generator, thereby producing electricity. This process is similar to energy generated in coal and oil stations.

2.8 THEORY OF NEUTRON THERMALIZATION

Neutrons are said to be thermalized if they are in thermo dynamic equilibrium with the moderator atoms. Thermalization is simply the reduction of neutron-energy, from the fast to the thermal region. It is achieved using a moderator, hence the term neutron moderation (Isa 2002). After a number of collisions (often in the range of 10–20) with nuclei, neutrons arrive at this energy level, provided that they are not absorbed. The name 'thermal' comes from their energy being that of the room temperature gas or material they are permeating. Elastic scatting is the main mechanism of energy loss for fast neutrons.

A necessary condition for the neutron slowing down process to be effective is that, the neutron scattering cross section must be much greater than the capture cross section. Under this condition, the neutron energy decreases until it becomes comparable with the thermal motion of the neutrons in the slowing down medium (Mukhin, 1970) i.e.

$$T_{therm} = kT_o \qquad (2.15)$$

where T_o is the absolute temperature (room temperature) and k is Boltzmann constant.

The neutrons are then referred to as thermal neutrons. "It can be shown that at room temperature (300K), the most probable velocity of thermal neutrons is $2.2 \times 10^5 cms^{-1}$ (2.2 km/s) and the corresponding thermal energy is

$$KT_o \approx 0.0253eV\ (4.0 \times 10^{-21}J) \qquad (2.16)$$

No further slowing down can take place since the probability of gaining or losing the energy is the same. The neutrons diffuse into the medium until they are either absorbed by nucleus, or leave the medium. This will confirm that neutron scattering is the most suitable for the analysis of light elements. Most fission reactors use a neutron moderator to slow down, or *thermalize* the neutrons that are emitted by nuclear fission so that they are more easily captured, causing further fission. Others called fast breeder reactors, use fission energy neutrons directly.

2.8.1 Interaction of Neutron with Matter

We are interested in the interaction with matter of the various neutrons' energy, since it must be detected, identified, and their numbers measured for scientific purposes. They must be stopped to prevent personnel working with radioactive sources. They may heat and cause damage to the substances through which they pass. Since a neutron has no

charge it can easily enter into a nucleus and cause reaction. Neutrons interact primarily with the nucleus of an atom, except in the special case of magnetic scattering where the interaction involves the neutron spin and the magnetic moment of the atomic. The interaction of neutron with matter can lead to so many phenomena, depending on the energy of the incident neutron and on whether the interaction is with a nucleus or with a bulk matter (Nicholas, 1972, Knoll, 1979). Generally, the interaction of neutron with matter depends greatly on the neutron's energy and nature of the target materials (Nucleus). The target nucleus can be a light (with $A < 25$), intermediate ($25 < A < 80$) and heavy ($A > 80$) where A is the atomic mass. The interaction with nuclei is used for probing the structure of the nucleus whereby important parameters such as nuclei cross section are determined. However, the interaction with bulk media is used for quantitative and qualitative analysis of such media. The experimental work of interest in this research is based on the latter type of neutron interaction. The probability of a particular event occurring between a neutron and a nucleus is expressed through the concept of the cross section. If a large number of neutrons of the same energy are directed into a thin layer of material, some may pass through with no interaction, others may have interactions that change their directions and energies, and still others may fail to emerge from the sample. There is a probability for each of these events.

In neutron interactions generally, the following two categories can be identified:

- Compound Nucleus Reaction (CNR)
- Direct Reaction (DR)

In the compound nucleus reaction, the incident projectile and target form a new nucleus referred to as compound nucleus (CN) that will live for a short period of time in an excited state and then decays. The excitation energy of this nucleus equals the sum of the kinetic energy and the binding energy (E_b) of the captured neutron. The lifetime of the typical CN is of the order 10^{-16}s. The duration 10^{-16}s is so short that the CN cannot be observed directly. However, it is much larger than the time a projectile takes to traverse a nuclear distance, which is of the order of 10^{-21}s. In this case the incident energy is much lower, the projectile and the target may fuse together for a long time, for example of the order of 10^{-14}s. In this case, a compound nucleus is formed as the intermediate state.

$$^{19}F_9 + P \rightarrow (^{20}Ne_{10})^* \rightarrow {}^{19}Ne_{10} + {}^{1}n_0 \qquad (2.17)$$

The nucleus decays to stability through any of the following processes.

- Compound elastic (or resonance) scattering the nucleus releases a neutron of same energy as the incident one, i.e. the (n, n) reactions
- Radioactive capture the excitation energy is given up, via emission of one or several γ- Ray i.e the (n, γ) reactions.
- Particle emission for sufficiently high excitation energies, the excitation energies, the nucleus can emit charged particles or two neutrons, i.e. the (n, α),(n, p),(n, np) or (n,2n) reactions.

In direct nuclear reaction, the interaction of fast nucleon with nucleus may be regarded as a two particle interaction between the incident projectiles with one or more nucleons in the target nucleus. A nucleon or a cluster of nucleons, in the projectile interacts with one of the nucleons, or a cluster, in the target without exciting the internal degrees of freedom in any

of the clusters or the rest of the nucleus. The basis for taking such direct reaction point of view is the short time, of the order of 10^{-22}s it takes for the projectile and the target to interact once with each other (Cohen, 1993). Since this is comparable to the transit time for an incident particle with kinetic energy greater than the order of 1 MeV per nucleon to travel over a distance of the order of the nuclear diameter, the probability for interacting more than once is small. Example of direct nuclear interaction is pickup and stripping reactions which are always observed at high enough energies and extremely very short time (10^{-22}s) that can assume the reaction to be direct.

2.8.2 Neutron Detection

A common method for detecting neutrons involves converting the energy released from neutron capture reactions into electrical signals. Therefore detection of neutron requires a transfer of all or part of its energy to the detector material. Certain nuclides have a high neutron capture cross section, which is the probability of absorbing a neutron. Upon neutron capture, the compound nucleus emits more easily detectable radiation, for example an alpha particle, which is then detected. The nuclides ^{3}He, ^{6}Li, ^{10}B, ^{233}U, ^{235}U, ^{237}Np and ^{239}Pu are useful for this purpose.

For thermal neutrons, detection is most efficiently done using the (n, γ) or (n, α) reactions. Element with high cross sections for these reactions e.g. ^{6}Li (900b) or ^{10}B (4, 000b) are most conveniently used in ionization chambers. Proportional counters can also be used for neutron detection by using a gas containing nuclei with neutron-capture cross sections and produce charged particles in the nuclear reaction, e.g. ^{10}B or ^{3}He. In BF_3- Counter, the gas is enriched in ^{10}B, which reacts with neutrons via

$$^{10}B + n \rightarrow {}^{7}Li + {}^{4}He \quad (Q = 2.78MeV) \qquad (2.18)$$

The ionization of the two products gives a heavy pulse, easily discriminated against an intense γ-background.

For fast and higher energy neutrons, detection relies mainly on detecting the recoil proton in (n, p) scattering reaction. Recoiling nuclei can ionize and excite further atoms through collisions. Charge and/or scintillation light produced in this way can be collected to produce a detected signal. Kinematically, a neutron can transfer more energy to light nuclei such as hydrogen or helium than to heavier nuclei. Plastics and other organic materials are particularly convenient, since they contain large amount of hydrogenous material. Detectors relying on elastic scattering are called fast neutron detectors. Fast neutron detectors have the advantage of not requiring a moderator, and therefore being capable of measuring the neutron's energy, time of arrival, and in certain cases direction of incidence. A major challenge in fast neutron detection is discerning such signals from erroneous signals produced by gamma radiation in the same detector. The standard scintillator in neutron spectroscopy is liquid organic scintillator (e.g. NE 213). This material offers excellent pulse shape discrimination properties and allows a rejection of the γ-ray background usually accompanying neutron reactions. It further easily handled and is adaptable to wide variety of geometries.

2.8.3 The Concept of Neutron Reflection

A special case of thermalization is the neutron reflection when slow neutrons are incident at a small angle 'θ' to the surface of a crystal (say); one would observe the reflection of monochromatic neutrons at angle equal to θ (incidence angle). Bragg's formula gives the

relation between the angle of incidence θ, the wavelength, λ of the reflected neutrons and the lattice constant d as

$$2d\sin\theta = n\lambda = 2\pi n\chi \qquad (2.19)$$

where n = order of reflection, since $\chi = h/2\pi p = h/2\pi (2mT)^{1/2}$ (2.20)

then equation (2.20) gives

$$T = \frac{h^2}{8md^2} \cdot \frac{n^2}{\sin^2\theta} \qquad (2.21)$$

Equation 2.21 implies that the energy of reflected neutrons can change by varying the angle θ and energies of the neutrons reflected at angle θ can be given by

$$T_n = n^2 T_0 \qquad (2.22)$$

where $T_0 = \frac{h^2}{8md^2\sin^2\theta}$, n = 1, 2, 3 … and by differentiating (2.21) with respect to θ, one gets

$$\frac{dT}{T} = -2\cot\theta d\theta \qquad (2.23)$$

It can be seen that angle θ in equations (2.21) and (2.22) are quite large. For example, for a lattice constant, d = 2.32Å and n=1, the angle θ for 1eV neutrons is 35^o while for l00eV neutrons it is only 0.35^o. The formulae above can hence be replaced by the approximate expression

$$T_n \approx n^2 T_o \qquad (2.24)$$

$$\text{where } T_o \approx \frac{h^2}{8md^2\theta^2} \qquad (2.24)$$

Equation 2.22 shows apparently that the resolution deteriorates with increasing neutron energy which limits the applicability of this method to energy ranges from $T_{min} \approx 0.01$eV to $T_{max} \approx$ 50- 100eV.

2.8.4 Neutron reflection property (Albedo, β)

The principle of albedo (reflection property of samples to thermal neutron) was introduced by Amaldi and Fermi (1936) and was subsequently generalized for two media of different neutron diffusion properties by Csikai (1987). The reflection cross section, σ_β (microscopic parameter) of the thermal neutrons is used for the characterization of the reflection property of substances.

For neutrons reflected (backscattered) from a homogeneous sample, of N' number of atoms/cm^2, the relative (excess) counts rate, R, is proportional to the reflective cross section, σ_β and number of atoms N' in the sample. i.e.

$$R \alpha \quad N' \sigma_\beta \tag{2.25}$$

It follows from (2.25), that $R = CN' \sigma_\beta$ (2.26)

where C is a constant of proportionality = 10^{-24}

The excess count R can be obtained from the relation

$$R = \left(\frac{I - I_o}{I_o} \right) = \left(\frac{A - A_o}{A_o} \right) \tag{2.27}$$

(Jonah et al, 1992, Kiraly B. and Csikai J, 2000, Akaho *et al,* 2001)

where I, I_o = intensity with and without sample respectively and A, A_o is the Activity with, without sample respectively. If N is the number of Atom per unit volume (cm^{-3}) and d is the sample thickness (cm) then $N' = Nd$ (2.28)

Also, if n is the total number of sample's atoms and S is the surface area of samples in cm^2, then

$$Nd = n/S \tag{2.29}$$

S is the surface area of the sample given by

$$S = \pi r^2 = \pi (d/2) \quad (2.30)$$

(This is for the shape of the sample holder used in this work).

But number of atoms (or number of moles), n is related to the mass of sample m, its atomic mass A, and the Avogadro's number N_A, by

$$n = mN_A/A \quad (2.31)$$

Therefore, $Nd = n/S = mN_A/AS$ (2.32)

For a two media sample, e.g. HC compounds, the number of moles is just a summation i.e.

$$n_{mol} = \left[\left(m_{gs} / A_{gs}\right) + \left(m_w / A_w\right)\right] N_A \quad (2.33)$$

Now substituting equations (2.29) and (2.27) into (2.26) gives

$$R = CNd\sigma_\beta = Cn\sigma_\beta/S \quad (2.34)$$

Now, the reflection cross section, σ_β is obtained as

$$\sigma_\beta = R/CNd = R.S/C.n = \left(I - I_o\right)S / I_o C.n \quad (2.35)$$

The result can be generalized for sample of molecules with atoms n_i of different reflection cross sections $\sigma_{\beta i}$, using

$$\sigma_{\beta,\,mol} = \sum n_i \sigma_{\beta i} \quad (2.36) \text{ or}$$

$$\sigma_{\beta,\,mol} = \sum n_i \sigma_{\beta i} = R/CNd = R.S/C.n_{mol} \quad (2.37)$$

It was observed that in most cases, the excess counts R, is reduced to density, ρ, of the material, as such, the normalized excess counts, η is used. This is obtained using

$$\eta = \frac{1}{\rho}\left(\frac{I - I_o}{I_o}\right) = \frac{1}{\rho} R \quad (2.38)$$

(Source: Zakari, 1997; Kiraly, B., and Csikai, J., 2000; Akaho *et al,* 2001; Isa, *et al,* 2002); where R is the excess count rate and S is the surface area of samples in cm^2.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 SAMPLING OF BIOMASS MATERIALS

Fourteen (14) selected plant biomass from herbaceous plants/grasses (perennial crops) and agricultural residues locally produced in Nigeria's farmlands were collected from farmlands and local community around Mairua, Funtua, Katsina State in November, 2011. They were kept under a room temperature and used in this experimental work without any pretreatment so as to represent the actual scenario (condition) by which they are used as fuel.

3.2 ANALYTICAL PROCEDURE USING BOMB CALORIMETER

The use of bomb calorimeter requires certain procedures recommended in the instrument's manual for determining the calorific values of the samples. This includes the requirement for a sample to be in powder form for a grain size analysis.

The bomb measurement is based on the oxygen depletion calorimetry which relies on the precisely known air flow through the system. In the process the fuel mass loss rate is converted to energy and the Calorific Value readily computed by the Bomb appears on the display screen.

3.2.1 Sample Preparation

The samples were cut to approximately 1mm size using stainless steel scissors and used for analysis. The wet samples were sun dried and finally dried by slowly heating from 80^{o}C to

135^{o}C using electric oven held isothermally for either 2 or 5 minutes depending on the observed moisture content. This is to assured that the moisture/water content of each sample is quite negligible. The dried samples were carefully pounded in a wooden mortar with wooden pestles and then sieved to obtain 500, 212 and 125μm mesh size samples. The powdered sample was prepared into a pellet (of about 2.5g mass) before burning in to the machine by means of a pellet press; this is done to prevent scattering of material during the combustion, with consequent incompleteness of combustion. These pellets samples were also kept in a polyethylene bags to prevent moisture absorption before experiment.

3.2.2 Experimental Set Up for the Bomb Measurements

The direct determinations of calorific values were made using a bomb calorimeter (model 6100 series manufactured by Parr Instrument Company) in the chemical engineering department, Ahmadu Bello University, Zaria. The calorific value from this machine is the high heat value (HHV), which includes the latent heat of the vapor emitted from the specimen.

The machine consists of a small cup to contain the sample, an 1108 oxygen bomb with an oval bucket which fits into the insulating water jacket, a built-in semi-automatic system for charging the bomb with oxygen, high precision electronic thermometer, a bright, color, touch screen display for data entry and operation control, Special communication ports for printer, computer and network (LAN) connections, the dewar (to prevent heat flow from the calorimeter to the surroundings), ignition circuit connected to the bomb and a removable compact flash memory card slot for simple program updates and test report

archiving. All steps in the test procedure are managed by a microprocessor control system programmed to operate the calorimeter in either the conventional equilibrium mode or in a faster dynamic mode. All data is handled automatically by a dedicated microcomputer. Electrical energy is used to ignite 0.025g of the fuel; as the fuel is burning, it will heat up the surrounding air, which expands and escapes through a tube that leads the air out of the calorimeter. When the air is escaping through the copper tube it will also heat up the water outside the tube. The temperature of the water allows for calculating calorie content of the fuel. Figure 3.1 shows the test assembly of the model Bomb calorimeter, oxygen bomb with an oval bucket used in this work.



Figure 3.1: Schematic diagram of the experimental set up (Source: www.rofa-praha.cz/upl/katalog/100112s_455M.pdf)

A full system of Bomb calorimeter shown in figure 3.2 consists of a small cup to contain the sample, an1108 oxygen bomb with an oval bucket which fits into the insulating water jacket, a built-in semi-automatic system for charging the bomb with oxygen, the dewar (to prevent heat flow from the calorimeter to the surroundings), ignition circuit connected to the bomb and a stirrer.

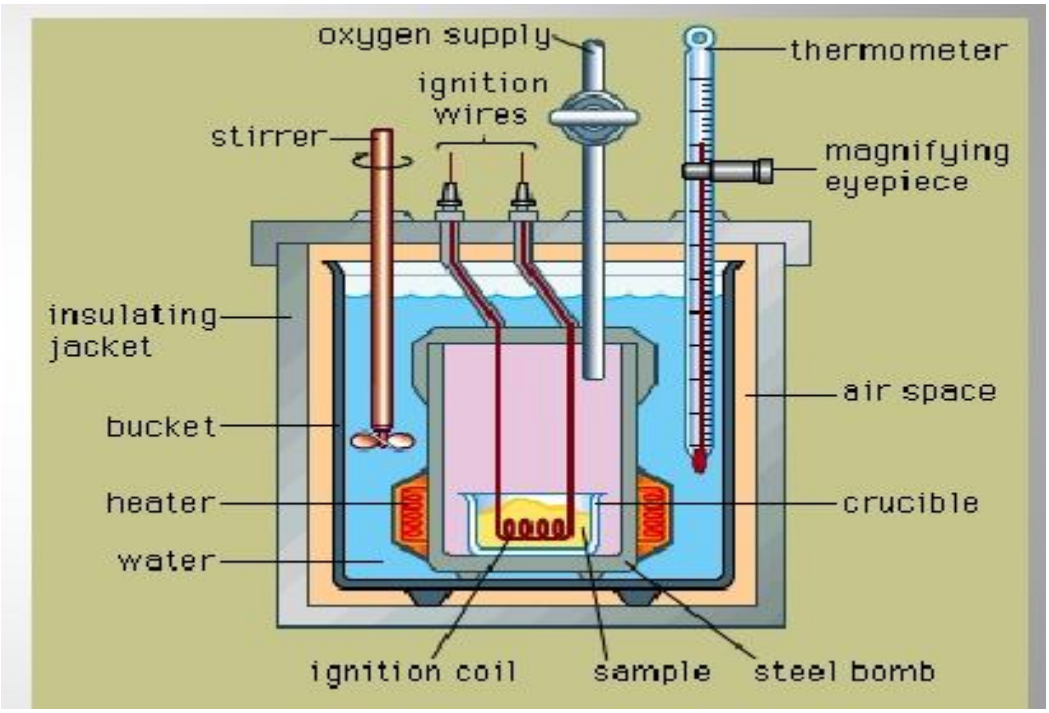


Figure 3.2: Schematic diagram of the Bomb Calorimeter (Source: www.encyclopedia.com)

3.2.3 Analysis Procedures for the Bomb Measurements

The use of Bomb calorimeter requires calibration so that the data reading from the machine can be measured accurately. Prior to burning the samples, the heat of combustion measured by the apparatus was calibrated using 1g mass (99.5% purity) of benzoic acid. The benzoic acid was prepared into a pellet before burning in to the machine by means of a pellet press; this is done to prevent scattering of material during the combustion, with consequent

incompleteness of reaction. The pellet is weighed and placed in the sample pan. A Nickel fuse wire (~10 cm) of known heat of combustion per unit length (0.9813 kcal/g) is attached to the two terminals of the ignition coil and adjusted to give firm contact with the pellet inside the bomb as described in the manufacturer's instruction manual. The cover is carefully assembled with the bomb and tightened. The bomb is then connected to the oxygen tank, and oxygen is admitted slowly until the pressure is 25 atm. The valves are then closed, the pressure in the line is relieved, and the bomb is removed.

About 2000 ml of distilled water, the temperature of which has been adjusted so as to be at least several degrees below the upper limit of the thermometer range close to room temperature, is placed in the calorimeter can; the latter is then placed within the adiabatic jacket. The ignition leads are connected, and the bomb is immersed in the water. The experiment was run and measured heat of combustion ((H_c) of benzoic acid was found to be 6318 cal/g. This is actually within the range specified in the instrument's manual for standardization of the machine. As the calorific value of the benzoic acid is determined, the bomb is standardized, and is ready for use to calculate heat of combustion of any compounds.

The bomb, with sample and oxygen, form a closed system – no air escapes during the reaction. The energy released by the combustion raises the temperature of the steel bomb, its contents, and the surrounding water jacket. The temperature change in the water is then accurately measured. This temperature rise, along with a bomb factor (which is dependent

on the heat capacity of the metal bomb parts) is used to calculate the energy given out by the sample burned.

3.3 ANALYTICAL PROCEDURES USISNG NEUTRON REFLCECTION SET UP

The procedure in determining the total hydrogen or moisture content of the sample by using neutron reflection method involves assembling the component, determining the ^{3}He probes operating voltage, pre-setting the electronic devices, obtaining the background count I_o and then the samples count I, computing the excess count rate, R and normalized count rate, η and finally determining the percentage of hydrogen content of the sample (s) from calibration line.

Standards in the form of compound of known hydrogen contents (100% graphite plus water) shown in table 3.1were used to obtain calibration line shown in figure 3.3 for thermal neutron reflection parameter as a function of hydrogen content. The total hydrogen content of the fourteen samples were calculated from the linear equation

$$\eta = 0.211H + 0.454 \qquad 3.0$$

where η represents normalized excess count rate, η (given in table 4.1, calculated using equation 2.38) and H is the total hydrogen content.

Table 3.1: Reflection Parameters of Compound (standard) used for the determination of H (wt %) (Source: Isa, 2002)

H_2O (wt %)	ρ g/cm^3	η (cm^3/g)	H (wt %)	$\sigma_{\beta mol}$ (b)
0	0.573	0.41	0	8.078
5	0.602	0.62	0.53	12.996
10	0.63	0.67	1.01	13.853
15	0.659	0.76	1.45	15.895
20	0.688	0.85	1.85	17.948
25	0.718	0.91	2.22	19.362
30	0.745	0.99	2.56	21.383

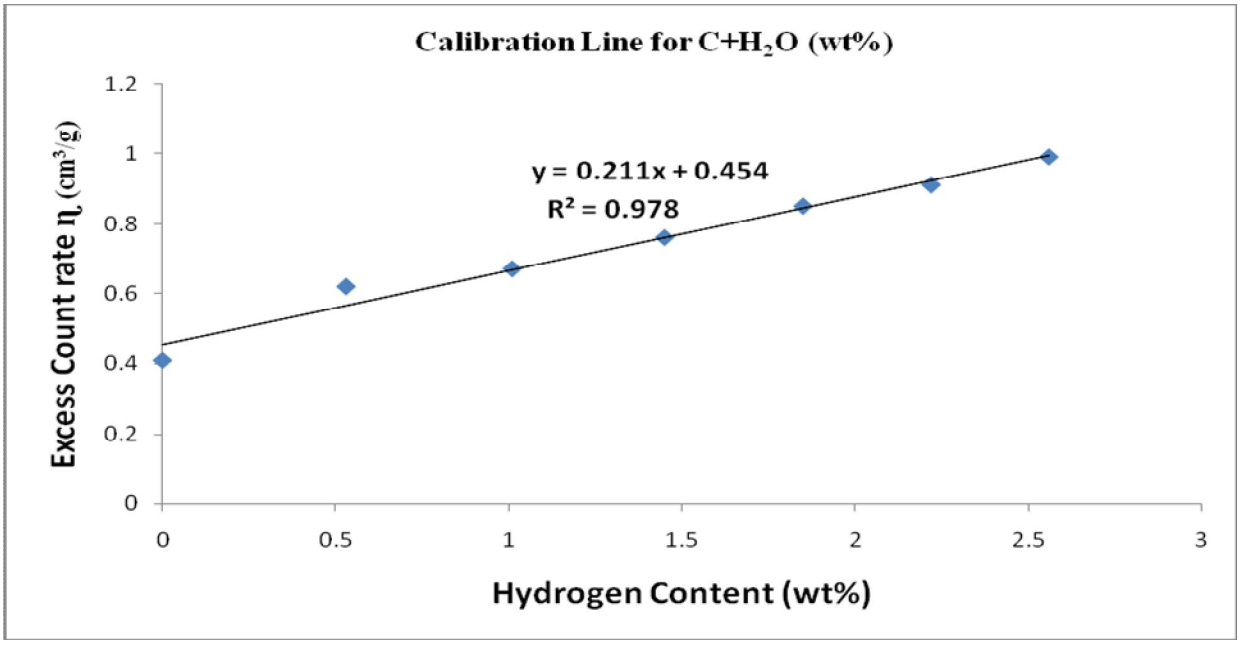


Figure 3.3: Calibration Line for Material (Standards) used for the determination of H(wt%)

3.3.1 Sample Preparation

The dried samples were carefully pounded in a local wooden mortar with wooden pestles and then sieved to obtain 500μm mesh size. The powdered samples were also kept in a polyethylene bags to prevent moisture absorption before experiment. All samples were prepared to powder and its total H-contents were calculated from equation 3.0.

3.3.2 Experimental Arrangement for the Determination of Hydrogen Using Neutron Reflection Facilities

The experimental set up consist of 1ci ^{241}Am-Be neutron source and ^{3}He detector embedded in a cylindrical aluminium (Al) container containing Paraffin moderator of diameter 10 cm and of height 10.4 cm, plate 1. Other experimental facilities in the set up include sample holder, an electronic counting set up attached to the source and a weighing balance. Figure 3.4 shows experimental set up for the neutron reflection method.



Plate 1: Neutron Reflection facility

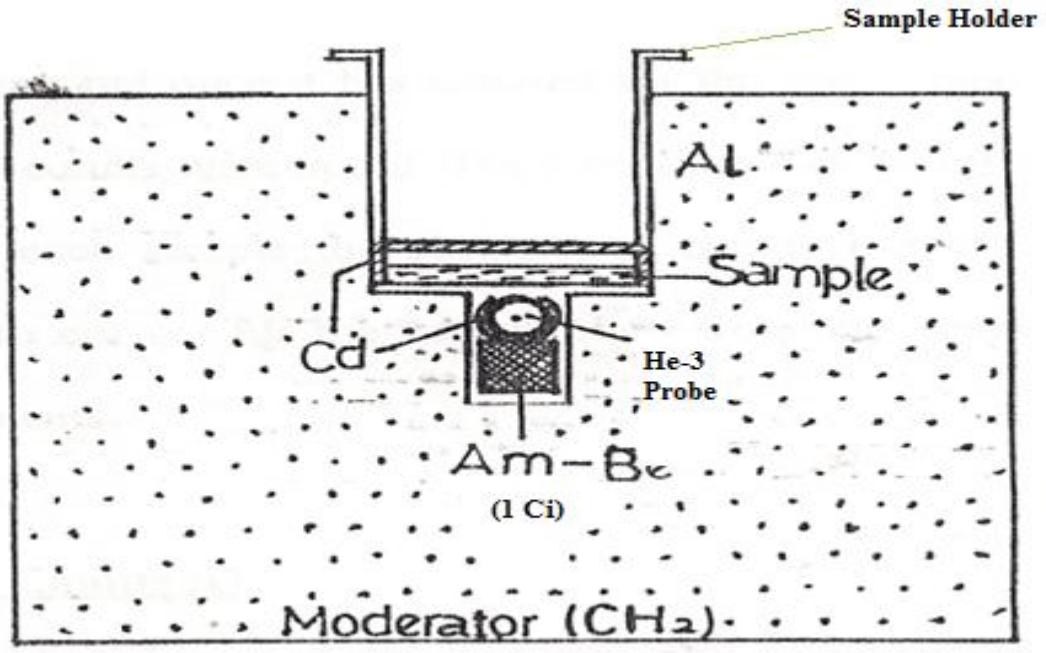


Figure 3.4: The arrangement of neutron reflection Technique

3.3.2.1 The ^{3}He Neutron Probe

A Helium-3 (^{3}He) neutron detector was used in this work. Its sensitivity to gamma rays is negligible. It provides effective neutron detection from material because it has a high absorption cross section (5400 barn) for thermal neutron beams and ^{3}He reacts by absorbing thermal neutrons, producing a ^{1}H and ^{3}H through the reaction

$$n\ (\text{thermal}) + {}^{3}\text{He} \rightarrow {}^{3}\text{H} + {}^{1}\text{H} + 0.764\ \text{MeV} \qquad (2.39)$$

Fast neutrons produced by the source (^{241}Am-Be) collide with the hydrogen in the bulk sample, the fast neutrons lose enough energy to become slow neutrons, and the slow neutrons rebound back towards the exposed active length of the probe and are absorbed by the nucleus of the helium-3 gas in the probe. When the slow neutrons enter the nucleus of the gas, a higher energy state results, and emitted photons is then detected as electrical

pulses with an electronic counting device. The number (s) obtained from the counting device are/is considered the count ratio and is used in a calculation to obtain the sample's hydrogen or moisture content.

The ^{3}He detector used in this work has an active length 3cm – 20cm, a total length 50cm and a diameter 2cm. It is housed in a 2.54-cm-diameter by 28-cm-long sealed stainless steel cylinder with ^{3}He gas at 6 Atmosphere of pressure.

Figure 3.5 shows the diagram of the ^{3}He probe model used in this work.



Figure 3.5: The ^{3}He Detector (Source: www.centronic.co.uk)

3.3.2.2 Electronic Counting Set-Up

The electronic counting systems consists of EG and G Ortec portable ratemeter (see Plate II) consisting of a BIN high voltage (HV) supply set (1.5KV), bias voltage supply (0.3KV), an amplifier (485), a counter, a timer set (10s) and a scalar. The above operating

parameters are considered to be appropriate setting of the components that enabled good data acquisition in this work.

Plate II: The Electronic Counting Set Up

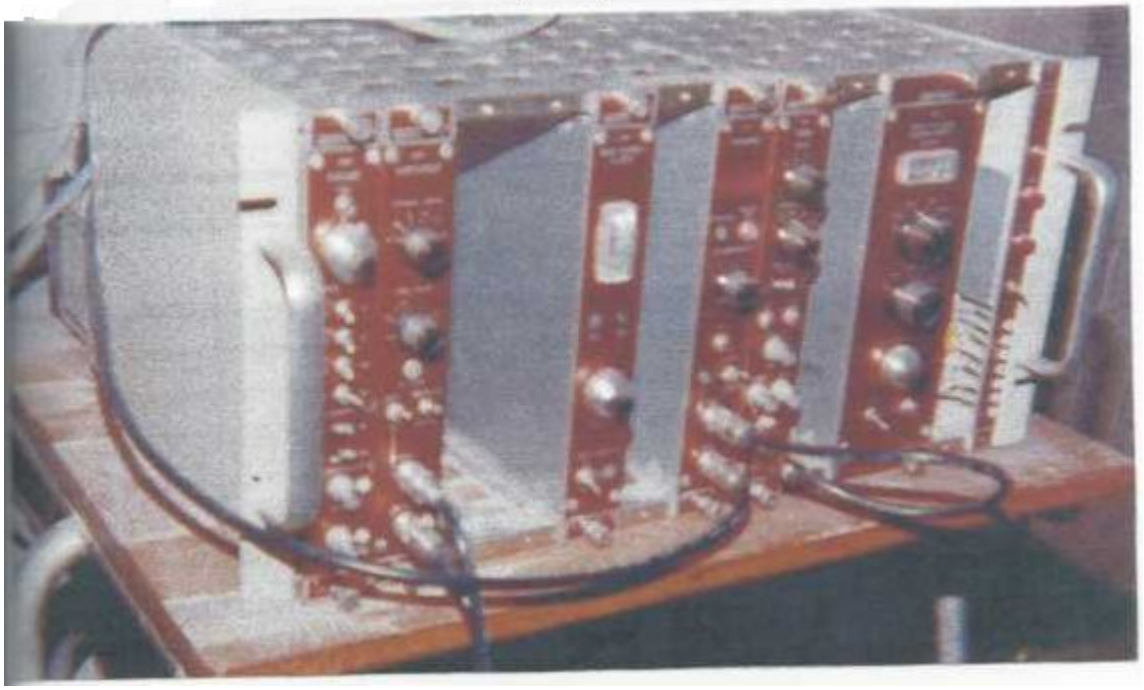


Plate II: The electronic counting Set Up

The emitted photons are detected as electrical pulses with an electronic counting device. The pulses coming from the detector are first pre-amplified in the probe (^{3}He). The pre-amplified pulses are transmitted to the electronic counting system through the cable that connects probe to the electronics. The number of thermalized neutrons is proportional to the sample hydrogen content. The microprocessor sums the returning thermalized neutrons over a 16-s sample time to provide a raw count in count per second (cps).

The Sample holder (dimensions: diameter = 9.69cm, h = 11.3cm) was fabricated from aluminium (Al). The bottom is exposed to neutrons from the source, which can then be thermalized and reflected by the sample into the exposed active length of the ^{3}He probe.

3.3.2.3 Analysis Procedure

The counting procedure is the most important aspect in calculating accurately the thermal neutron reflection parameter and hence total hydrogen. The method of counting is divided into two: the background counts and sample counts. The background counts were obtained by placing the empty sample holder in the 13cmϕ vertical shaft carved into the paraffin wax, coaxial with the cylindrical source holder, in such a way that the sample holder is always at the same separation from the ^{3}He probe and the source. This will keep the source-detector-sample array constant, which is absolutely necessary if the relative method is to be applied. The high voltage (HV) was connected and switch on and gradually increases until it reaches to 1.5KV. The counter was then reset to zero and count for a preset time of 10s, which allows the counter to automatically go off and the count noted. The procedure was repeated 10 times and the average was calculated for each of the fourteen samples.

The sample count was obtained by first weighing the sample holder using the weighing balance and its weight noted as M_h. The sample was then poured into the holder and then weighed again, this time the weight is noted as M_h+s. The difference (M_{h+s}-M_h) gave the sample mass, M_s.

The holder containing the sample was then placed into the source container and counted for 10seconds. The procedure was also repeated ten times and average counts obtained as I. This approach was used in obtaining counts with (I) and without (I_o) a sample for fourteen (14) dry samples.

The average of ten measurements of count rates were used as the excess count rate $\left(\frac{I-I_o}{I_o}\right)$, which was normalized using the density ρ of the samples to obtained the thermal neutron reflection parameter $\frac{1}{\rho}\left(\frac{I-I_o}{I_o}\right)$ and by this technique, the variation of the moisture/water content in the samples were measured.

3.4 DENSITY MEASUREMENT

The actual mass of the sample is measured with the mass scale and recorded. Enough water was added into a graduated cylinder and a volume marking was recorded as V_1. The fine powder of the sample is then added to the water and the new volume was recorded as V_2. The difference between the initial (V_1) and final volume (V_2) gives the actual volume of the sample. The measured mass of the sample is divided by its volume and its true density (ρ) is obtained.

This procedure was used in obtaining the actual density of all fourteen samples.

3.5 DETERMINATION OF NITROGEN, SULPHUR AND CARBON

The elemental (carbon, nitrogen and sulphur) composition by weight of the organic samples were obtained from the analytical experiments by the methods described in the next sections at the Soil Science Department, Institute of Agricultural Research, Samaru, Zaria. The total nitrogen for all samples was determined by Kjeldahl's method while sulphur was determined by slight modification of the Carius method. The total carbon was determined in the combustion analysis apparatus.

3.5.1 Determination of Nitrogen by Kjeldahl Method

In the method, a 0.4g of sample is placed in Kjeldahl flask and 25 ml of concentrated H_2SO_4 together with a little (0.05g) of potassium sulphate and copper sulphate is added. KSO_4 raises the boiling point and ensures complete reaction, while $CuSO_4$ acts as a catalyst. The flask is loosely stopped by a glass bulb and heated gently in an inclined position until the brown colour of the liquid first produced and disappeared on continuous heating. At this point all nitrogen in the substance is converted to ammonium sulphate. The flask is cooled and its contents diluted with distilled water and then carefully transferred into one-liter round bottomed flask. An excess of sodium hydroxide solutions poured down the side of the flask and it is fitted with a Kjeldahl trap and a water condenser. The lower end of the condenser dips in a measured volume of excess of the $N/10H_2SO_4$ solution. The liquid in the round bottomed flask is then heated and the librated ammonia distilled into H_2SO_4. The excess of acid was determined by titration with N/10 alkali, using phenolphthalein as the indicator. Total nitrogen content of the organic sample was calculated from the equation

$$\text{Percentage of nitrogen} = \frac{1.4VN}{w} \qquad (3.1)$$

where, N = Normality of the acid used

V = volume of the acid used

W = weight of the substance Kjeldahlised.

3.5.2 Determination of Sulphur

The total Sulphur content of the organic samples was estimated by heating about 0.35g of sample with fuming nitric acid. The sulphur is oxidized to sulphuric acid which is then precipitated as barium Sulphate ($BaSO_4$) by adding excess of barium chloride (BaCl) solution. The precipitate so formed is filtered, washed, dried and weighed. From the weight of $BaSO_4$ so obtained, the percentage of Sulphur was calculated as follows:

One mole of $BaSO_4$ contained one mole of S i.e $BaSO_4$ = S or

233g of $BaSO_4$ contains 32g of Sulphur

X g $BaSO_4$ contains $\frac{32}{233} x X_g$ of Sulphur $\frac{100}{0.35g}$

$$\text{Therefore, \% S} = \frac{32X_g}{233} x \frac{100}{0.35g} \qquad (3.2)$$

where, X_g is the mass of $BaSO_4$ so formed/produced.

3.5.3 Determination of Carbon Content

The total organic carbon was estimated by burning 0.32g of organic sample/substance in a slow stream of oxygen gas in a combustion tube. The vaporized sample is passed over hot copper oxide, which burns the sample completely to H_2O and CO_2. The increase in weight of the CO_2 absorbent tube (containing strong solution of potassium hydroxide) in the tube gives the weight of CO_2 formed by combustion of the sample. The percentage carbon was calculated from the equation

$$\%C = \frac{12y}{44} x \frac{100}{w} \qquad (3.3)$$

where y is the mass of CO_2 containing carbon and w is the weight of the substance/sample.

3.6 DETERMINATION OF ASH CONTENT

The ash content was measured as follows:

A prescribed amount of sample (2 g) was weighed in a ceramic crucible and was placed in an electric muffle furnace. Because the alkali oxides are volatile at high temperatures, the temperature was kept at 550^{o}C in the determination of ash for all samples. After 3 h, the furnace was turned off and was allowed to cool down. The crucible containing the ash was weighed and the ash content of each sample was determined by difference.

3.7 THE USE OF EMPERICAL EQUATIONS TO ESTIMATES HHVs

The indirect determination of high heating value (HHV) of biofuels samples were made from their ultimate analysis results and total ash contents using the equations recommended by Channiwala and Parikh (2002), and Boie (1953) (equation 2.06 and 2.07).

Direct (measured) and indirect (calculated) calorific values for each biofuel sample were compared and the results are presented in section 4.6.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0: RESULTS AND DISCUSSION

4.1 SAMPLES' DENSITIES

The actual density of the fouteen samples is presented in table 4.1. The measured density ranges beteween 0.1515 – 1g/cm^3 for Bagasse and Cocoanut shell respectively. The density of the materials was used to calculate the normalized count rate, η. It follows from the result that cocoanut shell appeared to be the densest having high mass per unit volume and hence theoretically should have high energy content. On the other hand, sugarcane bagasse is the lightest and hence low energy content.

4.1.1: Excess Count Rates for Fourteen biomass Samples

The reflection parameter i.e. normalises excess count rates (calculated from equation 2.38) for all samples are presented in table 4.1. The results show that the normalised count rate ranges as low as 0.978066 - 1.74148 cm^3/g for Cocoanut shell and Coffee senna respectively. It is confirmed from the results that the normalized count rate is a strong function of the sample's total hydrogen. Coffee senna with highest reflection parameter appeared to have high hydrogen content of 6.101802 (wt %) while cocoanut shell with smallest reflection parameter has low hydrogen value. A plot of normalized excess count rate against total hydrogen content of all samples will yield a linear graph.

4.1.2: Densities and Excess Count Rates for Fourteen biomass Samples

The measured relative excess activities, $R = \left(\frac{I - I_o}{I_o} \right)$ normalized to the physical density, ρ, of the given sample, i.e. $\eta = \frac{R}{\rho}$ were computed, the values are summarized in table 4.1 together with the hydrogen weight percent of all samples. Measured excess count rates with and without sample are used to calculate the excess count rate. Standards in the form of compounds of known hydrogen contents shown in table 3.1 were used to obtain calibration line for thermal neutron reflection parameter i.e. normalized excess counts rates, η, as a function of hydrogen content from which the total hydrogen contents of the fourteen samples are calculated from equation 3.0.

All values are obtained using the facilities presented in section 2.10, 2.11, 2.12 and procedure presented in chapter three. The observed total hydrogen contents of these plants biomass are in good agreement with widely reported values using other analytical methods except for rice straw and cocoanut shell, table 4.4.

Table 4.1: Densities and Excess Count Rates for Fourteen biomass Materials

S/N	Sample	$\rho(g/cm^3)$	I_o (cps)	I (cps)	R	$\eta\,(cm^3/g)$	H_2 (wt %)
1	Cocoanut Shells	1.0000	1003	1984	0.978066	0.978066	2.483724
2	Groundnut Shells	0.1720	1916	2354	0.228601	1.329077	4.147285
3	Coffeeweed (Senna Obtusifolia)	0.3077	4420	6587	0.490271	1.593343	5.399728
4	Coffee senna (Senna Occidentalis)	0.4167	4779	8247	0.725675	1.74148	6.101802
5	Rice Husks	0.4762	1003	1601	0.596211	1.252019	3.78208
6	Bagasse	0.1515	1871	2295	0.226617	1.49582	4.937537
7	Maize Cobs	0.5000	1019	1617	0.58685	1.1737	3.410899
8	Rice Straw	0.2759	1021	1324	0.296768	1.075636	2.946141
9	Cotton Stalks	0.3548	1007	1429	0.419067	1.181135	3.446135
10	Sawdust	0.2380	913	1224	0.340635	1.431241	4.631472
11	Flamboyant	0.4000	1106	1854	0.676311	1.690778	5.861505
12	Maize Husks	0.2800	1690	2243	0.327219	1.168639	3.386915
13	Corn Stalks	0.1724	982	1224	0.246436	1.429442	4.622949
14	Switch Grass	0.2571	1018	1326	0.302554	1.176795	3.425569

4.2 RELATIONSHIP BETWEEN HIGH HEATING VALUE (HHV) AND TOTAL HYDROGEN/CARBON CONTENTS (%WT) OF THE SAMPLES

The percentage hydrogen contents, the normalized excess count rate and high heating values for the fourteen plant samples are presented in table 4.2. The high heating value is measured directly with bomb calorimeter and estimated from equation 2.06.

A graph of high heating value against total hydrogen and carbon contents is plotted. From the data shown in table 4.2 and the trend of data plotted in figure 4.0 and 4.1, it is evident that the high heating values of the fourteen selected samples is not linearly related to their total hydrogen contents but directly related to their total carbon content, i.e. the higher the carbon content of plant biomass, the higher the heat energy to do a useful work. The co-efficient R^2, which represent the correlation between HHVs and total hydrogen and carbon contents were calculated as 0.001278 and 0.931541 respectively. These calculated values show that the relationship between HHVs and total carbon contents is positive/direct while for hydrogen content there is no correlation. These results are in good agreement with the theoretical equations derived by Tillman (1978), Yin (2011), Boie (1953) and Channiwala and Parikh (2001) that the high heating value of biomass materials is a very strong function of its fixed carbon content. The fixed carbon content represents the amount of combustible material present in the char residue after loss of moisture and volatile matter.

Table 4.2: Relationship between HHVs (MJ/Kg) and Hydrogen Contents (%wt) of the Samples

Fuel Name	$H_2(wt\%)$	C (wt %)	HHV (MJ/kg) (Measured)(125µm)	HHV (MJ/kg) (Channiwala and Parikh,2002)
Cocoanut Shell	2.483724	40.23	16.1228	15.24403
Groundnut Shells	4.147285	55.41	17.6236	20.86314
Coffee weed(Senna Obtusifolia)	5.399728	53.75	12.4379	21.91678
Coffee Senna (Senna Occidentalis)	6.101802	35.92	13.9546	14.81138
Rice Husks	3.78208	64.5	8.94868	25.61794
Bagasse	4.937537	45.21	30.3193	16.86594
Maize Cobs	3.410899	54.16	25.3422	19.60851
Rice Straw	2.946141	39.26	9.15308	12.87765
Cotton Stalks	3.446135	38	16.1025	11.93294
Sawdust	4.631472	46.12	21.1178	17.03614
Flamboyant	5.861505	61.94	32.26325	25.72979
Maize Husks	3.386915	75.98	21.1178	29.66653
Corn Stalks	4.622949	55.61	45.3495	24.04031
Switch Grass	3.425569	75.13	27.8379	28.7219

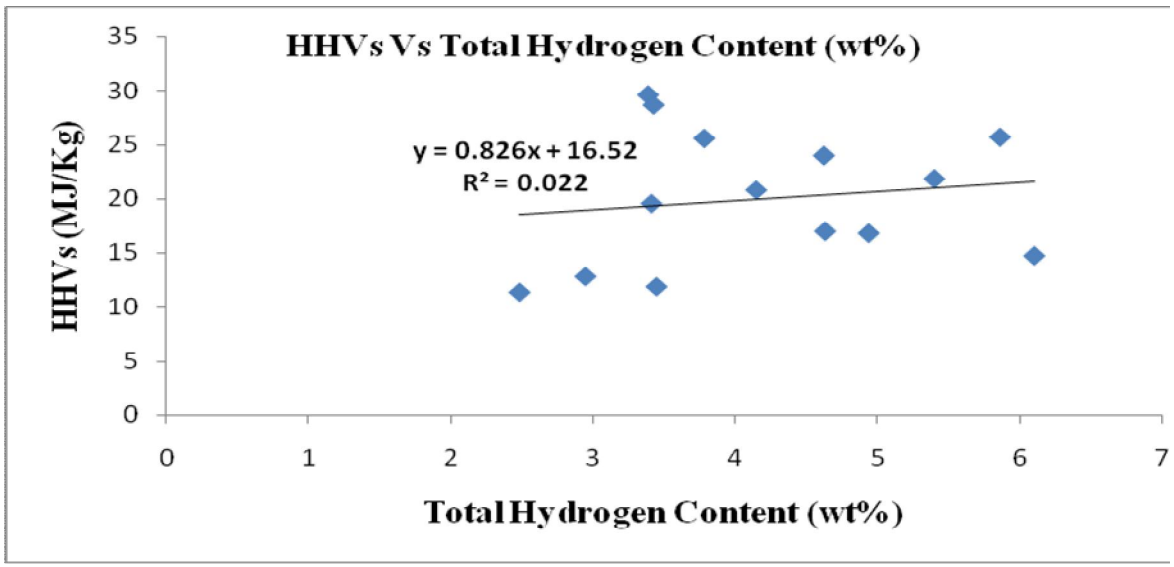


Figure 4.0: HHVs Against Total Hydrogen Content (%wt)

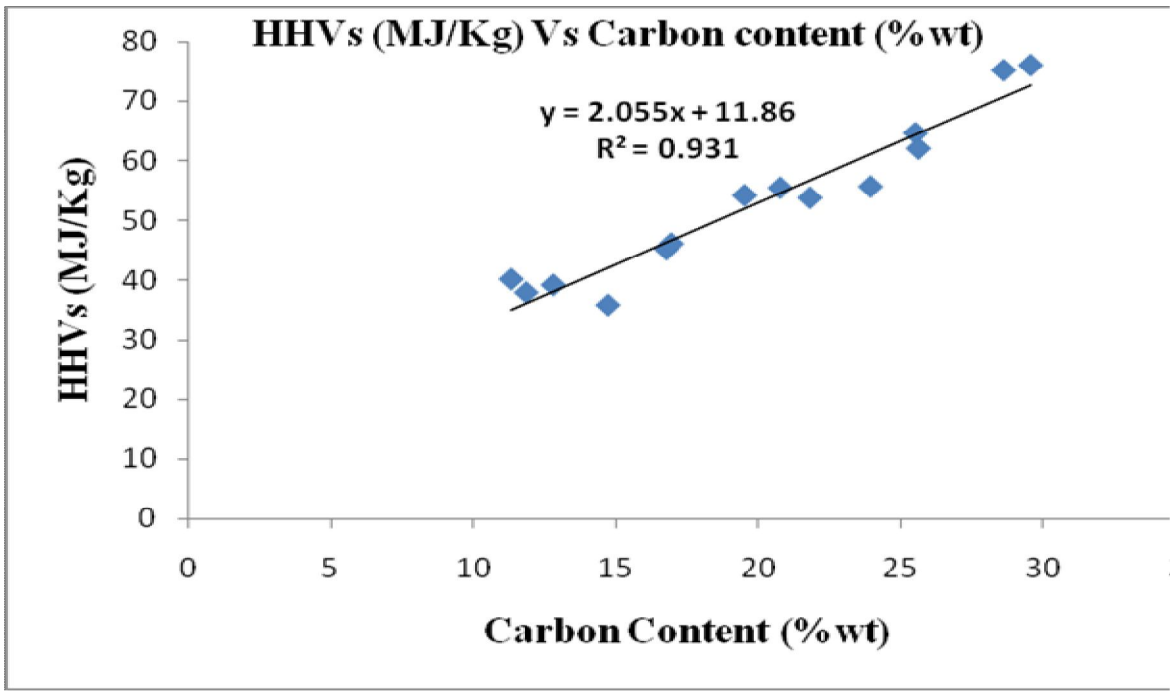


Figure 4.1: HHVs Against Total Carbon Content (%wt)

4.3 ULTIMATE ANALYSIS OF THE BIOMASS SAMPLES

The results of elementary and ash analyses for the fourteen samples are listed in table 4.3.

Table 4.3: Ultimate Analysis (% mass, dry basis) of Plant Biomass Samples

Fuel Name	C%	H%	S%	N%	O%	ASH%	HHV (MJ/kg) (dry basis)	HHV (MJ/kg) Boie's equation
Cocoanut Shells	40.23	2.483724	0.0151	0.88	56.39118	2.30	16.12275	11.07972
Groundnut Shells	55.41	4.147285	0.0136	3.50	36.92912	5.00	17.6236	20.25492
Coffee weed	53.75	5.399728	0.0196	1.05	39.78067	10.0	12.43788	20.78842
Coffeesenna	35.92	6.101802	0.0151	3.15	54.81310	8.50	13.95463	13.83635
Rice Husks	64.50	3.78208	0.0121	2.10	29.60582	20.0	8.948675	23.45964
Bagasse	45.21	4.937537	0.0106	0.88	48.96186	3.00	30.31925	16.46253
Maize Cobs	54.16	3.410899	0.0121	1.75	40.66700	10.0	25.34218	18.48514
Rice Straw	39.26	2.946141	0.0181	2.10	55.67576	17.0	9.153075	11.03164
Cotton Stalks	38.00	3.446135	0.0272	1.75	56.77667	5.00	16.1025	11.32648
Sawdust	46.12	4.631472	0.0242	0.70	48.52433	5.00	21.1178	16.42670
Flamboyant	61.94	5.861505	0.0302	1.58	30.58830	3.50	32.26325	25.27236
Maize Husks	75.98	3.386915	0.109	2.1	18.42409	12.0	21.1178	28.33641
Corn Stalks	55.61	4.622949	0.021	1.23	38.51605	37.5	45.3495	20.07040
Switch Grass	75.13	3.425569	0.0181	1.93	14.49633	5.00	27.8379	28.91979

A good estimate of high heating value of the fuels was obtained using their ultimate analysis results. The percentage of carbon, hydrogen, nitrogen and sulfur were determined analytically while the percentage of oxygen was obtained from the subtraction of the ultimate analysis result from 100: i.e.

$$\% \text{ Oxygen} = 100 - (\%C + \%H + \%N + \%S_{organic}) \quad (4.1)$$

The carbon and oxygen content is important in biomass energy analysis. High Oxygen content tends to lower the calorific value while high carbon content tends to form high-grade biomass fuel. It is evident from table 4.3 that high carbon contents contributes to the heating value positively and high oxygen content is contributes negatively. It is therefore important in biomass conversion routes to de-oxidize the biomass in order to increase the heating value.

The measured percentage H, N and S contents are generally much lower to that of hydrocarbon fuels and oxygen content is high to that of hydrocarbon. The total nitrogen varies in the range 0.88-3.50 (wt %) and the total sulphur range 0.0106-0.1090 (wt %). Both nitrogen and sulfur content are not important in biomass combustion. They tend to increase the release of toxic gases that are either irritants (NO_x, SO_2, aldehydes and acrolein) or asphyxiants (HCN) which may cause adverse effect to living organisms.

The ultimate analysis results of this work were found to be in good comparison with the ones obtained by Channiwala and Parikh (2002), see table 4.4 and figure 4.2 for comparison.

Table 4.4: Ultimate analysis % by wt (dry basis) Compared

Material	C	C*	H	H*	O	O*	N	N*	S	S*	A	A*	HHV MJ/kg
Cocoanut Shell	50.22	40.23	5.70	2.48	43.37	56.39	-	0.88	-	0.02	0.71	2.0	20.498
Groundnut Shell	48.59	55.41	5.64	4.15	39.49	36.93	0.58	3.50	-	0.01	5.70	5.0	19.849
Rice Straw	35.68	39.2	4.62	2.95	39.14	55.68	0.28	2.1	-	0.02	20.38	17.0	14.850
Rice Husk	38.50	64.50	5.20	3.78	34.61	29.61	0.45	2.1	-	0.01	21.24	20.0	14.693
Bagasse	45.48	45.21	5.96	4.94	45.21	48.96	0.15	0.88	0.01	0.01	3.20	3.0	17.330
Cotton Stalks	39.47	38.00	5.07	3.45	38.09	56.78	1.25	1.75	-	0.03	17.20	5.0	15.831
Saw dust	47.13	46.12	5.86	4.63	40.35	48.52	0.65	0.70	0.16	0.02	5.83	5.0	19.970

*This work

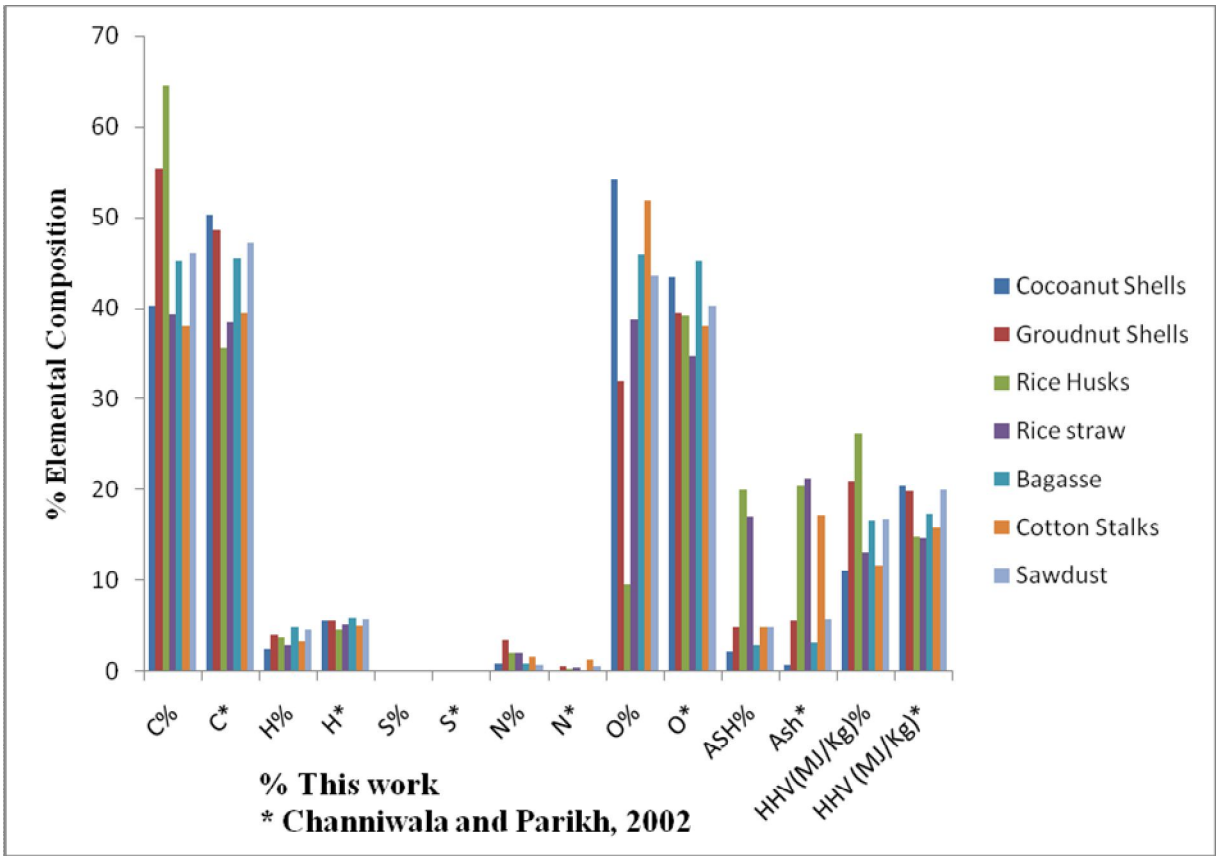


Figure 4.2: Comparison between Ultimate analysis results of this work and that of Channiwala and Parikh (2002)

4.4 EFFECT OF PARTICLE SIZE ON THE HIGH HEATING VALUES OF THE SAMPLES

The effect of particle size on the measured heating values of biomasses is presented in table 4.5 and figure 4.4 represent the bar chart of the results. It can be seen by comparison of the three mesh sizes; those bigger sizes (500µm and 212µm) have high calorific values than smaller (125µm) mesh size. The fine size (125µm) gives the smallest heating values in all the samples except for Flamboyant. The fine grinding resulted in a loss of some heat and made the sample vulnerable to air oxidation. This result agrees with that obtained by Kumar and Pratt (1996) when the effect of particle size on three plant biomass was analyzed.

It was observed that the measured heating values for all sizes are generally high when compared with the widely reported values in the range 17-21 MJ/kg for biomass materials. In all the sizes, 125 µm gives a better result that can be comparable to what is known in the literature. About ten data points (out of fourteen) are within the acceptable range of 17-21MJ/kg. The overestimation of high heating values in most of the data points might be due to compression force of 15 tons (15, 000Kg) that was applied in pelletizing (as the densification of the biomass increase its calorific value) or might be due to experimental condition.

The calculated high heating values were correlated as a function of their ultimate analysis results for all sizes and the following empirical correlations were obtained from regression analysis:

For 500 µm,

$$HHVs = 242.4535 - 1.8546C - 6.8718H - 122.2782S - 2.0293O - 1.9511A \quad (4.2)$$

With R-Squared = 0.5182. For 212 μm,

HHVs = 48.6348 - 0.1678C + 1.6773H + 84.7598S - 0.3239O - 0.6963A (4.3)

With R-squared = 0.1998 and for 125 μm,

HHVs = 4.8386C + 7.2062H - 25.6657S + 4.5627O + 4.8417A - 454.744 (4.4)

With R-Squared = 0.3734.

These equations, obtained from regression analysis by using the measured HHVs values as a function of their ultimate analysis results, shows that a better high heating values for biomass is obtainable with a larger particle size of 500 μm followed by 125 μm and 212 μm gives the least R-square value. These results imply that there should be certain size of the biomass that will give an optimum high heating value.

Table 4.5: Effect of Particle Size on HHVs Values of the Samples

Fuel Name	HHV (MJ/kg)(500 μm)	HHV (MJ/kg) (212 μm)	HHV (MJ/kg) (125 μm)
Cocoanut Shells	23.5636	18.73625	16.12275
Groundnut Shells	38.42588	51.8665	17.6236
Coffee weed (Senna Obtusifolia)	24.92278	41.49233	12.43788
Coffee Senna (Senna Occidentalis)	14.54073	17.07803	13.95463
Rice Husks	43.3076	9.403375	8.948675
Bagasse	30.5653	33.66293	30.31925
Maize Cobs	40.095	37.39783	25.34218
Rice Straw	40.105	33.9892	9.153075
Cotton Stalks	30.96895	26.33613	16.1025
Sawdust	29.39965	37.58613	21.1178
Flamboyant	19.08298	42.1115	32.26325
Maize Husks	29.39965	39.21535	21.1178
Corn Stalks	23.99553	34.8391	45.3495
Switch Grass	30.49055	29.02033	27.8379

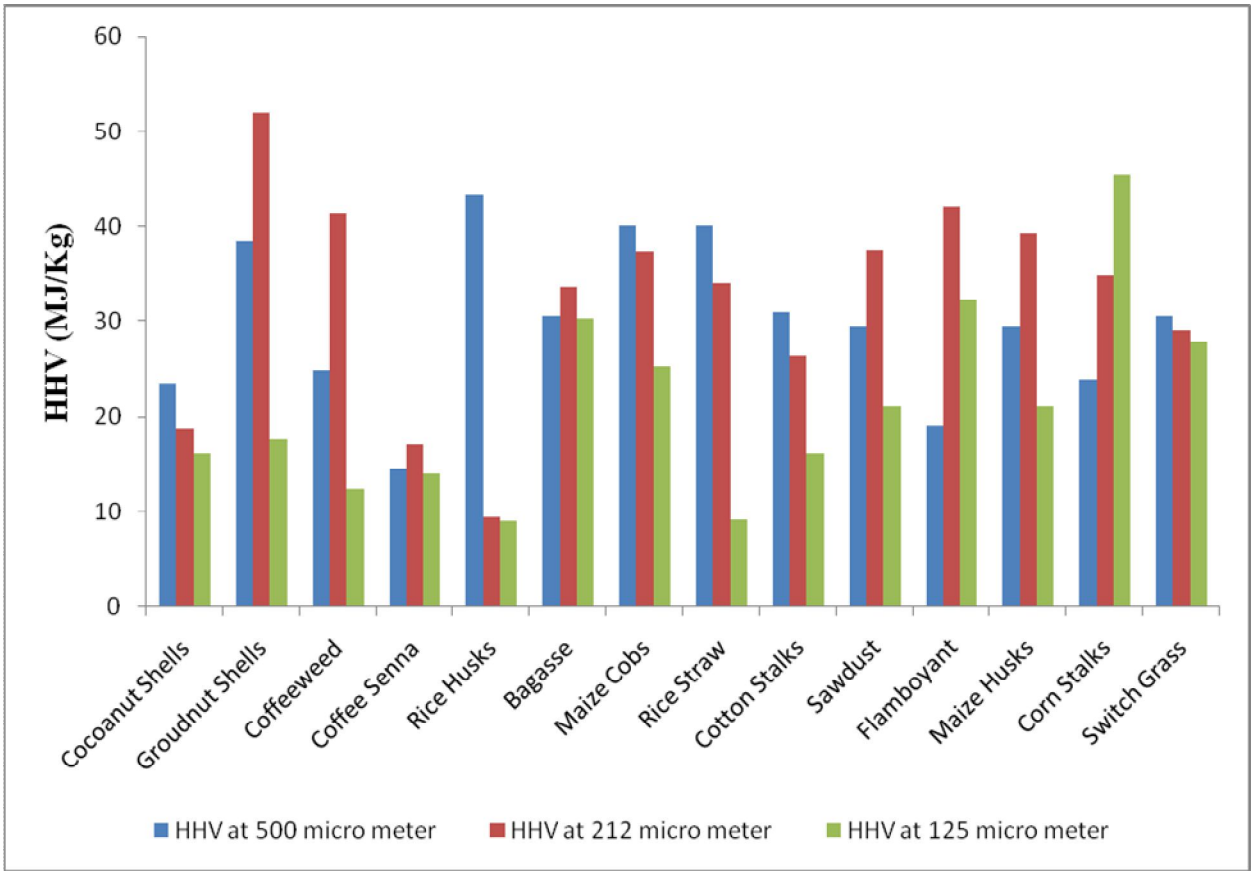


Figure 4.3: Effect of Particle Size on the High Heating Value

4.5: EFFECT OF BINDER ON THE HIGH HEATING VALUES

The results listed in table 4.6 reflect the effect of the addition of binder on the calorific value of biomass. Polyvinyl Chloride (PVC) dissolved in Toluene compound (organic binder) was used in this work. This class of binder is commonly used in sample preparation for XRF and XRD analysis in many laboratories. Addition of binders in the preparation of biomass is important for transport and storage purposes. It can be seen from figure 4.4 that the addition of this class of organic binder greatly decreases the heating value of most fuels. The calorific values decrease to about half in most of the data points. Decrease of high heating value would not be acceptable since the whole aim of biomass

combustion research is to enhance its heating values. It is therefore important to consider the effect of binder to be added in the solid Biofuel preparation as briquettes, pellets, bales, chips, etc. For cocoanut shell, the calorific value with binder is greater than that without binder. This is due to the fact that the effect of binder greatly depends on the elemental composition of the fuel in question. In the earlier work of Yakubu (2009), it was reported that briquettes produced from sawdust-gum Arabic binder is quite better in terms of calorific value, combustion characteristics, quality and ecological friendliness than does produced from sawdust-starch.

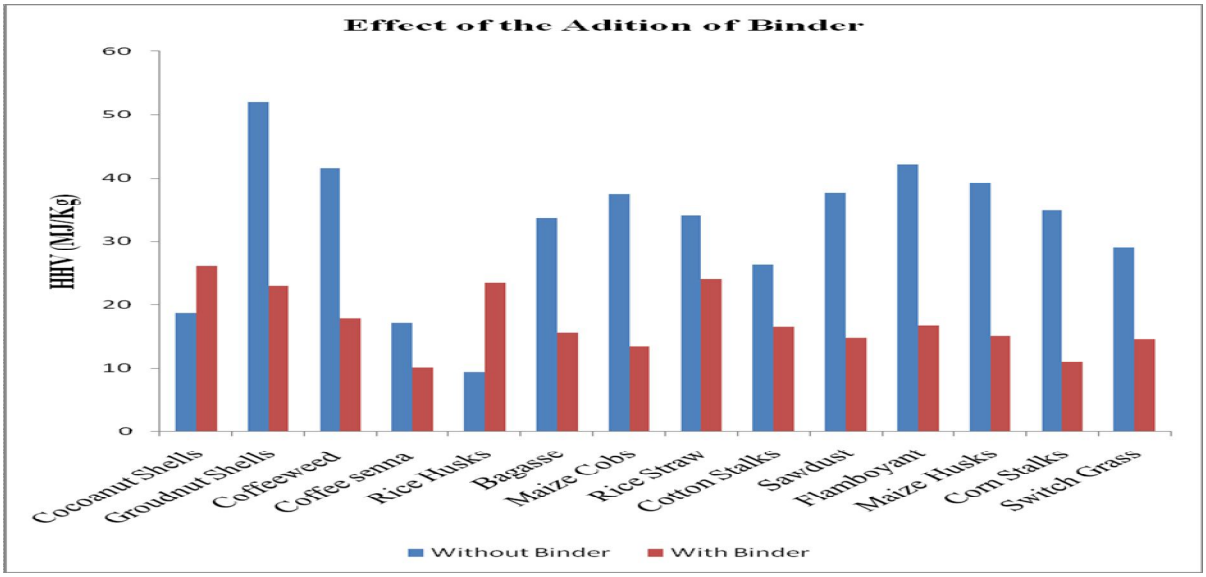


Figure 4.4: Measured High heating value with and without binder

Table 4.6: Effect of Binders on Gross Calorific Value

Fuel Name	Mesh Size (μm)	HHVs (MJ/kg)	HHVs (MJ/kg)*
Cocoanut Shells	212	18.73625	26.16468
Groundnut Shells	212	51.8665	23.0233
Coffee weed(Senna Obtusifolia)	212	41.49233	17.76208
Coffee senna (Senna Occidentalis)	212	17.07803	10.05858
Rice Husks	212	9.403375	23.5233
Bagasse	212	33.66293	15.57563
Maize Cobs	212	37.39783	13.4173
Rice Straw	212	33.9892	24.0586
Cotton Stalks	212	26.33613	16.46235
Sawdust	212	37.58613	14.89713
Flamboyant	212	42.1115	16.6632
Maize Husks	212	39.21535	15.18025
Corn Stalks	212	34.8391	10.97908
Switch Grass	212	29.02033	14.70883

* HHVs with Binder

4.6: COMPARISON BETWEEN MEASURED AND CALCULATED HHVS (DRY BASIS) OF BIOMASS FUELS

The higher calorific value (HCV) of biomass is most precisely determined by using a bomb

Calorimeter, as defined for example in the British Standard Methods (BS: 1016: part 5: 1977). High calorific value can also be estimated from empirical correlations, for example equation 2.06 and 2.07. Table 4.7 shows direct comparison between measured and estimated heating values. Comparisons of the results presented in this table showed that measured heating values do not excellently agreed with the calculated values estimated using empirical equations derived by Channiwala and Parikh (2001) and Boie (1953).

The calculated results are considered to be more accurate in this work due to the fact that the results of the two empirical equations fairly matched and are in good agreement with widely reported HHVs in the range of 17-21MJ/kg. Bomb measurements over predicts HHVs for a number of data points and some few data points matched the computed results. The over prediction might be due to densification of the powdered samples during preparation of biomass or may be due to experimental condition.

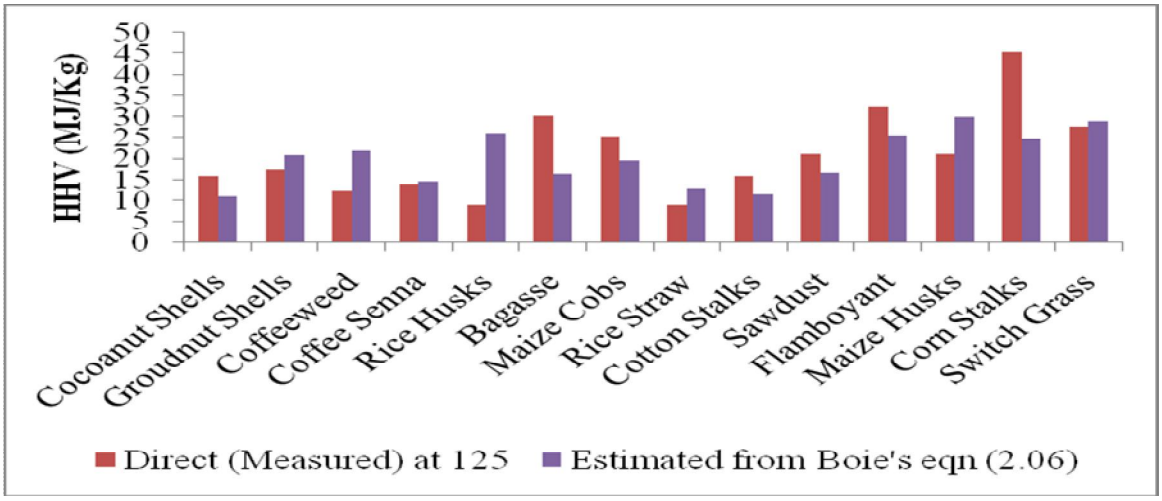


Figure 4.5: Comparison between Measured and Estimated HHV

Table 4.7: Comparison between Measured and Calculated HHVs (dry basis) of Biomass Fuels

Fuel Name	HHV (MJ/kg) (Measured)(125µm)	HHV (MJ/kg) Boie's equation	HHV(MJ/kg) (Channiwala & Parikh's equat.)	ASTM (MJ/kg)
Cocoanut Shells	16.1228	11.07972	11.31754	-
Groundnut Shells	17.6236	20.25492	20.77192	20.18
Coffeeweed (Senna Obtusifolia)	12.4379	20.78842	21.82242	-
Coffee senna (Senna Occidentalis)	13.9546	13.83635	14.71525	-
Rice Husks	8.94868	23.45964	25.52764	-
Bagasse	30.3193	16.46253	16.77273	17.33
Maize Cobs	25.3422	18.48514	19.51914	-
Rice Straw	9.15308	11.03164	12.78944	16.28
Cotton Stalks	16.1025	11.32648	11.84348	15.22
Sawdust	21.1178	16.42670	16.9437	16.23
Flamboyant	32.26325	25.27236	25.63426	-
Maize Husks	21.1178	28.33641	21.1178	-
Corn Stalks	45.3495	20.07040	23.9479	-
Switch Grass	27.8379	28.11549	28.63249	

CHAPTER FIVE

5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

5.1 SUMMARY

The relationship between the high heating values (HHVs) and total hydrogen and carbon contents of fourteen (14) selected biomass briquettes in terms of grain size, pressure and binders were investigated. Analyses of the data obtained from the study shows that the high heating values of the fourteen selected samples is not linearly related to their total hydrogen contents but directly related to their total carbon content. The co-efficient R^2, which represent the correlation between HHVs and total hydrogen and carbon contents were calculated as 0.001278 and 0.931541 respectively. These calculated values show that the relationship between HHVs and total carbon contents is positive/direct while for hydrogen content there is no correlation.

The measured elemental H, N and S contents are generally much lower to that of hydrocarbon fuels but oxygen content is high to that of hydrocarbon. The total nitrogen measured varies in the range 0.88-3.50 (wt %) and the total sulphur range 0.0106-0.1090 (wt %).

Comparisons of the measured (Bomb measurements) and calculated results showed that measured heating values do not excellently agreed with the calculated values estimated using empirical equations derived by Channiwala and Parikh (2001) and Boie (1953). The calculated results are considered to be more accurate in this work due to the fact that the

results of the two empirical equations fairly matched and are in good agreement with widely reported HHVs in the range of 17-21MJ/kg.

The effect of binder and particle size in the Biofuel preparation are also investigated. The investigation reveals that addition of polyvinyl chloride dissolved in toluene compound (binder) greatly decreases the heating value of most fuels to about half. Decrease of high heating value would not be acceptable as the prime aim of biomass combustion research is the enhancement of its heating values. The effect of particle size indicates that finely ground particles (about 125μm) had low calorific values than 500 μm or 212 μm as the grinding resulted in a loss of some heat and made the sample vulnerable to air oxidation.

5.2 CONCLUSION

A bomb calorimeter (Parr 6100) was used to measure directly the high heating values (HHVs) of fourteen selected plant biomass. C, N, S and ash contents were determined analytically and Oxygen (O) by subtraction. A non destructive technique based on the neutron reflection technique was used to determined total hydrogen (H) contents from the samples. Analysis of the experimental data confirmed the following:

1. HHVs of the fourteen biomass tested are not a function of their total hydrogen contents but a function of their total carbon contents as described in section 4.2.
2. Both particle size and addition of binder in the biofuels preparation have serious effect on the high heating values of the samples. Finely ground particle (with larger surface area, 125μm) tend to loss some heat and made the sample vulnerable to air oxidation and therefore gives low HHVs. The addition of PVC dissolved in toluene organic binder also decreased the HHVs of most samples by about half its original

values. This is not acceptable in energy research as its main aim is to enhance the HHVs.

3. The use of empirical equations to estimate the HHVs derived by Channiwala and Parikh (equation 2.06) and Boie (equation 2.07) is good as these equations predicts the American Standard of Testing Materials (ASTM) experimental results measured using Bomb calorimeter.
4. A thermal neutron reflection technique is a fast and non destructive method in determining the total hydrogen/moisture content of the biomass materials. The hydrogen contents of the biomass tested is in good agreement with the one determined using long analytical methods.

5.3 RECOMMENDATION FOR FURTHER WORK

- There is need to carry out more research to verify the major disagreement between the measured and calculated HHVs of biomass.
- There is also the need to repeat the experiment with the bomb machine for some other plants biomass in order to determine why the over prediction of the HHVs?
- The relationship between the HHVs and total hydrogen/carbon content of some other biomass fuels should also be investigated so as to confirm if a general statement can be drawn regarding the combustion relationship between biomass HHV and its total carbon or hydrogen content.
- Different particle sizes should be tested in order to obtain an optimum particle size that may give better HHVs.

- Other binders should also be tested in order to come up with a better one than PVC dissolved in toluene.

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