EFFECT OF BINDERS ON THE PROPERTIES OF COAL BRIQUETTE BLENDS PRODUCED WITH DIFFERENT BIOMASSES

BY

IKELLE, ISSIE IKELLE
2008547011P

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CERTIFICATION

This is to certify that this thesis was written by IKELLE, ISSIE IKELLE, a postgraduate student in the Department of Pure and Industrial Chemistry with the Registration Number 2008547011P.

The work embodied in the thesis is original and to the best of our knowledge has not been submitted in part or full for any other diploma or degree of this or any other University.

....   ………....................
Prof. J.O. Ogbuagu   Date
(Supervisor)

....
Prof. T.U. Onuegbu   Date
(Supervisor)

....
Dr. J.K. Nduka   Date
(Head of Department)

....
Prof. P.O. Ukoha   Date
External Examiner

....
Prof. Eric. Ofoedu   Date
(Faculty PG Sub-Dean)

....
Prof. A.J. Ekpunobi   Date
(Dean, Faculty of Physical Sciences)

....
Prof. Ike Odimegwu   Date
(Dean, School of Postgraduate Studies)

DEDICATION

With profound gratitude to the Almighty God for His mercy and kindness towards me and my family, I dedicate this work to my sons Prince Ebubechukwu Lucas Ikelle and Godswill Ikenna Ikelle, my lovely wife Ada Precious Ikelle. Her wisdom and support has been a great source of inspiration.

I dedicate this work to my father and mother, Elder Issie Ikelle and Mrs. Comfort Ikelle for laying the foundation of my educational pursuit and parental care.

I dedicate this work to my siblings, Gladys, Ogbonne, Nwanyigwe, Okamma, Okey, Onuoha, Chinwe and Chineme.

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ABSTRACT

The production and characterization of briquettes from mixtures of coal, corn cob and rice husk has been carried out. The briquette samples were produced by blending varying compositions of coal and rice husk, also coal and corn cob at the ratios of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 using bitumen, starch, calcium sulphate and cement as binders and calcium hydroxide as desulphurizing agent. The briquettes were produced mechanically using a manual briquetting machine with force and compression pressure of 276.36 N and 31.67 N/m^2 respectively. The results showed that the calorific values of the briquettes of coal and rice husk with the respective binders are in the following ranges, cement (19701.57-24441.12 kJ/kg), bitumen (20981.48-27083.07 kJ/kg), calcium sulphate (19615.16-24840.95 kJ/kg) and starch (21739.54-25921.82 kJ/kg). The calorific values for corn cob and coal are in the following ranges, cement (20364.34-22823.93 kJ/kg), bitumen (21691.64-23940.37 kJ/kg), calcium sulphate (19000.54-23219.07 kJ/kg) and starch (21450.82-23794.98 kJ/kg). The values showed that briquettes of coal and rice husk had higher calorific values than those of coal and corn cob. With regard to the binders used in the briquetting, briquettes produced with bitumen ignited faster with values (16.00-37.00 s), had much sulphur content values (3.01-8.22%) and lowest burning time (11.71-24.89 min) than other briquettes produced with other binders. Briquettes produced with binders cement and calcium sulphate had high ash contents (19.13-28.83 %) and (18.88-29.63 %) respectively due to the presence of non combustible material. Briquettes produced with starch as binder had highest compressive strength values ranging from 7.92-13.74 N/mm^3, had lowest values of sulphur content (3.03-6.21 %) and long burning time (15.27-26.21 min). These properties made it the best of all the binders studied. The briquettes produced with starch had the lowest sulphur content. Analysis of variance (ANOVA) showed significant difference ($p<0.05$) at 95 % confidence interval for sulpur content when it was compared to other briquettes produced with different binders. The briquettes produced with bitumen as binder ignited faster than the other briquettes produced at 95 % confidence interval ($p<0.05$). The calorific values (kJ/kg) of the different briquette compositions were in the order, 60 % coal : 40 % rice husk (24441.12-27083.07) and 60 % coal : 40 % corn cob (22823.93-23940.37). The ignition time (s) of the different briquette compositions were in the order 60 % coal: 40 % rice husk (21.67-33.67) while 60 % coal: 40 % corn cob (29.56-42.50). The burning time (min) of the different briquette compositions were in the order 60 % coal : 40 % rice husk (17.81-20.43) while 60 % coal : 40 % corn cob (19.76-22.20 min). The compressive strength (N/mm^3) of the different briquette compositions were in the order 60 % coal: 40 % rice husk (11.34-13.95) and 60 % coal: 40 % corn cob (12.75-14.46), the values are higher than those of 100 % coal that ranged from 7.05-7.92 N/mm^3. The lower sulphur contents for 60 % coal : 40 % rice husk (4.69-7.78%), and that of 60 % coal : 40 % corn cob values of (5.78-7.56 %), showed that the briquette compositions were of good quality. The briquettes did not disintegrate when handled. The elemental composition of the ashes of the raw materials was determined using X-ray fluorescence spectrometer. The result showed that the concentration of the heavy metals in the ashes of coal included (V_2O_5 0.29 ± 0.0048 %, Cr_2O_3 0.059± 0.0011 %, MnO 0.13 ± 0.0012 %, CuO 0.18 ± 0.0041 %, As_2O_3 0.05 ± 0.0023 %, PbO 0.31± 0.0081 %), rice husk (V_2O_5 0.002 ± 0.0011 %, MnO 0.153 ± 0.0013 %, CuO 0.012 ± 0.0031 %, As_2O_3 0.0063 ± 0.0001 %, PbO 0.004± 0.0001 %) and corn cob (Cr_2O_3 0.346± 0.0032 %, MnO 0.123 ± 0.0006 %, SrO 0.023± 0.0014 %).The results showed that the concentration of the heavy metals in the ashes of coal, rice husk and corn cob were relatively small, therefore the ashes can be disposed off after cooking.

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CHAPTER ONE

INTRODUCTION

In many countries of the developing world, the use of wood fuel as a source of energy is on the increase. It has been observed that the rate of consumption of this energy source in the country has been on the increase since the rural dwellers that constitute about 70 % of the population cannot afford the currently available alternative fuels to wood. The practice results in accelerated desertification in the northern part and erosion menace in the southern part of Nigeria. Both effects constitute serious ecological challenges (Olorunnisola, 1999).

An absolute minimum of 350 kg to 2,900 kg of dry wood is burnt annually, with the average being around 700 kg per person. Rural wood fuel supplies appear to be steadily collapsing in many developing countries, especially in Sub-Saharan Africa. At the same time, the rapid growth of agriculture, the pace of migration to cities, and the growing numbers of people entering the money economy are placing unprecedented pressures on the biomass base and increasing the demand for commercial fuels: from wood and charcoal to kerosene, liquid propane, gas, and electricity (Foley, 2005). Wood is being collected faster than it can re-grow in many developing countries that still rely predominantly on biomass wood, charcoal, dung, and crop residues - for cooking, for heating their dwellings, and even for lighting. Food and Agricultural Organization (FAO) stated that in 1990, around 1.3 billion people lived in wood-deficit areas. With the population-driven overharvesting that continued at that rate, some 3.4 billion people lived in areas where wood was acutely scarce or had to be obtained elsewhere. Precise data on

supplies are unavailable because much of the wood is not commercially traded but collected by the users, principally women and children, but there is no doubt that millions are hard put to find substitute fuels, and their numbers are growing (Mikdashi, 2003).

The pressure comes from various fronts, these include industrialization, farmers practicing slash and burn agriculture, fires set up deliberately or inadvertently through careless or uncaring acts. An inescapable consequence of the value of forest products to man is the huge pressure on native forests and wood lands. Fortunately, the attention of the government has been drawn to it. In Nigeria, government and research agencies are joining the conservation program, creation of shelterbelts, conservation of forest by discouraging the use of plants as wood fuel. Forest denudation is also another major problem faced in the country today. This is caused by excessive cutting down of forest trees that are primarily used for fuel production and other purposes. The use of wood fuel has increased the erosion problems, desert encroachment and deforestation. These problems can be prevented by diversion to the use of briquette as fuel source for cooking and other domestic uses like heating of the homes (Olorunnisola, 1999). A greater part of the population of Nigerians live in rural areas and most of this proportion of the population depend on wood fuel for supply of energy. This population thereby reduces the percentage of the area of forest cover to less than 25 % (United Nations Development Programme UNDP, 2000). Presently an average rural dweller in Nigeria consumes about 4300 kg of wood fuel annually. Therefore, any innovation that would lead to reduction in

the demand and use of wood in Nigeria will certainly reduce the pressure on the forest in the search of wood (Energy Commission, 2002).

Meanwhile the desert continues to creep in at the rate of 100 meters per annum in northern Nigeria. The problems of deforestation and wood fuel shortage are facing our country and as such attention has now been turned to other sources of biomass fuel. Agricultural residues are in principle, one of the most important sources of the biomass fuel. The large volume of agricultural waste generated in these rural areas when properly utilized can reduce the pressure on wood for heating purposes (Oladeji, 2012).

The intention for complete substitution of wood fuel by other sources such as electricity, solar, gas and kerosene will certainly take a few decades to materialize. In the interim, the development, production and active utilization of agro-residue briquettes will certainly be a step in the right direction. The briquetting of agro-residues is one of the numbers of ways that has been developed to solve the problem of over dependence on wood as source of fuel. Briquetting thereby puts the huge volume of waste from agriculture and agro processing to some useful purposes (Johannes, 1982).

1.1 Background of the study.

The following are advantages associated with coal briquette fuel; bio-coal briquettes can be made available and in abundance for consumption. Bio-coal briquettes are very low in price as compared to traditional energy resource such as diesel, petrol and lignite. They are less polluting than pure lignite briquettes. Burning of briquettes could be clean and smokeless and does not cause widespread eye and respiratory diseases in women and children, who are mainly involved with domestic activities (Shakya, 2002). They generally have high calorific value associated with a high bulk density. Bio-coal briquettes have lower moisture content and offer excellent combustion that does not cause ash-fly as against when the fuel material was in the raw state. The biomass materials are compressed into briquettes so that they can be used by energy producing companies to replace charcoal. These burn just like charcoal but they do not produce any harmful effects to the environment. They can be used to boil water and power turbines to generate electricity. The processes for the production are simple resulting in compact size and shape, the products are easy to store, transport and use.

Bio-coal briquettes have wide range of Industrial and domestic applications, with very lower ash content, long shelf-life and no danger of fire or explosion of the fuel. It saves the trees as the practice of cutting of trees for fuel is replaced by these better quality briquettes. The briquettes are bio-degradable fuel, hence it does not leave residues and cause contamination of the water and soil. It also acts as a good substitute for polluting fuels as well as costly renewable energy resource and they can be produced in almost every part of the world where bio-mass is easily available (Ndiema, *et al.*, 2002).

Biomass also gets rid of the need to have fossil fuels exported and imported around the world, since it can be made domestically from plants and animal waste. This will lower the price of electricity for many countries that do not have oil or coal reserves. It will mean affordable and safe energy for everyone. Briquettes are better than loose biomass since they are compressed. This compression allows them to burn for a lot longer than if it was loose. Also, it does not take too much money to compress these so it will be inexpensive for people to attain. Briquette lowers overall fuel costs for users as they are made from biomass waste. Finally, briquetting process provides job opportunities (El-Saeidy, 2004).

1.1.1 Challenges of Using Coal Briquettes

As good as briquetting process appears to be, it has the following drawbacks; briquettes can only be used as solid fuels. They have no application as liquid fuel such as the one being used in internal combustion engines. Combustion of briquette as a fuel also consumes it at a much faster rate than it can be replaced. This means that briquette is not a very efficient source of energy (Grover and Mishra, 1996). The second major problem identified with the briquetting process is the life of the screw, where dies screw is used. Usually the screw wears out within 3-4 hours and becomes unusable. Repairing of the screw causes interruption in the work and also one screw cannot be repaired more than 10 times (Mishra, 1996). Therefore, the cost of screw and its repair are one of the major barriers to further dissemination of briquetting technology (Moral and Nawasher, 2004). Briquettes cannot withstand direct contact with water, so a covered storage facility is

required. The maximum attainable temperature is 1000 ^{o}C due to their low carbon content. However, this temperature is more than adequate for cooking purpose, but may not be sufficient for industrial applications. The burning capacity per unit volume is low compared to coal, so a larger storage area is required (Oladeji, 2012).

The coal briquettes must first be ignited before use as heating fuel itself. There is also the issue of purchase of the briquettes, transportation to the house, and also need for sufficient space for storage. There is also need to feed the furnace and continous disposal of the ashes after cooking. There is also problem of the sulphur content of the coal. When coal is used for electricity generation in power plants, these oxides of sulphur are removed by filters (flue gas scrubbing). However, many stoves do not have such a filter and releases the sulphur oxides into the environment. In addition the relatively large amount of carbon IV oxide is released when coal briquettes are burnt, the amount is about twice as much as other fossil fuels, a further challenge (Oladeji *et al.,* 2009).

Through the waste-to-wealth scheme, some or many agricultural residues that are generated in large quantities can be turned into useful products as alternative energy resource. This will go a long way in making more lands available for better use rather than dumpsites and to create a clean, friendly and healthy environment for all and sundry. By the application of briquetting, which can be regarded as an attempt to link up two large or complex worlds, that of agriculture and that of fuel supply and use. Briquetting is also a densification process of loose organic materials such as rice husks, sawdust, corn

cob, tea waste, cashew nut shell, coconut shell, groundnut shell, oil palm fiber, coffee husk and coal aimed at improving handling and consumption characteristics for domestic and industrial use (Ogbuagu and Okeke, 1999). The world economy measures the standard of living of every nation and the level of its industrialization in terms of energy production and consumption. The level of energy consumption in sub-Saharan African countries is said to be 0.08 KW per capita as compared with the consumption in developed economy put at 7.0 KW per capital. Thus, if there are energy needs in our energy scenario, the overdependence on the highly favoured energy especially petroleum products can be reduced and will eventually lead to the increase in the standard of living of the growing population. Energy is thus an integral part of our economic, environment and political life and has a major role to play in the realization of people's social and economic aspiration for a better life (Ogbuagu, 1993).

1.2 Statement of the Problem

Solid waste management is one of the major problems in Nigeria. This is not only found in the urban areas but also at the rural areas. The major waste generated at the rural areas is agricultural waste or residue (crop by-product). Despite this level of waste generation, the rural dwellers still rely on wood fuel and charcoal fuel for heating, cooking and other purposes. In realization that deforestation and wood fuel shortages are likely to become serious problems in Nigeria, attention has been turned to other types of biomass fuel (Olorunnisola, 2007). Agricultural residues are, in principle, one of the major sources. They arise in large volumes both in the rural and urban areas which are

often subject to some of the worst pressures of wood shortage. The use of briquetting for conversion of agricultural residues is comparatively recent, however, and has only been taken up in developing countries in the last few years. Main agricultural residues that are produced are rice husk, coconut dregs, hay, groundnut skin, jatropha husk, palm nut shell, corn cob and cotton stem. Beside the problem of transportation, storage and operation, open burning of this bio waste with traditional style without control can cause critical air pollution.

The impact of agricultural waste on the environment depends not only on the amounts generated but also on the disposal methods used. Some of the disposal practices pollute the environment. The potential threat posed by climate change, due to high emission levels of greenhouse gases (CO_2 being the most important one), has become a major stimulus for renewable energy sources in general. When produced by sustainable means, biomass emits roughly the same amount of carbon during conversion as is taken up during plant growth. The use of biomass therefore does not contribute to a buildup of CO_2 in the atmosphere (Oladeji and Enweremadu, 2002). Hence the need at the moment in the densification of this agricultural waste in developing countries is the development of an appropriate briquetting machine suitable to the local communities. For biomass to make a significant impact as fuel for rural communities, it is imperative that an efficient, cost effective and easy to duplicate technology is developed specifically for rural communities.

1.3   Aim and Objectives of the Research.

The aim of this research is to determine the effect of binders on the properties of coal briquette blends produced with biomasses such as rice husk and corn cob.

The objectives of the study include:

i. To produce blends of briquettes from mixtures of coal and biomasses with binders such

as starch, bitumen, calcium sulphate and cement.

ii. To investigate the changes in the results of the proximate analyses of the briquettes

produced, as the proportion of rice husks and coal, corn cob and coal are varied.

iii. To compare the binding ability of the respective binders used in the briquette

production.

iv. To investigate whether the heavy metals present in the ashes of the raw materials

could constitute any human or environmental risk after burning the briquettes.

v. To convert the rice husk and corn cobs, which are environmental wastes and lump

coal into smokeless briquetted fuel.

1.4 Justification of Study

The study is desired to optimize production of cost effective briquettes. In this, two major economic and social impacts will be achieved. This means effective environmental clean up by consumption of bio-waste in briquettes which have been modified with agro-wastes. It will enable industries to reduce ignition in pure coal briquettes making them available for domestic use. The extent of desulphurization which will be determined through X-ray fluorescence spectrometric analysis that will provide scientific insight into method of producing coal based briquette. The work can contribute to the technological development of the briquette stove. The briquetting technology is relatively not a widely accepted innovation, the idea of its usage would lead to mass production of stoves. Thus, the innovation will create more job opportunities for artisans. Additionally more hand press hydraulic machines will be locally produced.

1.5   Scope of Study

The scope will cover the following:

Preparation of the coal briquettes containing 20 %, 40 %, 60 %, 80 % and 100 % biomass. The wastes biomass selected are rice husk and corn cob.

The study will involve the preparation of 50 coal briquettes modified with rice husk and corn cob. Each set comprising 10 of each set made with 20 %, 40 %, 60 %, 80 % rice husks. Similarly the same number will be produced for corn cob and coal dust. For each set of 20 %, 10 briquettes made of rice husks should contain 10 % of each of the respective binders. Therefore the total number produced will be 200 briquettes of coal and rice husk and a similar number of corn cob and coal that should give a total of 400 briquettes.

Proximate analyses (ash content, moisture content, fixed carbon, volatile matter and calorific value) of the coal, rice husk and corn cob will be carried out. The ashes of the raw samples (coal, rice husk and corn cob) will be subjected to X-ray fluorescence spectrometric analysis.

The proximate analyses (ash content, fixed carbon, moisture content, density, volatile matter, porosity index, calorific value, water boiling test, burning time, ignition time, sulphur content and compressive strength) of the respective briquettes produced will also be carried out.

The results obtained will be validated statistically by the application of Analysis of Variance (ANOVA), f-Test and t-Test.

CHAPTER TWO

LITERATURE REVIEW

2.1   Briquetting

Briquettes can be produced from sawdust, charcoal fines and rice husk. The briquettes are used basically for heating/cooking purposes and this is limited to households. Briquetting technology is yet to get a strong foothold in many developing countries because of the technical constraints involved and the lack of knowledge to adapt the technology to suit local conditions. Overcoming the many operational problems associated with this technology and ensuring the quality of the raw material used are crucial factors in determining its commercial success (Dermibas and Sahin, 1998).

Briquetting is the process of converting low bulk density biomass into high density and energy concentrated fuel briquettes. The technology uses either a dry or wet process to compress rice husk, corn cob and other agro-based wastes into shapes. The dry briquetting process requires high pressure equipment and does not need a binder. The process is expensive and recommended only for high production levels. On the other hand, using wet process allows for lower pressure equipment, but a binder is used (Belonio *et al.*, 1991).

At present two main high pressure technologies; ram or piston press and screw extrusion machines, are used for briquetting. According to Maninder *et al.*(2012), there are two types of piston press, the die and punch technology and hydraulic press. In the die

and punch technology, which is also known as ram and die technology, biomass is punched into a die by a reciprocating ram with a very high pressure thereby compressing the mass to obtain a compacted product. The standard size of the briquette produced using this machine is 60 mm, diameter. The power required by a machine of capacity 700 kg/h is 25 kW. The hydraulic press process consists of first compacting the biomass in the vertical direction and then again in the horizontal direction. The standard briquette weight is 5 kg and its dimensions are: 450 mm x 160 mm x 80 mm. The power required is 37 kW for 1800 kg/h of briquetting.

This technology can accept raw material with moisture content up to 22 %. The process of oil hydraulics allows a speed of 7 cycles/minute (cpm) against 270 cpm for the die and punch process. The slowness of operation helps to reduce the wear rate of the parts. The ram moves approximately 270 times per minute in this process. While the briquettes produced by a piston press are completely solid, screw press briquettes on the other hand have a concentric hole which gives better combustion characteristics due to a larger specific area. The screw press briquettes are also homogenous and do not disintegrate easily (Balatinecz, 1983). Having a high combustion rate, these substitute for coal in most application and in boilers. Briquettes can be produced with a density of 1.2 g/cm^3 from loose biomass of bulk density 0.1 to 0.2 g/cm^3. A higher density gives the briquette a higher heat value kJ/kg, and makes the briquettes burn slowly as compared to the raw materials from which the briquettes are made. The briquettes burn cleanly and

therefore are eco-friendly. These advantages are associated with the use of biomass that is present in the briquettes (Kaliyan and Morey, 2009).

India is the only country where the briquetting sector is growing gradually although challenges of technological and financial constraint are still there. A number of entrepreneurs are also making strenuous effort to improve both the production process and the technology (Belonio *et al.*, 1991). In underdeveloped African countries the demand for briquette is on the rise, for example in Uganda, over 93 % of domestic fuel is in the form of briquettes and wood charcoal (Wamukonya and Jenkins, 1995).

Historically, biomass briquetting technology has been developed in two distinct directions. Europe and the United States have pursued and perfected the reciprocating ram/piston press while Japan has independently invented and developed the screw press technology. In addition to this commercial aspect, the importance of this technology lies in conserving wood, a commodity extensively used in developing countries and leading to the widespread destruction of forests. Briquetting process helps to solve the disposal and pollution problems often created by biomass residues. Other notable advantages are: raw materials for briquetting are readily available world-wide, especially in the less developed countries and low cost machinery can be used (Ndiema *et al.*, 2002).

2.2 Briquette Making

Biomass briquetting plant can produce briquettes in many shapes such as cylindrical, hexagonal or square shapes; the diameters of the final briquettes ranging from 3mm to 100 mm or even bigger (Bhattacharya, 1985). Briquetting can be regarded as a waste control measure. Depending on the material of interest, briquetting can be used to provide fuel source, or as a preventive measure to many ecological problems. Certain materials like coal, agricultural waste such as rice husk, paper and saw dust can be briquetted to serve as cooking fuel (Hall and Scrase, 1998).

In rice husk briquetting, four stages are involved; carbonization within a temperature range of 150 – 200 ^{o}C in a coal-fired carbonizer, followed by separation using mesh of aperture 200-210 micron. The next stage is mixing in a mixer where the binders are added and the mixing lasts for five minutes. The final stage is moulding the plate in a mould with dimensions: length-10 cm, width-10 cm and thickness-5.2 cm. The moulded rice husk briquette is charged into an electrically heated oven at 50 ^{o}C for the first 30 minutes with increase in temperature to 100 ^{o}C for onward drying. The smokeless rice husk briquette is taken out and packed for use (Musa, 2007).

Countries rich in forestry biomass resource have already taken up biomass briquetting densification fuel as a development priority. For instance, if we consider countries such as Sweden, 30 % of the country's total energy consumption is renewable energy, 46.7 % of which is densified biomass briquettes for fuel. In the EU, biomass briquettes have become an integral part of domestic and ordinary merchandise in super

markets. More EU countries have established the corresponding industrial standards, technical specification for biomass briquettes and industrial development has entered into a rapid development stage of mature commercialization in those countries. It is highly likely that such a scenario would come into existence in other countries of the world especially Asia pacific and Africa (Vasudevan, 1993).

2.3   Characteristics of Briquettes.

According to Kaliyan and Morey, (2009) the main purpose of briquetting a raw-material is to reduce the volume and there-by increase the energy density. When densification has taken place, there are two quality aspects that need to be considered. Firstly, the briquette has to remain solid until it has served its purpose (handling characteristics). Secondly, the briquette has to perform well as a fuel (fuel characteristics).

2.3.1   Handling Characteristics.

Handling characteristics are important when considering ways of storing, transporting and handling briquettes. These are mainly determined by shape, density and raw-material. The density of a briquette can theoretically reach 1500 kg/m^3, but normally the maximum density of briquettes for commercial purposes are in the range of 1200-1400 kg/m^3. Mechanical piston presses can generally produce briquettes with a higher density than hydraulic piston presses. Increasing the density of briquettes is likely to be fruitless, as this probably would worsen the combustion characteristic (Stout and Best,

2001). The geometry of the briquette makes the hole density differ significantly from the bulk density due to the filled space between the briquettes (Eriksson, 2006).

When storing briquettes the air filled spaces between them reduce the energy density, the bulk density is normally 550-660 kg/m^3. Briquettes are sensitive to handling and transporting. Depending on production method and raw-material, the friability that is the resistance to mechanical action will vary. Observation at production plants have showed that the reliability is satisfactory in plants using mechanical piston presses, whereas plants using hydraulic piston presses have experienced reliability problems. The type of briquette press used in the production also influences the result, hydraulic presses were developed for use in small scale production and it produces a softer, more sensitive briquette. Briquettes from mechanical piston presses are more sensitive to foreign particles such as nails or screws. A nail in the raw-material would likely destroy parts of the equipment, whereas or hydraulic piston press probably would be unharmed by a nail. Finally another important aspect of the handling characteristics is the briquette resistance to humidity. Briquettes have a limited life time under humid conditions. The reason for this is the water solubility of the inherent binding agent in the briquette (Wilaipon, 2009).

2.3.2   Fuel Characteristics.

The energy characteristics describe the burning rate and the products when briquettes are burnt. The calorific value of briquette is an important measure of the amount of energy released from every kilogram burnt. Briquettes are normally priced by weight, but

still, the calorific value is the most important factor in determining the competitiveness of the fuel (Eriksson, 2006).

2.4   Process of Briquetting.

Briquetting is one of several compaction technologies in the general category of densification. In densification, a material is compressed to form a product of higher bulk density, lower moisture content, and uniform size shape, and material properties. There are two ways that compaction can be accomplished, with or without a binder (Belonio *et al.*, 1991).

Ugwu and Agbo (2013), reported that briquettes were produced from empty fruit bunches using starch as binder in one experiment and asphalt as binder in the second experiment. The empty fruit bunches briquettes made with starch as binder had more desirable performance. They also concluded that briquettes produced can be used in domestic cooking, in ironing of clothes, and in industrial heating such as in bakery and in raising steam in boilers. There are many binders but the most common effective binder is starch. About 4-8 % of starch made into paste with hot water is adequate. First, the fines are dried and screened, undersized fines are rejected and oversized hammer milled. This powder is blended with the starch paste and fed to the briquetting press. The briquettes are dried in a continuous oven at about 80 °C. The starch sets through loss of water, binding the charcoal into a briquette which can be handled and burned like ordinary lump charcoal in domestic stoves and grates. Generally briquettes are not suitable for use as industrial charcoal in blast furnaces and foundry cupolas, since the bond disintegrates on

slight heating. When briquettes are bonded with tar or pitch and subsequently carbonized in charcoal furnaces to produce a metallurgical charcoal briquette, adequate crushing strength are needed to break them. It is possible to add combustion aids such as waxes, sodium nitrate and so on, during manufacture to give a more acceptable product (Lehtikanga, 2001). Also clay as a binder, silica, and so on, can be mixed with the fines to reduce the cost of the briquette. This of course, lowers the calorific value and is merely a form of adulteration for which the user pays, though claims may have been made that burning had improved. But well made briquettes are an acceptable, convenient product. The virtual absence of fines and dust and their uniformity are attractive for barbecue purposes. Generally they sell at around the same cost per kg as lump charcoal in high price markets and have more or less the same calorific value as commercial charcoal of 10-15 % moisture content (Taulbee *et al.*, 2009)

It has been established that a sticking agent which acts as a binder must be incorporated. In some cases, especially under high temperature and pressure, a material can act as its own binder. Wood for example, becomes plastic and can be briquetted without a binder under such conditions. Many of the processes considered here, however will require the addition of a binder (Teixera *et al.*, 2010).

In most cases, the process of briquetting will consist of a series of steps:

1. Collection of materials to be densified.

2. Preparation of material.

3. Compacting of material.

4. Removing, drying or cooling and storing.

2.4.1 Collection of Materials to be Densified.

A wide variety of materials can be densified. Some can be bundled, or tied together, rather than briquetted. A partial list includes the following; rice husk, jute, coal dust, alfalfa, nutshells, bagasse, dung, wood waste, straw, sawdust, sunflower husks, bark, leather waste and charcoal fines (Nasrin *et al.*, 2011).

Industrial or automotive waste oils are not desirable for briquette formulation, such oils contain additives that could give off toxic fumes when burnt. Before they can be used, proper laboratory test is required to remove additives (Emerhi, 2011).

In general, any material that will burn but is not in a convenient size, shape or form to be readily useable as a fuel is a good candidate for briquetting. It may be necessary or desirable to make briquettes of more than one material (Adegbulugbe, 1994).

2.4.2   Preparation of Raw Material.

Once the raw material is collected, it must be assembled in a central location for processing. The method of preparation depends somewhat on the particular material being briquetted, but the procedure generally included some or all of these steps: the raw material was chopped, crushed, broken, rolled, hammered, milled, ground and cut to reduce the size until it passed through a screen or reached suitable small and uniform size. The process consumed a great deal of energy, the size reduction steps were made as short as possible. The method of mixing the raw material with the binder to produce the feed stock varied widely. The method involved the use of simple trough and hoe to a modified commercial cement mixer. The correct proportion of raw material to binder was determined before production started. This was accomplished by continous trial and error method in which several briquettes with different mixtures of binder material were produced. The briquettes produced were tested for mechanical strength and burning properties (Prasertsan and Sajjakulnukit, 2003).

2.4.3 Compaction of Material.

The next step involved compaction that was done in many ways. In general, a supply of prepared feed stock was loaded into a chamber, the chamber was covered with a close-fitting top, and pressure applied to compress the feedstock. The pressure applied was in the range of 0.5 to 1200 kilograms per square centimeter (kg/cm^2) depending on the process employed. In some cases, the feedstock was heated to aid the binding (Grover and Mishra, 1996).

Another method of compaction, employed by some of the more sophisticated briquetting machines was to heat the feed stock and then extrude it. Extrusion involved the process whereby the feedstock was forced through a small opening at a high pressure. The result was a continuous log that was cut to any length. The advantage of extrusion was that briquettes of many shapes and sizes were produced (Mani, Tabil and Sokhansanj, 2006).

2.4.4   Drying and Storage.

The feed stock when removed from the briquetting press was wet, they are subsequently dried very well before storage. Drying was done in the sun, with a heater, or by use of heated air. The material could be dried before or after size reduction. The dried briquettes were then stored in moisture or water free environment so that the heating ability was not reduced (Belonio *et al*., 1990).

Figure 2.1 represents the flow chart for all the processes involved in the production of briquettes.
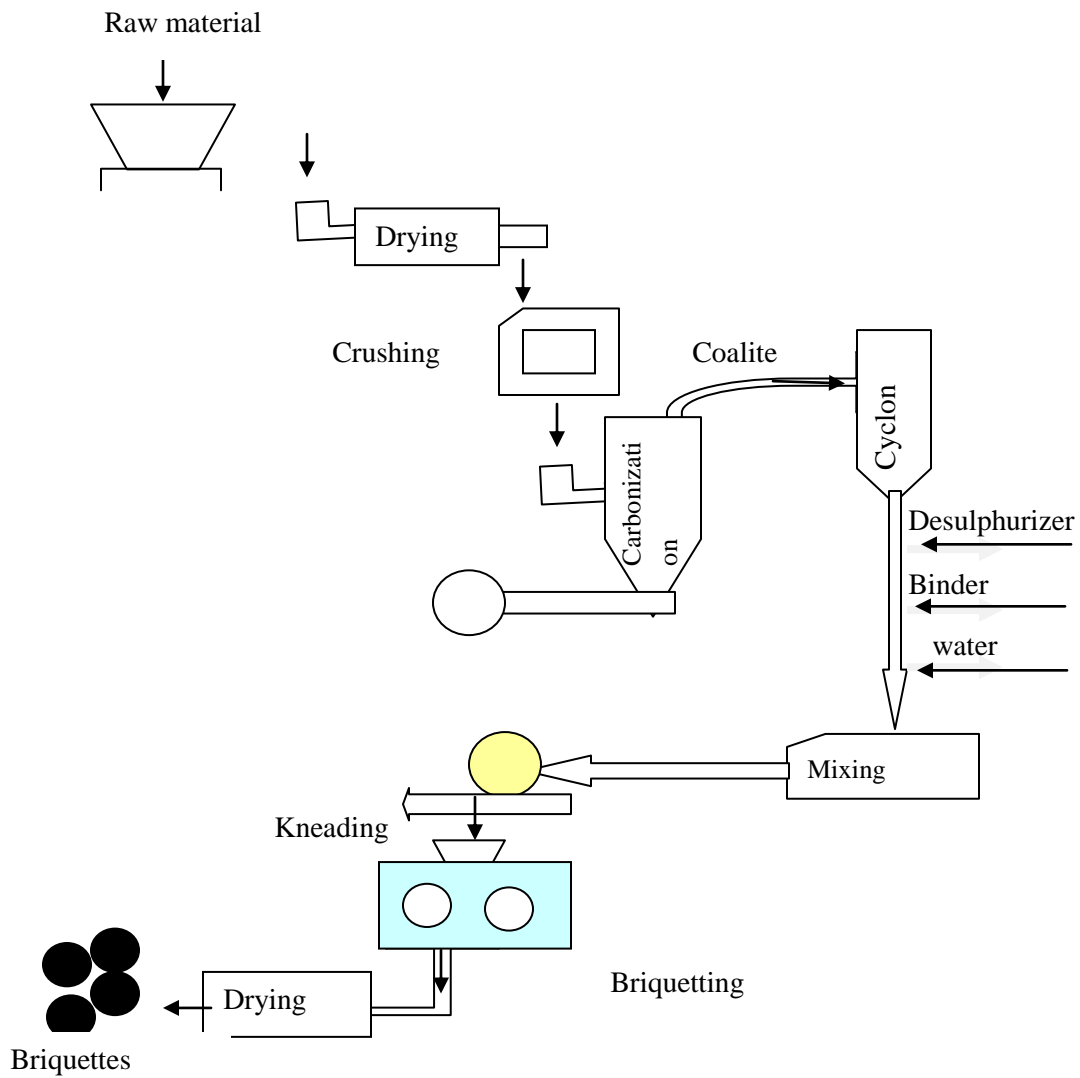
Fig.2.1: A typical flow process of briquette production (Hirsch, 1987).

2.5   Factors that Affect the Strength of Coal Briquettes

Mechanical strength of prepared coal briquettes affects its storage and transportation to the intended market. The studies show that the strength of coal briquettes depends on many factors such as moisture content, coal particle size and its distribution, time of compaction, compaction temperature and pressure, binder type and amount and grade of coal. Among these factors it can be shown from the experimental work that the compressive strength of briquettes is greatly affected by the amount of binder, curing temperature, size of coal, the type of coal and the ash content on burning. Parameters like moisture content, briquetting pressure and time for briquetting does not affect the briquetting strength significantly (Taulbee,2009).

i.   Size and Shape of Coal Briquettes

The size of the coal powder affects the mechanical properties of coal briquettes. Berkowitz (1953) and Gregory (1960) in their studies found that the coal particle size and its distribution affect the strength of coal briquettes. They showed that the strength of coal briquettes decreases with an increase in particle size (Habib *et al.*,2012). The durability of coal briquettes is enhanced when fine coal powder is used for making briquettes (Motaung, 2007). The size and shape of resulting coal briquettes also affect the product strength. The size and shape effect was studied by applying stress on cylindrical and pillow shaped briquettes. The results showed that the pillow shaped briquettes are stronger than the cylindrical shaped briquettes because there was a density difference with the cylindrical shaped briquettes with maximum density in the upper portion of the

briquettes. The size of briquettes and position of stress applied on pillow shaped briquettes does not affect its strength significantly. The experiments on cylindrical briquettes showed that the dimensions of briquettes and the position of the applied stress define the strength of coal briquettes (Rahman *et al*.,1989).

ii. Curing Temperature

The heat treatment and the temperature also affect the coal briquettes quality. Blesa *et al*., (2003) looked into the mechanical characteristics of heat cured coal briquettes made from molasses and suggested that curing brings a uniform morphology to the resulting structures. They also verified that low rank coal after pyrolysis can be used for producing high strength briquettes. The favorable temperature of pyrolysis was 600 °C in their work. The briquettes formed this way showed a higher calorific value and lower volatile matter upon combustion. The mechanical properties like strength and water resistance of fuel were also enhanced by heat treatment. The strength of heat cured briquettes can further be increased by the high temperature carbonization process. As the temperature of carbonization increases so does the strength but it makes the process uneconomical. So high temperature carbonization processes should only be followed when the strongest briquettes are required (Benk, 2010).

iii. Compaction Pressure

The briquette density is directly related to the pressure applied during the formation of coal briquettes (Habib *et al*.,2012). The maximum density can be obtained by applying pressure of up to 150 MPa. Miller recognized that abrasion resistance and density of coal

briquettes can be increased at pressure of 70 MPa, further increase in the pressure will slightly increase the density and abrasion resistance (Miller, 1979).

iv. Grade of Coal

The importance of the type of coal used for coal briquetting was assessed by the experimental work of Moghaddam *et al.,*(2011). Bituminous coal fines from three different fields were used in their work. The results showed that the type of coal affected the compressive strength and water resistance of coal briquettes produced. The quantity of mineral matter present in different amounts in the various types of coal was the cause of this behavior. Burchill *et al*., (1994) demonstrated that the difference in the surface and bulk compositions of the coal briquettes caused the deposition of large mineral content at some points and the formation of microscopic pores in the whole structure. Some other factors like refining, mining process and the physical properties of the coal also created minute spaces in the coal. The deposition of mineral matter and pores weakens the structure of briquettes and the resulting briquettes breaks under stress.

v. Moisture Content and the Time of Compaction

Berkowitz (1953) showed that coal briquettes can be formed easily by the addition of water up to a certain optimum value. Gregory (1960) revealed that optimum moisture content required for making high strength coal briquettes is between 50 to 100 percent of the actual moisture content found in the coal. Water helps to increase the strength of coal briquettes because water increases the adhesive forces of coal particles and decreases the free surface energy of coal particles. Rapid compaction can be done only if the optimum moisture content is provided (Habib *et al.*, 2012). On the other hand the amount of water

added during briquettes formation affects the drying time and the drying mechanism of the coal briquettes. So the cost of the product is increased because of the extra effort required for the drying process. Gunnink and Li (2000) suggested that the required briquettes strength can be achieved if the time of compaction is increased instead of increasing the moisture content. The time required for briquetting is an important parameter for coal briquettes strength (Habib *et al.*, 2012). Miller *et al.*,(1979) observed that increasing duration of compaction significantly increases the strength of coal briquettes.

2.5.1 The Factors that Influence Briquette Quality

Briquettes quality influences the burning of briquettes significantly. The quality of the briquettes is directly affected by physical parameters in briquetting process, these include pressing temperatures, compacting pressure, and moisture content.

i. Pressing Temperature

According to Kuti (2007), the pressing temperature influences briquette quality and strength significantly. Pressing temperature will impact on the softening and excretion of lignin which will function as natural binders to join the fibers of the feed stocks to form solid high density briquettes. The optimal pressing temperature is at the curve peak where maximum strength is achieved by briquettes. When the temperature is low, the briquettes are unstable and have less strength and are likely to crumble during burning. These briquettes subsequently have shorter burning time and eventually produce less heat.

When the temperature is higher, the volatile compounds may be burned out and cause burning during pressing.

ii. Compacting Pressure

Briquettes strength is increased with the increasing compacting pressure within the compacting limit of the feed stock. When the pressure is increased, the atmospheric humidity in the feed stock is decreased and briquettes durability is increased (Rabier *et al.*,2006).

iii. Moisture Content

Akowuah *et al.*,(2012) stated that the moisture content of a briquette is mainly affected by the feed stock species and their properties. The optimal moisture content is around 10 – 18 %. When the moisture content is lower than 10 % or higher than 18 %, particles of feed stock are not consistent and the briquettes tends to disintegrate or fall into pieces after a short period of time.

2.5.2   External Factors that Influence the Burning of Briquettes

Besides the factors that influence the quality of briquettes, there are other factors that affect the burning of briquettes. They are air flow, ash removal and the positioning of the briquettes in the stove.

i. Airflow

According to Ajueyitsi and Adegoke (2003), airflow is one of the most important factors to be considered for the burning of briquettes. Good airflow means that there is plenteous supply of oxygen which is necessary for burning to take place. Adequate supply of air guarantees burning of the briquettes at a high combustion rate. This means that optimal combustion is possible and incomplete combustion with resultant smoky fire is prevented.

ii. Ash Removal

The ash produced during burning of briquettes may cause problems. This is because the ash may block the air holes and eventually lower the oxygen supply to the combustion chamber. That is why ash content remains one of the criteria for deciding the quality of briquettes. It is therefore important to choose high quality briquettes with low ash content. Therefore research should be conducted on the ash content of the biomass or raw material before briquettes are produced. Even when high quality briquettes are used in the stoves, it is necessary to remove the ashes from time to time to ensure that the air holes are free to ensure efficient supply of oxygen that is needed for combustion (Weither *et al.*,2000).

iii. Briquettes Positioning

The positioning of briquettes may influence the air flow and eventually influence the burning characteristics. Generally, the main purpose of positioning briquettes is to put them in a position that they will enjoy good air flow. When positioning the briquettes, it is better to intentionally leave a path for the air flow which makes the oxygen available for the briquettes during combustion. It is therefore necessary to put the briquettes in an upright position, this makes air to easily pass through the inner hole, enlarges the contact surface of the air and briquettes, and improves the burning efficiency (Bruce *et al.*,2000)

2.6 Biomass

Biomass is a renewable energy source not only because the energy in it comes from the sun, but also because biomass can re-grow over a relatively short period of time compared with the hundreds of millions of years that it took for fossil fuels to form. Through the process of photosynthesis, chlorophyll in plants capture the sun's energy by converting carbon dioxide from the air and water from the ground into carbohydrates (complex compounds composed of carbon, hydrogen, and oxygen). When these carbohydrates are burnt, they produce carbon(IV) oxide and water and release the energy they captured from the sun (Huber *et al.*, 2006). Biomass is organic matter derived from living, or recently living organisms. Biomass can be used as a source of energy and it most often refers to plants or plant-based materials which are not used for food or feed, and are specifically called lignocellulosic biomass (Liu, *et al.,* 2011). As an energy

source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel. Conversion of biomass to biofuel can be achieved by different methods which are broadly classified into: thermal, chemical, and biochemical methods. Historically, humans have harnessed biomass-derived energy since the time when people began burning wood to make fire (Baxter, 2005). Even today, biomass is the only source of fuel for domestic use in many developing countries.

Biomass is all biologically-produced matter based on carbon, hydrogen and oxygen. The estimated biomass production in the world is about 105 billion metric tons of carbon per year, about half in the ocean and half on land (Randor, 2010). Wood remains the largest biomass energy source today, examples include forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even municipal solid waste. Wood energy is derived by using lignocellulosic biomass (second-generation biofuels) as fuel. Harvested wood may be used directly as a fuel or collected from wood waste streams. The largest source of energy from wood is pulping liquor or "black liquor," a waste product from processes of the pulp, paper and paperboard industry (Naik, 2010). In the second sense, biomass includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuels (Martin, 2010). Industrial biomass can be grown from numerous types of plants, including miscanthus, switchgrass, hemp, corn, rice, willow, sorghum, sugarcane, bamboo, and a variety of tree species, ranging from eucalyptus to oil palm trees (Field, 1998).

Based on the source of biomass, biofuels are classified broadly into two major categories. First-generation biofuels are derived from sources such as sugarcane and corn starch. Sugars present in this biomass are fermented to produce bioethanol, an alcohol fuel which can be used directly in a fuel cell to produce electricity or serve as an additive to gasoline. However, utilizing food-based resources for fuel production only aggravates the food shortage problem (Munnings *et al.,*2014). Second-generation biofuels, on the other hand, utilize non-food-based biomass sources such as agriculture and municipal waste. These biofuels mostly consist of lignocellulosic biomass, which is not edible and is a low-value waste for many industries (Huber *et al.,* 2006). Despite being the favored alternative, economical production of second-generation biofuel is not yet achieved due to technological issues. These issues arise mainly due to chemical inertness and structural rigidity of lignocellulosic biomass (Kunkes *et al.*,2008)

Plant energy is produced by crops specifically grown for use as fuel that offer high biomass output per hectare with low input energy. Some examples of these plants are wheat, which typically yields 7.5–8 tonnes of grain per hectare, and straw, which typically yields 3.5–5 tonnes per hectare in the UK. The grain can be used for liquid transportation fuels while the straw can be burned to produce heat or electricity (Munnings *et al.*,2014). Plant biomass can also be degraded from cellulose to glucose through a series of chemical treatments, and the resulting sugar can then be used as a first-generation biofuel.

The main contributors of waste energy are municipal solid waste, manufacturing waste, and landfill gas. Energy derived from biomass is projected to be the largest non-hydroelectric renewable resource of electricity in the US between 2000 and 2020 (Huber *et al.*, 2006)

Biomass can be converted to other usable forms of energy like methane gas or transportation fuels like ethanol and biodiesel. Rotting garbage, and agricultural and human waste, all release methane gas, also called landfill gas or biogas. Crops such as corn and sugarcane can be fermented to produce the transportation fuel ethanol. Biodiesel, another transportation fuel, can be produced from leftover food products like vegetable oils and animal fats. Also, biomass-to-liquids (called "BTLs") and cellulosic ethanol are still under research (Mafakheri and Nasiri, 2014).

2.7 Rice Husk

Many of the developing countries produce huge quantities of agro residues but they are used inefficiently causing extensive pollution to the environment. Rice husks are residues of rice harvesting and processing operations for which rather minimum utilization outlets have been found in Nigeria despite its vast potentials. Rice husk is the outermost layer of the paddy grain that is also called rice hull. It is separated from the brown rice in rice milling (Bhattacharya and Shrestha, 1998). Burning rice husk produces rice husk ashes, if the burning process is incomplete carbonized rice husk is produced. Around 20 % of the paddy weight is husk. In 2004 the world paddy production was 661

million tonnes and consequently 132 million tonnes of rice husk were also produced. While there are some uses of rice husk, it is still often considered a waste product in the rice mill and therefore often is either burned or dumped on waste lands. Husk has a high calorific value and therefore can be used as a renewable fuel. Rice husk is produced in the first step in the milling process when the husk is removed from the grain in the husking stage of the rice mill (Beloilo, 2005). It is not uncommon to find man-made mountains of rice husk in drainage channels and market places in rice producing areas such as Abakaliki, Ezillo, Ogbaru, Ugboka and Adani. The tasks of clearing the refuse heaps created often appear problematic. Apart from the problems of transportation, storage, and handling, the direct burning of loose biomass in conventional grates is associated with very low thermal efficiency and widespread air pollution. The conversion efficiencies are as low as 40 % with particulate emissions in the flue gases in excess of 3000 mg/Nm^3. In addition, a large percentage of un-burnt carbonaceous ash has to be disposed off (Ogbuagu, 1993).

In these areas, the rice husks are used mainly as fuel products in its natural state. However, rather than being used as the main fuel material, they are used as a fire-sustaining agent with wood fuel, being the major fuel. This mode of utilization limits the quantities of rice husk being put into economic use. Another use of rice husk is in serving as filler in rigid polyurethane foam. Rice husk ashes are used also in the generation of silica and silicate products. This shows that rice husk ash contains a commercializable quantity of silica that can be used for the manufacture of silicates which can be used for

various industrial purposes. Tables 2.1 and 2.2 show the composition of rice husk and rice husk ash respectively, (Mehta, 1994).

Table 2.1: Composition of Rice Husk on Dry Basis

Element	Mass Fraction (%)
Carbon	41.44
Hydrogen	4.94
Oxygen	37.32
Nitrogen	0.57
Silicon	0.57
Potassium	0.59
Sodium	0.035
Sulphur	0.3
Phosphorus	0.07
Calcium	0.06
Iron	0.006

Table 2.2: Composition of Rice Husk Ash on Dry Basis

Compounds	Mass Fraction (%)
Silica (SiO_2)	80-90
Alumina (Al_2O_3)	1-2.5
Ferric Oxide (Fe_2O_3)	0.5
Calcium Oxide (CaO)	1-2
Magnesium Oxide (MgO)	0.5-2.0
Sodium Oxide (Na_2O)	0.2-0.5
Potash (K_2O)	0.2
Loss on ignition	10-20

From Table 2.2 it is clear that silica is the major constituent of rice husk ash. Rice husk is difficult to ignite and it does not burn easily with open flame unless air is blown through the husk. It is highly resistant to moisture penetration and fungal decomposition. Husk therefore makes a good insulation material. Rice husk has high silica (SiO_2) content which means that it decays slowly when dumped in the open field. It makes it a poor animal fodder (Permchart and Tanatvanit, 2009). Handling of rice husk is difficult because it is bulky and dusty. It has angle of repose that is about 40-45 ^{o} which means that its flow ability, example in feed hoppers is very poor. Rice husk has a low bulk density of only 70-110 kg/m^3, 145 kg/m^3 when vibrated or 180 kg/m^3 in form of briquettes or pellets (Jekayinfa, and Omisakin, 2005).

It thus requires large volumes for storage and transport, which makes transport over long distances un-economical. When burned, the ash content is 17-26 % a lot higher than fuels (wood 0.2-2 %, coal 12.2 %). This means that when used for energy generation large amount of ash needs to be handled (Olutayo, 1989). Rice husk has a high average calorific value of 3410 kcal/kg and therefore is a good, renewable energy source. One concern in rice husk firing is the behaviour of the ash that is its slagging and fouling tendency caused by a low melting point of the rice husk ash. Rice husk is produced centrally at rice mills and has low moisture content since the paddy is dried to 14 % or less before milling. The disadvantage is that rice husk has very low density (Weither *et al.,* 2000).

Some typical applications of rice husk include incorporation into the soil as a bio-fertilizer additive. It is used in animal husbandry as low quality and litter material. It is incorporated into building material because of the good thermal insulation property. It is also used for heat generation in cook stoves, furnances for heating the air in rice dryers, brick kilns and at large scale for generation of Syngas for electricity generation (Oliver, 2005).

Major ways of expanding the potential usage of rice husk is first by carbonizing and briquetting, then utilizing it as the major fuel product which will reduce its current nuisance and improve the standard of living of the populace. Converting rice husk into various energy forms can help minimize the problem on fuel cost as well as on rice husk disposal. Moreover, this would minimize excessive cutting of trees for fuel. Efficient operation of thermo-chemical conversion systems requires a thorough understanding of the influence on the composition and thermal properties of rice husks on their behaviour during the conversion process (Permchart and Kouprianov, 2002).

2.8   Corn Cobs

Corn is a significant crop all around the world. The annual production worldwide is about 520109 kg. The major production regions are North America (42 %), Asia (26 %), Europe (12 %) and South America (9 %) (Kim and Dale, 2004). According to FAO (2004) worldwide production of corn in 2002 was 604106 tonnes cultivated in 1383106 m^2, of which 134 m^2 were cultivated in Europe. Most corn though (about 64 % of global production) is used for animal food. For human needs the percentage is 19 %, while only

5 % of global production is lost as waste. Wasted corn can be utilized as feedstock for bio-ethanol production (Kim and Dale, 2004).

The past 15 years, maize is used as raw material for bio-ethanol production, which has tripled up to 28106 tonnes in 2003. Corn residues may contain valuable materials and the current economic values are less than the apparent cost of collection, transportation and processing for beneficial use (Tsai *et al.*, 2001).

Recently, this agricultural waste is being studied as a raw material for energy and active carbon preparation. Cao *et al.* (2004) studied the behaviour of corn cob pyrolysis, where Sun *et al.* (2002) studied the pyrolysis of corn stalk, both in a tube-type reactor. Putun *et al.* (2005) also studied pyrolysis in a fixed-bed reactor focusing on the liquid and solid products. Lanzetta and Di Blasi (1998) also studied the pyrolysis of corn straw focusing on the kinetics of the reactions. Rapid pyrolysis in a free-fall reactor was performed by Zanzi *et al.*(2002), Encinar *et al.*(1997) and Wei *et al.*(2006), using different kinds of biomass. In their studies it was observed that hydrogen content was favored by a higher temperature and cellulose and hemi-cellulose content. The research of Tsai *et al.* (2005) and Lee *et al.* (2007) was concerned about fast pyrolysis conditions, where Lee *et al.* (2007) focused on the prediction of gaseous products from biomass pyrolysis.

Cobs represent about 8 to 9 % of the above ground dry matter (grain plus residues) at grain physiological maturity (Pordesimo *et al.*, 2005). The yield of corn cobs may range from 1.42 - 1.53 dry tonnes/hectare. Currently, after combining the grain, corn residues

are collected as baled corn stover, which includes cobs, husks, leaves and stalks. About 15 to 20 % of above ground corn residues (non-grain) are corn cobs (Sokhansanj *et al.*, 2002). Corn cob moisture content may range from 20 to 55 % depending on the grain moisture content at the time of harvest. With the existing corn stover collection process, most of the corn cobs are left on the field. The higher heating value (HHV) of corn cobs ranges from 18.3 to 18.8 kJ/kg of dry matter (Morey and Thimsen, 1980). The proximate analysis of corn cobs gave 80.10 % volatiles, 1.36 % ash, and 18.54 % fixed carbon on a dry mass basis. Jau-Jang and Wei-Hsim, (2014) reported that the ultimate analysis of corn cobs resulted in 46.58 % carbon, 5.87 % hydrogen, 45.46 % oxygen, 0.47 % nitrogen, 0.01 % sulfur, 0.21 % chlorine, and 1.40 % ash on a dry mass basis. Thus, corn cobs are suitable for heating applications especially due to their low ash contents compared to other agricultural residues (Ebeling and Jenkins, 1985).

The need for densification of corn cobs into briquettes/pellets could be justified based on the end use. Corn cobs can be used for producing heat, power, gas/liquid fuels, and a wide variety of chemical products such as furfural, xylitol and activated carbon (Jiang and Morey, 1992). A greater yield of glucose (i.e., ethanol) was found from corn cobs than other corn residues such as stalks or leaves plus husks (Crofcheck and Montross, 2004). Cobs are already used for burning, they are just burnt straight in the fire, making a very smoky, dirty fire. Cobs are also used as small additives of fertilizer for the fields, but there is not much emphasis on this usage. The corn cobs must be free of kernels and husks, and well dried. This type of cob is easy to find because a lot of corn is dried on the cob and stripped off for making corn flour, so the cobs are left over. Corn

cobs are one of the potential agricultural biomass feed stocks for renewable energy industries in the United States to abate the current energy and the greenhouse gas problems (Christiansen, 2009).

Corn cobs are a part of the corn stover. Corn stover includes a mixture of individual pieces of cobs, husks, stalks and leaves having different shapes and sizes. Baling of corn stover can gather these individual pieces into a large cylindrical compact with density of up to 150 kg/cm^3. Chopping or grinding of corn stover could result in a relatively uniform product; however, chopping/grinding may not increase the bulk density significantly higher than the baled density. Corn cobs exist as individual pieces with similar shapes and sizes. The bulk density of whole corn cobs would range from 160 to 210 kg/ cm^3, which is higher than the density of corn stover bales, 150 kg/cm^3 (Shinners *et al*., 2003).

Either in baled form or chopped/ground form, corn stover may be difficult to handle, transport, store and use, whereas the whole corn cobs could be handled, transported, stored and used relatively easily compared to the baled or chopped/ground corn stover. It appears that briquetting or pelleting of corn stover or corn cobs can produce uniform products with bulk density of 500-600 kg/cm^3. Therefore, changing the physical form of corn stover into briquettes/pellets is essential to improve its transportation, handling, storage, and use. But, corn cobs can be used without briquetting/pelleting for majority of applications such as industrial scale heating. For applications requiring high quality feedstock such as home heating, corn cobs may need to be pelleted. Furthermore, although corn cobs are almost cylindrical in shape, a mixture of whole and broken pieces of cobs may result due to breakage of cobs during combining.

Therefore, corn cobs may lack free-flowing properties. Therefore, the densification of corn cobs into briquettes/pellets resulted in consistent, high density products with uniform shapes and sizes, that were efficiently handled, transported, stored, and used (Kaliyan *et al.*, 2009).

2.9   Coal

Coal is one of the oldest fuels known to man. It was formed from the dead remains of plants that were buried and subjected to pressure and heat over a long period of time. Plant materials have a high content of cellulose, a complex molecule whose empirical formula is $(CH_2O)_n$ with n up to 500,000. After the death and burial of trees and plants materials, chemical changes gradually lower the oxygen and hydrogen content of cellulose molecules (Zumdahl, 2002).

Coal is a readily combustible black or brownish-black sedimentary rock normally occurring in rock strata in layers or veins called coal beds or coal seams. The harder forms, such as anthracite coal, can be regarded as metamorphic rock because of later exposure to elevated temperature and pressure. Coal is composed primarily of carbon along with variable quantities of other elements, chiefly sulphur, hydrogen, oxygen and nitrogen (Mitchell, 1997). Coal begins as layers of plant matter accumulate at the bottom of a body of water. For the process to continue the plant matter must be protected from biodegradation and oxidization, usually by mud or acidic water. The wide shallow seas of the carboniferous period provided such conditions. This trapped atmospheric carbon in the ground in immense peat bogs that eventually were covered over and deeply buried by

sediments under which they metamorphosed into coal. Over time, the chemical and physical properties of the plant remains (believed to mainly have been fern-like species antedating more modern plant and tree species) were changed by geological action to create a solid material (Smith,1997).

Coal a fossil fuel, is the largest source of energy for the generation of electricity worldwide, as well as one of the largest worldwide anthropogenic sources of carbon dioxide emissions. Gross carbon dioxide emissions from coal usage are slightly more than those from petroleum and about double the amount from natural gas. Coal is extracted from the ground by mining, either underground by shaft mining through the seams or in open pits (Mancuso and Seavoy, 1981).

The geochemical process that transforms plant material into coal is called coalification. Coalification can be described as consisting of three processes: the microbiological degradation of cellulose of the initial plant material, the conversion of the lignin of plant material into humus substances and the condensation of these humus substances into larger coal molecules. The physical force exerted upon the deposit play the largest role in the coalification process (Cantril, 1984).

As the process of coal "maturity" proceeds, the carbon content gradually increases. Coal constitutes about 90 % of the world's fossil fuel reserves and has been used as fuel both in homes and industries for many centuries. Currently, it is furnishing about 40% of the U.S.A's energy needs. As the supply of petroleum dwindles, the share of the energy

supply from coal could increase to as high as 50 % by the next decade. World coal consumption was about 6.7 billion tonnes in 2006 and is expected to increase to about 9.98 billion tonnes by 2030, with about 40 % of the world's electricity coming from coal (Huffman *et al*., 1994).

The quality and type of coal varies from high quality anthracite (high % carbon, few volatile impurities and burns with clean flame) to bituminous (high % volatile impurities and burns with smoky flame) to lignite (softer than bituminous coal, contains vegetable matter not fully converted to carbon and burns with very smoky flame). Coal is burned in coal-fired plants to produce energy in the form of electricity. Domestically, coal is burnt in un-vented stoves producing heat energy for cooking and heating up homes. Over the years, it has been recognized that certain impurities in coal can have a significant impact on the types of emissions produced during coal combustion. However, various processes employed in converting coal into more useful forms emit considerable amounts of pollutants such as SO_2, NO_X and CH_4. Notwithstanding, even if coal were pure carbon, the CO_2 produced during its combustion still has significant effects on the environment. These effluent gases interact with other atmospheric gases as well as with each other. There is the possibility that the global average air temperature may be increasing due to these chemical changes which in turn may cause a greater variability in precipitation. Soil and plants absorb a portion of these gases and the remainder can cause a variety of harmful effects to normal ecosystems and agriculture as well as, in some cases, to human health (EPA, 1997). The absorption of inorganic air pollutants by soils is primarily by

chemical and physical means. Absorption of SO_2 by soil increases the acidity of the soil surface layers. Elevated levels of CO_2 increase plant's photosynthetic rates, leaf area, biomass and yield. On the other hand it reduces the transpiration rate per unit leaf area. Plants absorb significant amounts of NOx gases and they contaminate air and remove all the nitrogenous components (Rahman *et al*., 2000)

Bio-coal briquette is a type of solid fuel prepared by compacting pulverized coal, biomass, binder and a sulphur fixation agent. The high pressure involved in the process ensures that the coal and the biomass particles are sandwiched and adhere together, as a result do not separate during transportation, storage and combustion (Onuegbu *et al.*,2010). The co-combustion of the coal and the biomass gives a better combustion performance and reduces pollutant emission. Bio-coal briquette has a favourable ignition, better thermal efficiency, emits less dust and soot. The mechanism behind this is that, since the biomass component of the briquette ignites at low temperature when compared to the coal, this ensures that the volatile matter in the coal which would have otherwise be liberated as smoke at low combustion temperature combusts completely. The complete combustion of the volatiles reduces smoke and as well, contributes to the total heat released by the fuel. This technique has advantages over coal briquette in the sense that any grade of coal can be used without carbonization. Additional cost of carbonization of low grade coal before briquetting is saved. Furthermore, the presence of sulphur fixation agent otherwise known as desulfurizing agent ensures that most of the sulphur content of

the coal is converted to ash instead of being liberated into the atmosphere as SO_2 (Somchai *et al.,* 1988).

The combustion of all types of coal produces CO_2 emissions and other hazardous gases like SO_2. The use of high grade coal such as anthracite coal for briquette makes an environmentally friendly fuel. The anthracite coal is a naturally occurring clean fuel but the cost and limited reserves of anthracite coal restricts its use for the briquette formation. Environmentally safe briquettes can be produced by applying various techniques during manufacturing. De-volatilization is the most common technique applied for producing low smoke briquettes. De-volatilization can be done by a heat treatment process involving the inclusion of chemicals like calcium hydroxides. Heat treatment and additives decrease the emissions of harmful gases by fixing the sulfur and nitrogen content in the coal (Blesa *et al.,* 2003).

Ryu *et al.,*(2008) proposed a novel technique used for the reduction of pollutants in the air via the utilization of biomass in combination with coal to make bio-coal briquettes. Biomasses are naturally occurring organic materials that help to complete the combustion of the coal with liberation of less poisonous gases. Large amounts of fine coal powder are made from coal cleaning and other coal processing. These fine coal powders can be combined with agricultural waste like exhausted mushrooms for making environmentally safe briquettes.

According to Kwong *et al.,*(2007) they implied by a new technology, that pollution problems associated with burning of coal was to a great extent taken care of by de-

sulphization. Calcium hydroxide $Ca(OH)_2$ and calcium oxide (CaO) are common desulfurizing agents used for this purpose. For instance when CaO is used it follows this equation.

$$CaO_{(s)} + SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CaSO_{4(s)}. \dots\dots\dots\dots(2.1)$$
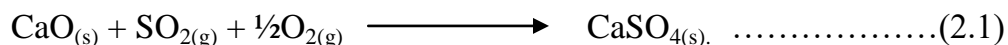
The ash of bio-coal has been shown to be effective for soil treatment and enrichment. However, preserving the forest resources by substituting wood fuel with bio-coal, along with the use of the ash from this briquette for soil treatment will compensate for fossil carbon emitted by the coal component of the briquette. Therefore bio-coal is considered to be a clean technology.

2.10   Coal in Nigeria

In other parts of the world, coal is the oldest commercial fuel, dating in Nigeria from 1916 when 24,000 tonnes were produced. Production peaked at near one million tonnes in 1959, before declining to the present insignificant level. This is due to the reduction in the demand for coal arising from death of rail transportation, and switching from coal to gas for thermal power generation. Coal production is from the cretaceous Anambra basin which extends to Dekina in the northern part of the basin in Benue State and to Okigwe in the south.

From north to south, the reserves from seams over one meter thick, are in million tonnes; Ogboyoga (100), Okaba (70), Orukpa (60), Ezimo (50), and Enugu (50). Coal seams also occur at Gombe in Gombe State. Mine production capacities after full

rehabilitation and privatization could attain the following levels: Onyeama and Okpara (150,000-400,000 tonnes/year), Owukpa (2,500 tonnes/year) and Okaba (15,000-300,000 tonnes/year). Nigerian sub-bituminous coal has a high calorific value (5,000-6,000 cal/g or 5500-6500 air dried), low ash and low sulphur contents, with good storage characteristics.

In the Lafia-Obi area of Nassarawa State, good quality cooking coal has been discovered which is suitable for use in the iron and steel industry. If utilized, the Lafia-Obi coal would save the country the high cost of importing cooking coal. Since the Nigerian Coal Corporation has lost nearly all its traditional customers, notably railways and power authority, while the drive to market its coal overseas offered some hope of recovery (Afonja, 1979).

2.11 Chemistry of Coal.

Coal can simply be defined as a sedimentary rock that burns. It is a complex organic substance formed from the decomposition of plant matter over years of exposure to high temperature and pressure. Coal constitutes mainly of carbon, hydrogen and oxygen, to a lesser amounts nitrogen and sulphur. Metals such as Al, Hg, Se, As, Mg and Na have been reported in coal samples. Also, trace quantities of uranium and thorium have been detected. The quantity of uranium in coal samples ranges from less than 1ppm in some samples to about 10 ppm in others. Generally, the average amount of thorium in coal is usually 2.5 times greater than that of uranium. The elemental analysis of coal samples

gives empirical formulae like $C_{135}H_{97}O_9NS$ for bituminous coal and $C_{240}H_{90}O_4NS$ for high grade anthracite (Chang, 2002).

As a result of coal combustion, coal injects mainly CO_2, NO_x, SO_2, CO, and to a lesser amount, fluorine, mercury and arsenic into the environment. These effluents interact with each other as well as with other atmospheric gases resulting in atmospheric oxygen depletion. The chemical structure in Fig. 2.2 shows a long chain of elemental linkage in the compound.
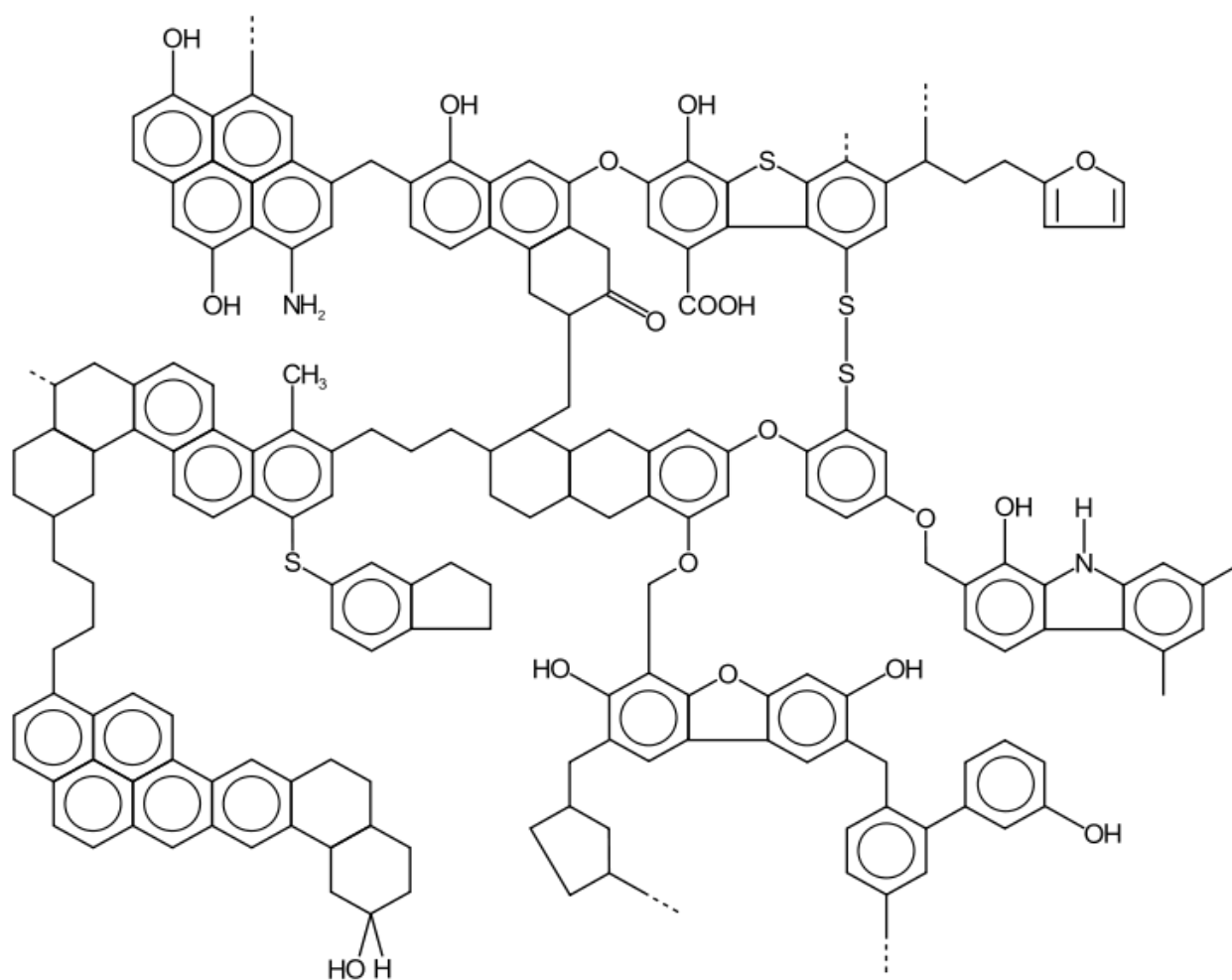
Fig. 2.2: Chemical structure of coal (Tyler *et al.*, 1985).

The environmental and health effects of these effluents from coal combustion are discussed briefly.

2.11.1   Carbon(II) Oxide

Carbon (II) oxide is produced from the partial combustion of coal (i.e. combustion in limited amount of oxygen). It is a poisonous, colourless, odourless and tasteless gas that binds to haemoglobin about 320 times faster and more tightly than oxygen. Such a great affinity implies a very easy displacement of oxygen from O-Fe bond in the blood to form carboxy-haemoglobin (Goldstein, 2008). The severity of CO effects however, depends on the duration of exposure because it takes some time for the inhaled CO to equilibrate with the circulating blood. At concentrations above 750 ppm of air, loss of consciousness and death occur quickly (Struttman, 1998).

2.11.2   Sulphur (IV) Oxide

Sulphur(IV) oxide is a colourless, water-soluble gas that is reactive and has a choky smell. It is detectable to the human nose at concentrations of around 0.5-0.8 ppm. SO_2 is a lung irritant known to be harmful to people suffering from respiratory diseases. Suspended SO_2 in the atmosphere is easily oxidized to tetraoxosulphate(VI) acid aerosol according to the reaction equations,

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)} \quad \text{……………………….(2.2)}$$

$$SO_{3(g)} + H_2O_{(g)} \longrightarrow H_2SO_{4(g)} \quad \text{……………………..(2.3)}$$
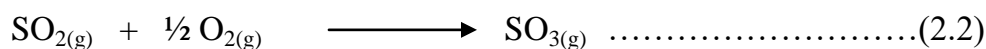
The aerosol irritates the fine vessels of the pulmonary region causing it to swell and block the respiratory passage. It easily and gradually dissolves everything made of cement according to the reaction equation:

$$CaCO_3 \quad + \quad 2H^+ \longrightarrow \quad Ca^{2+} \quad + \quad CO_2 \quad + \quad H_2O \quad ………………..(2.4)$$
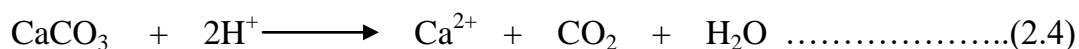
The presence of SO_2 in the atmosphere has also been linked to the formation of acid rain due to its solubility in water thereby forming tetraoxosulphate (VI) acid as described above. Environmental effects of sulphur compounds include impaired visibility, damage to materials and deposition as acid rain. Fine particles in the atmosphere reduce the visual range by scattering and absorbing light. Aerosols of sulphuric acid and other sulfates comprise from 5 to 20 % of the total suspended particulate matter in urban air, thus contributing to the reduction in visibility (Wark *et al.*, 1998).

2.11.3   Nitrogen Oxides (NOx)

Nitrogen oxides are volatile organic compounds (VOCs), but are not direct air pollutants in that they rarely affect life directly. They are however, the main ingredients in the formation of photochemical smog. In particular, NO_2 takes part in photochemical reactions that produce the most unpleasant of all the chemicals present in photochemical smog called peroxyacetyl nitrate, $CH_3CO_3NO_2$, with the structure as represented in Figure 2.3.
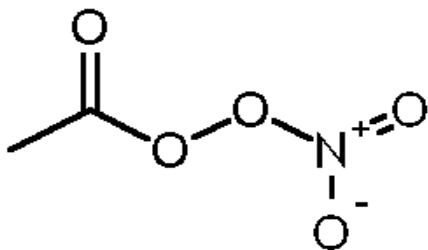
Fig. 2.3: Structure of Peroxyacetyl nitrate.

It is toxic by inhalation, detectable by smell at low concentrations. Symptoms of poisoning (lung edema) tend to appear several hours after inhalation of a low but potentially fatal dose. Long-term exposure to NO_2 at concentrations above 40-100 $\mu g/m^3$ causes adverse health effects. It facilitates the formation of ozone at ground level which goes ahead to produce other pollutants.

$$NO_2 \xrightarrow{\text{h}\nu} NO_{(g)} + O_{(g)} \quad \text{...........................(2.5)}$$

$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)} \quad \text{................................... (2.6)}$$
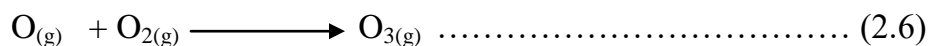
Nitrogen oxides are also involved in the precipitation of acid rain through the precipitation of nitric acid. Seven oxides of nitrogen are present in ambient air. These include nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), NO_3, N_2O_3, N_2O_4, and N_2O_5. Nitric oxide and nitrogen dioxide are collectively referred to as NOx due to their interconvertibility in photochemical smog reactions. The term NOy is often used to represent the sum of the reactive oxides of nitrogen and all other compounds that are atmospheric products of NOx. NOy includes compounds such as nitric acid (HNO_3), nitrous acid (HNO_2), nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5), and peroxyacetyl

nitrate (PAN). It excludes N_2O and ammonia (NH_3) because they are not normally the products of NOx reactions (Wark *et al*., 1998).

Both NOx and NOy (*i.e.*, HNO_3) have been shown to accelerate damage to materials in the ambient air. NOx affects dyes and fabrics, resulting in fading, discoloration of archival and artistic materials and textile fibres, and loss of textile fabric strength. NO_2 absorbs visible light and at a concentration of 0.25 ppm will cause appreciable reduction in visibility. NO_2 affects vegetation, as studies have shown suppressed growth of pinto beans and tomatoes and reduced yields of oranges. In the presence of sunlight, nitrogen oxides react with unburned hydrocarbons—volatile organic compounds (VOCs) that are emitted primarily from motor vehicles but also from chemical plants, refineries, factories, consumer and commercial products, and other industrial sources to form photochemical smog. Nitrogen oxides also contribute to the formation of acid rain. NO and NO_2 in the ambient air can react with moisture to form NO^{3-} and H^+ in the aqueous phase (*i.e.*, nitric acid), which can cause considerable corrosion of metal surfaces (Wark *et al.*, 1998).

2.11.4   Carbon(IV) oxide

Carbon(IV) oxide is the major by-product of coal combustion. It absorbs infrared radiation in the region 15 μm of the electromagnetic spectrum and as a result, its presence in the atmosphere decreases the loss of heat from the earth surface by radiation. Consequently, most of the radiant energy from the sun is retained and this leads to warming of the atmosphere popularly referred to as global warming. As at October 2010,

carbon(IV) oxide in the Earth's atmosphere was at a concentration of 388 ppm by volume.

Again, CO_2 is also involved in the precipitation of acid rain through the formation of carbonic acid. It is responsible for the rusting of iron according to the equations below:

$$CO_2 + H_2O \longrightarrow H_2CO_3 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.7)$$

$$Fe + H_2CO_3 \longrightarrow FeCO_3 + H_2 \dots\dots\dots\dots\dots\dots\dots(2.8)$$

$$2H_2 + O_2 \longrightarrow 2H_2O \dots\dots\dots\dots\dots\dots\dots\dots\dots(2.9)$$

$$4FeCO_3 + 10H_2O + O_2 \longrightarrow 4Fe(OH)_3 + 4H_2CO_3 \dots\dots\dots(2.10)$$
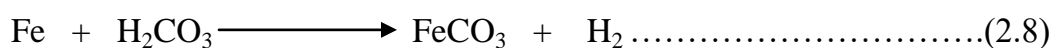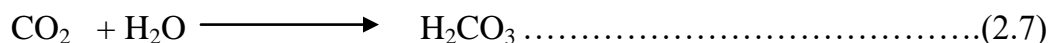
The carbonic acid is regenerated which ensures that the corrosion reaction continues (Thoning *et al.*,1989).

2.11.5 Fluorine

Fluorine volatilizes during the combustion of coal. Exposure to fluorine results in a disease condition called fluorosis, symptoms of which include mottling of the tooth enamel (dental fluorosis) and various forms of skeletal fluorosis including limited movement of the joints (osteosclerosis) and outward manifestations such as knock knees, bow legs and spinal curvature.

Fluorine is the main ingredient in the formation of a newly discovered greenhouse gas, trifluoromethyl sulphur pentafluoride (SF_5CF_3), known to be the most powerful

absorber of infrared radiation. This gas is known to absorb infrared radiation about 18,000 times as much as CO_2 (Connett, 2011).

2.11.6   Particulate Matter (PM)

Particulate matter is the general term used for a mixture of solid particles and liquid droplets found in the air. Some particles are large or dark enough to be seen as soot or smoke, while others are so small that they cannot be seen with the naked eye. These small particles, which come in a wide range of sizes, originate from many different stationary and mobile sources as well as natural sources (EPA, 1997). Fine particles, those less than 2.5 μm, result from fuel combustion from motor vehicles, power generation, industrial facilities, and residential fireplaces and woodstoves. Coarse particles, those larger than 2.5 μm but classified as less than 10 μm, are generally emitted from sources such as vehicles traveling on unpaved roads, materials handling, crushing and grinding operations, and windblown dust (Davis, 2000).

Some particles are emitted directly from their sources, such as smokestacks and cars. In other cases, gases such as SO_2, NOx, and VOCs react with other compounds in the air to form fine particles. Coal generally contains from 5 to 20 weight percent mineral matter (*i.e.*, ash content per proximate analysis) (Marcus, 1997). During combustion, most of the minerals are transformed into dust-sized glassy particles and, along with some unaltered mineral grains and unburned carbon, are emitted from smokestacks. Particle composition and emission levels are complex functions of firing configuration, boiler operation, and coal properties. In dry-bottom, pulverized coal-fired systems, combustion is very good,

and the particles are largely composed of inorganic ash residue. In wet-bottom, pulverized coal-fired units and cyclone-fired boilers, the amount of fly ash is less than in dry-bottom units because some of the ash melts and is removed from the system as slag. Spreader stokers, which fire a mixture of fine and coarse coal, tend to have a significant quantity of unburned carbon in the fly ash. Overfed and underfed stokers emit considerably less particulate than pulverized coal-fired units or spreader stokers because combustion takes place on a relatively undisturbed bed. Fly ash reinjection for increased consumption of unburned carbon or load changes can also affect particulate emissions (Davis, 2000).

2.12   Peculiarity of Various Coal Materials.

i. Peat: It is considered to be a precursor of coal. It has industrial importance as a fuel in some regions like Ireland and Finland. In its dehydrated form, peat is a highly effective absorbent for fuel and oil spills on land and water. It is also used as conditioner for soil to make it more able to retain and slowly release water (Smith, 1997).

ii. Lignite: It is also referred to as brown coal, it is the lowest ranked coal and used almost exclusively as fuel for electric power generation. Jet is a compact form of lignite that is sometimes polished and has been used as an ornamental stone since the iron-age (Hook and Aleklett, 2009).

iii. Sub-bituminous coal: Its properties range from those of lignite to those of bituminous coal. It is an immature coal with a carbon content of only about 25%-35% and corresponding lower energy content. They are used primarily as fuel for steam-

electric power generation. Additionally, it is an important source of light aromatic hydrocarbons for the chemical synthesis industry (Tarka *et. al.*,2009)

iv. Bituminous coal: It is a dense, black but sometimes dark brown mineral, often with well-defined bonds of bright and dull material. It is used primarily as fuel in steam-electric power generation, with substantial quantities used for heat and power applications in manufacturing and to make coke for the steel industry (Zumdahl, 2002).

v. Anthracite: It is a harder, glossy, black coal used primarily for residential and commercial space heating. It may be divided further into metamorphically altered bituminous coal and petrified oil, as from the deposits in Pennsylvania. It has the highest carbon content, between 86 and 98 percent and a heat value of nearly 15000 BTU/pound (He and Wu, 1997).

vi. Graphite: It is technically the highest ranked but difficult to ignite coal. It is not commonly used as fuel but mostly used in pencils and in powdered form as a lubricant.

 A typical elemental composition of coal is given in Table 2.3 (Zumdahl, 2002).

Table 2.3: Elemental Composition of Coal.

	Types of Coal	%C	%H	%O	%N	%S
1	Lignite	71	4	23	1	1
2	Sub-bituminous	77	5	16	1	1
3	Bituminous	80	6	8	1	5
4	Anthracite	92	3	3	1	1

2.13   Coal Conversion.

Coal conversion is all about the various processes and techniques employed in energy generation from coal. It involves breaking of the complex structure of coal to simpler units and replacing most of the C-C bonds with C-O and C-H bonds. Some of the major processes being used in coal conversion are as follows.

2.13.1   Coal Gasification.

Before cheap natural gas became available in 1940s, gas produced from coal (sometimes called producer gas, town gas, city gas, and syngas) was widely used in the United States. This gas was manufactured by passing steam and air through heated coal.

The reactions involved are;

$$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)} \qquad \Delta H^o = +131.3 kJ…………..(2.11)$$

$$CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)} \qquad \Delta H^o = -41.2 kJ…………..…(2.12)$$

$$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)} \qquad \Delta H^o = -221.0kJ\ldots\ldots\ldots\ldots\ldots(2.13)$$

$$C_{(g)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H^o = -74.8kJ\ldots\ldots\ldots\ldots\ldots(2.14)$$
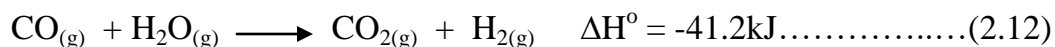
The principal gasification reaction equation (2.11) is highly endothermic. The heat requirements for this reaction are met by the carefully controlled partial combustion of coal given by equation (2.13) (Petrucci and Harwood, 1997).

During gasification, the coal is mixed with oxygen and steam (water vapour) and heated under pressure. During the reaction, oxygen and water molecules oxidize the coal into carbon (II) oxide while releasing hydrogen gas. This process has been conducted in both underground coal mines and coal refineries (Speight, 2001),

$$(Coal) + O_{2(g)} + H_2O_{(g)} \longrightarrow H_{2(g)} + CO_{(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.15)$$
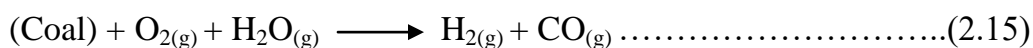
If the refiner wants to produce gasoline, the syngas is collected at this state and routed into a Fischer-Tropsch reaction. If hydrogen is the desired end product, however, the syngas is fed into water gas shift reaction where more hydrogen is liberated (Speight, 2008),

$$CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.16)$$
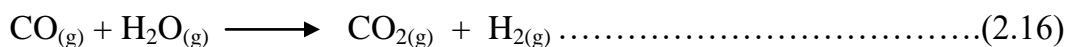
2.14 Binding in Briquette

Binders are agents used to impart cohesive qualities to the powdered material during the production of briquettes. They impart cohesiveness to the briquette formulation, which ensures that the briquette produced remains intact after compression

as well as improving the flowing quality on extrusion from the mould (Iwuagwu, 1991). Many materials contain naturally occurring binders such as resin, wax or wood lignin. For example, where plant matter is concerned, it is the lignin constituent of the biomass material, a major component of most plant matter, which, under suitable compression conditions, acts as a binder and holds the briquette together. However, adequate pressure is required to break cell walls and allow amalgamation. This occurs at moderate pressures greater than or around 5.0 MPa but of course this depends on the specific properties of the material (Olorunnisola, 2004). In some processes, heat can be applied before or during compaction to activate the material's built-in binder and reduce the pressure required (Svenningson, 1987). Manufacture of briquettes by compaction at high pressures, requiring a hydraulic press for example, while applying heat is, however, an energy intensive process, and often unpractical for a rural setting. Moreover, equipment is expensive and more than likely unavailable, but even if it were available, it would be unaffordable for subsistence communities (Engelleitner, 2001).

Basic hand presses that could be fabricated from limited equipment in rural areas might only be able to achieve low pressures of less than 1 MPa. However, the compaction of partly dried biomass material (which has a moisture content of <25 %) at such low pressures (less than 5 MPa), is unlikely to produce stable briquettes. This was demonstrated in attempting to compress straw with a moisture content of 8 % at such pressures, found it was impossible to form briquettes that held together (Faborode and O'Callaghan, 1987). For briquetting to be feasible in rural locations, an appropriate

method is needed that will bind the residue matter together at low compression pressures. Examples of some combustible binders include natural resins, tar, animal manure, fish waste algae and starch. Some common non-combustible binders would be clay, mud and cement (Cosgrove, 1985). Generally, the greater the quantity of binder used in the mix, the greater the resulting relaxed briquette density, durability and sheer strength of the briquettes (Chin and Siddiqui, 2000). The amount of binder selected should give the final product its required strength, so that it is able to withstand handling, transportation and storage, and for the safety of those manufacturing the briquettes it should be non-toxic (Engelleitner, 2001).

Altun *et al.*, (2001) looked into the burning characteristics of coal briquettes from a combustion kinetics point of view. They suggested that coal briquettes ignition efficiency and effectiveness of combustion reaction was considerably dependent on the binder type, amount of binder agent and water addition. Coal tar pitch and petroleum residues are the common binders used for the coal briquetting process. These binders give high strength briquettes but they have a hazardous effect on human beings and are also involved in environmental pollution. Environmentally safe binders like molasses gave briquettes of comparatively low strength. Mehmet and Gulhan showed that using humic acid as a binder can solve these problems to some extent. In their work the optimum conditions required for high strength briquettes were found to be heat treatment of 1 h at 165 °C, 5 % humic acid as a binder and a moisture content of 10.50 % (Yildirim and Ozbayoglu, 2010).

The type of binder used for making coal briquettes not only affects the strength but also has an effect on the burning properties of coal briquettes. Altun *et al*., (2001) studied the burning properties of coal briquettes by using different binders. They used different binders like molasses, sulfide liquor, sodium silicate, corn starch, lime, peridur, polyvinyl acetate, bentonite and carboxyl methylcellulose. The results of revealed that the heating value of briquettes is increased by using binders of sulfide liquor, corn starch and heavy crude oil while the molasses and carboxyl methylcellulose decreased the ash content of briquettes on burning (Altun *et. al.*, 2001). The cost of the binder is another important parameter in binder selection for the briquetting process. Taulbee performed an economical and technical investigation of briquettes by using different binders in combination with the coal and saw dust. Out of the 50 binders used for briquette making, guar gum, wheat starch and lignosulfate (lime) were found to be the most cost effective binders (Taulbee *et al.,* 2009). Ellison and Stanmore (1981) have looked into producing high mechanical strength coal briquettes without the addition of any binder.

On the other hand, the effect of the binder and the amount present on a briquette's combustion, the emissions given off when it burns and the residue left after combustion, also need to be considered carefully.

2.14.1   Types of Binders.

i. Bitumen

Bitumen may refer to either a naturally occurring mixture of various organic liquids, also called crude bitumen, or a residue yielded in the distillation process of coal or petroleum, called refined bitumen. It is a brown-black, extremely viscous, tar-like material that was the first oil product utilized by humans because of its adhesive and cohesive properties. Crude bitumen can be found as a solid or semi-solid material, and consists mainly of hydrocarbons. Its formation can be traced to the decomposition of organisms deep within the earth's crust, where they were affected by intense pressure and heat. This process produced materials such as bitumen. Natural bitumen dumps can be found all over the world, with the largest deposits located in Canada and Venezuela. Bitumen uses varies according to geographical and societal contexts; however, it was historically employed for tasks such as water-proofing, building, construction and the composition of more complex tools that required some binding element (Connan *et al*., 2004).

ii. Calcium tetraoxosulphate (VI)

Calcium tetraoxosulphate(VI) is made by calcining gypsum ($CaSO_4.2H_2O$), a process which involves the exposing of the gypsum to very high temperatures to create calcium tetraoxosulphate(VI) and then grinding it into a fine white powder. Calcium tetraoxosulphate(VI) can exist as a hemihydrates, $CaSO_4.\frac{1}{2}H_2O$, which is an important material in the building trade where it is known as plaster of paris.

$$CaSO_4.2H_2O \longrightarrow CaSO_4.\frac{1}{2}H_2O \longrightarrow CaSO_4 \longrightarrow CaO+SO_3 \ \ldots\ldots\ldots.(2.17)$$

Gypsum   plaster of paris   anhydrite
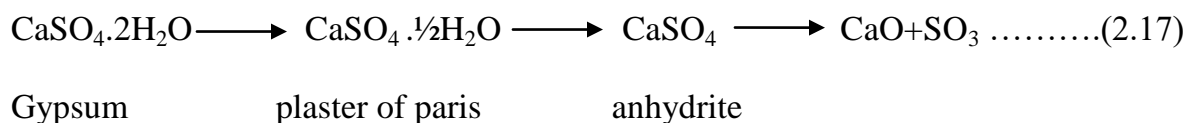
It is also formed by replacing hydrogen in an acid by a metal species. When powdered plaster of paris ($CaSO_4.\frac{1}{2}H_2O$) is mixed with the appropriate amount of water it sets into a solid mass of $CaSO_4.2H_2O$ (gypsum) (Lee, 2009). When water is added to the powder to make slurry, the slurry can be moulded in a variety of ways, and as it sets, a firm matrix is created, creating a solid shape which is also smooth. In the anhydrous form, it is used as a desiccant, it is also used as a coagulant. In the natural state, unrefined calcium tetraoxosulphate(VI) is translucent, crystalline white rock (Gangolli, 1999).

iii. Cement

Cement in the most general sense of the word is a binder, a substance that sets and hardens independently, and can bind other materials together. It is a fine, soft powdery-type substance (Gartner and Macphee, 2011). Cement is the general term given to the powdered materials which initially have plastic flow when mixed with water or other liquid, but has the property of setting to a hard solid structure in several hours with varying degree of strength and bonding properties. A cementing material (binder) is a semi-finished product that is processed at construction sites in making concrete (mortar) mixes. Lime (CaO) is the principal constituent of cement. Excess of lime reduces the strength of cement and presence of lime in amount lesser than needed also reduces the strength of cement and makes it quick setting. Silica (SiO_2) imparts strength to cement. Alumina (Al_2O_3) increases the rate of setting but excess of alumina weakens the strength

of cement. Calcium sulphate or gypsum retards the rate of setting of cement and actually enhances the initial setting time of cement. Iron oxide (Fe_2O_3) gives colour, strength and hardness to cement. SO_3 is desirable in small proportion, because it imparts soundness to cement. Alkalies should be present in small amounts. In excess, they can cause the cement to efflorescent (Sharma, 2011). It is made from a mixture of elements that are found in natural materials such as limestone, clay, sand and/or shale. The four essential elements needed to make cement are calcium, silicon, aluminium and iron. Calcium which is the main ingredient can be obtained from limestone, whereas silicon can be obtained from sand and/or clay. Aluminium and iron can be extracted from bauxite and iron ore, and only small amounts are needed. Cement is usually gray. White cement can also be found but it is usually more expensive than gray cement (Shultz *et. al.*, 2009).

iv.   Starch

Starch is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. This polysaccharide is produced by all green plants as an energy store. It is the most common carbohydrate in the human diet and is contained in large amounts in such staple foods as potatoes, wheat, maize, rice and cassava. Cassava plants are the major source of starch. The plant thrives in the equatorial region between the tropics of Capricon, and as well it thrives well in Nigeria. There are many varieties of cassava of which the sweet and bitter species are widely grown for starch production in commercial quantity and they contain 12- 33 %. A typical composition of the cassava root is moisture (70 %), starch (24 %), fiber (2 %), protein (1 %) and other substances

including minerals (3 %). The general formula for starch is $C_6H_{10}O_5$. Starch obtained from cassava tubers has high polymeric structure the granule size in microns is between 5–36 μm. The granule size maybe truncated, round or oval (Nyerhovwo, 2000).

Pure starch is a white tasteless and odourless powder that is insoluble in cold water and alcohol. Dissolving starch in warm water gives white paste that can be used as a thickening, stiffening or binding agent (Brown and Poon, 2005). The production of starch uses many different extraction techniques. In principle, they are differentiated by the origin of the raw materials. There are cereal starches, root starches and tuber starches. The processing of supplied raw materials starts with a cleaning step. After that, the material is crushed and then the components are separated by various physical means. Then the separated starch passes on to one more cleaning step and finally it is dehydrated and dried.

However, recently in the United States of America, a binder obtained from the direct liquefaction of biomass has been successfully used in the production of coal briquettes and is known to react chemically with the coal structure. This greatly increased the bond strength and ability to resist compressive force of the resulting briquettes (Smith, 2001). According to Emerhi, (2011), he concluded that the quality of the briquettes that were produced using starch as binder was higher than those bonded with cow dung and ash.

CHAPTER THREE

MATERIALS AND METHODS

3.1   Materials collection

The bitumen that was used as binder for the production of the briquettes was sourced from Conpro Bitumen Works Emene, Enugu State. Sub-bituminous coal from Onyeama mine was sourced at Nigeria Coal Corporation, Enugu. The rice husk was sourced from rice mill in Abakaliki and the corn cob was from dump site at the local Kpirikpiri market Abakaliki. The binders that were used in the production of the briquettes are; cassava starch extracted from cassava tubers bought from Relief market in Enugu, Portland cement brand 42.5 R was also bought from Kenyatta market in Enugu. The briquettes produced were of various mixtures of coal and rice husk / corn cob with binders such as starch, cement, $CaSO_4$ and bitumen.

All chemicals used were BDH grade. These are calcium hydroxide, calcium sulphate, sodium carbonate, barium chloride and sodium nitrite.

Equipment:

(i) Diesel operated UT grinding machine, UT-280.

(ii) Manual briquette machine model Hand Press Hydraulic machine, Energymix Nigeria.

(iii) Digital weighing machine model Vibra 8J, Sansui Electronics.

(iv) Vibrator Sieve Shaker AS 450, Retsch, mesh size 450 microns.

(v) Adiabatic bomb calorimeter, model OSK 100A, Ckic.

(vi) Electric muffle furnance ST-1700M, Zhengzhou Sutong.

(vii) Electric oven, Model DHG, SANFA.

(viii) Locally made briquette stove, Abacha stoove

(ix) Digital stop watch, Seiko.

(x) Rigaku ZSX100e X-ray fluorescence, 51 mm (diameter) by 30 mm (high) 30 rpm instrument at ABU Zaria.

(xi) Instron Model 4400 Universal strength testing machine 100 kN.

3.2 Methods

3.2.1 Preparation of pulverized coal:

The lumps of coal obtained from the coal mine was sun dried, pulverized and ground to powdery form to pass through sieve of 4 mm and stored in polyethene bags in an aerated area till use to prevent caking.

3.2.2 Preparation of rice husk

Rice husk was sourced from the rice mill Abakaliki and sieved to remove any other grains of rice that might be left in the rice husk. It was ground to powdery form, passed through sieve of 4 mm, aerated to prevent caking and moulds formation and stored.

Plate 1: The ground samples of coal dust and rice husk.

3.2.3 Preparation of corn cob

The corn cob was sourced from waste dump site of Kpirikpiri market in Abakaliki. The corn cob were pulverized, dried for five days and ground to dust, sieved through 4 mm sieve, aerated and stored in polyethene bag.

Corn cob

Plate 2: The ground samples of corn cob.

3.3 Proximate analyses of raw materials.

3.3.1. Moisture content of raw materials: Using a digital weighing balance a portion each of the coal, corn cob and rice husk (2 g) were weighed out into a watch glass. The samples were placed in an oven for 24 h at temperature of 105 ^{o}C. The moisture content was determined according to ASTM Standards, (1992).

$$MC = \frac{W_1 - W_2}{W_1} \times 100$$
……………………………………… (3.1)

W_1 = Initial weight

W_2 = Final weight after drying

MC = Moisture content

3.3.2 Volatile matter of raw materials: Again another portion (2 g) each of corn cob and rice husk were heated to 400 ^{o}C for 10 min, while coal was heated to 400 ^{o}C for 2 h all in a partially closed crucible in a muffle furnace. The crucible and its contents were retrieved and cooled in a desiccator. The differences in weights were recorded and the volatile matter was calculated based on ASTM Standards, (1992):

$$VM = \frac{W_1 - W_2}{W_1} \times 100$$
……………………………………. (3.2)

VM = Volatile matter

W_1 = Initial weight of the sample

W_2 =   Final weight of sample after cooling.

3.3.3 Ash content of raw materials: Another 2 g each of coal, corn cob and rice husk were placed in a pre weighed porcelain crucible and transferred into a preheated muffle furnace at a temperature of 600 ^{o}C for 1 h after which the crucibles and their contents were transferred to a desiccator and allowed to cool. The crucibles and their contents were reweighed and the new weight noted. The percentage ash content was calculated based on ASTM Standards, (1992).

$$AC = \frac{W_2}{W_1} \times 100$$

……………………………………………… (3.3)

AC = Ash content

W_2 = Final weight of ash after cooling

W_1 = Original weight of dry sample

3.3.4 Fixed carbon of raw materials: The fixed carbon was determined using the formula.

$$FC = 100 - (\%VM + \%AC + \%MC)$$ ……………………………….. (3.4)

Where VM, AC and MC are volatile matter, ash content and moisture content respectively (ASTM Standards, 1992).

3.3.5 Calorific values of raw materials: The calorific values of the coal, corn cob and rice husk were determined using oxygen bomb calorimeter. The samples were crushed and sieved through a screen with 0.3 mm perforations. For each, 1 g was weighed with an electronic balance and wrapped with a thin rice paper of known heat capacity, after which the rolled racer was tied to the ignition wire connected to the electrodes.

Samples were placed in the bomb, oxygen was admitted through a reducing valve until the pressure was 25 to 30 bar. The bomb was lowered into the inner vessel containing a known quantity of water and water was introduced into the outer jacket from an overhead inlet until it overflowed. The water temperatures in the two vessels were taken as the temperatures before ignition. The ignition button was switched on and the heat generated within the bomb was quickly conducted to increase the temperature of water in the inner vessel.

Temperatures were read on certified Beckman thermometers at 1 min intervals until steady readings were attained and the reading were taken for a further 3 min. The steady temperature was taken as the maximum temperature from which the temperature rise for the sample under test was obtained. The Beckman thermometers were graduated to 0.001 ^{o}C scale divisions.

The calorific values (kJ/kg) of the raw samples under consideration were calculated from the temperature rise in the calorimeter vessel and the mean effective heat capacity of the system given by the equation 3.5.

$$VI = (Ee + W1)TR - \frac{(C)}{S} \times 4.16868$$ (Sumner *et al.*, 1983) ………………… (3.5)

Where Ee is water equivalent of the calorimeter (581kg)

W1 = quantity of water in the vessel

TR = Temperature rise (^{o}C)

C = Correction factor for ignition (154 cal)

S = Weight of sample (g)

VI = Calorific value

3.3.6 X-ray resonance fluorescence (XRF) analysis of raw materials.

An x-ray resonance fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength dispersive spectroscopic principles that are similar to an electron microprobe. The relative ease and low cost of sample preparation, and the stability and ease of use of x-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals and sediment (Fitton, 1997).

The analysis of major and trace elements in geological materials by XRF is made possible by the behavior of atoms when they interact with x-ray radiation. An XRF spectrometer works because if a sample is illuminated by an intense x-ray beam, known as the incident beam, some of the energy is scattered, but some is also absorbed within the sample in a manner that depends on its chemistry. The incident x-ray beam is

typically produced from a Rh target, although W, Mo and Cr can be used depending on the application (Potts, 1987).

When the sample was introduced into the x-ray spectrometer primary x-ray beam illuminated the sample and it was excited. The excited sample then emitted x-rays along a spectrum of wavelengths characteristics of the types of atoms present in the sample. The atoms in the sample absorbed x-ray energy by ionizing, ejecting electrons from the lower (usually K and L) energy levels. The ejected electrons were replaced by electrons from an outer, higher energy orbital. The energy that was released due to the decreased binding energy of the inner electron orbital was compared with an outer energy. The energy that was released was in the form of emission of characteristic x-ray that indicated the type of atom present (Rollinson, 1993). Each of these transitions yielded a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital (Clark *et al.*, 1999).

The wavelength of the fluorescent radiation was calculated from Planck's law:

$\lambda = h.c/E$ …………………………………………………………………….. (3.6)

(Where λ is wavelength, *h* is Planck's constant, c is the speed of light and *E* is the energy of the photon (Shefsky, 1995).

3.3.7 Calculation of pressure exerted by the machine

The briquetting machine was fabricated to yield (3) three briquettes at a time, according to Osarenmwinda and Ihenyen, (2012), the pressure was calculated thus,

Total area of pressure = Number of mould die X Cross sectional area of die

$$= 3 \ x \ \pi/3d^2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3.7)$$

Where d= diameter of moulding die = 60 cm^3 =0.6m, $\pi = 3.142$

Total area = $\dfrac{3 \ x \ 3.142}{3 \ x \ (0.6)^2}$ = 8.728 m^2

Pressure = $\dfrac{Force}{Cross \ sectional \ area}$

But   F= M x a

Where M= Mass of beam = 9.5 kg

a = acceleration due to gravity (9.8 m/s)

Mass of screw jack = 18.70 kg

Force = (9.5 + 18.70) x 9.8 = 276.36 N

Pressure = $\dfrac{Force}{Cross \ sectional \ area}$

= $\dfrac{276.36 \ N}{8.728 \ m^2}$

= 31.67 N/m^2

3.4 Preparation of the various briquette samples.

The briquettes were produced in the laboratory of Industrial Chemistry Department, Ebonyi State University Abakaliki. A manual hydraulic briquetting machine with three cubic moulds of 500 g each and with a total capacity of 1.5 kg was used. Briquettes of varied mixtures of coal dust and rice husks; coal dust and corn cob were produced with different binders of 150 g each for starch, cement, bitumen and calcium sulphate. The mixture of coal dust, rice husk, corn cob, binder, calcium hydroxide which was used as the desulphuriser and water were thoroughly mixed to avoid formation of lumps, the mixtures were then fed into the three moulds of the hydraulic briquetting machine. The pressure and compression force of 276.36 N and 31.67 N/m^2 was maintained for 20 min before the briquettes were extruded. The machine is based on hydraulic principle and consists of three moulds, where biomass feed stocks were fed as seen in Plate 3. The briquettes produced for each composition were three (3). The briquettes were removed from the mould and dried in the sun for 6 days. The different briquettes produced are showed in Plates 4, 5, 6 and 8 representing briquettes produced with bitumen, $CaSO_4$, starch and cement binders respectively. The briquettes produced were used for heating purposes as seen in Plate 7. Different compositions of briquettes were produced using the formulation in Table 3.1.

Table 3.1: The amount of materials used for the production of briquettes.

Percentage composition	Coal (g)	Raw Material(g)	Binder (g)	$Ca(OH)_2$ (g)	Water (cm^3)
100%CD	1500	0.0	150	70	400
80%CD:20%RM	1200	300	150	60	470
60%CD:40%RM	900	600	150	50	550
40%CD:60%RM	600	900	150	40	620
20%CD:80%RM	300	1200	150	30	690
100%RM	0.0	1500	150	20	750

RM= Raw Material (corn cob or rice husk), CD= Coal dust

Plate 3:   The manual briquetting machine.

Plate 4: Samples of coal-rice husk briquettes made using bitumen as binder.

Plate 5: Samples of coal-rice husk briquettes made using $CaSO_4$ as binder.

Plate 6: Samples of coal-rice husk briquettes made using starch as binder.

Plate7: A typical coal briquette stove used for cooking in Ikwo, Ebonyi state. Ash is collected in a compartment below the briquettes, making it easier to clean.

Plate 8: Sample of coal-corn cob briquettes produced with cement as binder.

3.5 Analyses of the Briquette Samples.

3.5.1. Moisture content of the briquettes: Using a digital weighting balance a portion each of the briquette samples (2 g) was weighed out into a watch glass. The samples were placed in an oven for 24 h at temperature of 105 ^{o}C. The moisture content was determined as according to ASTM Standards, (1992).

$$MC = \frac{W_1 - W_2}{W_1} \times 100$$

………………………………………. (3.7)

W$_1$ =   Initial weight

W$_2$ =   Final weight after drying

MC   =   Moisture content

3.5.2 Volatile matter of the briquettes: Again another portion (2 g) of the sample was heated to about 300 ^{o}C for 10 min in a partially closed crucible in a muffle furnace. The crucible and its content were retrieved and cooled in a desiccator. The difference in weight was recorded and the volatile matter was calculated using the formula of ASTM Standards, (1992).

$$VM = \frac{W_1 - W_2}{W_1} \times 100$$

………………………………………. (3.8)

VM   =   Volatile matter

W$_1$ =   Initial weight of the sample

W$_2$ =   Final weight of sample after cooling.

3.5.3 Ash content of the briquettes: In a pre-weighed porcelain crucible, 2 g of the sample was weighed out and transferred into a preheated muffle furnace at a temperature of 600 ^{o}C for 1 h after which the crucible and its content were transferred to a desiccator and allowed to cool. The crucible and its content were reweighed and the new weight noted. The percentage ash content was calculated based on ASTM Standards,(1992).

$$AC = \frac{W_2}{W_1} \times 100$$

…………………………………….. (3.9)

W_2 = Final weight of ash after cooling

W_1 = Initial weight of dry sample

AC = Ash content

3.5.4 Fixed carbon of the briquettes: The fixed carbon was determined using the formula.

$$FC\,(\%) = 100 - (\%\,VM + \%\,AC + \%\,MC) \quad …………………………… (3.10)$$

Where VM, AC and MC are volatile matter, ash content and moisture content respectively according to ASTM Standards, (1992).

3.5.5 Density of the briquettes: Density is a physical property of briquettes. Since the briquettes have the shape of a cuboid, the length, breadth and height were measured with metre rule. The volume was evaluated using *V=lbh.* The density was computed as ratio of mass to the volume of the briquette (Sotanndes *et. al.,* 2010)

$$\text{Density (g/cm}^3) = \text{Mass (g)/Volume (cm}^3) \quad \ldots\ldots\ldots\ldots\ldots \quad (3.11)$$

3.5.6 Porosity index of the briquettes: The following procedure was carried out to compare the porosity of the briquettes. Each briquette sample was weighed, immersed in a separate beaker containing a known volume of water for 20 min, brought out and reweighed after they seemed to have absorbed water to their full capacity. The porosity of the briquettes was determined based on the amount of water each sample was able to absorb. The porosity index was calculated as the ratio of the mass of water absorbed to the mass of the sample immersed in the water (Montgomery, 1978).

$$\text{Porosity Index} = \frac{\text{Mass of water absorbed}}{\text{Mass of the sample}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots.. \quad (3.12)$$

3.5.7 Calorific value of the briquettes: The calorific value of the briquette samples were determined using oxygen bomb calorimeter. The samples were crushed and sieved through a screen with 0.3mm perforations. For the different briquettes, 1 g each was weighed with an electronic balance and wrapped with a thin rice paper of known heat capacity, after which the rolled racer was tied to the ignition wire connected to the electrodes. Samples were placed in the bomb, oxygen was admitted through a reducing valve until the pressure was 25 to 30 bar. The bomb was lowered into the inner vessel containing a known quantity of water and water was introduced into the outer jacket from an overhead inlet until it overflowed. Then the stirrers were started and stabilized. The water temperatures in the two vessels were taken as the temperatures before ignition. The ignition button was then pressed and the heat generated within the bomb was quickly conducted to increase the temperature of water in the inner vessel.

Temperatures were read on certified Beckman thermometers at 1 min intervals until steady readings were attained and the reading were taken for a further 3 min. The steady temperature was taken as the maximum temperature from which the temperature rise for the sample under test was obtained. The Beckman thermometers were graduated to 0.001 ^{o}C scale divisions.

The calorific value (kJ/kg) of the samples under test was calculated from the temperature rise VI in the calorimeter vessel and the mean effective heat capacity of the system as given by the equation 3.7,

$$VI = (Ee + W1)TR - \frac{(C)}{S} \times 4.16868$$ (Sumner *et al.*, 1983) ……………. (3.13)

Where Ee is water equivalent of the calorimeter (581 kg)

W1 = Quantity of water in the vessel

TR = Temperature rise (^{o}C)

C = Correction factor for ignition (154 cal)

S = Weight of sample (g)

VI = Calorific value

3.5.8 Ignition time of the briquettes: The different samples were ignited at the edge of their bases with a bunsen burner. The time taken for each briquette to catch fire was recorded as the ignition time using a stopwatch (Kim *et al.,* 2001).

3.5.9 Water boiling test of the briquettes: This was carried out to compare the cooking efficiency of the briquettes. It measured the time taken for each set of briquettes to boil an equal volume of water under similar conditions. For each briquette sample, 100 g was

used to boil 250 cm^3 of water using small stainless cups and domestic briquette stove (Kim *et al.,* 2001).

3.5.10 Burning time of the briquettes: This is the time taken for each briquette sample to burn completely to ashes. The difference between the time the briquettes turned into ashes and the ignition time gave the burning rate (Kim *et al.,* 2001).

Burning time = Ashing time – Ignition time ………………… (3.14)

3.5.11 Total sulphur content:

The different samples of the briquettes were pulverized, 1g each of finely powdered sample was mixed with 5 g of NaNO$_3$ in a crucible. The mixture was preheated at 400 ^{o}C for 30 min in an electric muffle furnance and then fused at 950 ^{o}C, after fussion, the crucible was allowed to cool and was placed on its side in a 150 cm^3 beaker. Enough deionized water barely to cover the contents of the crucible was added and the beaker was heated at a temperature just below boiling in a hot plate, until the melt was thoroughly disintegrated. The crucible was then removed and washed with deionized water. At this point 20 cm^3 of 6 M HCl was added to neutralize the Na$_2$CO$_3$ and the solution was made slightly acidic. This was filtered into a 100 cm^3 volumetric flask and the volume was made up to the mark with deionized water. The solution was brought to boiling and 10 cm^3 of 10 % BaCl$_2$.2H$_2$O was slowly added to precipitate the sulphate. The solution was allowed to cool and was filtered. The residue was washed with deionized water. The paper (BaSO$_4$) was ignited at a low temperature of 40 ^{o}C and the

precipitate weighed. The ignited precipitate was treated with drops of HF and H_2SO_4, cautiously ignited and weighed again. The determination was carried out in triplicate. The percentage sulphur in the precipitate was calculated from the expression (Jackson, 1988).

$$\text{Sulphur Content} = \frac{BaSO_{4(g)} \times 13.7}{\text{Weight of sample}} \times 100 \qquad \text{.........................(3.15)}$$

$$CaSO_{4(s)} + 2NaNO_{3(aq)} \longrightarrow Ca(NO_3)_{2(aq)} + Na_2SO_{4(aq)}$$

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow BaSO_{4(S)} + 2NaCl_{(aq)}$$
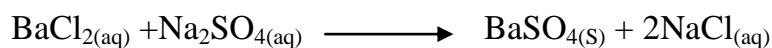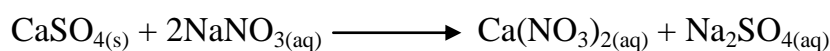
3.5.12 Determination of the Compressive Strength :

Compressive strength in cleft of briquettes was determined in accordance with ASTM, (2008) using an Instron Universal Strength testing machine with load cell capacity of 100 kN. The cross-head speed was 0.305 mm/min. A sample of briquette to be tested was placed horizontally in the compression test fixture and a load was applied at a constant rate of 0.305 mm/min until the briquette failed by cracking. The compressive strength in cleft was then computed as follows:

Compressive strength in cleft (N/mm)= $\dfrac{3 \times \text{The load at fracture point(N)}}{[l_1(\text{mm})+l_2(\text{mm})+l_3(\text{mm})]}$, ...(3.10)

Where l_1, l_2 and l_3 were lengths of briquettes at points one, two and three, respectively in (mm).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 The Proximate Analyses

The results of proximate analyses of raw coal, rice husk and corn cob are shown in Table 4.1.

Table 4.1: Proximate analyses of raw materials

Proximate Analyses	Coal	Rice husk	Corn cob
Moisture content (%)	3.25±0.021	8.48±0.012	7.03±0.015
Volatile matter (%)	20.12±0.017	35.14±0.028	39.21± 0.016
Ash content (%)	10.12±0.023	19.53±0.013	12.56±0.012
Fixed carbon (%)	66.51±0.013	36.85±0.016	41.2±0.021
Calorific value (kJ/kg)	29573.13±0.014	24421.19±0.011	27277.84±0.013

The results of the proximate analyses show that raw coal had a moisture content of 3.25 ±0.021 %, volatile matter of 20.12 ±0.017 %, ash content of 10.12 ±0.023 % showing the presence of non combustible matter. The raw coal sample had the value of fixed carbon of 66.51±0.013 % and with a calorific value of 29573.13±0.014 kJ/kg. The values for the proximate analyses of coal are similar to those obtained by Majumder *et al.,* (2008). The high calorific value showed that coal is a good fuel source that releases enough heat upon combustion. The rice husk on the other hand had moisture content of 8.48 ± 0.012 %, volatile matter of 35.14 ±0.028 % which signified that it would readily ignite unlike coal. The results also showed an ash content value of 19.53± 0.013 %, fixed carbon of 36.85

±0.016 % which showed that it contained less carbon content for char formation. The rice husk had a lower calorific value of 24421.19 ±0.011 kJ/kg as against the coal sample that was higher. The results for the corn cob showed that it had a moisture content of 7.03 ±0.015 %, volatile matter of 39.21 ±0.016 %, ash content of 12.56 ±0.012 %, fixed carbon of 41.2 ±0.021 %, and a calorific value of 27277.84 ±0.013 kJ/kg. The reasonable calorific value of the corn cob wastes signified that it could be used as a source of fuel for domestic cooking. The results are similar to the study carried out by Ioannidou *et al.,* (2009), they concluded that based on the calorific value that corn cob was a good solid biofuel, due to the high heating value of the produced char.

4.2 The elemental composition of ashes of the raw materials.

Table 4.2 showed the XRF results of the elemental composition of ashes of coal dust, rice husks and corn cob. From the results obtained, it could be seen that there is a high concentration of silicon oxide (74.8 ±0.0357 %) present in rice husk followed by P_2O_5 (14.90 ±0.0715 %), K_2O (5.19 ±0.0241 %) and arsenic oxide having the lower concentration while other compounds were found in varying little amounts and Eu_2O_3 was not found present. The values are comparable with the work of Mehta (1994). The significant amount of phosphorus and potassium would have come from the use of N.P.K fertilizer during rice farming. The XRF results for coal dust showed that coal contained more of solid compounds such as SiO_2 (52 ±0.7889 %), K_2O (1.2 ±0.0567 %), CaO (4.19 ±0.0058 %), Fe_2O_3 (12.9 ±0.0536 %), ZrO_2 (2.3 ±0.0881 %), Ag_2O (3.4 ±0.0548 %), all above 1 %. The amount of SO_3 of 15 ±0.0842 % in coal made it imperative that $Ca(OH)_2$

must be added to coal to desulphurize the briquettes produced. Desulphurization reduces the amount of oxides of sulphur emitted into the atmosphere when the briquettes are burnt. Coal contained more solid compounds than rice husk and corn cob, this feature could explain why briquettes with higher amount of coal had higher density than other briquettes produced.

The result showed that corn cob also contained high concentration of silicon oxide (58.205 ±0.6556 %) followed by oxides of potassium (17.801 ±0.4625 %), phosphorus (4.677 ±0.0025 %), aluminium (4.378 ±0.0023 %), sulphur (3.863 ±0.0008 %), iron (3.317 ±0.0041 %), calcium (2.467 ±0.0042 %) all with reasonable compositions. The significant amount in the concentration of oxides of sulphur made it necessary to desulphurize the briquettes produced to reduce emission of sulphur oxides when the briquettes are burnt. The oxides of manganese, zinc, titanium, magnesium, chromium are all below 1% as such are removed in the ash formed when the briquettes are burnt. The XRF results showed that for the coal sample under consideration there are no trace of compounds such as P_2O_5, ZnO, BaO, Eu_2O_3, Yb_2O_3, Rb_2O, Al_2O_3, Cl and SrO. For the rice husk sample there are also no trace of compounds such as ZnO, Cr_2O_3, Eu_2O_3, Al_2O_3, Cl and SrO. For the corn cob there were also no trace of compounds such as V_2O_5, NiO, CuO, As_2O_3, ZrO_2, Ag_2O, Re_2O_7, PbO, BaO, Eu_2O_3, Yb_2O_3 and Rb_2O. X-ray fluorescence results of the elemental composition of the ashes of the raw material are shown in Table 4.2.

Table 4.2: Elemental composition of ashes of the raw materials.

Compound	Coal (%)	Rice Husk (%)	Corn Cob (%)
SiO_2	52±0.7889	74.8±0.0357	58.205±0.6556
SO_3	15±0.0842	0.28±0.0057	3.863±0.0008
K_2O	1.2±0.0567	5.19±0.0241	17.801±0.4625
CaO	4.19±0.0058	1.66±0.0425	2.467±0.0042
TiO_2	6.92±0.0112	0.14±0.0034	0.358±0.0021
V_2O_5	0.29±0.0048	0.002±0.0011	NA
Cr_2O_3	0.059±0.0011	NA	0.346±0.0032
MnO	0.13±0.0012	0.153±0.0013	0.123±0.0006
Fe_2O_3	12.9±0.0536	1.05±0.0088	3.317±0.0041
NiO	0.15±0.0023	0.004±0.0006	NA
CuO	0.18±0.0041	0.012±0.0031	NA
As_2O_3	0.05±0.0023	0.0063±0.0001	NA
ZrO_2	2.3±0.0881	NA	NA
Ag_2O	3.4±0.0548	1.62±0.0321	NA
Re_2O_7	0.32±0.0073	0.025±0.0001	NA
PbO	0.31±0.0081	0.004±0.0001	NA
P_2O_5	NA	14.90±0.0715	4.677±0.0025
ZnO	NA	0.0582±0.0014	0.200±0.0035
BaO	NA	0.049±0.0034	NA
Eu_2O_3	NA	NA	NA
Yb_2O_3	NA	0.001±0.0035	NA
Rb_2O	NA	0.017±0.0014	NA
Al_2O_3	NA	NA	4.378±0.0023
Cl	NA	NA	3.787±0.0017
SrO	NA	NA	0.023±0.0014

Key: NA= Not available

4.3 The effect of ash content on the briquettes.

Table 4.3a, Table 4.3b and Fig.4.1 showed the result of the ash content of the briquettes produced from different binders.

Table 4.3a: Ash contents of the briquette samples

Briquette samples (%)	Cement (%)	Bitumen (%)	$CaSO_4$ (%)	Starch (%)
100% C	28.83	21.05	29.63	22.06
80% C : 20% RH	26.22	20.27	26.38	21.79
60% C : 40% RH	24.80	19.67	25.92	20.26
40% C : 60% RH	23.21	18.21	24.86	19.45
20% C : 80% RH	21.78	17.56	23.45	18.91
100% RH	19.13	16.23	19.23	16.82
100% CCB	22.00	17.69	18.88	18.67
80% CCB : 20% C	22.50	18.81	23.00	19.72
60% CCB : 40% C	23.40	19.42	23.45	20.46
40% CCB : 60% C	24.84	20.17	25.30	21.00
20% CCB : 80% C	28.00	20.63	27.69	21.70

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.3b. ANOVA results of ash contents of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	242.2848	3	80.76158	13.72663	2.66413E-06	2.83874541
Within Groups	235.3429	40	5.883572			
Total	477.6276	43				

The ash content of the coal briquette is the amount of ash that remains after the briquette is burned or incinerated. It was noticed from the results that the binder concentration of cement and calcium sulphate affected the ash content of the coal briquettes, since there briquettes had higher ash content. According to Loo and Koppejan, (2008), the higher the fuel's ash content, the lower the calorific value. The briquettes produced with binders of cement and calcium sulphate had higher ash contents in the

ranges of (19.13-28.83 %) and (18.88-29.63 %) respectively unlike the briquettes that were produced with binders such as starch with values (16.82-22.06 %) and bitumen briquettes with lowest values in the ranges (17.69-21.05 %) confirming the position of Loo and Koppejan, (2008). The presence of more non combustible compounds in cement and calcium sulphate resulted in their briquettes with lower calorific values when compared to briquettes of similar compositions produced with starch and bitumen as binders.

The one-way ANOVA in Table 4.3b shows significant differences (p<0.05) in the ash contents for the respective binders used in this study at 95 % confidence interval. The one-way analysis ANOVA (Appendix 1b) of the ash contents of briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, showed that there is no significant difference (p>0.05) at 95 % confidence interval. For the f-Test (Appendix 1c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} which is 1.45 is less than $F_{critical}$ (0.05,3,3) which is 15.4, we retain the null hypothesis and have no evidence of a difference between the variances at α of 0.05. The t-Test (Appendix 1d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), showed that for the T_{stat} which is -0.08 is less than $t_{critical}$ (0.05,6) which is 2.45, confirmed that at 95% confidence interval that there is no significant difference between the means at an α of 0.05.

Fig. 4.1: Ash content versus briquettes samples with different binders.

4.4 The effect of fixed carbon on the briquettes.

Table 4.4a, Table 4.4b and Fig.4.2 show results of fixed carbon of the respective briquettes made with the binders under study.

Table 4.4a: Amount of fixed carbon in the briquette samples

Briquette samples (%)	Cement (%)	Bitumen (%)	$CaSO_4$ (%)	Starch (%)
100% C	58.34	65.04	57.46	61.76
80% C : 20% RH	53.76	60.95	53.59	53.71
60% C : 40% RH	48.83	57.94	47.18	50.06
40% C : 60% RH	41.01	49.75	38.88	39.87
20% C : 80% RH	34.33	40.90	32.74	31.55
100% RH	32.02	37.37	32.30	27.00
100% CCB	25.17	32.48	22.98	26.92
80% CCB : 20% C	27.15	36.40	26.10	33.95
60% CCB : 40% C	35.54	40.96	30.93	37.47
40% CCB : 60% C	38.79	44.83	37.48	42.24
20% CCB : 80% C	40.15	50.69	41.63	45.01

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.4b. ANOVA results of fixed carbon of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	494.899334	3	164.9664	1.405283	0.255340536	2.83874541
Within Groups	4695.60785	40	117.3902			
Total	5190.50719	43				

Essentially, the fixed carbon of a fuel is the percentage of carbon available for char combustion. This is not equal to the total amount of carbon in the fuel (the ultimate carbon) because there is also a significant amount released as hydrocarbons in the volatiles. Fixed carbon gives an indication of the proportion of char that remains after the devolatization phase. The results show that the carbon content of 100 % coal briquettes

(58.34 -61.76 %) for the respective binders was higher than those of 100 % rice husk briquette (27.00-37.37 %) and 100 % corn cob briquette (22.98-32.48 %) respectively.

The results also show that for the respective binders used in the production, the briquettes produced using bitumen as binder had values with the highest amount of fixed carbon in the range (32.48-65.04 %) followed by briquettes produced with starch as binder (26.92-61.76 %). This is because the binder bitumen contained the highest amount of carbon content than the other binders under consideration. The result also show that the briquettes produced with the binder cement (25.17-58.34 %), and the briquettes produced with calcium sulphate (22.98-57.46 %) having the least values. Since coal contained higher amount of fixed carbon (66.51± 0.013 %) the briquettes with higher percentage composition of coal had higher values of carbon content. The higher the number of carbon content of the briquettes the higher the calorific values, while the briquettes with low carbon content do have lower calorific values. The findings of this study compared favourably with that of Adetogun *et al.*,(2014). The production of briquettes from mixtures of coal and rice husk, coal and corn cob by varying their compositions resulted in briquettes with reduced fixed carbon content.

The one-way ANOVA analysis in Table 4.4b show no significant difference (p>0.05) in the values of the fixed carbon for the respective binders used at 95 % confidence interval. For the fixed carbon of briquette samples (100 %C, 60 %C: 40 %RH and 60 %C:40 %CCB) produced, the one-way ANOVA analysis show significant difference since p<0.05 (Appendix 2b). The f-Test (Appendix 2c) of the briquette

samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 2.05 is less than $F_{critical}$ (0.05,3,3) which is 15.4, therefore there is no significant difference between the variances at α of 0.05. The t-Test (Appendix 2d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), showed that for the T_{stat} which is 3.49 is greater than $t_{critical}$ (0.05,6) which is 2.45, there is significant difference between the means at an α of 0.05.

Fig. 4.2: Fixed carbon versus briquettes samples with different binders.

4.5 The effect of moisture content on the briquettes.

Table 4.5a, Table 4.5b and Fig.4.3 show the results of the moisture contents of the

briquettes produced.

Table 4.5a: Moisture content of the briquette samples

Briquette samples (%)	Cement (%)	Bitumen (%)	$CaSO_4$ (%)	Starch (%)
100% C	2.52	2.15	2.47	2.78
80% C : 20% RH	2.56	2.34	2.71	3.37
60% C : 40% RH	3.45	2.92	3.82	4.42
40% C : 60% RH	4.14	3.51	4.21	4.55
20% C : 80% RH	4.75	4.08	5.17	5.68
100% RH	5.65	4.68	5.94	6.95
100% CCB	5.83	4.06	4.14	5.14
80% CCB : 20% C	5.69	3.38	3.89	4.05
60% CCB : 40% C	4.06	3.50	3.48	3.38
40% CCB : 60% C	3.04	2.50	3.02	3.01
20% CCB : 80% C	2.80	2.20	2.77	2.87

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.5b. ANOVA results of moisture contents of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	6.23388	3	2.07796	1.579638	0.209326	2.838745
Within Groups	52.61862	40	1.315465			
Total	58.8525	43				

The moisture content is a measure of the amount of water in the fuel material. In

solid fuels, moisture can exist in two forms: as free water within the pores and interstices

of the fuel, and as bound water which is part of the chemical structure of the material

(Borman and Ragland, 1998). Moisture content is a very important property and can

greatly affect the burning characteristics of the briquettes (Yang *et al*., 2005). The results

show that briquettes of rice husk had the highest moisture content for the different

binders used for briquettes production. The results show that briquettes of rice husk produced with starch as binder had the highest values in the range of (3.37-6.95 %), followed by briquettes of rice husk produced with calcium sulphate as the binder (2.71-5.94 %). The results also show that briquettes produced with bitumen as the binder had the lowest values for briquettes of corn cob (2.20-4.06 %) and rice husk briquettes (2.34-4.68 %). The low moisture values are due to the sticky nature of the binder that made absorption of water molecules into the pores of the briquettes difficult. The sticky coating thereby reduces the rate at which water molecules are absorbed from the air by the briquettes upon exposure before they are used for fuel or heating purposes. The effect is that the loosely held particle of the raw material creates more space for absorption of moisture than the compact coal particles. The resultant effect was that as the pores are been introduced with the blending of the coal dust with the agro-wastes, there is an increase in the ignition time of the briquettes produced.

The one-way ANOVA analysis in Table 4.5b shows no significant difference ($p>0.05$) in the moisture content for the respective binders used in this study at 95 % confidence interval. The moisture contents of briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced were subjected to one-way ANOVA analysis (Appendix 3b) and the results showed significant difference ($p<0.05$) at 95 % confidence interval. The f-Test (Appendix 3c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 5.80 is less than $F_{critical}$ (0.05,3,3) which is 15.4, therefore there is no significant difference between the variances at α of 0.05. The t-Test (Appendix 3d) of the

briquette samples (60 %C: 40 %RH and 60 %C: 40% CCB), showed that for the T_{stat} which is 2.23 is less than $t_{critical}$ (0.05,6) which is 2.45, there is no significant difference between the means at an α of 0.05.
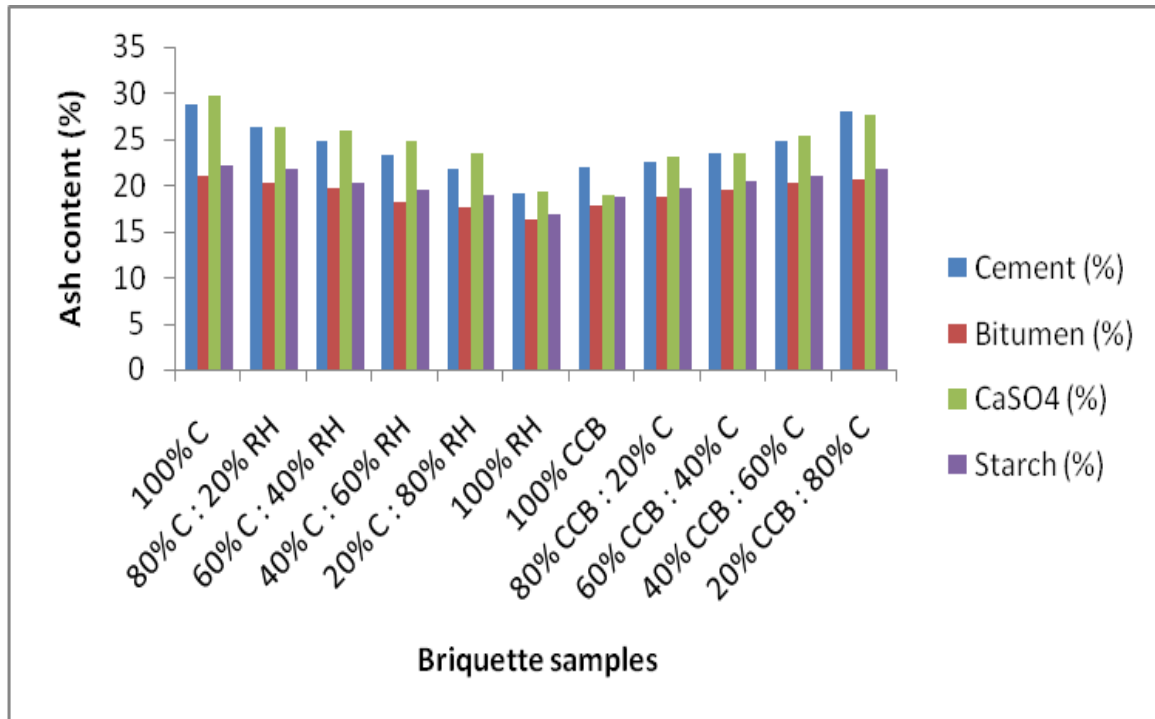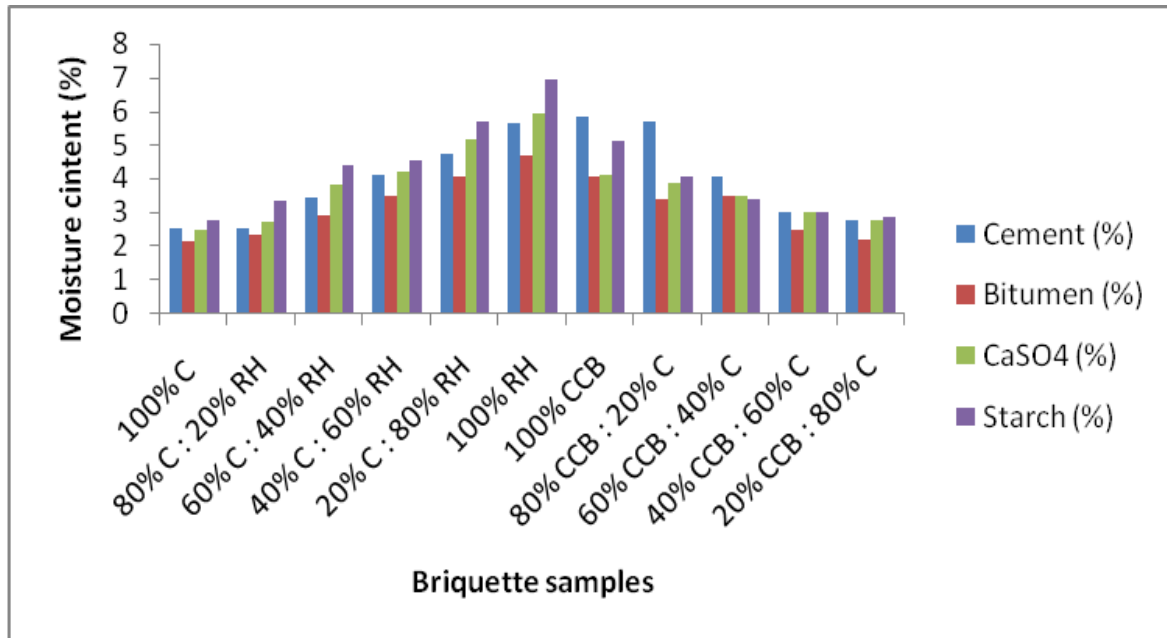

Fig.4.3: Moisture content versus briquettes samples with different binders.

4.6 The effect of density on the briquettes.

Table 4.6a, Table 4.6b and Fig.4.4 contained results of the density of the briquettes

produced from mixtures of coal, rice husk and corn cob with different binders.

Table 4.6a: Density of the briquette samples

Briquette samples (%)	Cement (g/cm^3)	Bitumen (g/cm^3)	$CaSO_4$ (g/cm^3)	Starch (g/cm^3)
100% C	0.854	0.714	0.824	0.724
80% C : 20% RH	0.694	0.574	0.684	0.594
60% C : 40% RH	0.474	0.401	0.474	0.414
40% C : 60% RH	0.344	0.294	0.374	0.334
20% C : 80% RH	0.284	0.264	0.304	0.274
100% RH	0.234	0.201	0.244	0.224
100% CCB	0.254	0.154	0.163	0.213
80% CCB : 20% C	0.273	0.222	0.303	0.284
60% CCB : 40% C	0.393	0.242	0.344	0.323
40% CCB : 60% C	0.433	0.414	0.443	0.363
20% CCB : 80% C	0.474	0.453	0.503	0.482

Key: C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.6b. ANOVA results of density of the briquette binders

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.037321	3	0.01244	0.381323	0.766985	2.838745
Within Groups	1.304958	40	0.032624			
Total	1.342279	43				

The higher the density of the fuel, the greater the energy density for a stoked fire.

This therefore influences the ratio of energy input per unit volume into a cook stove's

combustion chamber. The fuel briquette's density will affect its bulk thermal properties,

the thermal conductivity will be reduced as the density is decreased (increased fuel

porosity), but the lower the density, the less heat is required for a specific volume of fuel

to reach the ignition temperature (Loo *et al.*, 2008). This effect is seen in the increased burning time of briquettes of such binders like calcium sulphate and cement which tend to exhibit greater burning time than those of starch and bitumen.

Since coal is denser than rice husks and corn cob, the briquettes produced with higher composition of coal had a higher density value than those briquettes with higher amount of rice husk and corn cob. Additionally, if the raw material is finer, it gives a larger surface area for bonding which results in the production of briquette with higher density. The lower the porosity index of the briquettes the higher the density of the briquettes produced. These values show that for 100 % coal briquettes which values range from 0.714-0.854 g/cm^3 had a higher density than 100% rice husk with range of 0.201-0.244 g/cm^3 and followed by 100 % corn cob briquettes with values in the range of 0.154-0.254 g/cm^3. The results also show that for the binders used in the production of the briquettes, the briquettes produced with the binder cement with values in the range 0.234-0.854 g/cm^3 was the most dense followed by calcium sulphate with values (0.163-0.824 g/cm^3). The results also showed that briquettes of starch which values ranged from (0.213-0.724 g/cm^3) was denser than briquettes of bitumen with values in the range (0.154-0.714 g/cm^3). These results suggest that the relaxed density of the briquettes produced from coal dust with smaller particle size are likely to have higher relaxed density than those with larger particle size of rice husk and corn cob. The results obtained confirmed the work of Krizan (1990), who reported that in reality, in briquetting, when a large proportion of the raw material is of smaller particles, the briquette produced will have a higher density.

The one-way ANOVA analysis in Table 4.6b shows no significant difference (p>0.05) in the density for the respective binders used in this study at 95% confidence interval. For the ash contents of briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, the one-way ANOVA (Appendix 4b) showed significant difference (p<0.05) at 95 % confidence interval. The f-Test (Appendix 4c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 1.19 is less than $F_{critical}$ (0.05,3,3) which is 9.28, the null hypothesis is retained since no evidence of difference between the variances at an α of 0.05. The t-Test (Appendix 4d) of the briquette samples (60 %C:40 %RH and 60 %C:40 %CCB), showed that for the T_{stat} which is 1.05 is less than $t_{critical}$ (0.05,6) which is 2.45, there is no significant difference between the means at an α of 0.05.
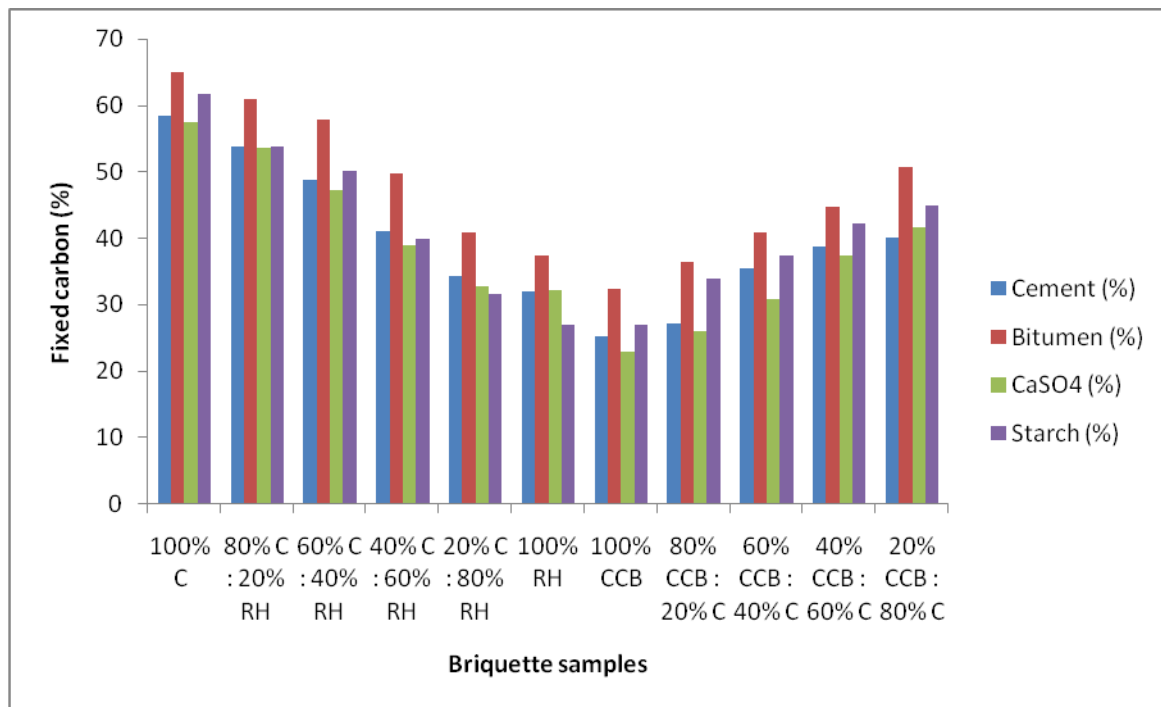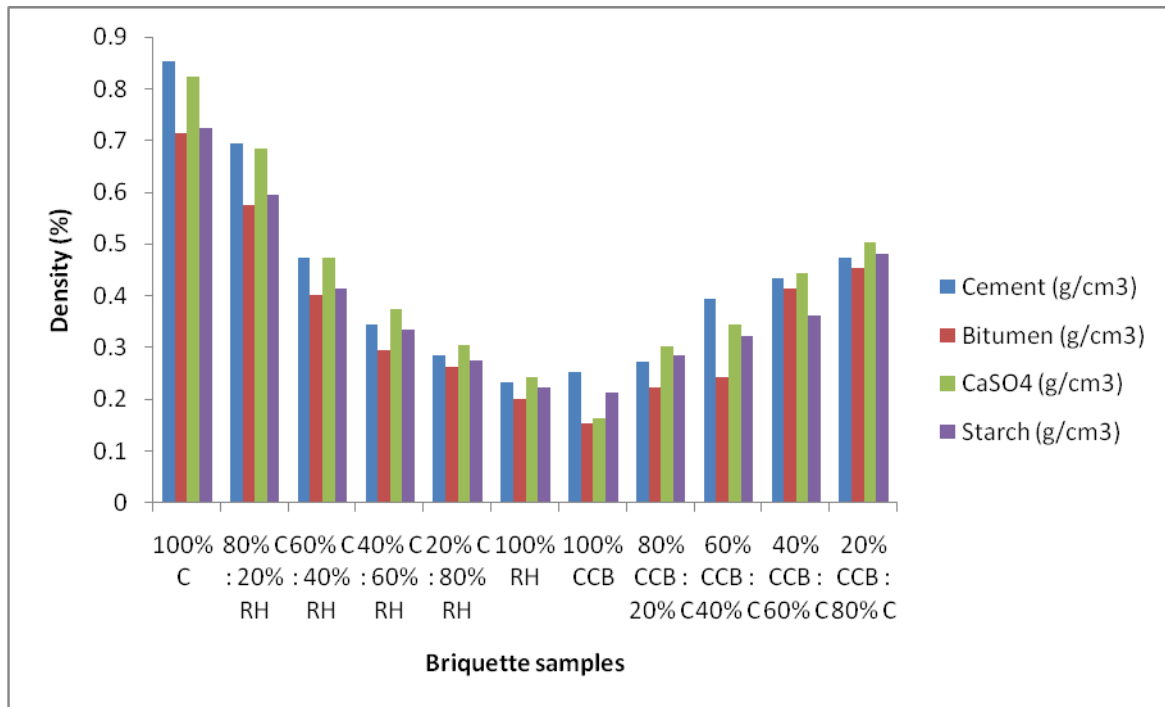
Fig. 4.4: Density versus briquettes samples with different binders

4.7 The effect of volatile matter on the briquettes.

Table 4.7a, Table 4.7b and Fig.4.5 show the results of the volatile matter in the briquettes

produced.

Table 4.7a: Amount of volatile matter of the briquette samples.

Briquette samples (%)	Cement (%)	Bitumen (%)	CaSO$_4$ (%)	Starch (%)
100% C	10.31	11.76	10.44	13.40
80% C : 20% RH	17.46	16.44	17.32	21.13
60% C : 40% RH	22.92	19.47	23.08	25.26
40% C : 60% RH	31.64	28.53	32.05	36.13
20% C : 80% RH	39.14	37.46	38.64	43.86
100% RH	43.20	41.72	42.53	49.23
100% CCB	47.00	45.77	54.00	49.27
80% CCB : 20% C	44.66	41.41	47.01	42.28
60% CCB : 40% C	37.00	36.12	42.14	38.69
40% CCB : 60% C	33.33	32.50	34.20	33.75
20% CCB : 80% C	29.05	26.48	27.91	30.42

Key: C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.7b. ANOVA results of volatile matter of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	103.9550432	3	34.65168106	0.244777969	0.864548342	2.838745406
Within Groups	5662.549	40	141.563725			
Total	5766.504043	43				

In almost all biomass, the amount of volatile matter is higher than in bituminous coal. Biomass generally has a volatile content of around 70-80 % of the weight of the dry biomass, compared to coal, which contains only about 35 % volatile matter (Loo *et al.*, 2008). Consequently, the fractional heat contribution of the volatiles is more for biomass (Demirbas, 1999). This makes biomass a more reactive fuel than coal, giving a much faster combustion rate during the devolatization phase. The volatile content has shown to

influence the thermal behavior of the solid fuel, but this is also influenced by the structure and bonding within the fuel and is therefore hard to quantify (Loo *et al.*, 2008). When the particles of a combustible material are loose, the briquettes produced would have more volatile matter during pyrolysis. Since particles of rice husk and corn cob are less bonded to each other than coal dust, 100 % rice husk briquettes which values ranged from (41.72-49.23 %) and 100 % corn cob briquettes with values in the range (45.77-54.00 %) produced more volatile matter than 100 % coal briquettes with values in the range (10.31-13.40 %) for the different binders under consideration.

The results also showed that for the binders under study that briquettes produced with calcium sulphate as binder had highest amount of volatile matter in the range 10.44-54.00 %. The volatile matter released during burning could then be reduced by producing briquettes with varying compositions of rice husk and coal, corn cob and coal thereby yielding better quality briquettes. This is true of the briquettes produced when the compositions of coal, corn cob and rice husk were varied as seen in the sample 60 % C: 40 % RH with values in the range of 19.47-25.26 % for the respective binders, and for the sample 60 % C:40 % CCB which ranged from 32.50-33.75 %. The reduction in the amount of the volatile matter made the briquettes to combust slowly and with a resultant increase in the calorific values.

The one-way ANOVA in Table 4.7b shows no significant difference ($p > 0.05$) in the volatile matter for the respective binders used in this study at 95 % confidence interval. The one-way ANOVA (Appendix 5b) of the volatile matter of the briquette samples (100

%C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, however showed significant difference (p<0.05) at 95 % confidence interval. The f-Test (Appendix 5c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 10.95 is less than $F_{critical}$ (0.05,3,3) which is 15.44, therefore there is no significant difference between the variances at α of 0.05. The t-Test (Appendix 5d) of the briquette samples (60 %C:40 %RH and 60 %C:40 %CCB), showed that for the T_{stat} which is -8.61 is less than $t_{critical}$ (0.05,6) which is 2.45, therefore no significant difference between the means at an α of 0.05.
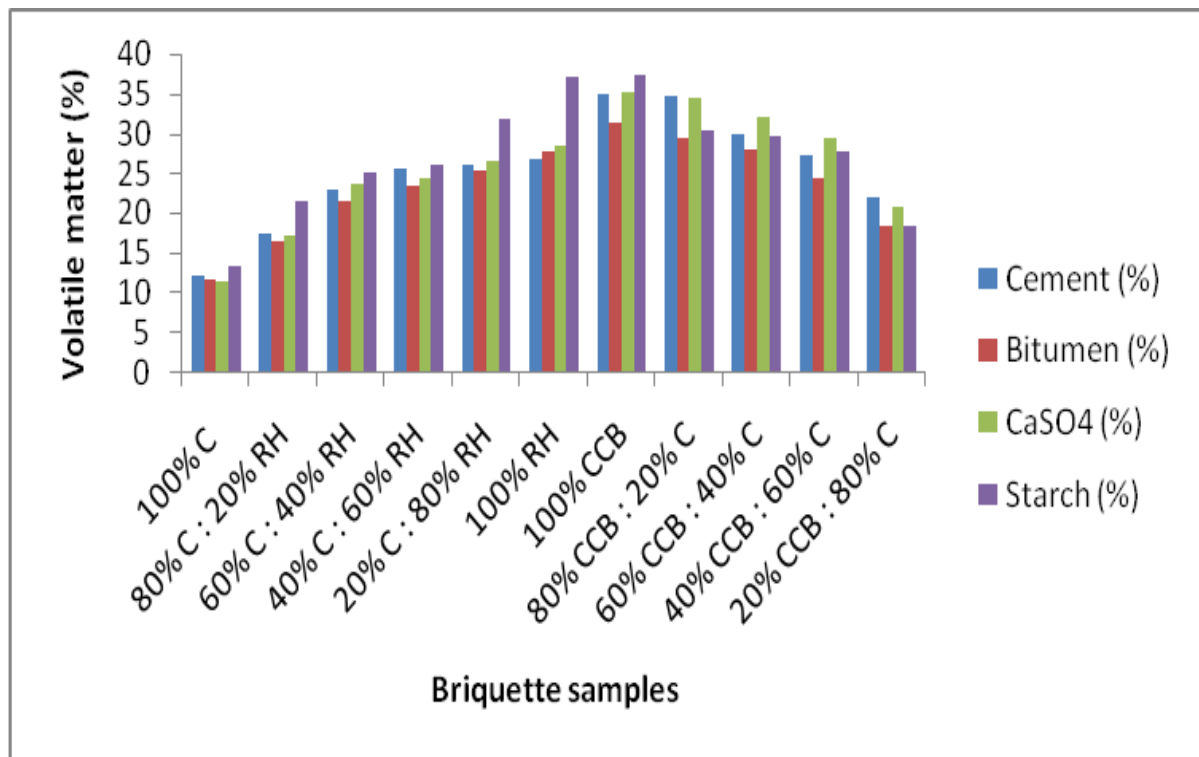
Fig. 4.5: Volatile matter versus briquettes samples with different binders

4.8 The effect of porosity index on the briquettes.

Table 4.8a, Table 4.8b and Fig.4.6 show the porosity index of the briquettes produced

with different binders.

Table 4.8a: Porosity index values of the briquettes samples.

Briquette samples (%)	Cement (%)	Bitumen (%)	CaSO$_4$ (%)	Starch (%)
100% C	24.82	22.02	25.10	24.96
80% C : 20% RH	32.55	31.33	34.01	33.66
60% C : 40% RH	42.47	38.74	42.53	40.76
40% C : 60% RH	57.83	47.61	59.98	50.48
20% C : 80% RH	66.21	56.95	66.72	62.52
100% RH	72.09	64.72	73.65	70.13
100% CCB	80.11	78.69	80.25	79.26
80% CCB : 20% C	76.33	69.87	71.86	70.80
60% CCB : 40% C	69.47	53.66	66.78	62.88
40% CCB : 60% C	50.21	48.12	53.62	49.64
20% CCB : 80% C	45.38	39.68	41.11	40.12

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.8b. ANOVA results of porosity index of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	263.7021	3	87.90072	0.281497	0.838431	2.838745
Within Groups	12490.47	40	312.2618			
Total	12754.17	43				

In effect the values of porosity index show that the briquettes of biomass in which

the particles are more adhered to each other do have lower value than those that are made

up of loose particles. The coal dust particles are more adhered to each other than the

coarse loose particles of rice husks and corn cob. For this reason, when 100 % coal

briquettes which ranged from 22.02-25.10 % are compared with 100 % rice husk

briquettes with values 64.72-73.65 % or 100 % corn cob briquettes 78.69-80.25 % for the

respective binders, the briquettes of coal had lower porosity index values than briquettes made from rice husks with the briquettes of corn cob being the most porous. The formation of briquettes by the blending of rice husk or corn cob to coal produces different briquettes with different porosity indices. The values for coal and rice husk briquettes of 60 % C: 40 %RH are 38.74-42.53 %, coal and corn cob of 60 % C:40 % CCB ranged from 53.66-69.47 %. The possibility of briquetting coal with rice husk or corn cob, introduces more pores into the briquettes which would aid in the passage of oxygen that is needed for complete combustion to take place when the briquettes are burnt.

The one-way ANOVA in Table 4.8b shows no significant difference (p>0.05) in the values of the porosity index for the respective binders used in this study at 95% confidence interval. The one-way ANOVA (Appendix 6b) of the porosity index of briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, showed significant difference (p<0.05) at 95 % confidence interval. For the f-Test (Appendix 6c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} which is 0.59 is greater than $F_{critical}$ (0.05,3,3) which is 0.07, there is evidence of a significant difference between the variances at α of 0.05. Also the t-Test (Appendix 6d) of the briquette samples (60 %C:40 %RH and 60 %C:40 %CCB), showed that for the T_{stat} which is -6.33 is less than $t_{critical}$ (0.05,6) which is 2.45, confirmed that at 95% confidence interval that there is no significant difference between the means at an α of 0.05.
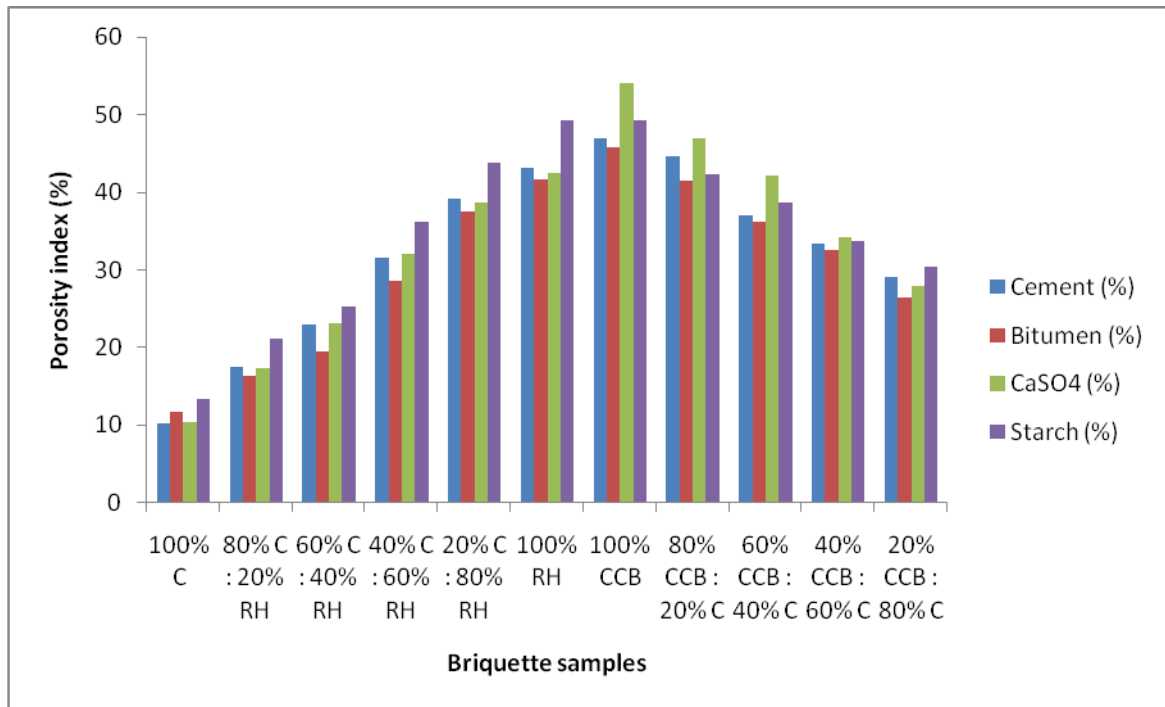
Fig. 4.6: Porosity index versus briquettes samples with different binders.

4.9 The effect of calorific values on the briquettes.

Table 4.9a, Table 4.9b and Fig.4.7 show the calorific values of the briquettes of coal, rice husk and corn cob with different binders.

Table 4.9a: Calorific values of the briquette samples.

Briquette samples (%)	Cement (kJ/kg)	Bitumen (kJ/kg)	$CaSO_4$ (kJ/kg)	Starch (kJ/kg)
100% C	23482.42	25238.36	23558.79	25519.89
80% C : 20% RH	24304.88	26088.37	24199.62	25650.93
60% C : 40% RH	24441.12	27083.07	24840.95	25921.82
40% C : 60% RH	22667.42	24961.28	22567.52	23813.43
20% C : 80% RH	20541.53	22569.36	20506.44	22532.94
100% RH	19701.57	20981.48	19615.16	21739.54
100% CCB	20364.34	21691.64	19000.54	21450.82
80% CCB : 20% C	21273.55	22347.46	22817.89	21864.73
60% CCB : 40% C	22600.12	23274.92	23083.75	23057.21
40% CCB : 60% C	22823.93	23940.37	23219.07	23794.98
20% CCB : 80% C	21512.56	23249.22	21295.99	22309.03

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.9b. ANOVA results of calorific value of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	22057669	3	7352556	2.361895	0.085681	2.838745
Within Groups	1.25E+08	40	3112990			
Total	1.47E+08	43				

The calorific (heating) value is the standard measure of the energy content of a fuel. It is defined as the amount of heat evolved when a unit weight of fuel is completely burnt and the combustion products are cooled to 298 K. However, in stoves, any moisture that is contained in the fuel and which formed in the combustion process is removed as water vapour, and so its heat is not available (BSI, 2005).

The heating value of a particular fuel relates to the amount of oxygen that is required for complete combustion. For every gram of oxygen burnt, 14,022 Joules of energy are released. Consequently, fuels containing carbon with a higher degree of oxidation will have a lower heating value, because less oxygen is required for their complete oxidation. In contrast, when fuels contain compounds such as hydrocarbons, these possesses lower degree of oxidation, they tend to raise the heating value of the biomass (Jenkins *et al*., 1998). It is for this reason that biomass fuels, in which the carbon is present in a partly oxidized form, have a lower heating value than coal (Buckley, 1991). The calorific value is limited by fuel moisture content, because heat is used to vaporize the water, lowering the heat released (Ragland and Aerts, 1991). The results show that 60 % coal: 40 % rice husk, and 60 % coal: 40 % corn cob briquettes of all the binders had the highest calorific values that ranged from (244412.12-27083.07 kJ/kg) and (22823.93-23940.37 kJ/kg) respectively. The calorific values of briquettes made with binders such as starch (21450.82-25921.82 kJ/kg) and bitumen (20981.48-27083.07 kJ/kg) as binders had higher values, but those briquettes produced with bitumen had the highest values. The higher carbon atom number of bitumen makes available more carbon that is used up during combustion since bitumen has carbon atom from C-70 and above. The briquettes burned with much smoke as a result of incomplete combustion introducing carbon(II) oxide into the air. This position was confirmed by the works of Taulbee *et al.*(2009) and Emerhi (2011).

The calorific values show that 100 % rice husk briquettes in which different binders had significant values in the range 19615.16-21739.54 kJ/kg and 100 % corn cob

briquettes (19000.54-21691.64 kJ/kg). It could also be seen that briquettes produced with cement as binder with values in the range 19701.57-24441.12 kJ/kg and briquettes made with calcium sulphate as binder have values between 19000.54-24840.95 kJ/kg had lower calorific values. These binders had higher ash content values and as such lower calorific values, this is in agreement with the work of Loo and Koppejan (2008). The energy values and combustion qualities of the briquettes produced in this study are sufficient enough to produce the required heat for domestic cooking and for industrial application especially the energy requirement of the small-scale industries.

The one-way ANOVA in Table 4.9b shows no significant difference (p>0.05) in the calorific values for the respective binders used in this study at 95 % confidence interval. The one-way ANOVA (Appendix 7b) of the calorific value of the briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, however showed significant difference (p<0.05). The f-Test (Appendix 7c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 5.24 is less than $F_{critical}$ (0.05,3,3) which is 15.4, therefore there is no significant difference between the variances at α of 0.05. The t-Test (Appendix 7d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), show that for the t_{stat} which is 3.29 is greater than $t_{critical}$ (0.05,4) which is 2.78, there is significant difference between the means at an α of 0.05.
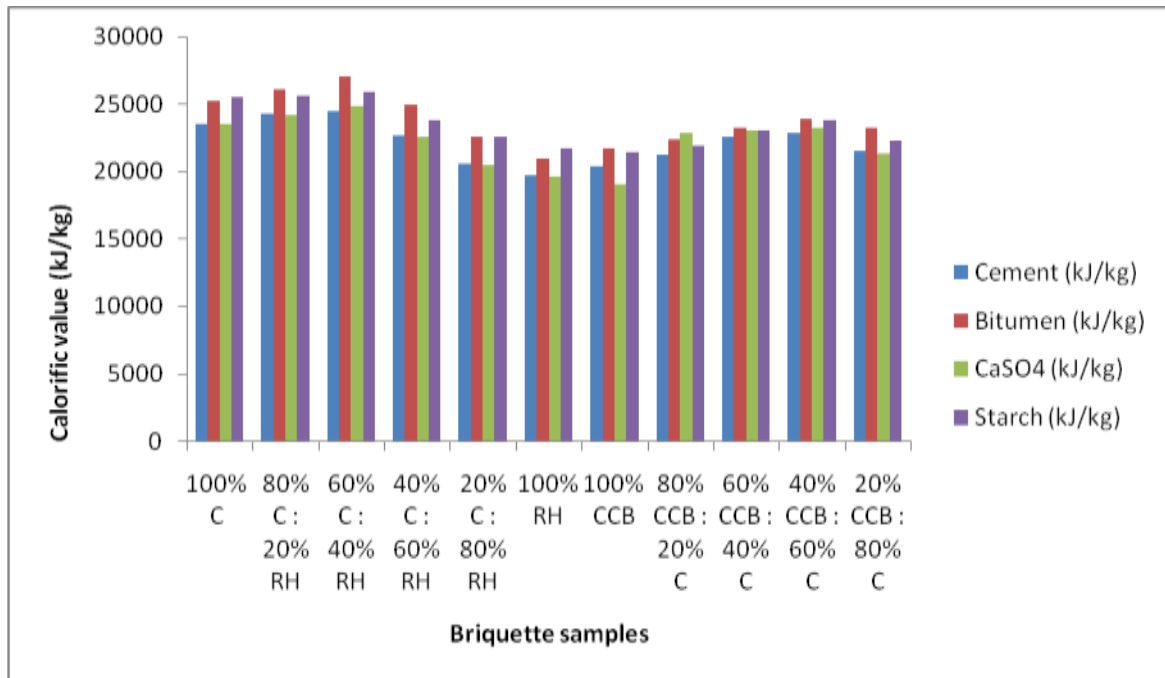
Fig. 4.7: Calorific values versus briquette samples with different binders.

4.10 The effect of water boiling test on the briquettes.

Table 4.10a, Table 4.10b and Fig.4.8 show the water boiling tests of the briquettes produced with different binders.

Table 4.10a: Water boiling test of the briquette samples.

Briquette samples (%)	Cement (g/min)	Bitumen (g/min)	$CaSO_4$ (g/min)	Starch (g/min)
100% C	1.58	1.63	1.44	1.42
80% C : 20% RH	1.79	1.84	1.60	1.62
60% C : 40% RH	2.10	2.25	2.14	2.15
40% C : 60% RH	2.86	3.17	2.85	2.91
20% C : 80% RH	3.26	3.75	3.28	3.42
100% RH	4.05	4.38	4.07	4.12
100% CCB	4.75	4.57	4.87	4.32
80% CCB : 20% C	3.46	3.14	3.71	3.22
60% CCB : 40% C	2.70	2.62	2.87	2.69
40% CCB : 60% C	2.12	2.10	2.24	2.05
20% CCB : 80% C	1.72	1.64	1.71	1.65

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.10b. ANOVA results of water boiling test of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	0.045570455	3	0.0151902	0.013079	0.997921	2.838745
Within Groups	46.45605455	40	1.1614014			
Total	46.501625	43				

The water boiling test measures the time taken for a given quantity of fuel to heat and boil a given quantity of water (Mangena and Cann, 2007). In this case a known mass of briquette (100 g) each of the different compositions of briquettes made with different binders was used to boil a given quantity of water (250 cm^3) using small stainless cup and domestic briquette stove. The results showed that briquettes produced using calcium

sulphate as binder with values in the range (1.44-4.87 g/min) took longer time to boil water when compared with the other briquettes produced. For the other binders the values are cement (1.58-4.75 g/min), bitumen (1.63-4.57 g/min) and starch (1.42-4.32 g/min). The high amount of ash content of calcium sulphate also affected the water boiling property. For the briquettes produced, the results showed that 100 % coal briquettes for the different binders (1.42-1.63 g/min) burned water faster than the briquettes of 100 % rice husk (4.05-4.38 g/min) and 100% corn cob (4.57-4.87 g/min). The results also show that there were not much differences in the time it took 100 %C (1.42-1.63 g/min) for the different binders under consideration to boil water as against briquette samples 60 %C: 40 %RH (2.10-2.15 g/min) and briquette samples 60 %C: 40 %CCB (2.05-2.24 g/min). The results obtained are in line with the work of Onuegbu *et. al*.,(2011).

The one-way ANOVA in Table 4.10b show no significant difference (p>0.05) in the water boiling test for the respective binders used in this study at 95 % confidence interval. The one-way ANOVA (Appendix 8b) of the water boiling test of the briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, however showed significant difference (p<0.05) at 95 % confidence interval. The f-Test (Appendix 8c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 0.63 is greater than $F_{critical}$ (0.05,3,3) which is 0.05, therefore there is significant difference between the variances at α of 0.05. The t-Test (Appendix 8d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), showed that for the T_{stat} which is 0.63 is less than $t_{critical}$

(0.05,4) which is 2.45, there is no significant difference between the means at an α of 0.05.
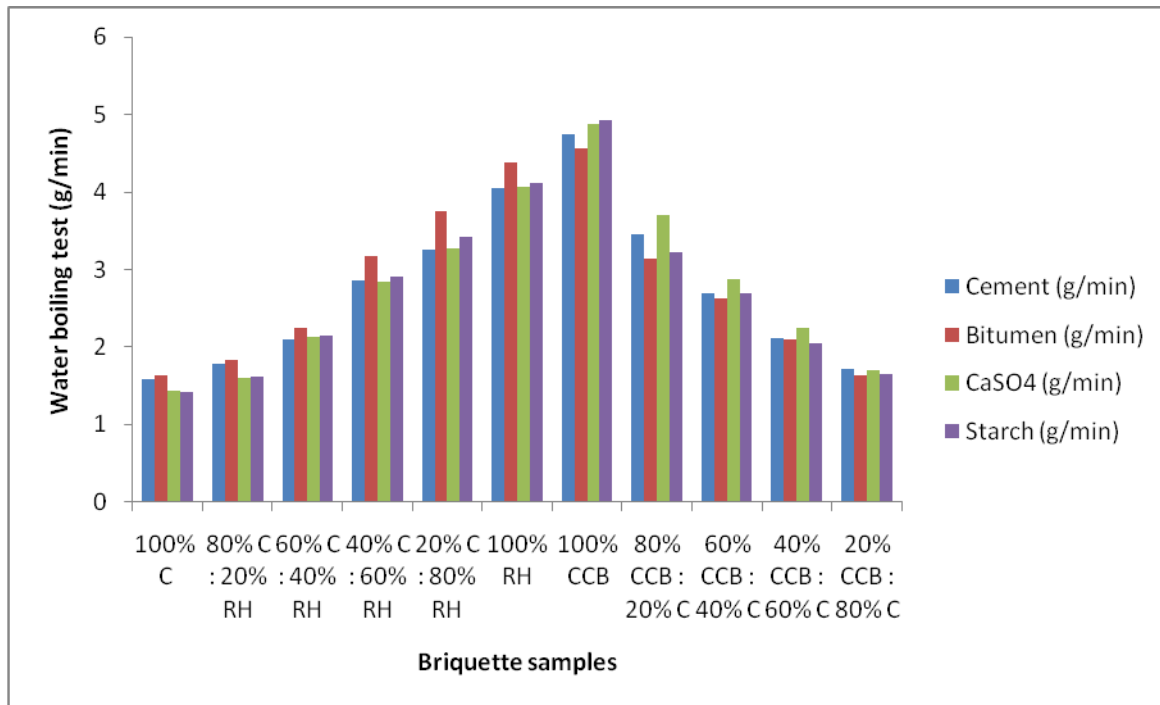
Fig. 4.8: Water boiling test versus briquettes samples with different binders.

4.11 The effect of burning time of the briquettes.

Table 4.11a, Table 4.11b and Fig.4.9 show the burning time of the briquettes produced.

Table 4.11a: Burning time of the briquette samples.

Briquette samples (%)	Cement (min)	Bitumen (min)	$CaSO_4$ (min)	Starch (min)
100% C	26.27	24.89	26.84	26.21
80% C : 20% RH	23.31	20.76	23.75	24.15
60% C : 40% RH	20.42	17.81	19.85	20.43
40% C : 60% RH	17.55	14.55	18.96	19.22
20% C : 80% RH	16.09	12.88	16.34	17.48
100% RH	15.57	11.71	15.68	16.17
100% CCB	16.23	14.13	16.00	15.27
80% CCB : 20% C	17.34	16.43	18.01	16.28
60% CCB : 40% C	19.45	18.56	20.14	19.69
40% CCB : 60% C	21.12	19.76	22.20	20.75
20% CCB : 80% C	24.34	23.28	25.91	24.42

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.11b. ANOVA results of burning time of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	46.75736	3	15.58578788	1.039619811	0.38547459	2.83874541
Within Groups	599.6726	40	14.991815			
Total	646.43	43				

Biomass briquettes, due to their varied nature in terms of constituent materials, the conditions under which they are formed and the moisture content of their briquettes are likely to show significant differences in their thermal properties. These properties are not only for briquettes of different materials, but also for briquettes of same material formed (Ravi *et al.*,2003). From the results, 100 % coal briquettes of the different binders in the range 24.89-26.84 min had the longest burning time for all the briquettes produced followed by 100 % corn cob briquettes (14.13-16.23 min) while 100 % rice husk

briquettes (11.71-16.17 min) of all the different binders had the least burning time. The briquetting of rice husk/corn cob and coal yielded briquettes with improved burning time. The briquettes of binders such as cement (15.57-26.27 min) and briquettes produced with the binder calcium sulphate (15.68-26.84 min) had reasonable burning time. This might be due to the presence of incombustible compounds that are likely to take long time before complete pyrolysis takes place. The briquette produced with bitumen as binder had lower burning time (11.71-24.89 min), the smoky nature of briquettes made them burn much faster thereby affecting the rate of combustion of the briquettes produced. The smoke generated during burning by briquettes of that were produced with bitumen made them environmentally unfriendly because the smoke contained carbon(II) oxide that irritated the eyes during cooking. The briquettes produced with starch as the binder on the contrary combusted and burned much freely with the production of blue flame which was due to complete combustion, making the briquettes to be environmentally friendly. The burning time of the briquettes showed improvement as the compositions increased with regards to coal.

The one-way ANOVA in Table 4.11b showed no significant difference (p>0.05) in burning time for the respective binders used at 95 % confidence interval. The one-way ANOVA (Appendix 9b) of the burning time of the briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced, however showed significant difference (p<0.05) at 95 % confidence interval. The f-Test (Appendix 9c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 1.52 is less than $F_{critical}$ (0.05,3,3) which

is 15.44, we retain the null hypothesis and no evidence of a difference between the variances at α of 0.05. The t-Test (Appendix 9d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), showed that for the T_{stat} which is -1.66 is less than $t_{critical}$ (0.05,4) which is 2.45, there is no significant difference between the means at an α of 0.05.
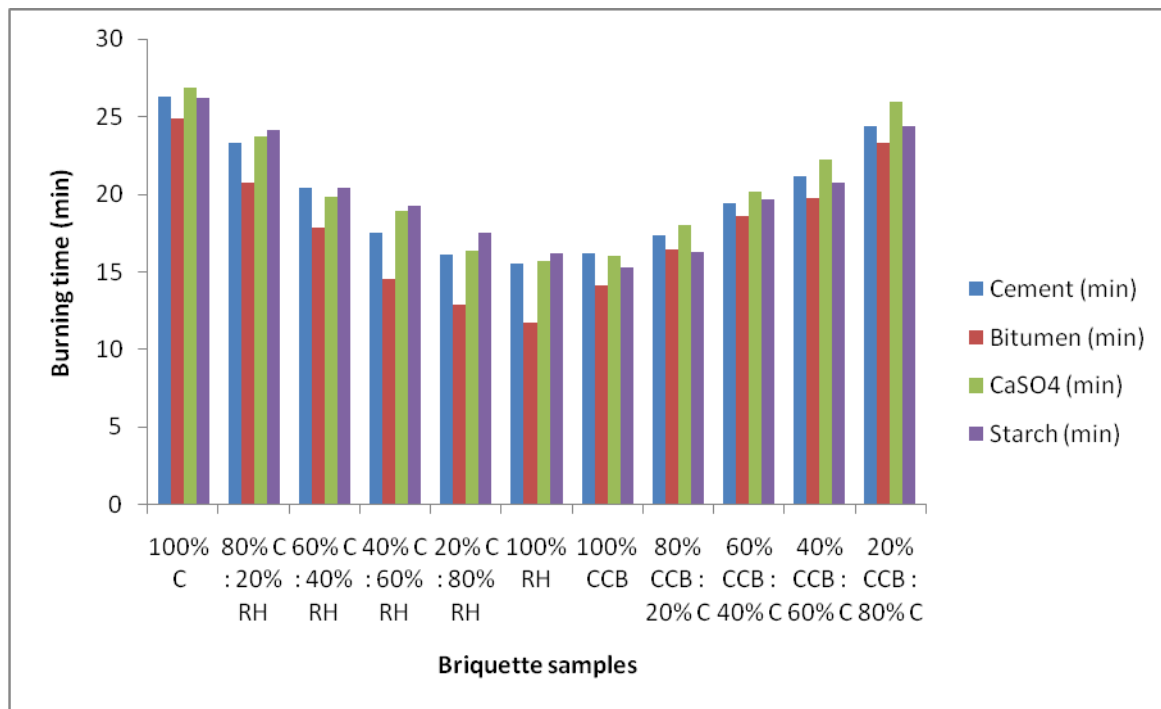

Fig. 4.9: Burning time versus briquettes samples with different binders.

4.12 The effect of ignition time of the briquettes.

Table 4.12a, Table 4.12b and Fig.4.10 show the ignition time of the briquettes produced.

Table 4.12a: Ignition time of the briquette samples.

Briquette samples (%)	Cement (s)	Bitumen (s)	CaSO$_4$ (s)	Starch (s)
100% C	46.00	37.00	46.66	47.33
80% C : 20% RH	37.33	27.67	39.33	41.00
60% C : 40% RH	29.30	21.67	33.10	33.67
40% C : 60% RH	25.30	19.33	28.67	29.67
20% C : 80% RH	23.60	17.67	25.67	27.00
100% RH	23.00	16.00	24.33	23.33
100% CCB	25.50	23.20	30.36	29.60
80% CCB : 20% C	32.65	24.10	32.50	31.44
60% CCB : 40% C	37.00	27.70	34.54	32.52
40% CCB : 60% C	42.50	29.56	37.12	34.40
20% CCB : 80% C	44.00	35.14	41.40	41.22

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.12b. ANOVA results of ignition time of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	571.0770182	3	190.3590061	3.552303	0.022677	2.838745
Within Groups	2143.499655	40	53.58749136			
Total	2714.576673	43				

Briquettes are a blend of substances, when they are heated their temperature rises, the heat propagates into the briquette, evaporating moisture and when the surface becomes sufficiently hot a process of thermal decomposition of the briquettes takes place. The pyrolysis front moves into the briquette, driven by the temperature gradient. The small volume of the solid which is undergoing pyrolysis at any one moment in time is known as the pyrolysis reaction zone (Kung, 1972). The ignition of a briquette sample occured when the briquette was lighted, combusts and heat propagated through the block

of briquette. The 100 % C briquette samples (37.00-47.33 s) ignited much slower for the different binders than the 100 % RH briquette samples (16.00-24.33 s) and 100 % CCB (23.20-30.36 s). The briquettes with more composition of biomass ignited faster than coal briquettes because of the porous nature of the briquettes of the biomass that allowed more passage of oxygen which supports combustion. The briquettes showed a progression in values of the ignition time of the briquettes produced. Therefore, as the composition of coal and rice husk/corn cob briquettes were varied, it was found that the rate of ignitability of the briquettes improved tremendously. Coal briquettes would not ignite very fast but the briquetting of coal with either corn cob or rice husk would produce fuel sources that would solve the problem of fast ignitability of sources of fuel. This is in agreement with the work of Raju *et al.,* (2014), where they reported that the ignition time of the briquettes increased with increase in biomass concentration.

The one-way ANOVA (Table 4.12b) shows significant difference (p<0.05) in the values of the ignition time for the respective binders at 95 % confidence interval. The one-way ANOVA (Appendix 10b) of the ignition time of the briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced showed significant difference since p<0.05. The f-Test (Appendix 10c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 1.05 is less than $F_{critical}$ (0.05,3,3) which is 15.44, we retain the null hypothesis and no evidence of a difference between the variances at α of 0.05. The t-Test (Appendix 10d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB),

showed that for the T_{stat} which is -1.66 is less than $t_{critical}$ (0.05,4) which is 2.45, there is no significant difference between the means at an α of 0.05.
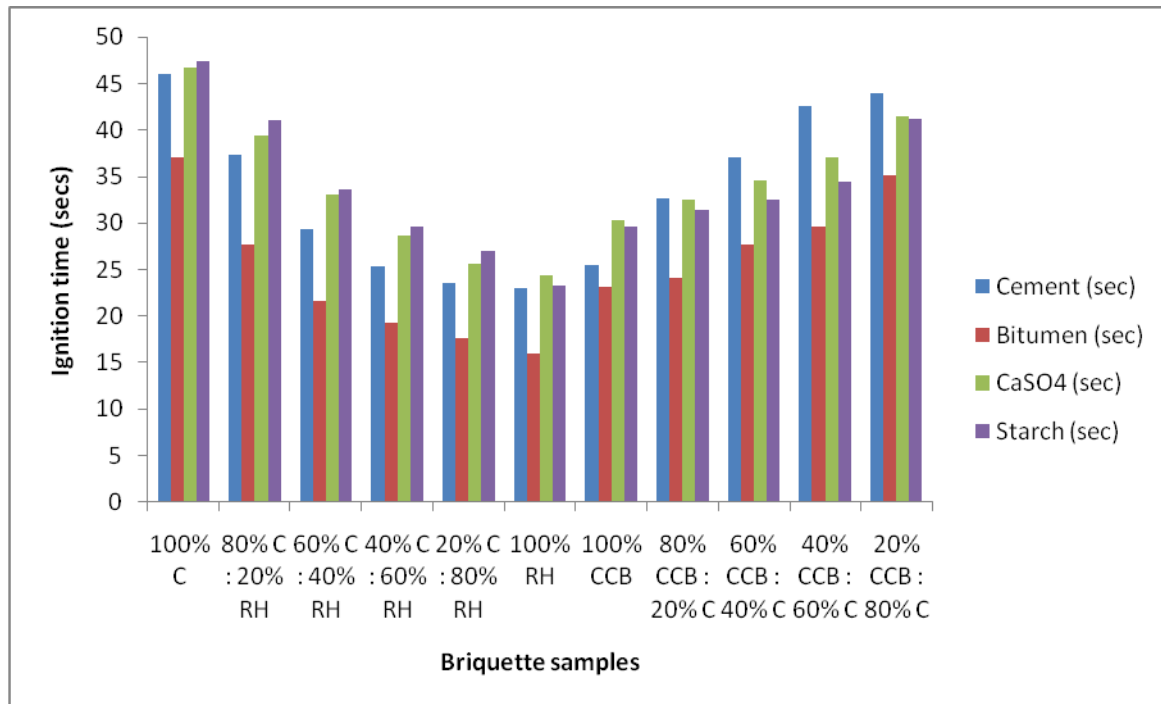

Fig. 4.10: Ignition Time versus Briquettes Samples with Different Binders.

4.13 The sulphur content of the briquettes.

Table 4.13a, Table 4.13b and Fig. 4.11 shows the total sulphur content of the briquettes produced with the different binders.

Table 4.13a: Sulphur contents of the briquette samples.

Briquette samples (%)	Cement (%)	Bitumen (%)	$CaSO_4$ (%)	Starch (%)
100% C	8.20	8.22	7.87	6.21
80% C : 20% RH	7.17	8.02	7.18	5.52
60% C : 40% RH	7.02	7.78	7.04	4.69
40% C : 60% RH	6.68	7.43	6.72	4.42
20% C : 80% RH	6.02	6.29	5.91	4.14
100% RH	4.17	4.21	4.12	3.45
100% CCB	4.91	3.01	3.18	3.03
80% CCB : 20% C	6.88	5.89	5.92	4.12
60% CCB : 40% C	7.01	6.39	6.98	4.98
40% CCB : 60% C	7.56	7.56	7.13	5.78
20% CCB : 80% C	8.03	8.19	7.42	6.05

Key: C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.13b. ANOVA results of sulphur contents of the briquette binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	27.23574	3	9.078579	4.723111	0.006496	2.838745
Within Groups	76.88644	40	1.922161			
Total	104.1222	43				

The methods to control sulphur dioxide emissions from coal-fired briquettes include switching to a lower sulphur fuel, cleaning the coal to remove the sulphur bearing components such as pyrite (Davis, 2000). Coal preparation processes, which are physical processes designed mainly to provide ash removal, energy enhancement and product stabilization. Sulphur reduction is required because the ash produced contains pyritic

sulphur. Coal cleaning is used for moderate sulphur dioxide emissions control, as physical coal cleaning is not effective in removing organically bound sulphur (Elliot, 1998). Since the above processes are difficult for the rural dwellers, the introduction of the desulpurizer $Ca(OH)_2$ in the briquettes helped to solve the problem of coal-sulphur cleaning. The amount of total sulphur content in the range 6.21-8.20 % were highest for 100 % coal briquettes for the different binders when compared to the values of 60 %C: 40 %RH which is 4.69-7.78 % and for 40 %CCB: 60 %C (5.78-7.56 %) for the binders used in the production. The addition of the desulphurizer in the coal and rice husk/corn cob briquettes reduced the sulphur content for the briquettes for different binders. On the average 100 % corn cob briquettes with values in the range 3.01-4.91 % had the least values of sulphur content but when other properties are considered especially the calorific value, there is the need therefore to introduce desulphurizing agents during coal briquetting. The results are in agreement with the study carried out by Osuwan *et. al.*,(1989). Optimum addition of calcium oxide in coal briquetting can improve the stove efficiency, and calcium oxide functions as a desulpurizing agent effectively. With no calcium oxide, only 15-30 % of the sulphur originally present in coal will be retained in the ash after combustion, mostly in the form of sulphates. With the rest released into the atmosphere as sulpur oxides, thereby causing pollution.

The one-way ANOVA in Table 4.13b showed significant difference ($p<0.05$) in the sulpur content of the respective binders at 95 % confidence interval. The one-way ANOVA (Appendix 11b) of the sulphur content of the briquette samples (100 %C, 60

%C: 40 %RH and 60 %C: 40 %CCB) produced showed no significant difference (p>0.05) at 95 % confidence interval. The f-Test (Appendix 11c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 2.54 is less than $F_{critical}$ (0.05,3,3) which is 15.44, we retain the null hypothesis and no evidence of a difference between the variances at α of 0.05. The t-Test (Appendix 11d) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), showed that for the T_{stat} which is -0.47 is less than $t_{critical}$ (0.05,4) which is 2.45, there is no significant difference between the means at an α of 0.05.
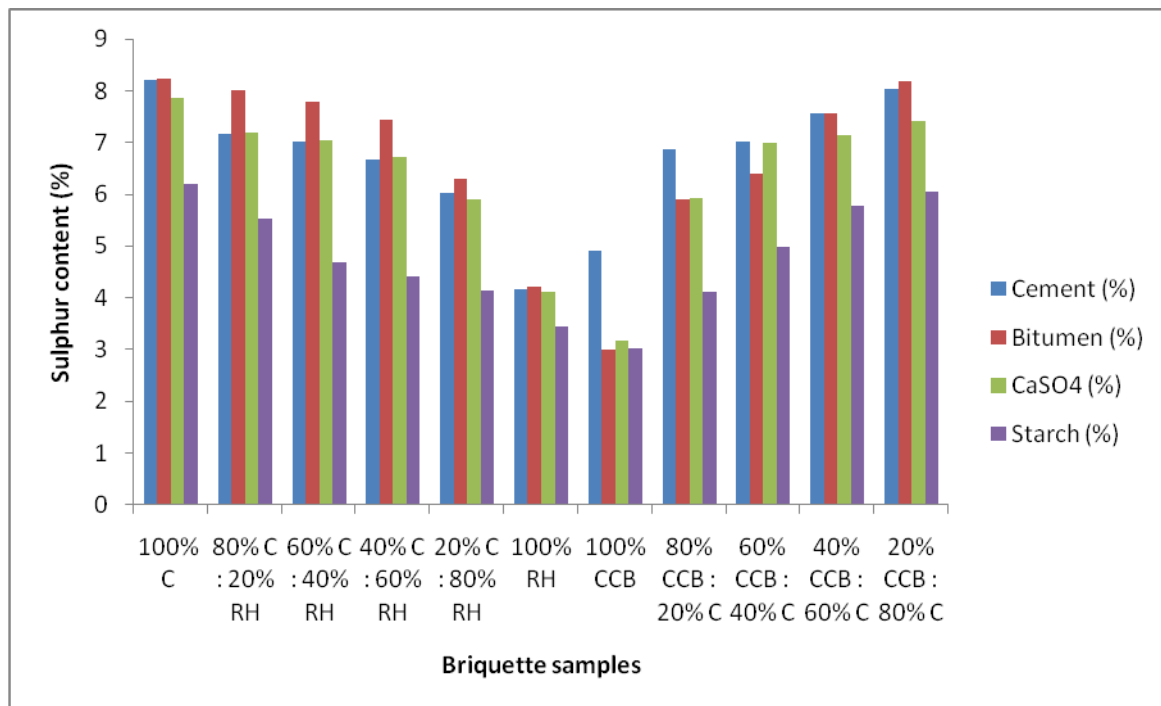
Fig. 4.11: Sulphur content versus briquettes samples with different binders.

4.14 The compressive strength of the briquettes.

Table 4.14a, Table 4.14b and Fig. 4.12 shows the compressive strength of the briquettes produced with the different binders.

Table 4.14a: Compressive strength of the briquette samples

Briquette samples (%)	Cement (N/mm^3)	Bitumen (N/mm^3)	CaSO$_4$ (N/mm^3)	Starch (N/mm^3)
100% C	7.23	7.05	7.11	7.92
80% C : 20% RH	7.74	9.42	8.22	9.78
60% C : 40% RH	10.47	11.76	11.52	13.02
40% C : 60% RH	11.34	13.56	12.63	13.95
20% C : 80% RH	11.82	12.57	12.36	13.74
100% RH	10.98	11.94	12.24	12.36
100% CCB	11.19	12.03	11.61	12.72
80% CCB : 20% C	11.67	13.14	12.57	13.89
60% CCB : 40% C	12.06	13.65	12.75	14.13
40% CCB : 60% C	12.75	14.01	13.17	14.46
20% CCB : 80% C	12.30	12.96	12.90	14.25

Key : C=Coal, RH=Rice husk and CCB=Corn cob

Table 4.14b. ANOVA Results of Compressive Strength of the Briquette Binders

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	20.5695	3	6.8565	1.733092	0.175651	2.838745
Within Groups	158.249	40	3.956224			
Total	178.8185	43				

The compressive strength of briquettes is one of the indices used to assess its ability to be handled, packed and transported without breaking (Onuegbu *et al.,*2010). The results show that the compressive strength in cleft for the briquettes increased with the briquetting of the coal with the biomass. The values for the compressive strength in cleft for briquettes produced with starch as the binder ranged from 7.92-14.46 N/mm^3 to record the highest values. This is probably due to the nature of biomass with the presence

of cellulose which helps to bind the briquette together and probably reduce the brittleness of the briquette. The briquettes produced using cement as binders with values ranging from 7.23-12.75 N/mm^3 and the briquettes produced with calcium sulphate as binders with values ranging from 7.11-13.17 N/mm^3 had lower compressive strength values. This might be due to the lower amount of cellulosic matter that is needed to bind the briquettes stronger during compression. The values obtained from the study are similar to the values obtained in the study carried out by Mitchual *et al.*,(2014). This result contradicts the values obtained in the work of Križan, (2007) where it was reported that mechanical strength of pellets are inversely proportional to particle size since smaller particles have greater surface area for moisture addition during steam conditioning, this result in increased starch gelatinization and better binding. The reason for the deviation is that, in this study, the briquettes were formed at room temperature, therefore the formation of strong bond resulting from the natural bonding of chemicals may be absent or minimal.

The one-way ANOVA in Table 4.14b show no significant difference (p>0.05) in the compressive strength for the respective binders at 95% confidence interval. The one-way ANOVA (Appendix 12b) of the compressive strength of the briquette samples (100 %C, 60 %C: 40 %RH and 60 %C: 40 %CCB) produced showed significant difference (p<0.05) at 95 % confidence interval. The f-Test (Appendix 12c) of the briquette samples (60 %C: 40 %RH and 60 %C: 40 %CCB), F_{exp} is 1.81 is less than $F_{critical}$ (0.05,3,3) which is 15.44, we retain the null hypothesis and no evidence of a difference between the variances at α of 0.05. The t-Test (Appendix 12d) of the briquette samples

(60 %C: 40 %RH and 60 %C: 40 %CCB), showed that for the T_{stat} which is -2.92 is less than $t_{critical}$ (0.05,4) which is 2.45, there is no significant difference between the means at an α of 0.05.
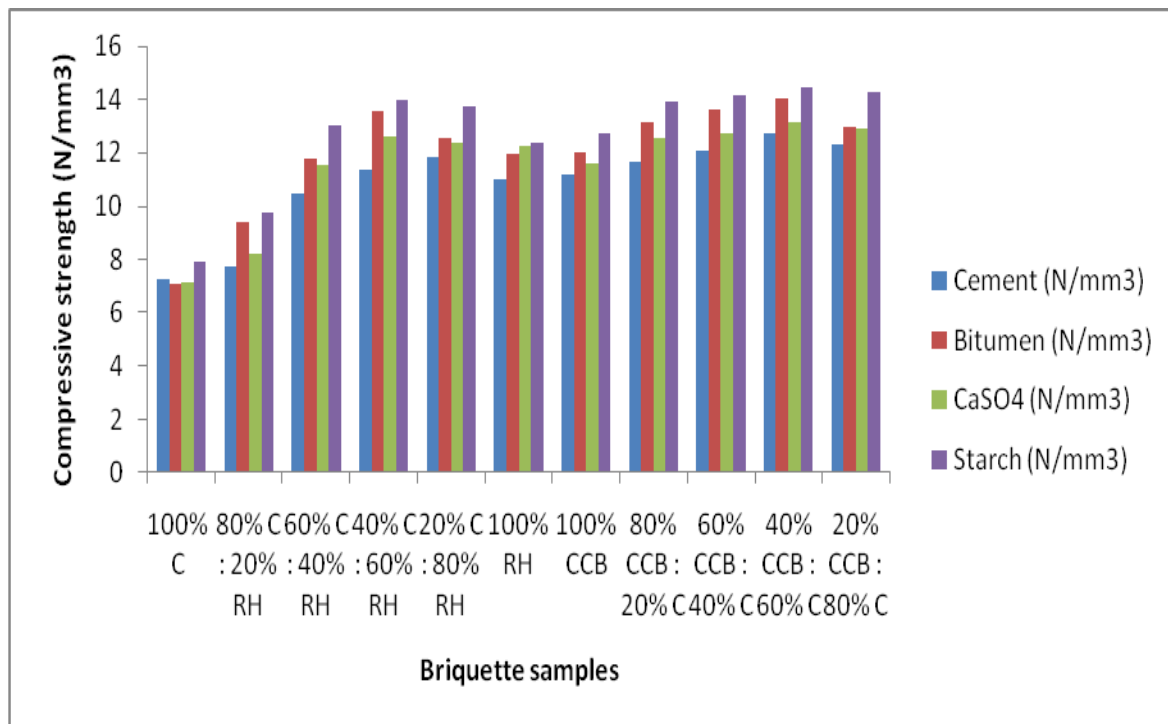

Fig. 4.12: Compressive Strength versus Briquettes Samples with Different Binders.

CHAPTER FIVE

5.1   Conclusions

From the investigations carried out in the study, the following conclusions were arrived at:

The 100 % coal briquettes had high calorific values in the range of 23558.79-25519.89 kJ/kg for the respective binders used in the production of briquettes, therefore the briquettes are very suitable sources of fuel. The calorific values of 100 % rice husk briquettes was found to be in the range of 19615.16-21739.54 kJ/kg and that of 100% corn cob briquettes was in the range of 19000.54-21691.64 kJ/kg, which showed significant calorific value, and as such they are also good sources of cooking fuel. Briquettes produced from blending 60 % coal and 40 % rice husk had higher calorific values which range from 24441.12-27083.07 kJ/kg, while 60 %C: 40 %CCB briquettes had calorific values in the range of 22823.93-23940.37 kJ/kg are significantly high. The calorific values are comparable to the sample of 100 % coal briquettes produced with different binders. The 60 % coal 40 % rice husk ignited between 21.67-33.67 s while that of 60 % coal and 40 % corn cob ignited in the range of 29.56-42.5 s, these briquettes ignited much faster than the 100 % coal briquettes for the respective binders under consideration. A relatively long burning time in the range of 17.81-20.43 minutes was recorded for 60 % coal and 40 % rice husk and 19.76-22.20 minutes for 60 % coal and 40 % corn cob, the values are comparable to 100 % coal briquettes with values in the range of 24.89-26.84 minutes. According to the sulphur contents of the briquettes after

combustion, it reduced from 6.21-8.22 % sulphur content value for 100 % coal to the range of 4.69-7.78 % for 60 % coal and 40 % rice husk and from 5.78-7.56 % for 60 % coal and 40 % corn cob for the different binders used. This reduction was due to the desulphurizing agent, $Ca(OH)_2$ that was added to the briquettes during blending, this gave briquettes with lower sulphur contents thereby making these briquettes environmentally friendly.

The research also showed varying amounts of fixed carbon for the briquettes. Although 100 % coal briquettes had highest amount of fixed carbon ranging from 57.46-65.04 % for the briquettes produced with the different binders used, the values observed in 60 % coal and 40 % rice husk (47.18-57.94 %) and for 60 % corn cob and 40 % coal (30.93-40.96 %) for the respective binders under consideration are comparable to the 100 % coal. It could be suggested that the higher number of carbon atoms of the binder bitumen contributed to higher amount of fixed carbon noticed in the briquettes as against the briquettes of cement (25.17-58.34 %), calcium sulphate (22.98-57.46 %) and starch (26.92-61.76 %).

The respective binders used for the briquetting (cement, calcium sulphate, bitumen and starch) could be used when producing briquettes because they contributed in making the briquettes produced portable, easy to handle and stable after production. A comparison of some of the tests carried out showed that the ignition time of the briquettes produced with different binders are in the order bitumen (17.67-35.14 s), calcium sulphate (25.67-41.40 s), cement (23.60-44.00 s) and starch (27.00-41.22 s). This showed

that briquettes produced with bitumen ignited much faster than all the briquettes under consideration. This could be attributed to the presence of hydrocarbon fractions in bitumen. The results of the calorific values of the briquettes produced with the different binders are in the following range, starch (21450.82-25921.82 kJ/kg), bitumen (20981.48-27083.07 kJ/kg), calcium sulphate (19000.54-24840.95 kJ/kg) and cement (19701.57-24441.12 kJ/kg). The results showed that briquettes produced with bitumen as binder had the highest calorific values. This is possibly due to higher amount of carbon atoms in bitumen which is C-70 and above as against other binders used for briquette production. The results of the burning time for the briquettes produced with respective binders are in the range, calcium sulphate (16.34-25.91 min), starch (17.48-24.42 min), cement (16.09-24.34 min) and bitumen (14.55-23.28 min). The briquettes produced with calcium sulphate had the longest burning time due the presence of non combustible materials. The high ash content values of briquettes produced with binders like cement (21.78-28.00 %) and calcium sulphate (23.45-27.69 %) respectively, showed that the briquettes produced fouled the stoves when used. The briquettes produced with bitumen as binder emitted more smoke during combustion than other briquettes thereby making it not eco-friendly, this could be attributed to the presence of heavy oils in bitumen.

For the binders under consideration the use of starch as a binder is strongly recommended during briquetting because the briquettes produced with starch as the binder had better results for ignition time ranging from (27.00-41.22 s), highest compressive strength values (7.92-13.95 N/mm^3), lowest sulphur emission values (4.14-

6.05 %), significantly high calorific values in the range (21450.82-25921.82kJ/kg) and relatively longer burning time (17.48-24.42 min) for the different binders under consideration. The binder bitumen is not suitable for briquetting due to the much smoke emitted by the briquettes produced with it due to incomplete combustion. Cement and calcium sulphate are expensive, their briquettes fouls stoves during cooking producing much ash and are not easily affordable to the rural dwellers. Therefore, they are not recommended for use as binders.

In this work when the properties of the different briquette compositions produced were compared, the briquette sample 60 % coal and 40 % rice husk briquettes had highest calorific values (24441.12-27083.07 kJ/kg) and 60 % coal and 40 % corn cob (22823.93-23940.37 kJ/kg), speedy ignitable property for 60% coal and 40% rice husk (21.67-33.67 sec) while 60 % coal and 40 % corn cob (29.56-42.50 s). The burning time for 60 % coal and 40 % rice husk values are (17.81-20.43 min) while 60 % coal and 40 % corn cob (19.76-22.20 min). The compressive strength values for 60 % coal and 40 % rice husk in the range of (11.34-13.95 N/mm^3) and 60 % coal and 40 % corn cob (12.75-14.46 N/mm^3) were higher than those of 100 % coal with values ranging from (7.05-7.92 N/mm^3). The briquettes did not disintegrate when handled. The lower amount of sulphur contents for 60 % coal and 40 % rice husk (4.69-7.78 %), while 60 % coal and 40 % corn cob values are (5.78-7.56 %) when combusted as against the values of (6.21-8.22 %) for 100 % coal briquettes made the briquettes better alternative source of fuel. These features

made the composition very good for domestic cooking and even better than the 100 % coal briquettes.

The concentration of heavy metals determined using X-ray fluorescence spectrometer, showed that the concentration of the heavy metals in the ashes of coal included (V_2O_5 0.29 ± 0.0048 %, Cr_2O_3 0.059± 0.0011 %, MnO 0.13 ± 0.0012 %, CuO 0.18 ± 0.0041 %, As_2O_3 0.05 ± 0.0023 %, PbO 0.31± 0.0081 %), that of rice husk are (V_2O_5 0.002 ± 0.0011 %, MnO 0.153 ± 0.0013 %, CuO 0.012 ± 0.0031 %, As_2O_3 0.0063 ± 0.0001 %, PbO 0.004± 0.0001 %) and the concentration of heavy metals in corn cob are (Cr_2O_3 0.346± 0.0032 %, MnO 0.123 ± 0.0006 %, SrO 0.023± 0.0014 %), the values are all less than 1 % respectively in the ashes. Thus the concentrations are relatively small, the ashes therefore can be disposed off after cooking.

Therefore, the research showed that agricultural wastes in terms of rice husk and corn cob that are generated in large quantity and disposed indiscriminately can be utilized for the production of smokeless briquette fuel. A measure that would curb the environmental hazards posed by poor methods of agricultural waste disposal as well as converting waste- to- wealth.

5.2   Contributions to Knowledge

The innovation that was also developed in this study was the use of starch as a binder and it was observed that briquettes produced with starch as binders had complete combustion with high calorific value, low ash content, high compressive strength and longer burning time.

The materials and method used in the production of the briquettes from agro-wastes can be easily adopted at the local communities as it does not require expertise or special training before implementation.

The biomass briquettes gave efficient fuel source through which the carbon(IV) oxides mitigation and other climate changing problems can be easily reduced. Therefore, the technology indirectly contributes in the saving of the environment.

The elemental composition of the ashes of coal, rice husk and corn cob showed low level in the concentration of heavy metals, therefore the ashes of the briquettes can be used for soil enrichment.

5.3   Recommendations

The following recommendations are necessary from the work:

1. The cooking efficiency of coal briquettes can be improved by blending with wastes such as rice husk and corn cob thereby reducing the environmental problems associated with the open burning of the wastes.

2. The use of briquette should be given wide publicity in Nigeria due to the imminent wood shortage and scarcity of other energy sources.

3. Since briquetting technology is not a new innovation, it is therefore recommended that the rural population should be encouraged to adopt the technology by making available to them the fabricating machines to reduce the pressure mounted on the forest in search of fuel wood.

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APPENDIX 1A

ANOVA Table of the Ash content of the briquette binders

Groups	Count	Sum	Average	Variance
Cement (%)	11	264.71	24.06455	8.143647
Bitumen (%)	11	209.71	19.06455	2.254347
CaSO$_4$ (%)	11	267.79	24.34455	10.63599
Starch (%)	11	220.84	20.07636	2.500305

APPENDIX 1B

ANOVA Table of the ash content of some briquette composition

Groups	Count	Sum	Average	Variance
100%C	4	101.57	25.3925	19.91189
60% C : 40% RH	4	90.65	22.6625	9.969092
40% CCB : 60% C	4	91.31	22.8275	6.855158

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	18.7458	2	9.3729	0.765423	0.493181175	4.25649473
Within Groups	110.2084	9	12.24538			
Total	128.9542	11				

APPENDIX 1C

F-Test Two-Sample for Variances (Ash content)

	60% C : 40% RH	40% CCB : 60% C
Mean	22.6625	22.8275
Variance	9.969091667	6.855158333
Observations	4	4
Df	3	3
F	1.454246741	
P(F<=f) one-tail	0.382846829	
F Critical one-tail	15.43918238	

APPENDIX 1D

t-Test: Two-Sample Assuming Equal Variances (Ash content)

	60% C : 40% RH	40% CCB : 60% C
Mean	22.6625	22.8275
Variance	9.969091667	6.855158333
Observations	4	4
Pooled Variance	8.412125	
Hypothesized Mean Difference	0	
Df	6	
t Stat	-0.080453711	
P(T<=t) one-tail	0.469246427	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.938492854	
t Critical two-tail	2.446911846	

APPENDIX 2A

ANOVA Table of the fixed carbon of the briquette binders
SUMMARY

Groups	Count	Sum	Average	Variance
Cement (%)	11	435.09	39.55364	110.4749
Bitumen (%)	11	517.31	47.02818	115.5225
$CaSO_4$ (%)	11	421.27	38.29727	119.6615
Starch (%)	11	449.54	40.86727	123.9018

APPENDIX 2B

ANOVA Table of the fixed carbon of some briquette composition
SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	242.6	60.65	12.00547
60% C : 40% RH	4	204.01	51.0025	22.78283
40% CCB : 60% C	4	163.34	40.835	11.12403

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	785.448717	2	392.7244	25.66137	0.000191393	4.25649473
Within Groups	137.736975	9	15.30411			
Total	923.185692	11				

APPENDIX 2C

F-Test Two-Sample for Variances (fixed carbon)

	60% C : 40% RH	40% CCB : 60% C
Mean	51.0025	40.835
Variance	22.782825	11.12403333
Observations	4	4
Df	3	3
F	2.048072342	
P(F<=f) one-tail	0.285493221	
F Critical one-tail	15.43918238	

APPENDIX 2D

t-Test: Two-Sample Assuming Equal Variances (fixed carbon)

	60% C : 40% RH	40% CCB : 60% C
Mean	51.0025	40.835
Variance	22.782825	11.12403333
Observations	4	4
Pooled Variance	16.95342917	
Hypothesized Mean Difference	0	
Df	6	
t Stat	3.492210396	
P(T<=t) one-tail	0.006474234	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.012948469	
t Critical two-tail	2.446911846	

APPENDIX 3A

ANOVA Table of the moisture content of the briquette binders
SUMMARY

Groups	Count	Sum	Average	Variance
Cement (%)	11	44.49	4.044545	1.641947
Bitumen (%)	11	35.32	3.210909	0.733209
$CaSO_4$ (%)	11	41.62	3.783636	1.147445
Starch (%)	11	46.2	4.2	1.73926

APPENDIX 3B

ANOVA Table of the moisture content of some briquette composition
SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	9.92	2.48	0.066867
60%C:40%RH	4	14.61	3.6525	0.398225
60%C:40%CCB	4	11.57	2.8925	0.068625

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	2.830017	2	1.415008	7.953705	0.010247	4.256495
Within Groups	1.60115	9	0.177906			
Total	4.431167	11				

APPENDIX 3C

F-Test Two-Sample for Variances (moisture content)

	60%C:40%RH	60%C:40%CCB
Mean	3.6525	2.8925
Variance	0.398225	0.068625
Observations	4	4
Df	3	3
F	5.80291439	
P(F<=f) one-tail	0.091339907	
F Critical one-tail	15.43918238	

APPENDIX 3D

t-Test: Two-Sample Assuming Equal Variances (moisture content)

	60%C:40%RH	60%C:40%CCB
Mean	3.6525	2.8925
Variance	0.398225	0.068625
Observations	4	4
Pooled Variance	0.233425	
Hypothesized Mean Difference	0	
Df	6	
t Stat	2.224615231	
P(T<=t) one-tail	0.033883068	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.067766137	
t Critical two-tail	2.446911846	

APPENDIX 4A

ANOVA Table of the density of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement	11	4.711	0.428273	0.037744
Bitumen	11	3.933	0.357545	0.029855
CaSO4	11	4.66	0.423636	0.037516
Starch	11	4.229	0.384455	0.02538

APPENDIX 4B

ANOVA Table of the density of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	3.116	0.779	0.004967
60%C:40%RH	4	1.763	0.44075	0.001502
60%C:40%CCB	4	1.653	0.41325	0.001267

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.331923	2	0.165962	64.36084	4.66E-06	4.256495
Within Groups	0.023208	9	0.002579			
Total	0.355131	11				

APPENDIX 4C

F-Test Two-Sample for Variances
(Density)

	60%C:40%RH	60%C:40%CCB
Mean	0.44075	0.41325
Variance	0.00150225	0.001266917
Observations	4	4
Df	3	3
F	1.185752812	
P(F<=f) one-tail	0.445963051	
F Critical one-tail	9.276628154	

APPENDIX 4D

t-Test: Two-Sample Assuming Equal Variances (Density)

	60%C:40%RH	60%C:40%CCB
Mean	0.44075	0.41325
Variance	0.00150225	0.001266917
Observations	4	4
Pooled Variance	0.001384583	
Hypothesized Mean Difference	0	
Df	6	
t Stat	1.045172903	
P(T<=t) one-tail	0.168105479	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.336210958	
t Critical two-tail	2.446911846	

APPENDIX 5A

ANOVA Table of the volatile matter of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement (%)	11	355.71	32.33727273	136.0359018
Bitumen (%)	11	337.66	30.69636364	125.2264655
$CaSO_4$ (%)	11	369.32	33.57454545	172.1292073
Starch (%)	11	383.42	34.85636364	132.8633255

APPENDIX 5B

ANOVA Table of the volatile matter of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	45.91	11.4775	2.071758333
60%C:40%RH	4	90.73	22.6825	5.726025
60%C:40%CCB	4	133.78	33.445	0.5231

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	965.27265	2	482.636325	174.0090465	6.41188E-08	4.256494729
Within Groups	24.96265	9	2.773627778			
Total	990.2353	11				

APPENDIX 5C

F-Test Two-Sample for Variances (volatile matter)

	60%C:40%RH	60%C:40%CCB
Mean	22.6825	33.445
Variance	5.726025	0.5231
Observations	4	4
Df	3	3
F	10.94632957	
P(F<=f) one-tail	0.040066255	
F Critical one-tail	15.43918238	

APPENDIX 5D

t-Test: Two-Sample Assuming Equal Variances (volatile matter)

	60%C:40%RH	60%C:40%CCB
Mean	22.6825	33.445
Variance	5.726025	0.5231
Observations	4	4
Pooled Variance	3.1245625	
Hypothesized Mean Difference	0	
Df	6	
t Stat	-8.610602763	
P(T<=t) one-tail	6.74951E-05	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.00013499	
t Critical two-tail	2.446911846	

APPENDIX 6A

ANOVA Table of the porosity index of the briquette binders
SUMMARY

Groups	Count	Sum	Average	Variance
Cement (%)	11	617.47	56.13364	339.3791
Bitumen (%)	11	551.39	50.12636	287.012
CaSO4 (%)	11	615.61	55.96455	324.5265
Starch (%)	11	585.21	53.20091	298.1294

APPENDIX 6B

ANOVA Table of the porosity index of some briquette composition
SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	96.9	24.225	2.173967
60%C:40%RH	4	164.5	41.125	3.2015
60%C:40%CCB	4	201.59	50.3975	5.393492

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	1408.78535	2	704.3927	196.2286	3.78E-08	4.256495
Within Groups	32.306875	9	3.589653			
Total	1441.092225	11				

APPENDIX 6C

F-Test Two-Sample for Variances (porosity index)

	60%C:40%RH	60%C:40%CCB
Mean	41.125	50.3975
Variance	3.2015	5.393491667
Observations	4	4
Df	3	3
F	0.593585788	
P(F<=f) one-tail	0.339419618	
F Critical one-tail	0.064770269	

APPENDIX 6D

t-Test: Two-Sample Assuming Unequal Variances (porosity index)

	60%C:40%RH	60%C:40%CCB
Mean	41.125	50.3975
Variance	3.2015	5.393491667
Observations	4	4
Hypothesized Mean Difference	0	
Df	6	
t Stat	-6.325634693	
P(T<=t) one-tail	0.000364827	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.000729654	
t Critical two-tail	2.446911846	

APPENDIX 7A

ANOVA Table of the calorific values of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement (kj/kg)	11	243713.4	22155.77	2553729
Bitumen (kj/kg)	11	261425.5	23765.96	3603224
$CaSO_4$ (kj/kg)	11	244705.7	22245.97	3573586
Starch (kj/kg)	11	257655.3	23423.21	2721420

APPENDIX 7B

ANOVA Table of the calorific values of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100% C	4	97799.46	24449.87	1165547
60% C : 40% RH	4	102287	25571.74	1406343
40% CCB : 60% C	4	93778.35	23444.59	268216.4

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	9058619	2	4529309	4.784301	0.038422	4.256495
Within Groups	8520321	9	946702.4			
Total	17578940	11				

APPENDIX 7C

F-Test Two-Sample for Variances (calorific value)

	60% C : 40% RH	40% CCB : 60% C
Mean	25571.74	23444.5875
Variance	1406343.328	268216.3555
Observations	4	4
Df	3	3
F	5.243316819	
P(F<=f) one-tail	0.103435397	
F Critical one-tail	15.43918238	

APPENDIX 7D

t-Test: Two-Sample Assuming Unequal Variances (calorific value)

	60% C : 40% RH	40% CCB : 60% C
Mean	25571.74	23444.5875
Variance	1406343.328	268216.3555
Observations	4	4
Hypothesized Mean Difference	0	
Df	4	
t Stat	3.287594965	
P(T<=t) one-tail	0.015141909	
t Critical one-tail	2.131846782	
P(T<=t) two-tail	0.030283819	
t Critical two-tail	2.776445105	

APPENDIX 8A

ANOVA Table of the water boiling test of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement	11	30.39	2.7627273	1.063782
Bitumen	11	31.09	2.8263636	1.123765
CaSO4	11	30.78	2.7981818	1.219056
Starch	11	30.17	2.7427273	1.239002

APPENDIX 8B

ANOVA Table of the water boiling test of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	6.07	1.5175	0.010692
60%C:40%RH	4	8.64	2.16	0.004067
60%C:40%CCB	4	8.51	2.1275	0.006492

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.04795	2	0.523975	73.97294	2.59E-06	4.256495
Within Groups	0.06375	9	0.007083			
Total	1.1117	11				

APPENDIX 8C

F-Test Two-Sample for Variances (water boiling test)

	60%C:40%RH	60%C:40%CCB
Mean	2.16	2.1275
Variance	0.004066667	0.006491667
Observations	4	4
df	3	3
F	0.626444159	
P(F<=f) one-tail	0.355079348	
F Critical one-tail	0.064770269	

APPENDIX 8D

t-Test: Two-Sample Assuming Equal Variances (water boiling test)

	60%C:40%RH	60%C:40%CCB
Mean	2.16	2.1275
Variance	0.004066667	0.006491667
Observations	4	4
Pooled Variance	0.005279167	
Hypothesized Mean Difference	0	
df	6	
t Stat	0.632580314	
P(T<=t) one-tail	0.275169419	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.550338839	
t Critical two-tail	2.446911846	

APPENDIX 9A

ANOVA Table of the burning time of the briquette binders
SUMMARY

Groups	Count	Sum	Average	Variance
Cement	11	217.69	19.79	13.25568
Bitumen	11	194.76	17.70545455	18.05838727
CaSO4	11	223.68	20.33454545	15.25268727
Starch	11	220.07	20.00636364	13.40050545

APPENDIX 9B

ANOVA Table of the burning time of some briquette composition
SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	104.21	26.0525	0.681225
60%C:40%RH	4	78.51	19.6275	1.541625
60%C:40%CCB	4	83.83	20.9575	1.01575833

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	92.0114	2	46.0057	42.6161752	2.57E-05	4.256495
Within Groups	9.715825	9	1.079536111			
Total	101.727225	11				

APPENDIX 9C

F-Test Two-Sample for Variances (Burning time)

	60%C:40%RH	60%C:40%CCB
Mean	19.6275	20.9575
Variance	1.541625	1.015758333
Observations	4	4
Df	3	3
F	1.517708444	
P(F<=f) one-tail	0.37002233	
F Critical one-tail	15.43918238	

APPENDIX 9D

t-Test: Two-Sample Assuming Equal Variances (Burning time)

	60%C:40%RH	60%C:40%CCB
Mean	19.6275	20.9575
Variance	1.541625	1.015758333
Observations	4	4
Pooled Variance	1.278691667	
Hypothesized Mean Difference	0	
Df	6	
t Stat	-1.663350302	
P(T<=t) one-tail	0.073650676	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.147301352	
t Critical two-tail	2.446911846	

APPENDIX 10A

ANOVA Table of the ignition time of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement (sec)	11	366.18	33.28909	73.17921
Bitumen (sec)	11	279.04	25.36727	46.2565
$CaSO_4$ (sec)	11	373.68	33.97091	46.10775
Starch (sec)	11	371.18	33.74364	48.80651

APPENDIX 10B

ANOVA Table of the ignition time of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100% C	4	176.99	44.2475	23.63982
60% C : 40% RH	4	117.74	29.435	30.5603
40% CCB : 60% C	4	143.58	35.895	29.16463

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	441.208	2	220.604	7.938751	0.010303	4.256495
Within Groups	250.0943	9	27.78825			
Total	691.3023	11				

APPENDIX 10C

F-Test Two-Sample for Variances (ignition time)

	60% C : 40% RH	40% CCB : 60% C
Mean	29.435	35.895
Variance	30.5603	29.16463333
Observations	4	4
Df	3	3
F	1.047854765	
P(F<=f) one-tail	0.485124673	
F Critical one-tail	15.43918238	

APPENDIX 10D

t-Test: Two-Sample Assuming Equal Variances (ignition time)

	60% C : 40% RH	40% CCB : 60% C
Mean	29.435	35.895
Variance	30.5603	29.16463333
Observations	4	4
Pooled Variance	29.86246667	
Hypothesized Mean Difference	0	
Df	6	
t Stat	-1.67180137	
P(T<=t) one-tail	0.072797639	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.145595279	
t Critical two-tail	2.446911846	

APPENDIX 11A

ANOVA Table of the sulphur content of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement (%)	11	73.65	6.695455	1.527787
Bitumen (%)	11	72.99	6.635455	2.940247
CaSO$_4$ (%)	11	69.47	6.315455	2.114967
Starch (%)	11	52.39	4.762727	1.105642

APPENDIX 11 B

ANOVA Table of the sulphur content of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	30.5	7.625	0.915633
60% C : 40% RH	4	26.53	6.6325	1.802092
40% CCB : 60% C	4	28.03	7.0075	0.710758

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	2.009317	2	1.004658	0.879099	0.447985	4.256495
Within Groups	10.28545	9	1.142828			
Total	12.29477	11				

APPENDIX 11C

F-Test Two-Sample for Variances (sulphur content)

	60% C : 40% RH	40% CCB : 60% C
Mean	6.6325	7.0075
Variance	1.802091667	0.710758333
Observations	4	4
Df	3	3
F	2.535449227	
P(F<=f) one-tail	0.232471194	
F Critical one-tail	15.43918238	

APPENDIX 11D

t-Test: Two-Sample Assuming Equal Variances (sulphur content)

	60% C : 40% RH	40% CCB : 60% C
Mean	6.6325	7.0075
Variance	1.802091667	0.710758333
Observations	4	4
Pooled Variance	1.256425	
Hypothesized Mean Difference	0	
Df	6	
t Stat	-0.47312727	
P(T<=t) one-tail	0.326422028	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.652844056	
t Critical two-tail	2.446911846	

APPENDIX 12A

ANOVA Table of the compressive strength of the briquette binders

SUMMARY

Groups	Count	Sum	Average	Variance
Cement (N/mm^3)	11	119.55	10.86818	3.207976
Bitumen (N/mm^3)	11	132.09	12.00818	4.296256
$CaSO_4$ (N/mm^3)	11	127.08	11.55273	4.003282
Starch (N/mm^3)	11	140.22	12.74727	4.317382

APPENDIX 12 B

ANOVA Table of the compressive strength of some briquette composition

SUMMARY

Groups	Count	Sum	Average	Variance
100%C	4	29.31	7.3275	0.161625
60% C : 40% RH	4	46.77	11.6925	1.097025
40% CCB : 60% C	4	54.39	13.5975	0.605025

ANOVA

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	82.6602	2	41.3301	66.53	4.05E-06	4.256495
Within Groups	5.591025	9	0.621225			
Total	88.25123	11				

APPENDIX 12C

F-Test Two-Sample for Variances (compressive strength)

	60% C : 40% RH	40% CCB : 60% C
Mean	11.6925	13.5975
Variance	1.097025	0.605025
Observations	4	4
df	3	3
F	1.813189538	
P(F<=f) one-tail	0.318572535	
F Critical one-tail	15.43918238	

APPENDIX 12D

t-Test: Two-Sample Assuming Equal Variances (compressive strength)

	60% C : 40% RH	40% CCB : 60% C
Mean	11.6925	13.5975
Variance	1.097025	0.605025
Observations	4	4
Pooled Variance	0.851025	
Hypothesized Mean Difference	0	
df	6	
t Stat	-2.920376323	
P(T<=t) one-tail	0.013309132	
t Critical one-tail	1.943180274	
P(T<=t) two-tail	0.026618264	
t Critical two-tail	2.446911846	

APPENDIX 13

PAGE OF ABBREVIATIONS

ABBREVIATIONS	MEANING
SiO_2	Silicon IV oxide
SO_3	Sulphur VI oxide
CaO	Calcium oxide
TiO_2	Titanium IV oxide
V_2O_5	Vanadium pentaoxide
Cr_2O_3	Chromium VI oxide
MnO	Manganese II oxide
Fe_2O_3	Iron III oxide
NiO	Nickel II oxide
CuO	Copper II oxide
As_2O_3	Arsenic trioxide
ZrO_2	Zirconium IV oxide
Ag_2O	Silver I oxide
Re_2O_7	Rhenium oxide
PbO	Lead II oxide
P_2O_5	Phosphorus pentaoxide
ZnO	Zinc oxide
BaO	Barium oxide
Eu_2O_3	Europium sesquioxide
Yb_2O_3	Ytterbium oxide
Rb_2O	Rubidium oxide
Al_2O_3	Aluminium oxide
Cl	Chlorine
SrO	Strontium oxide
$NaNO_3$	Sodium nitrate
$BaCl_2$	Barium chloride
CCB	Corn cob
CD	Coal dust
RM	Raw material